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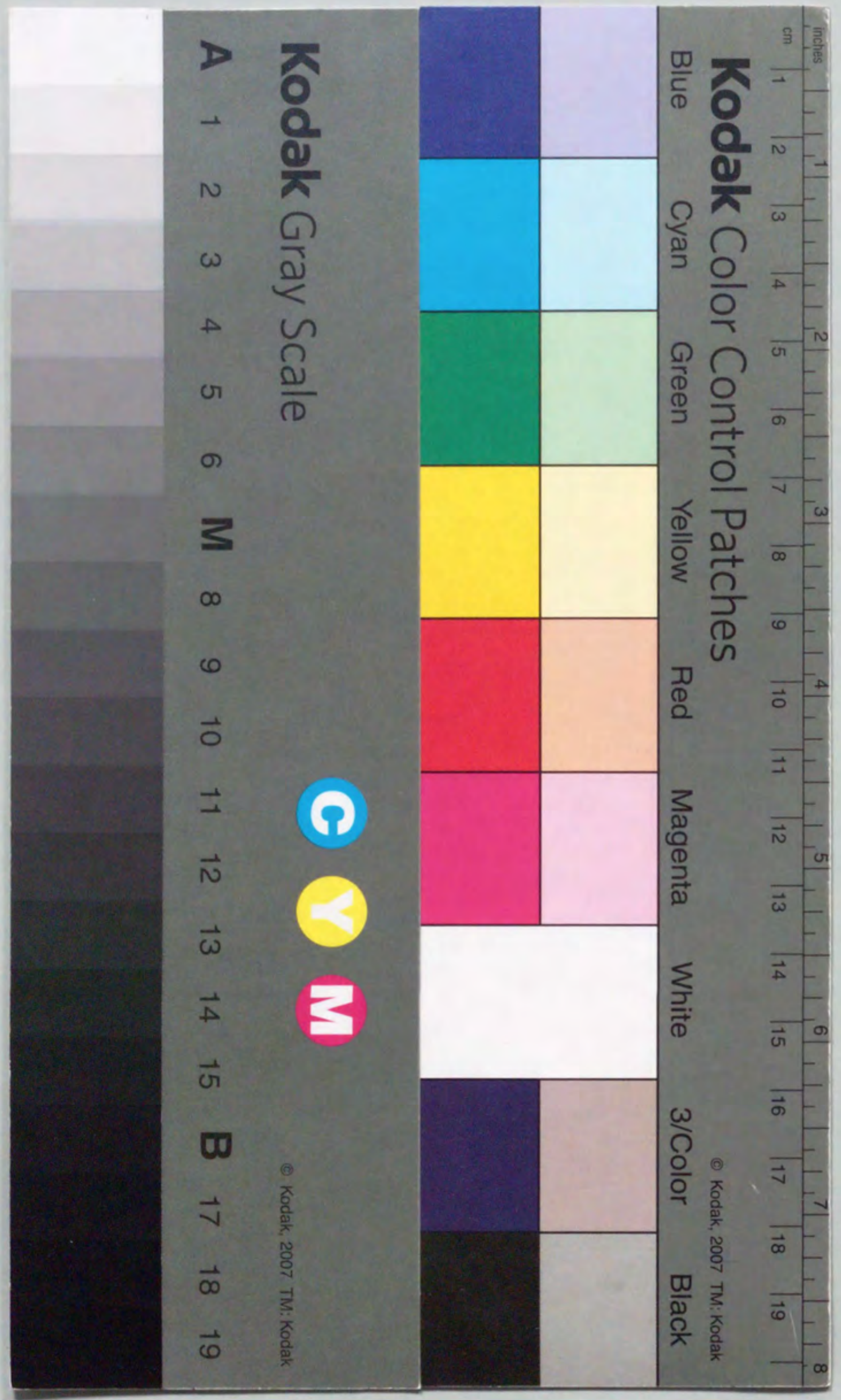

Heterotactic Living Polymerization of Methacrylates

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1999

Heterotactic Living Polymerization of Methacrylates

A Doctoral Thesis
by
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Osaka University

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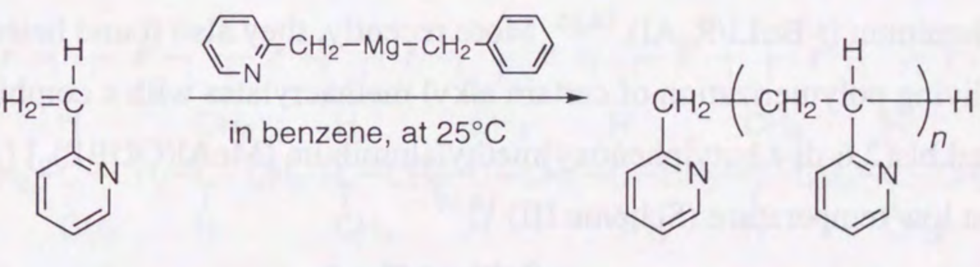
General Introduction

1. Stereospecific Living Polymerization

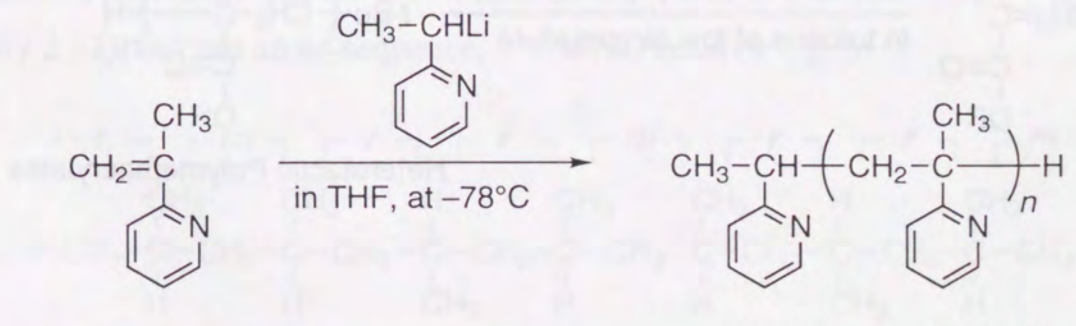
Structure control of polymer molecule is a primary step toward precise control of polymer properties that is required for the advanced polymeric materials such as functional and specialty polymers. Living polymerization, the concept of which was first proposed by Szwarc in 1956,[1] is one of the most promising ways for controlling the molecular weight and its distribution (MWD) as well as the structure of end groups. Another important structural feature to be controlled is stereoregularity. With one preceding finding of stereoregular poly(vinyl ether) by Schildknecht in 1947,[2] the field of stereospecific polymerization actually came into existence when Ziegler[3] and Natta[4] developed new polymerization systems which exhibited unique stereoregulating powers in olefin polymerization. For the precise control of structures of polymer molecule, combination of these two types of polymerizations is desirable, that is, stereospecific living polymerization. The term "stereospecific living polymerization" was first proposed

Scheme I



mm : *mr* + *rr* = 93 : 7

Scheme II



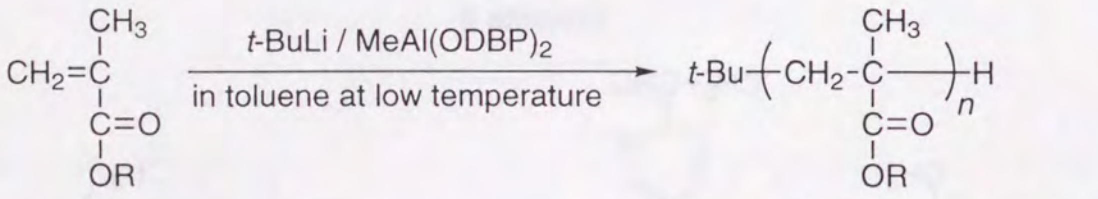
mm : *mr* : *rr* = 3 : 8 : 89

by Soum and Fontanille in 1980[5] regarding an isotactic (*it*-) living polymerization of 2-vinylpyridine in benzene with an organomagnesium compound (Scheme I). Later a syndiotactic (*st*-) living polymerization was also reported for 2-isopropenylpyridine in tetrahydrofuran (THF) with alkyllithium.[6]

Methacrylate is one of the most extensively studied classes of vinyl monomer, particularly, in regard of stereoregularity of the obtained polymers. The stereoregularity is a function of monomer structure (structure of ester group), initiator, solvent, temperature and so on. Proper selection of conditions allows preparation of a wide variety of stereoregular polymethacrylates.[7,8] On the other hand, living polymerizations of the polar monomers have been developed in the last decade.[9] However, living polymerizations which afford stereoregular polymers have still been limited. Yasuda and his coworkers found that organolanthanide complexes such as $[(C_5Me_5)_2SmH]_2$ give high molecular weight *st*-poly(methyl methacrylate)s (PMMAs) with narrow MWD in a living manner.[10,11]

In the 1980's, Hatada and his coworkers found two stereospecific living polymerizations of methacrylates: one is *it*-specific, initiated with *t*-butylmagnesium bromide (*t*-BuMgBr),[12,13] and the other *st*-specific, initiated *t*-butyllithium/trialkylaluminum (*t*-BuLi/R_3Al).[14,15] More recently, they also found heterotactic (*ht*-) specific living polymerization of certain alkyl methacrylates with a combination of *t*-BuLi and bis(2,6-di-*t*-butylphenoxy)methylaluminum $[MeAl(ODBP)_2]$ (Al/Li ≥ 2) in toluene at low temperature (Scheme III).[16,17]

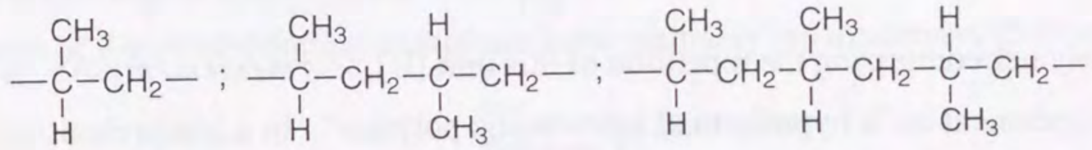
Scheme III



Heterotactic Polymethacrylates

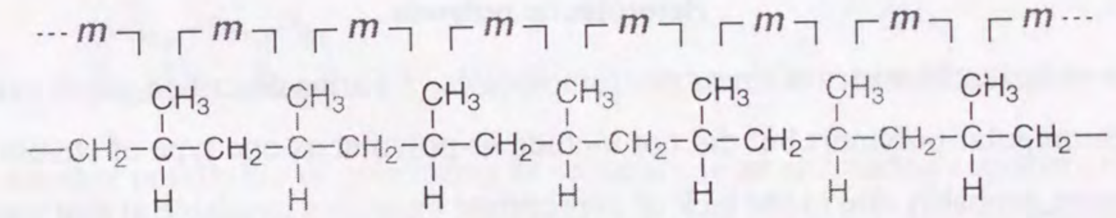
2. *Heterotactic Polymer*

"Heterotactic" is defined as an adjective for a triad sequence composed of meso (*m*) and racemo (*r*) diads; *cf.* degree of triad heterotacticity. An IUPAC document on the "Basic Definitions of Terms Relating to Polymers (1974)" describes the following three stereorepeating units for explanation:[18]

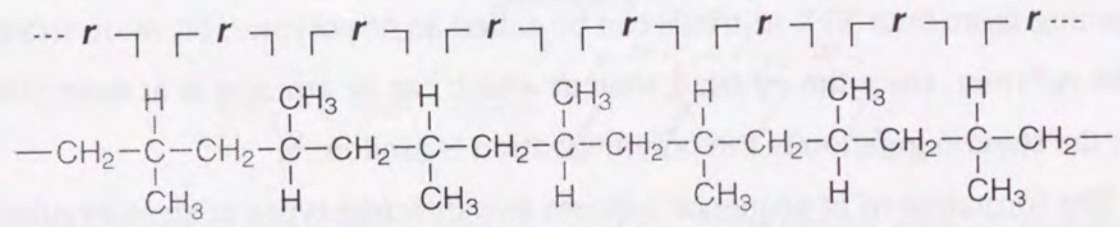


[A] [B] [C]

Stereoregular polymers formed by the repetitions of the first two stereorepeating units, [A] and [B], are *it*- and *st*-polymers, respectively. Though the last one [C] resembles a

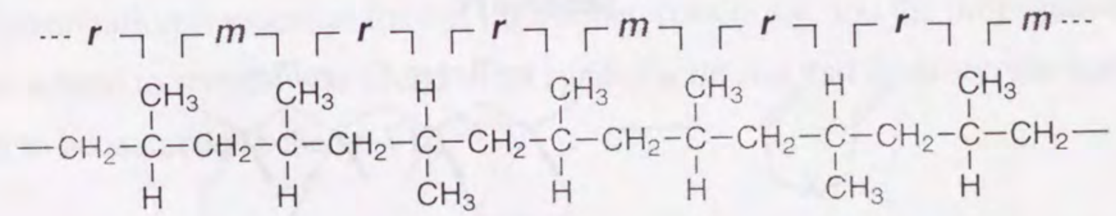


Isotactic polymer

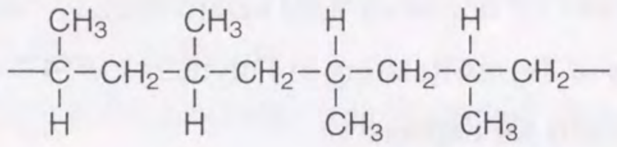


Syndiotactic polymer

ht-triad sequence, the repetition of it gives a sequence, ∿∿*mrrmrrmrr*∿∿ (*mm* / *mr* / *rr* = 0 / 2 / 1), but not an *ht*-sequence, ∿∿*mrmrmrmr*∿∿.



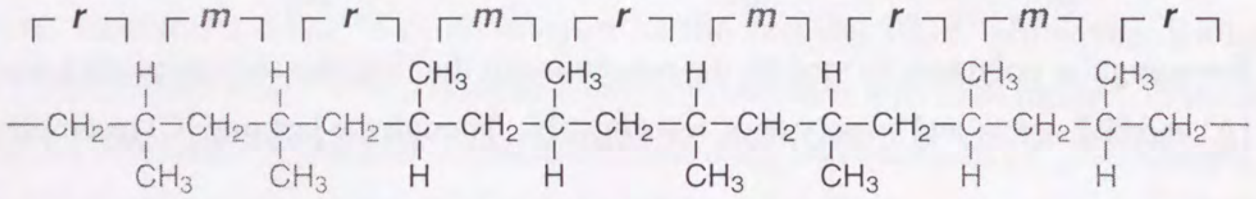
Another IUPAC document describes the following stereorepeating unit comprising four propylene units:[19]



$$-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-$$

[D]

The polymer comprising the repetition of this unit [D], ∿∿*mrmrmrmr*∿∿, is termed in the document as "a **hypothetical** heterotactic polymer". In a comprehensive review article on stereochemistry of linear macromolecules,[20] Farina described ample examples of stereoregular polymers but did not include *ht*-polymer as one type of stereoregular polymers, probably due to the lack of appropriate examples available at that time.



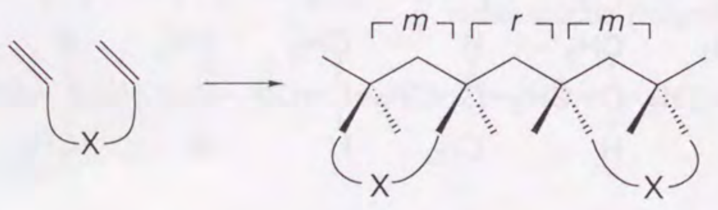
$$-\text{CH}_2-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-$$

Heterotactic polymer

Though the definition of *ht*-polymer is given for an ideal polymer, polymers containing more than 50% *ht*-triads can be called an *ht*-polymer, or, more strictly, an *ht*-rich polymer, since the *mr* triad content which can be attained is at most 50% even when the stereoregulation in the polymerization is random.[8]

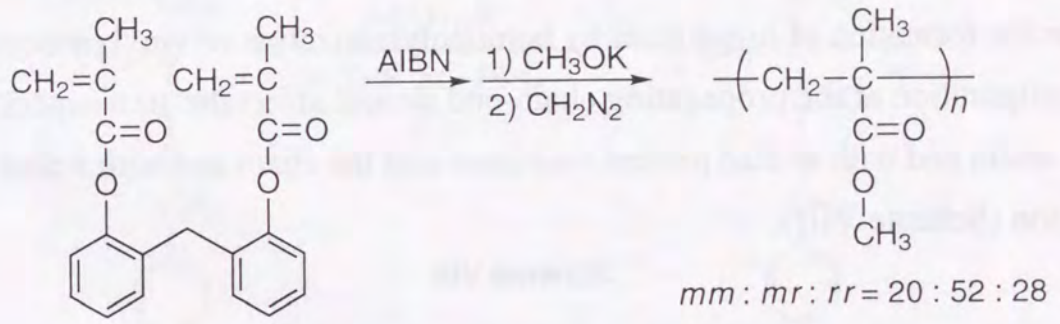
The formation of *ht*-sequence requires two different types of stereoregulation, *m*- and *r*-additions,[21] to occur in an alternate manner. One of the rational strategies for this is cyclopolymerization of divinyl monomers where intramolecular and intermolecular additions occur alternately. If these two processes exhibit opposite stereoregulations, *m*- and *r*-additions, the obtained polymer should have *ht*-sequence in the main chain (Scheme IV).

Scheme IV



Kämmerer and his coworkers studied cyclopolymerization of 2,2'-methylenebis(4-methyl-1,2-phenylene) dimethacrylate. Hydrolysis and methylation of the radically prepared polymer gave a PMMA rich in *ht*-triads ($mr = 52\%$).[22] Though the *mr* content is only a little higher than 50%, the value is much larger than those for radically prepared polymers of the corresponding monofunctional methacrylate monomers (Scheme V).

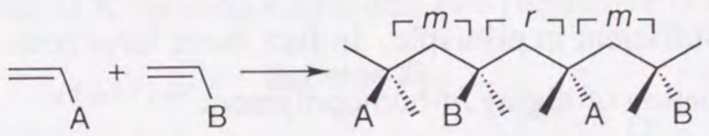
Scheme V



$mm : mr : rr = 20 : 52 : 28$

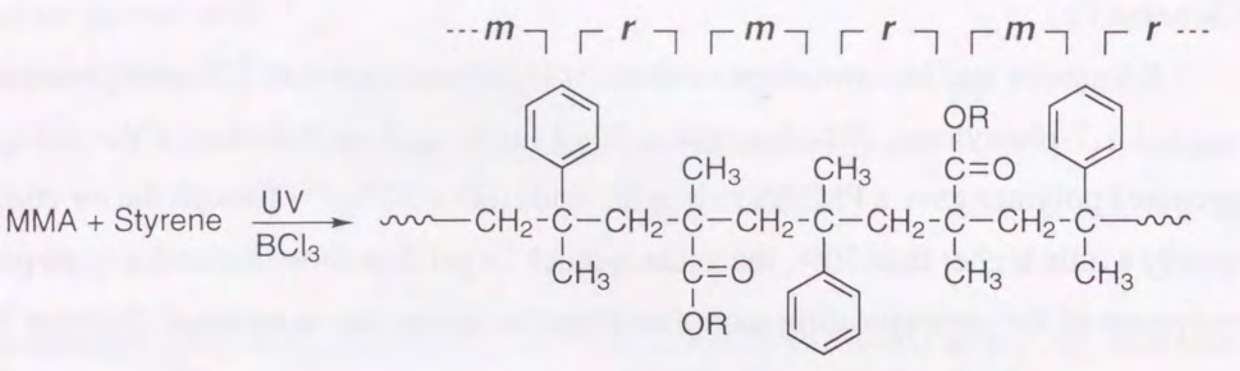
Another possibility of generating *ht*-sequence is an alternating copolymerization in which stereospecificities in two cross-propagation processes are opposite (Scheme VI).

Scheme VI



Gotoh and coworkers succeeded in preparing highly coheterotactic alternating copolymer of MMA and styrene by a radical copolymerization in the presence of BCl_3 at –95 to –100°C.[23] The cotacticity of MMA-centered triad is $mm : mr : rr = 9 : 89 : 2$ and that of styrene-centered triad $mm : mr : rr = 9 : 88 : 3$. The alternating tendency of the copolymerization is essential for this high coheterotacticity, and the propagation from MMA radical to styrene was found to be syndiotactic and that from styrene radical to MMA to be isotactic (Scheme VII).[24]

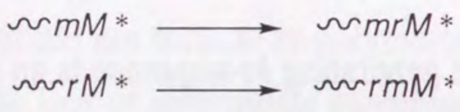
Scheme VII



MMA / *mm* : *mr* : *rr* = 9 : 89 : 2
Styrene / *mm* : *mr* : *rr* = 9 : 88 : 3 .

For the formation of *ht*-polymer by homopolymerization of vinyl monomers, the diad configuration at the propagating chain-end should affect the stereospecificity so that the chain end with *m* diad prefers *r*-addition and the chain end with *r* diad prefers *m*-addition (Scheme VIII).

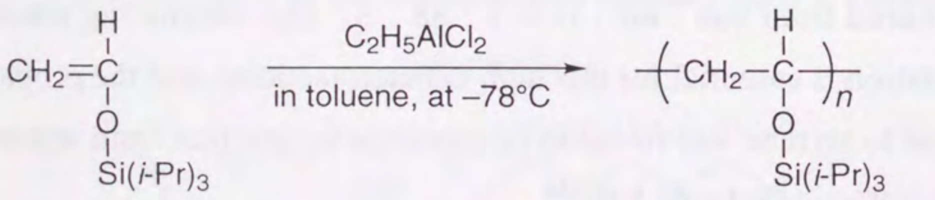
Scheme VIII



This obviously requires a higher order stereoregulation than those for *it*- and *st*-polymers: for the latter the control of configurational relationship between neighboring constitutional repeating units is sufficient in principle. In fact, there have been a limited number of reports on the formation of highly *ht*-homopolymers.[16,17,25-30]

Before the present study was started, the highest heterotacticity for homopolymer was reported by Nozakura *et al.* for poly(triisopropylsilyl vinyl ether) prepared with $C_2H_5AlCl_2$ in toluene at –78°C (Scheme IX).[25] The authors proposed that the side-chain ether group in antepenultimate (or penpenultimate) unit interacts with a terminal methine hydrogen, to form a cyclic transition state, through which the configurations at the penultimate and antepenultimate units may affect the stereoregulation.

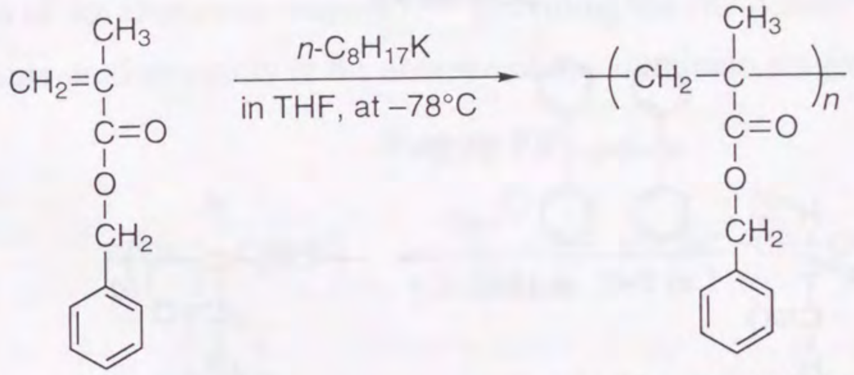
Scheme IX



mm : *mr* : *rr* = 26 : 69 : 5

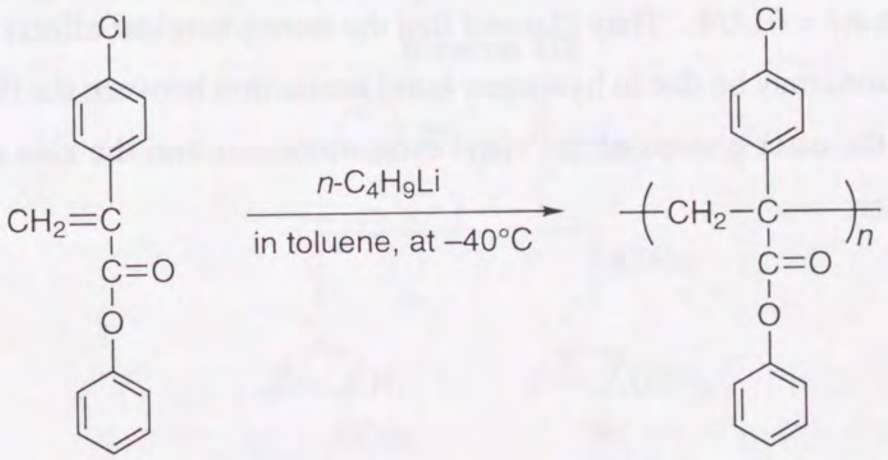
Among methacrylate polymerizations, the polymerization with octylpotassium in THF gives *ht*-rich polymers. The heterotacticity depends on the ester group (mr = 51-65%) and is the highest for the benzyl ester (Scheme X).[26] The mechanism for the *ht*-propagation in THF with octylpotassium was suggested as a combined effect, *i.e.*, *st*-placement is favored in the polymerization in THF but the bulkiness of the substituent and/or the steric effect of K^+ counterion hinders two successive *st*-additions.

Scheme X



mm : *mr* : *rr* = 13 : 65 : 22

Scheme XI

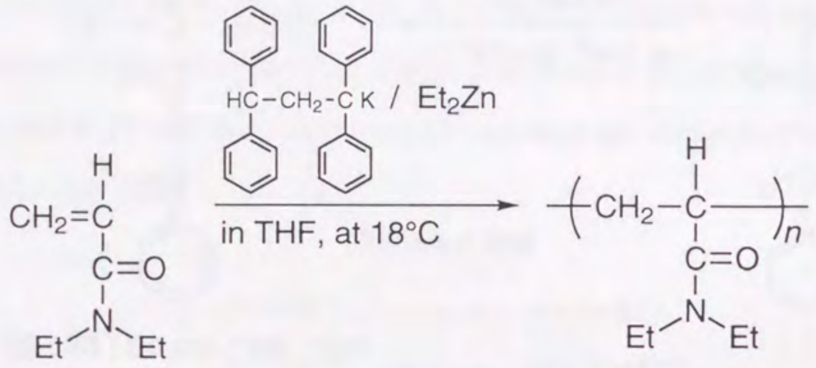


mm : *mr* : *rr* = 13 : 67 : 20

Some α-phenylacrylate derivatives also give *ht*-rich polymers.[26,27] Polymerization of phenyl α-(*p*-chlorophenyl)acrylate in toluene with butyllithium gives a polymer with *mr* of 67% (Scheme XI).[27]

Nakahama and his coworkers reported three types of stereospecific polymerization of *N,N*-diethylacrylamide.[28] All polymerizations were carried out in THF for 1h under high vacuum. When the combination of Li^+ / LiCl were used as countercation and additive at –78°C, *it*-polymer was obtained ($mm = 78\%$, $\overline{M}_w / \overline{M}_n = 3.00$). With Li^+ / Et_2Zn at –78°C, *st*-polymer was obtained ($rr = 88\%$, $\overline{M}_w / \overline{M}_n = 1.29$). With K^+ / Et_2Zn at +18°C, *ht*-polymer was obtained ($mr = 92\%$, $\overline{M}_w / \overline{M}_n = 1.10$) (Scheme XII).

Scheme XII



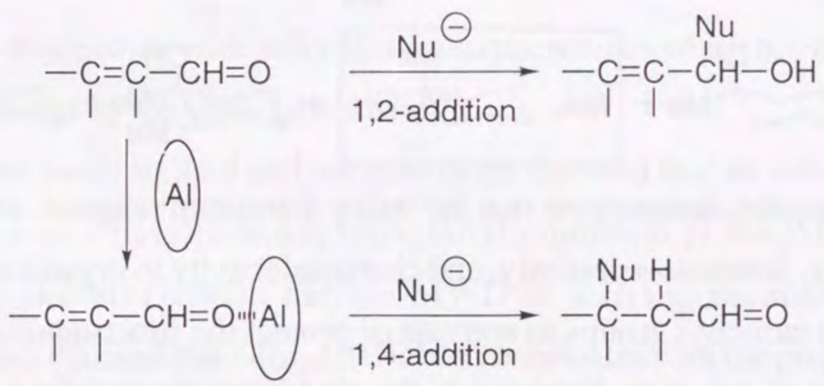
mm : *mr* : *rr* = 4 : 92 : 4

More recently, Okamoto and his coworkers reported *ht*-radical polymerization of vinyl pivalate (VPi) using fluoroalcohols as solvents.[29] The polymerization of VPi with n-Bu_3B in the presence of a small amount of air in $(CF_3)_3COH$ at –40°C gave *ht*-polymer with $mr = 61.0\%$. They claimed that the stereochemical effects observed in the polymerizations may be due to hydrogen-bond interaction between the fluoroalcohol molecules and the ester groups of the vinyl ester monomer and the side chain of the growing polymer.

3. *Bulky Aluminum Phenoxides in Organic Synthesis and Polymer Synthesis*

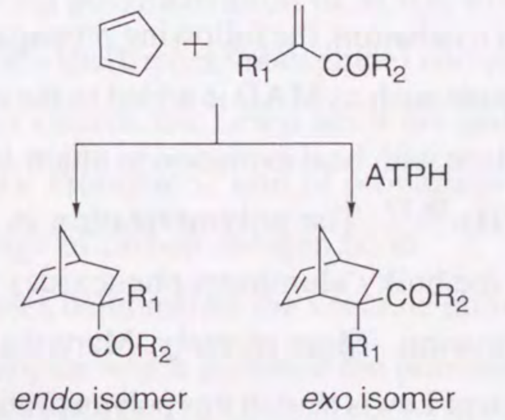
Bulky organoaluminum reagents such as methylaluminum bis(2,6-di-*t*-butyl-4-methylphenoxide) (MAD) and aluminum tris(2,6-diphenylphenoxide) (ATPH) have been recognized as promising Lewis acids in selective organic synthesis. The unique character of the bulky aluminum reagents is essentially related to the remarkable ability as a Lewis-acid receptor to recognize oxygen-containing organic molecules and activate certain functionalities. For example, ATPH facilitates selective 1,4-addition of nucleophiles to α,β-unsaturated carbonyl substrates due to efficient stabilization of carbonyls by coordination of the aluminum reagent,[31,32] providing the chemoselectivity, while 1,2-addition occurs predominantly in the absence of the aluminum reagent (Scheme XIII).

Scheme XIII



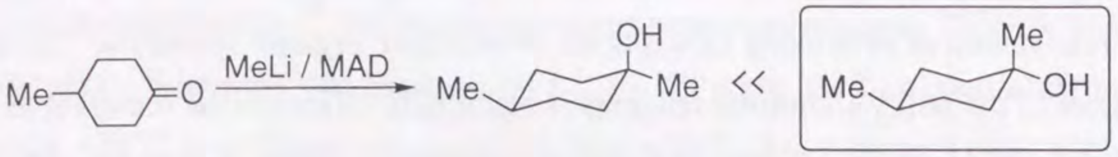
ATPH has also been utilized in *exo*-selective Diels-Alder reaction of α,β-unsaturated carbonyl compounds owing to steric repulsion of coordinating ATPH[33] (Scheme XIV).

Scheme XIV



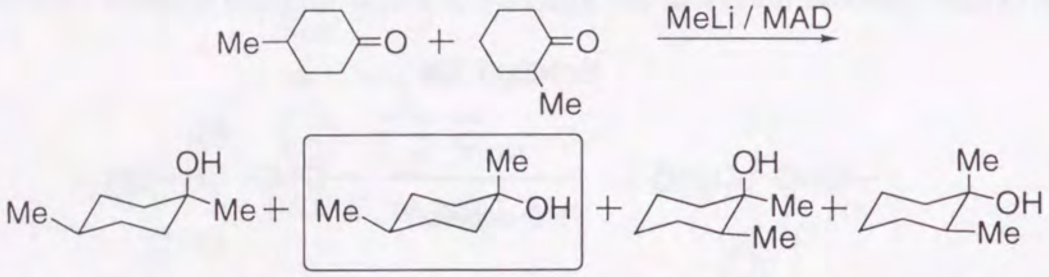
MAD facilitates the formation of *equatorial* alcohol in the alkylation reaction of cyclohexanone derivatives with methyllithium (MeLi), while the reaction with the nucleophile alone predominantly produces *axial* alcohol[34,35] (Scheme XV).

Scheme XV



Treatment of the equimolar mixture of 2- and 4-methylcyclohexanones and MAD with a nucleophile gives mainly an *equatorial* alcohol derived from the less hindered ketone, exhibiting substrate-selectivity and stereoselectivity at the same time[34,35] (Scheme XVI).

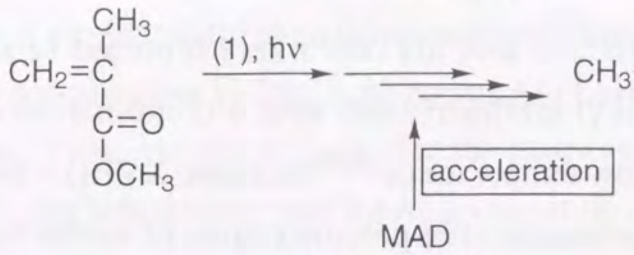
Scheme XVI

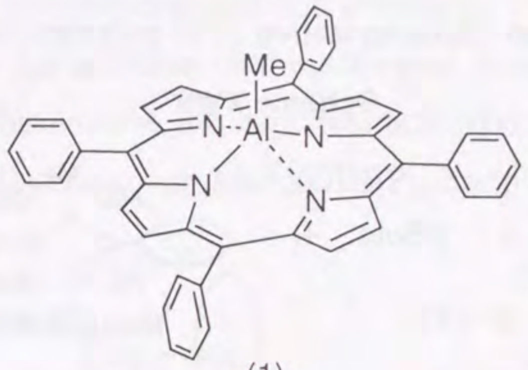


These examples demonstrate that the bulky aluminum reagents are able to provide stereoselectivity, substrate-selectivity, and chemoselectivity in organic synthesis through coordination to carbonyl groups to activate or protect the functionalities.

In the field of polymer chemistry, bulky aluminum phenoxides have been used as a Lewis-acid activator in the polymerizations of polar vinyl monomers such as methacrylates[36,37] and heterocyclic monomers such as lactones[38] and oxetane.[39] The polymerization of MMA with aluminum tetraphenylporphyrin complexes such as (1) is initiated with visible-light irradiation, the following propagation being very slow. When a bulky aluminum phenoxide such as MAD is added to the reaction mixture, a strikingly vigorous reaction takes place with heat evolution to attain 100% conversion within only 3 seconds (Scheme XVII).[36,37] The polymerization is termed "high-speed living polymerization", where the bulky aluminum phenoxides are assumed to activate the monomer through coordination. More recently, Maruoka and his coworkers claimed that ATPH is a more efficient Lewis acid in this polymerization to give narrower MWDs.[40] Miyamoto and his coworkers reported that enamines can initiate the polymerization of methacrylate in combination with bulky aluminum phenoxides which activate the monomer enough to be attacked by the weak Lewis base.[41]

Scheme XVII





(1)

On the other hand, Ballard and his coworkers reported that an initiator comprising *t*-BuLi and (2,6-di-*t*-butylphenoxy)diisobutylaluminum $[i\text{-Bu}_2\text{Al(ODBP)}]$ gave predominantly *st*-PMMA with narrow MWD in a living manner even at room temperature. They claimed that $i\text{-Bu}_2\text{Al(ODBP)}$ coordinates with the propagating species to stabilize them and the bulkiness of the phenoxide "screened" the polymer anion from possible side reactions to afford the living polymerization at ambient temperature.[42]

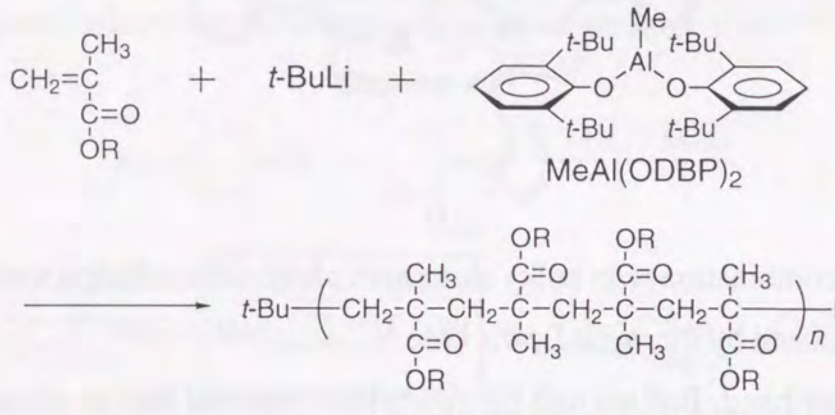
Among living radical polymerizations developed recent years, Sawamoto and his coworkers reported the living polymerization of MMA with a combination of alkyl halide, ruthenium(II) chloride tris(triphenyphosphine) complex, and Lewis acids such as MeAl(ODBP)_2.[43] In this system, the Lewis acids are assumed to coordinate to the carbonyl oxygen of terminal monomeric unit of propagating species to facilitate the reversible homolytic cleavage of carbon-halogen bond.

Although these examples demonstrate the versatile utility of bulky Lewis acids in polymer synthesis, the examples which illustrate the potential of bulky Lewis acids in the control of stereostructure of obtained polymers have scarcely been reported.

4. Heterotactic Living Polymerization — Outline of Thesis

As mentioned above, Hatada and his coworkers reported *ht*-specific living polymerization of certain alkyl methacrylates with a combination of *t*-BuLi and MeAl(ODBP)$_2$ in toluene at low temperatures[16,17] (Scheme XVIII). In this thesis are described the study on the mechanism of *ht*-polymerization of methacrylates with *t*-BuLi / MeAl(ODBP)$_2$ and characterization of *ht*-polymers obtained.

Scheme XVIII

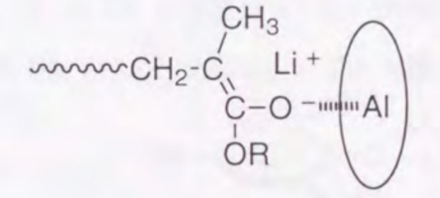


heterotactic polymethacrylate

The author describes an outline of methacrylate polymerization with *t*-BuLi / MeAl(ODBP)$_2$ in **Chapter 1**. In particular, effects of ester groups, Al / Li ratio, and temperature on the stereospecificity are demonstrated. Several primary and secondary alkyl methacrylates gave *ht*-polymers, especially primary alkyl methacrylates, except for MMA, gave highly *ht*-polymers whose heterotacticities exceeded 80% in triad. On the other hand, tertiary alkyl methacrylates gave *st*-polymers, particularly *st*-polymer with *rr* = 98%, the highest syndiotacticity among methacrylates ever reported, was obtained in the polymerization of trimethylsilyl methacrylate at –95°C.[44]

The polymerization of ethyl methacrylate (EMA) showed a linear dependence of $\bar{M}_n$ on conversion, keeping narrow MWD, and a repeated-monomer-addition experiment showed a linear increase of $\bar{M}_n$ of the polymers with conversion. These results indicate the livingness of this *ht*-specific polymerization.

The Al / Li ratio affect drastically on stereospecificity and yield in this polymerization system. The existence of an excess amount of MeAl(ODBP)$_2$ over *t*-BuLi is essential for the formation of the *ht*-polymer. In fact, at the ratio of Al / Li = 1, where most of the aluminum phenoxide might coordinate with the propagating species, an *st*-polymer forms in low yields.[17] At higher Al / Li ratios, *ht*-polymers are obtained quantitatively. These results suggest that the propagating species coordinated with MeAl(ODBP)$_2$ are less reactive and the *ht*-propagation requires excess MeAl(ODBP)$_2$ which might coordinate with the monomer and activate it. Thus the propagation process involves preferentially the addition of the activated monomer by the less reactive propagating anions. In this process, the steric interaction between the sterically crowded active-end (2) and the bulky monomer–MeAl(ODBP)$_2$ complex (3) might be an important factor for the *ht*-propagation. Thus MeAl(ODBP)$_2$ in this polymerization plays roles of the stabilization of the propagating species and of the activation of the monomer, thereby providing not only livingness but also the unique stereospecificity.



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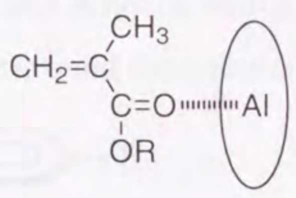
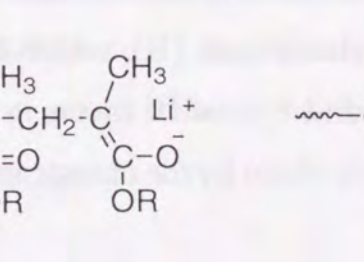
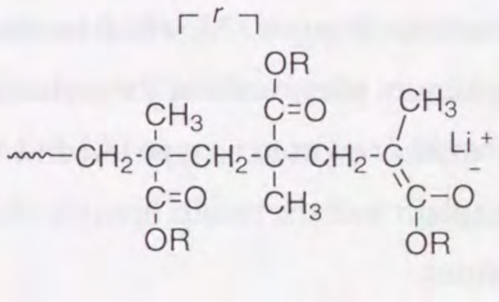


(3)

Heterotacticities of the polymers obtained at Al / Li ≥ 2 are almost constant. However, statistical analysis of stereoregularity distribution in main chain revealed that with increasing Al / Li ratio *ht*-selectivity of *r*-ended anion (~~~rM^-) increased drastically and that of *m*-ended anion (~~~mM^-) decreased slightly, resulting in a small change of heterotacticity for the polymers obtained as a whole.



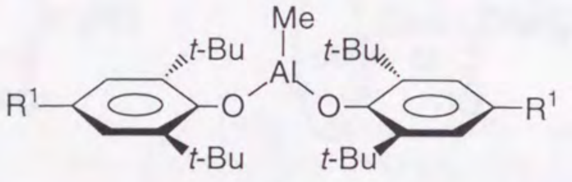
~~mM^-



~~rM^-

Polymerization temperature also affects the stereospecificity in this polymerization system. The stereoregularity of the polymers obtained changed drastically from heterotactic to syndiotactic with increasing polymerization temperature.

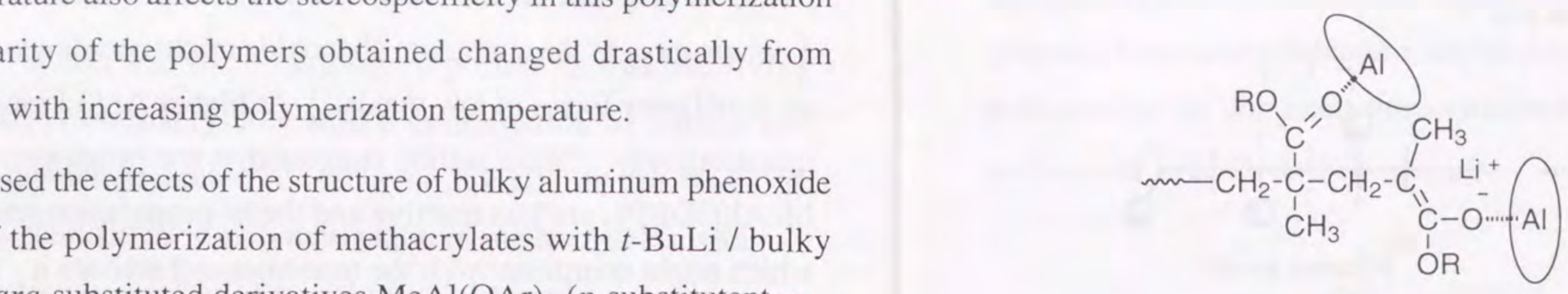
In **Chapter 2** is discussed the effects of the structure of bulky aluminum phenoxide on the stereospecificity of the polymerization of methacrylates with *t*-BuLi / bulky aluminum phenoxide.[45] *Para*-substituted derivatives $MeAl(OAr)_2$ (*p*-substitutent = –Me, –*t*-Bu, or –Br) of $MeAl(ODBP)_2$ gave *ht*-polymers, though heterotacticity of the polymers decreased slightly as compared with that of the polymer prepared with $MeAl(ODBP)_2$.



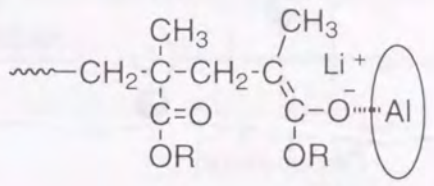
$MeAl(OAr)_2$

R^1 = H, Me, *t*-Bu, Br

The analysis of stereochemical sequence distribution in the main chain of the obtained polymers revealed that weaker Lewis acidity of the aluminum phenoxides led to a decrease of *ht*-selectivity of $\sim\sim\sim rM^{-}$ and an increase of *ht*-selectivity of $\sim\sim\sim mM^{-}$, and *vice versa* in the cases of the stronger Lewis acid. Based on the result (*cf.* Chapter 1) that it is necessary for the formation of *ht*-polymers to react between the stabilized anion and the activated monomer, the author proposed the structure models of two types of propagating species; anion bearing two phenoxides at the terminal unit and the penultimate ester group [A], which presumably favors *m*-addition, and anion coordinating one aluminum phenoxide at the terminal unit [B], which favors *r*-addition. Suppose that $\sim\sim\sim rM^{-}$ favors to be type [A] and $\sim\sim\sim mM^{-}$ favors to be type [B], these structures could explain well the results brought about by the change in Lewis acidity of aluminum phenoxides.

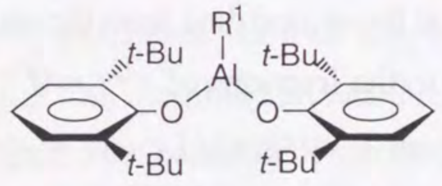


[A]



[B]

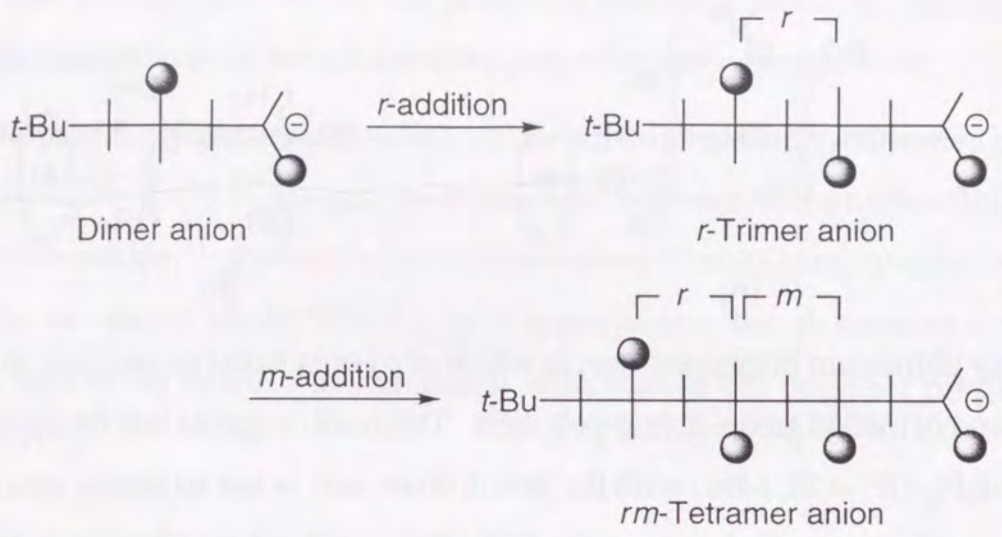
Bulky aluminum bisphenoxides, in which ethyl or isobutyl group binds to aluminum atom instead of methyl group, give *st*-polymers. This result suggests that the coordination of $R^1Al(ODBP)_2$ (R^1 = Et, *i*-Bu) with the penultimate unit is not so strong enough to stay there even with the small change in the steric factor around the aluminum center.



R^1 = Me, Et, *i*-Bu

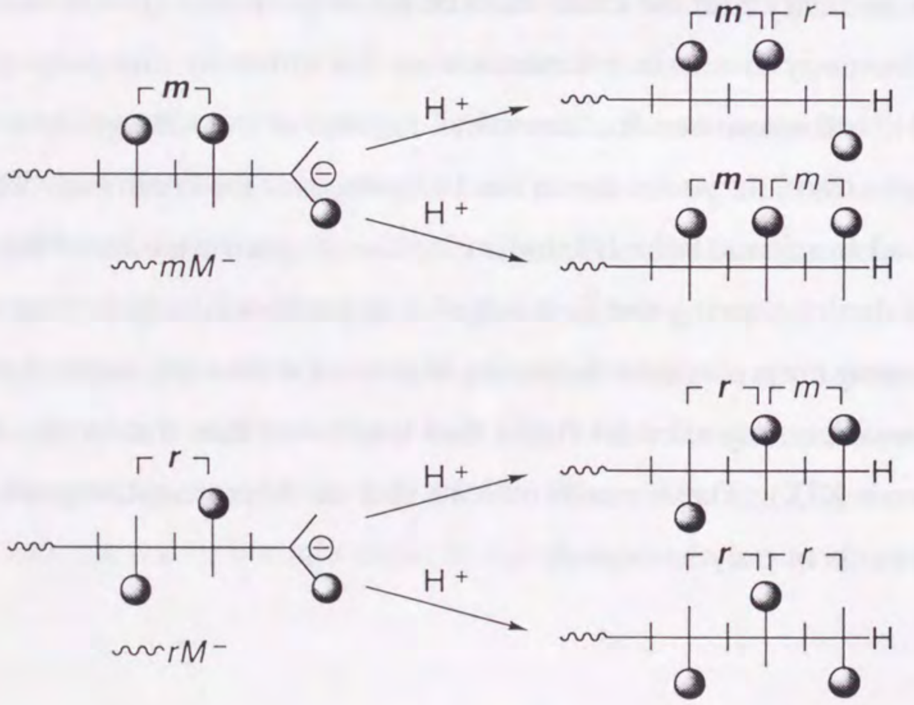
Stereochemistry near the chain ends of the *ht*-poly(EMA)s was examined by ^{13}C NMR spectroscopy to obtain information on the initiating and propagating species (**Chapter 3**).[46] Resonances due to methyl carbons of the *t*-Bu group at the initiating chain-end split into four peaks due to triad sequences at the chain end. The *m*/*r* ratio of the initial diad was found to be 1/9, indicating the *st*-specific nature of the dimer anions. The second diad following the first *r* diad was predominantly *m* (*rm* / *rr* = 3 / 1, at –78°C), indicating the preferential formation of *ht*-triad in the early stage of polymerization, though the *m*-selectivity after the first *r* diad was lower than that in the chain (*rm* / *rr* = 95 / 5) (Scheme XIX). These results indicate that the *ht*-propagation predominates even in the early stage of polymerization.

Scheme XIX

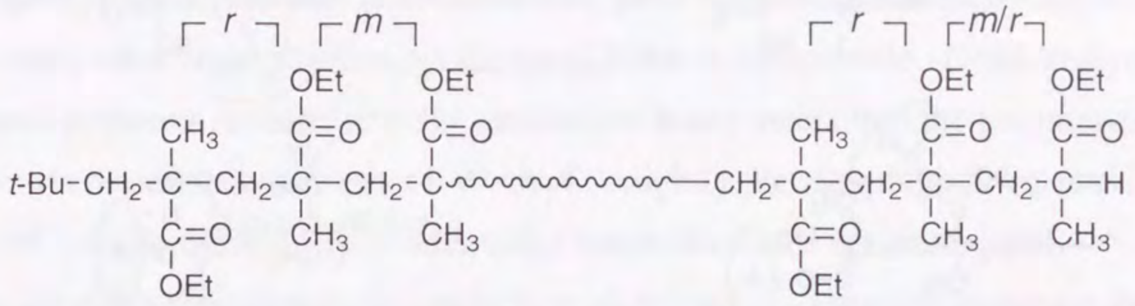


The methine carbon at the terminating chain-end showed splittings due to triad configuration. The *m*/*r* ratio at the second diad from the end, estimated from the terminal triad fractions, corresponds to the fractions of $\sim\sim mM^-$ and $\sim\sim rM^-$ existed in the polymerization system; $(\sim mr + \sim mm) / (\sim rr + \sim rm) = \sim\sim mM^- / \sim\sim rM^-$ = 1/2 (Scheme XX). The ratio indicates higher stability of the $\sim\sim rM^-$ anions and

Scheme XX



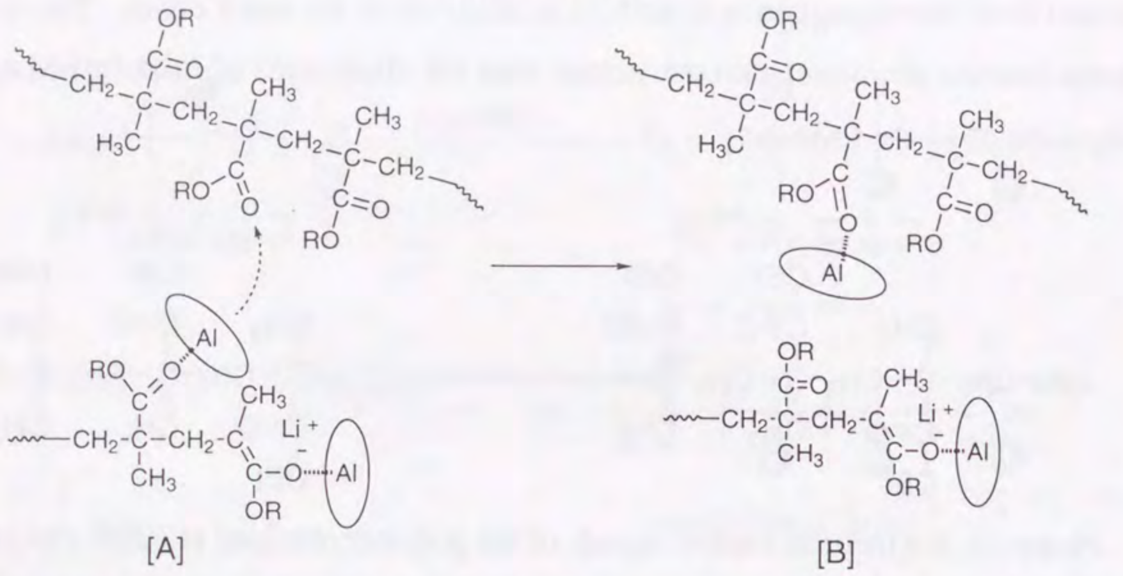
seems consistent with the fact, higher stereoselectivity of $\sim\sim rM^-$ than $\sim\sim mM^-$, obtained from stereosequence distribution analysis in the main chain. These results indicate that the dominant stereostructure near the chain ends of *ht*-poly(EMA) could be depicted as in the following:



However, the methine carbon signals of the polymer obtained at 100% yield showed splittings due to longer stereosequences than triad level, while those of the polymer obtained in the middle of polymerization showed simple four peaks due to terminal triad sequence.[47] In particular, the methine carbons due to $\sim rr$ and $\sim rm$ triads showed two and three split signals with comparable intensity, respectively. This suggests that the stereospecificities of the propagating anions decrease under the conditions where the monomer concentration is very low. In fact, the polymers obtained by termination reaction in the later stage of polymerization showed gradual complication in the resonances of methine carbons at the terminating chain-end with conversion.[48]

The stereostructure at the terminal diad is determined by the stereospecificity in termination reaction. The chain-end analysis demonstrated that living anions under the conditions where the monomer remained in the polymerization system favored *r*-termination. After the polymerization completed, however, the stereospecificity in termination reaction changed gradually from *r*-selective to *m*-selective. This result suggests that living anions transform gradually from type [A], which are coordinated with two $MeAl(ODBP)_2$, into [B], which coordinates with one $MeAl(ODBP)_2$, by releasing weakly coordinated $MeAl(ODBP)_2$ at the penultimate unit, probably through exchange with in-chain monomeric units (Scheme XXI).[48]

Scheme XXI



The methylene and carbonyl carbon NMR signals of *ht*-polymers were assigned in terms of stereochemical sequence at hexad and pentad levels in addition to chain-end analysis. Stereochemical sequence in main chain was found to obey first-order Markov model by statistical analysis of tacticity distribution in *ht*-poly(EMA) prepared with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at –95°C. Based on the results described in this thesis, the mechanism of *ht*-polymerization was proposed.

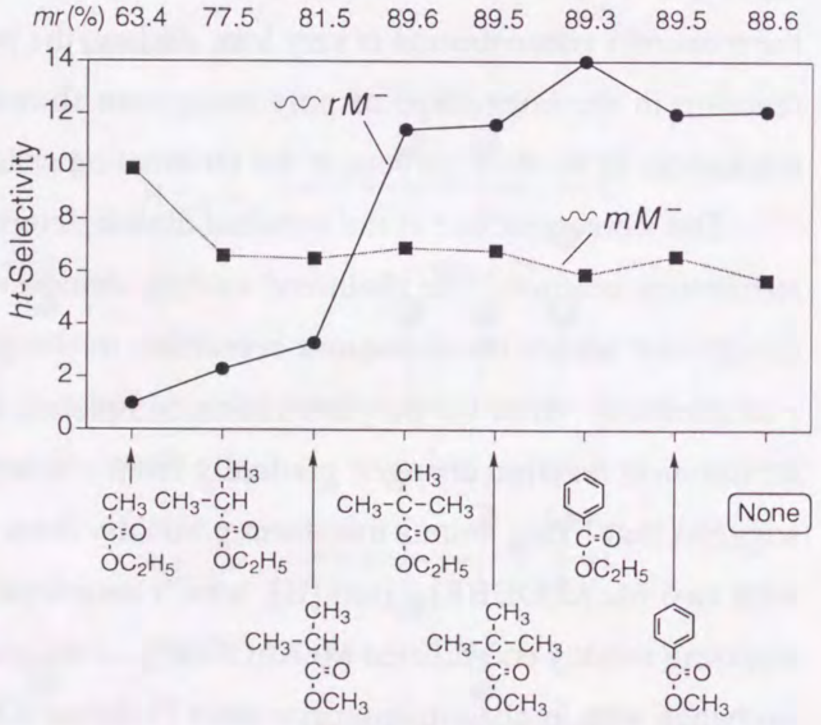


Figure I. Effect of added esters on the stereoselectivity of 〰rM^- and 〰mM^-.

Chapter 4 describes the effects of ester compounds, which may coordinate with MeAl(ODBP)$_2$, on the stereoselectivities of the propagating anions.[49] The addition of bulky esters, such as ethyl benzoate and ethyl pivalate, to the polymerization system of EMA led to the slight increase in heterotacticity of the obtained polymer (Figure I). In contrast, less bulky carbonyl compounds, such as ethyl acetate and ethyl isobutyrate, lowered heterotacticity. ^{13}C NMR spectra of the mixtures of EMA, MeAl(ODBP)$_2$, and ester compounds indicated that MeAl(ODBP)$_2$ favored to coordinate with less bulky esters such as ethyl isobutyrate than EMA monomer, while the coordination of MeAl(ODBP)$_2$ with bulky ester such as ethyl pivalate and EMA is comparable. NMR analysis of obtained polymers revealed that the addition of bulky esters into the polymerization system increased *ht*-selectivity of 〰mM^- slightly, keeping high *ht*-selectivity of 〰rM^-, while the addition of less bulky esters decreased *ht*-selectivity of 〰rM^- drastically with a slight increase in *ht*-selectivity of 〰mM^-. These results suggest that the addition of ester compound with appropriate bulkiness could increase selectively *ht*-selectivity of 〰mM^-, resulting in a slight increase in heterotacticity of the obtained polymers.

Consequently, the stereoselectivities of the propagating species, 〰mM^- and 〰rM^-, in methacrylate polymerizations with *t*-BuLi / bulky aluminum phenoxides were found to be affected either strongly or slightly by a slight change in the polymerization conditions. In Figure II are summarized the factors which were examined in this thesis.

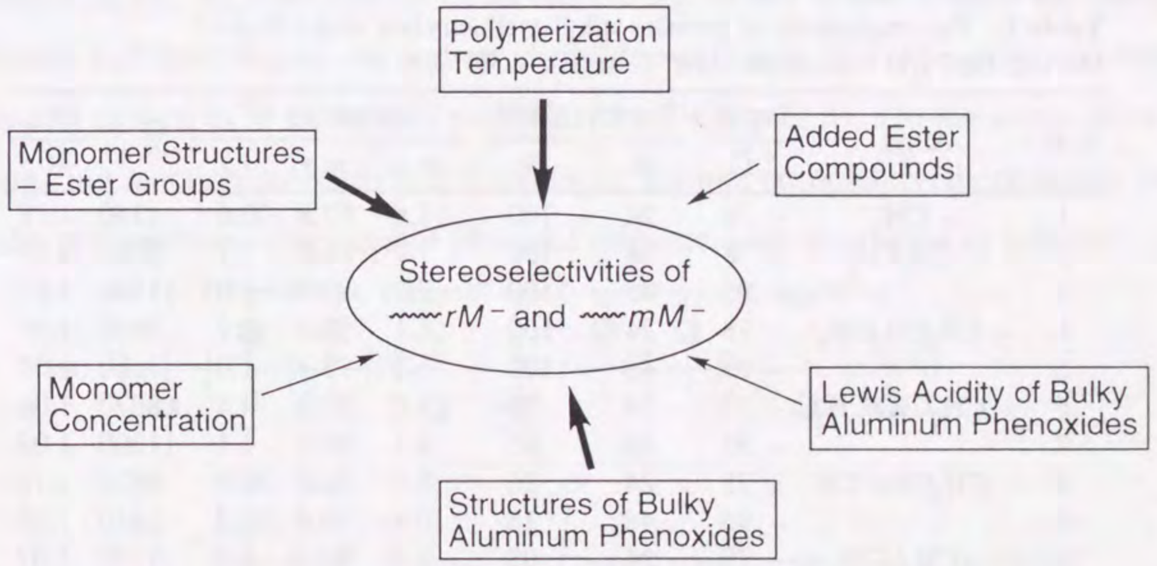


Figure II. The factors which affect the stereoselectivities of 〰rM^- and 〰mM^- in methacrylate polymerization with *t*-BuLi / bulky aluminum phenoxides.

Polymerization of several methacrylates, in particular primary alkyl methacrylates, with *t*-BuLi/MeAl(ODBP)$_2$ gives *ht*-polymers (*cf.* Chapter 1). When MMA was used as a monomer, the polymer with *mr* = 68% was obtained. On the other hand, ethyl and butyl esters gave *ht*-polymers whose *mr* contents were over 87%, and heterotacticity of poly(hexyl methacrylate) decreased to 84%. Keeping in mind the high sensitivity of the stereospecificity of the *ht*-polymerization upon the steric factors involved in the system, the author sought the possibility that the stereoselectivity in the *ht*-polymerization reaches the maximum between 2 and 4 carbon esters, and examined the polymerization of propyl (PrMA) and allyl methacrylates (AlMA) which have 3 carbons in the ester side group. In **Chapter 5** are described the polymerization of primary alkyl methacrylates having linear C-3 ester group (Table I).

The polymerizations of PrMA and AlMA at –78°C gave *ht*-polymers whose *mr* contents were 91 and 90%, respectively, with narrow MWD. By lowering the polymerization temperature to –95°C, the heterotacticities of poly(PrMA) and poly(AlMA) increased up to 93 and 96%, respectively. The heterotacticity of the latter is the highest among those of the *ht*-polymers so far reported.[50] On the other hand, propargyl methacrylate also having 3 carbons in the ester side group gave polymers with lower heterotacticity in much lower yield.

Table I. Polymerization of primary alkyl methacrylate with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at – 78° C and/or – 95° C[a]

Run	Alkyl	Temp. / ° C	Time / h	Yield / %	Tacticity / %[b] *m m*	*m r*	*r r*	$\bar{M}_n$[c]	$\bar{M}_w$[c] / $\bar{M}_n$
1	$-CH_3$	– 78	24	100	11.6	67.8	20.6	8330	1.18
2	$-CH_2CH_3$	– 78	24	100	7.7	88.6	3.7	7010	1.07
3		– 95	48	100	7.0	92.0	1.0	11100	1.07
4	$-CH_2CH_2CH_3$	– 78	24	100	6.1	91.2	2.7	7650	1.07
5		– 95	48	100	5.7	93.3	1.0	7680	1.09
6	$-CH_2CH{=}CH_2$	– 78	24	94	5.8	89.8	4.4	8070	1.06
7		– 95	48	85	3.1	95.8	1.1	11200	1.08
8	$-CH_2CH{\equiv}CH$	– 78	24	26	8.4	52.0	39.6	4170	1.15
9		– 95	48	18	10.4	79.4	10.2	3410	1.18
10	$-(CH_2)_3CH_3$	– 78	24	98	8.4	87.1	4.5	9300	1.07
11	$-(CH_2)_5CH_3$	– 78	24	100	12.0	83.7	4.3	13460	1.41

a Monomer 10mmol, toluene 10ml, *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol.
b Determined by ^{13}C NMR. c Determined by SEC.

ht-Poly(AlMA) was converted into *ht*-PMMA through the reaction with pyrrolidine in acetonitrile in the presence of Pd(PPh$_3$)$_4$, followed by methylation with diazomethane.[50] DSC curve of the *ht*-PMMA annealed at 130°C for 144h showed a melting endotherm at 166°C, while the melt-quenched *ht*-PMMA showed a glass transition at 91°C (Figure III). The annealed *ht*-PMMA showed X-ray powder diffraction peaks at 2θ = 7.9°, 13.9°, and 15.9°, while *it*-PMMA annealed at 80°C for 72h, showed diffraction peaks at 2θ = 8.4°, 14.2°, and 16.8°. Crystalline *it*-PMMA is known to adopt a double-strand helix with 10/1 helices.[51] The present result implies the possibility that *ht*-PMMA also takes a double-strand helix in the crystal state.

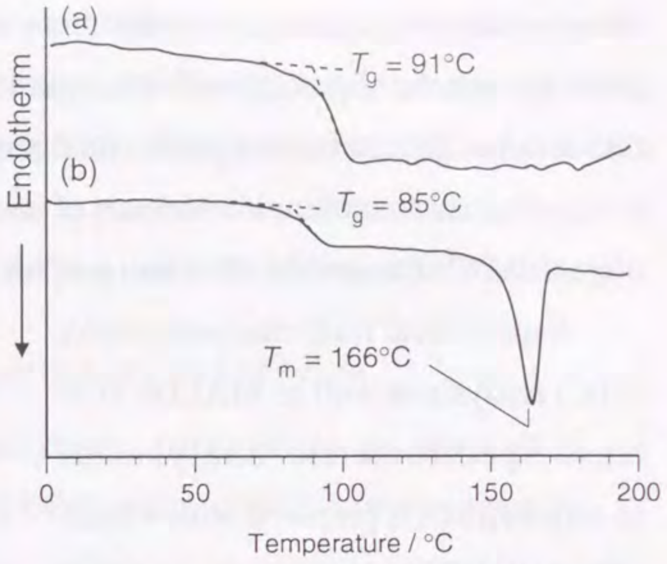
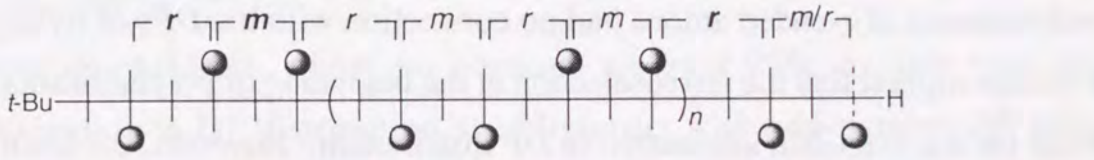
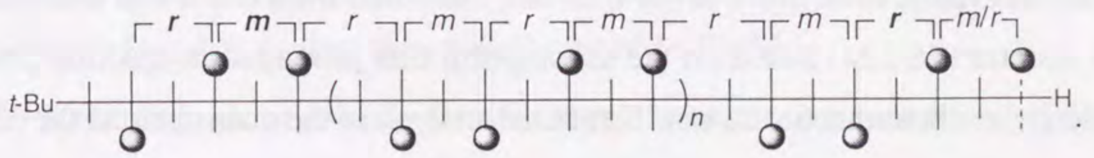


Figure III. DSC curves of *ht*-PMMA derived from *ht*-poly(AlMA), recorded at a heating rate of 10°Cmin^{-1}.
(a) melt-quenched;
(b) annealed at 130°C for 144h.

In the ^{13}C NMR spectrum of oligo(AlMA), prepared with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at –95°C, were mainly observed the signal due to *rm*– triad at the initiating chain-end and those due to –*rm* and –*rr* triads, derived from $\sim\!\sim rM^-$, at the terminating chain-end as well as in the case of poly(EMA) (*cf.* Chapter 3). On the supposition that propagating reaction proceeds in a heterotactic manner completely, these results imply that the predominant structures of obtained oligomers are expressed as follows;



or



These structures represent the oligomers with odd-number degree of polymerization (*DP*), but not the oligomers with even-number *DP*. This implies that *ht*-oligomers with odd-number *DP* are formed preferentially over those with even-number *DP*. **Chapter 6** describes chromatographic analysis of *ht*-oligo(AlMA) and NMR analysis of uniform oligo(AlMA) obtained by chromatographic separation with respect to *DP*.

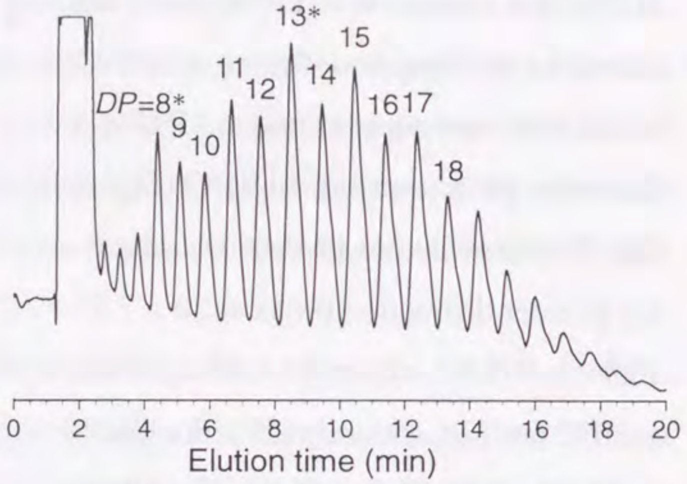


Figure IV. SFC trace of *ht*-oligo(AlMA) (*The *DP*s of the fractions were determined by FD mass spetrometry.)

Supercritical fluid chromatography (SFC) analysis as well as MALDI-TOF mass spectrometric analysis of *ht*-oligo(AlMA)s prepared with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at –95°C revealed that the population of the oligomers with respect to *DP* showed even-odd alternation, the oligomer with odd-number *DP* being formed preferentially (Figure IV).[52] The oligomers were fractionated into uniform oligomers with respect to *DP* by SFC, and the stereostructures of uniform oligomers were investigated by ^{13}C NMR spectroscopy.[53] Initiating chain-end analysis of uniform oligomers indicated clearly even-odd alternation in stereostructures near the initiating chain-end, while the signal due to *rm*– triad was observed with the strongest intensity in both cases of even- and odd-number oligomers. On the other hand, terminating chain-end analysis showed that the predominance of *r*-ended anions had no connection with the *DP*s of living anions. These results suggest that the stereoselection at the beginning of polymerization is very important for the even-odd alternation in *DP* distribution. However, the fraction ratio of odd- and even-number oligomers (55 : 45) obtained from the peak intensities in SFC analysis was found to be much lower than that estimated from chain-end analysis by ^{13}C NMR spectra (76 : 24) based on the assumption that propagation reaction proceeded completely in a heterotactic manner. Structural analysis in the main chain of the oligomers demonstrated that even-number oligomers contained *mm* sequence, while odd-number oligomers hardly contained such a defective sequence. One mistake in stereoregulation causes an increase of one degree of polymerization. These results indicate that a mistake in stereoregulation by propagating species, in particular by $\sim\!\sim\!\sim mM^{-}$ to form *mm* sequence, also plays an important role for the even-odd alternation in *DP* distribution.

The conclusions drawn in the thesis are summarized as below.

1. Polymerizations of several methacrylates, particularly primary alkyl methacrylates, with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at low temperature give *ht*-polymers with narrow MWDs.
2. For the formation of highly *ht*-polymers, MeAl(ODBP)$_2$ at least twice as much as *t*-BuLi and low temperature is necessary.
3. The slight change in bulkiness around the aluminum center of bulky aluminum phenoxide alters drastically the stereospecificity in the methacrylate polymerization [MeAl(ODBP)$_2$; heterotactic, EtAl(ODBP)$_2$; syndiotactic].
4. Propagating reaction proceeds in a heterotactic manner even in the beginning of the polymerization.
5. Propagating species stay longer in $\sim\!\sim\!\sim rM^{-}$ state than in $\sim\!\sim\!\sim mM^{-}$ state.
6. $\sim\!\sim\!\sim rM^{-}$ exhibits higher *ht*-selectivity than $\sim\!\sim\!\sim mM^{-}$.
7. The addition of bulky ester compounds such as pivalate into the polymerization system increases slightly *ht*-selectivity of $\sim\!\sim\!\sim mM^{-}$, keeping high *ht*-selectivity of $\sim\!\sim\!\sim rM^{-}$.
8. *ht*-Oligo(AlMA)s, whose *mr* contents are over 95%, exhibit even-odd alternation in *DP* distribution, the oligomers with odd-number *DP* being formed preferentially than those with even-number *DP*.
9. DSC and X-ray analyses of *ht*-PMMA, derived from *ht*-Poly(AlMA), annealed at 130°C for 144h proved the crystallinity of *ht*-PMMA.
10. ^{13}C NMR analysis of *ht*-polymer with regard to stereosequence revealed that

the stereocontrol in *ht*-polymerization obeys first-order Markovian statistics.

11. The mechanism in polymerization with *t*-BuLi and bulky aluminum phenoxide was proposed. The proposed mechanism interprets well the results described in this thesis.

In nearly a half century of history of stereoregular polymers and stereospecific polymerizations, highly stereoregular *ht*-polymer was prepared for the first time. The high *ht*-specificity is attained with a good balance of two types of stereocontrol, *m*-selectivity by $\sim\sim\sim rM^-$ anion and *r*-selectivity by $\sim\sim\sim mM^-$ anion. The improvement of the both selectivities by changing the polymerization conditions is often difficult and requires precise matching of every factors involved in the polymerization such as temperature, monomer concentration, structure of monomer, structure of bulky aluminum phenoxide, and additives if any. Nevertheless, these findings may contribute to the understanding of the stereoregulation not only in *ht*-polymerization but also in *it*- and *st*-polymerizations.

Polymer properties depend on many factors such as molecular weight, MWD, stereoregularity, end groups, and so on. Chemical structure of the *ht*-polymers prepared with *t*-BuLi / MeAl(ODBP)$_2$ is identical with those of *it*- and *st*-polymers prepared with *t*-BuMgBr and *t*-BuLi / R$_3$Al, respectively. Through the present study we now have these three types of stereoregular polymethacrylates which have the same chemical structures from one end to other end but differ in their stereochemical structures. These polymer samples may thereby contribute the understanding stereochemical effect in polymer properties without disturbance from the end group effect.

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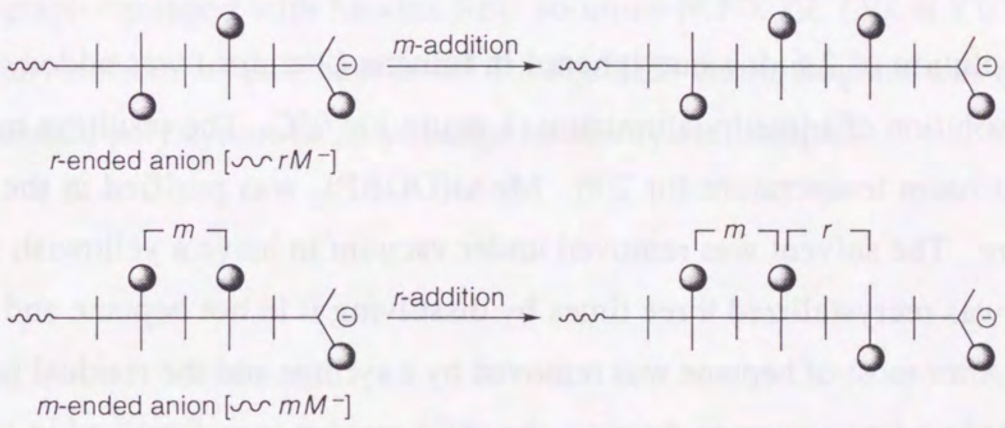
Chapter 1

Heterotactic Living Polymerization of Methacrylates

Introduction

In 1994, a combination of *t*-butyllithium (*t*-BuLi) and bis(2,6-di-*t*-butylphenoxy)-methylaluminum [MeAl(ODBP)$_2$] was found to give heterotactic (*ht*-) polymers with narrow molecular weight distribution (MWD) in the polymerization of certain alkyl methacrylates in toluene at low temperature.[1,2] Heterotactic polymer is one kind of stereoregular polymers, which comprises an alternating sequence of meso (*m*) diad and racemo (*r*) diad. For the formation of *ht*-sequence in anionic polymerization is needed an alternating opposite stereocontrol, *m*-addition by *r*-ended anion forming *rm*– sequence and *r*-addition by *m*-ended anion forming *mr*– sequence. It is obvious that *ht*-propagation requires higher order stereocontrol than those for isotactic (*it*-) and syndiotactic (*st*-) propagations. In fact, there are limited reports on the formation of *ht*-polymers.[1-8]



In this Chapter is described the outlined features of this unusual stereospecific living polymerization, placing particular emphasis on the relationship between the polymerization conditions and the stereospecificity in this polymerization system.

Experimental

Materials

Methacrylate monomers were purified by fractional distillation under reduced nitrogen pressure, dried over calcium dihydride and vacuum-distilled just before use. Toluene, heptane, and methylcyclohexane were purified in the usual manners, mixed with a small amount of *n*-BuLi, and distilled under high vacuum. Benzene was distilled, and dried over sodium.

2,6-Di-*t*-butylphenol, obtained commercially, was fractionally distilled, dried over Molecular Sieves (MS) 4A, and used as a toluene solution.

t-BuLi in pentane (Aldrich Co. Ltd.) was used as a heptane solution. The concentration was determined by titration with butan-2-ol.[9] Trimethylaluminum (Nippon Aluminum Alkyls) was used as toluene solutions.

Preparation of MeAl(ODBP)$_2$[10]

A solution of 2,6-di-*t*-butylphenol in toluene (2 equiv.) was added slowly to a toluene solution of trimethylaluminum (1 equiv.) at 0°C. The resulting mixture was stirred at room temperature for 20h. MeAl(ODBP)$_2$ was purified in the following procedure. The solvent was removed under vacuum to leave a yellowish solid. The product was recrystallized three times by dissolving it in hot heptane and cooling to –78°C. After most of heptane was removed by a syringe and the residual heptane was evaporated under vacuum to dryness, the solid residue was dissolved in toluene and used for the polymerization reactions.

Polymerization

All the polymerizations were carried out in a glass ampoule filled with dried nitrogen passed through MS 4A cooled at –78°C. A heptane solution of *t*-BuLi was added to MeAl(ODBP)$_2$ in toluene at polymerization temperature. The polymerization reaction was initiated by adding the monomer slowly to this mixture at polymerization temperature. The reaction was terminated by adding methanol containing HCl at the polymerization temperature. The reaction mixture was poured into a large amount of hexane to precipitate the polymeric product. The polymeric product was precipitated by cooling the hexane to –78°C and organic impurities such as monomer and 2,6-di-*t*-butylphenol derived from MeAl(ODBP)$_2$ were removed by repeated decantation. The product was redissolved in acetone and the solution was poured into a large amount of water to reprecipitate the polymeric product. The precipitate was collected by filtration, washed with dilute HCl and water, successively, and dried under vacuum.

Measurements

Tacticities of the polymers were determined from ^{13}C NMR signals due to the carbonyl carbons measured in $CDCl_3$ at 55°C on a Varian Unity Inova 500 spectrometer operated at 125MHz. Molecular weight and its distribution of the polymers were determined by size exclusion chromatography (SEC) using a JASCO 880-PU chromatograph equipped with Shodex SEC columns [KF-806L (30cm x 0.8cm) x2] using tetrahydrofuran as an eluent at 40°C. The SEC chromatogram was calibrated against standard polystyrene or poly(methyl methacrylate) samples.

Results and Discussion

Table 1-I shows compiled results of polymerization of several methacrylates with *t*-BuLi / MeAl(ODBP)$_2$ in toluene. The primary and secondary esters of methacrylic acid gave *ht*-polymers with narrow MWDs. In particular, ethyl and *n*-butyl esters gave the best results. Interestingly, *t*-butyl and trimethylsilyl methacrylates (TMSMA), tertiary alkyl methacrylates, gave *st*-polymers under the same conditions. In particular, polymerization of TMSMA gave highly *st*-polymers with *rr* triad of 96% at –78°C and 98% at –95°C, the latter being the highest syndiotacticity ever reported for polymethacrylates.[11] Methacrylates having a functional group, such as vinyl and *N,N*-dimethylaminoethyl methacrylates, gave *st*-polymers, suggesting the possibility of interaction between the functional groups and the aluminum compound.

In Figure 1-I is shown the relationship between the polymer yield and both $\overline{M}_n$ and $\overline{M}_w / \overline{M}_n$ for EMA polymerization. This demonstrates a linear dependence of $\overline{M}_n$ on

Table 1-I. Polymerization of alkyl methacrylate with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at – 78° C or – 95° C[a]

Alkyl	Temp. °C	Time h	Yield %	Tacticity / %[b] *m m*	*m r*	*r r*	$\overline{M}_n$[c]	$\overline{M}_w / \overline{M}_n$[c]
$-CH_3$	– 78	24	100	11.6	67.8	20.6	8330	1.18
$-CH_2CH_3$	– 78	24	100	7.7	88.6	3.7	7010	1.07
	– 95	48	100	7.0	92.0	1.0	11100	1.07
$-(CH_2)_3CH_3$[d]	– 78	24	98	8.4	87.1	4.5	9300	1.07
$-CH_2CH(CH_3)_2$	– 78	24	84	12.1	78.4	9.5	6350	1.07
$-CH_2Ph$	– 78	48	51	0.5	65.9	33.6	6010	1.08
$-CH(CH_3)_2$[d]	– 78	24	50	2.1	69.2	28.7	4730	1.07
$-C(CH_3)_3$[d]	– 78	48	19	7.4	8.5	84.1	3050	1.19
$-Si(CH_3)_3$[e]	– 78	24	100	0.3	3.3	96.4	7030	1.16
	– 95	48	48	0.5	1.4	98.1	3410	1.18
$-CH=CH_2$	– 78	24	100	0.0	18.7	81.3	5660	1.85
$-CH_2CH_2N(CH_3)_2$	– 60	24	90	0.9	11.0	88.1	nd	nd

a Monomer 10mmol, toluene 10ml, *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol.
b Determined by NMR. c Determined by SEC.
d Taken from Ref. 1. e Taken from Ref. 11.

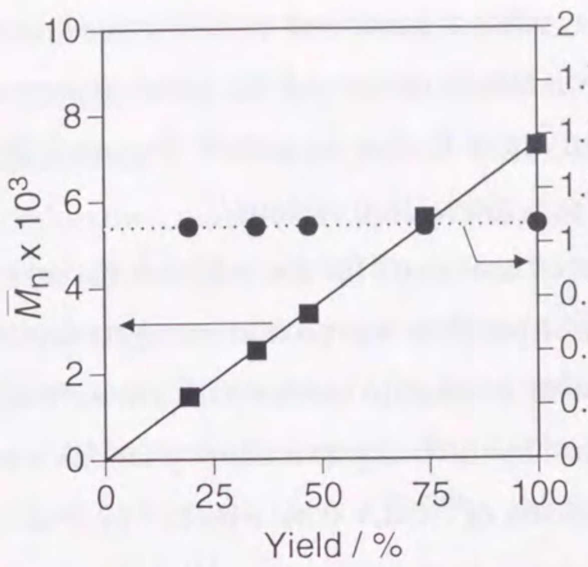


Figure 1-I. Polymerization of EMA with *t*-BuLi /MeAl(ODBP)$_2$ in toluene at –78°C ([M]/[I]=50). $\overline{M}_n$ ($\overline{M}_w$ / $\overline{M}_n$)-polymer yield relationship.

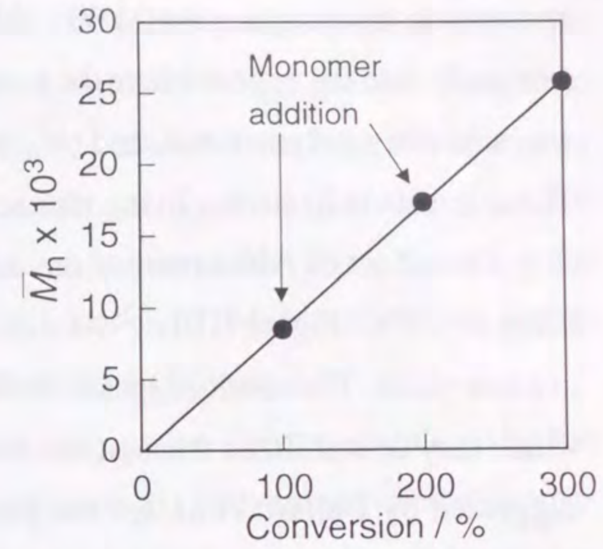


Figure 1-II. Polymerization EMA with *t*-BuLi/MeAl(ODBP)$_2$ (1/5 mol/mol) in toluene at –78°C [M]$_0$ = [M]$_{add}$ = 10mmol, [M]$_0$/[I]=50.

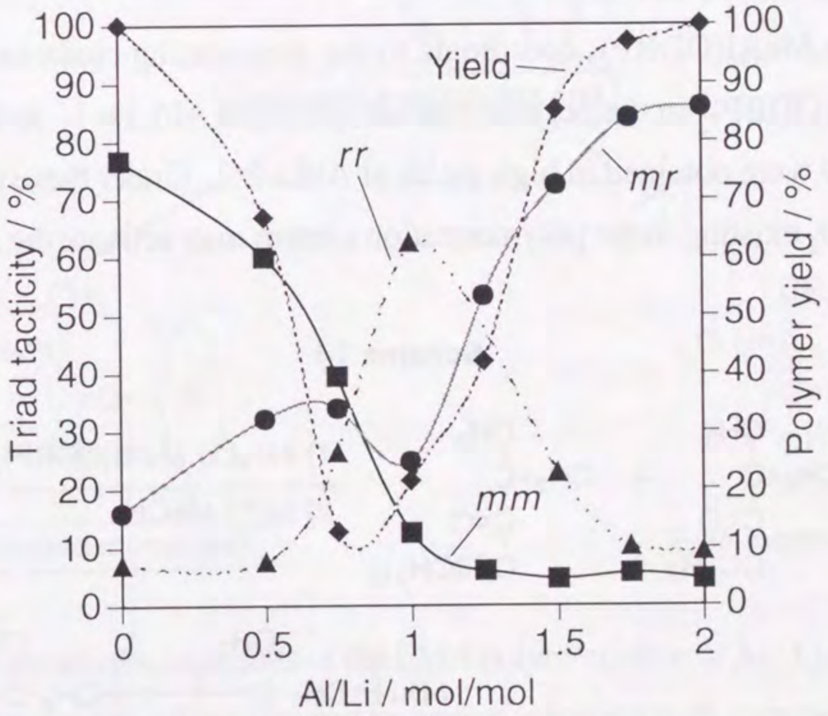
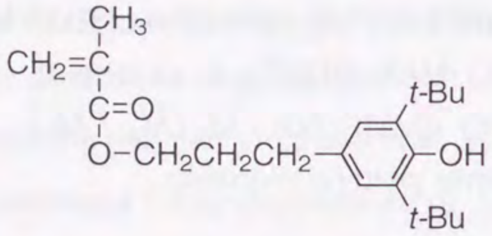


Figure 1-III. Effect of Al/Li ratio on the triad tacticity and polymer yield of poly(EMA) formed with *t*-BuLi/ MeAl(ODBP)$_2$ in toluene at –78°C for 24h.

conversion, keeping narrow MWD. Moreover, when a fresh feed of EMA was added repeatedly into the system where the monomer was almost consumed, the added monomer was smoothly polymerized, and $\overline{M}_n$ of the polymers further increased (Figure 1-II). These results indicate the living nature of this polymerization system.[12]

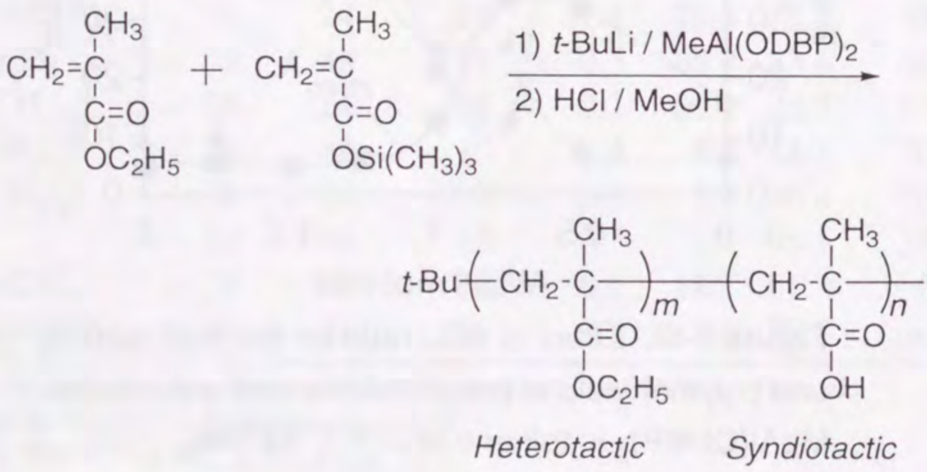
The effect of Al/Li ratio of the initiator was examined for the polymerization of EMA at –78°C (Figure 1-III).[12] At Al/Li = 1, an *st*-polymer was predominantly obtained in a low yield. The result suggests the formation of *st*-specific species with low activity, which may be stabilized through the coordination by the bulky aluminum phenoxide as suggested by Ballard *et al.* for the polymerization of MMA with *t*-BuLi / (2,6-di-*t*-butylphenoxy)diisobutylaluminum.[13] In fact, this initiator system can polymerize MMA even in the presence of 2,6-di-*t*-butylphenol[2] and a methacrylate monomer (1), which has an acidic hydrogen, without protection,[14] giving polymers with narrow MWDs.



(1)

If all the $MeAl(ODBP)_2$ coordinate to the propagating chain-end, there exists no excess $MeAl(ODBP)_2$ in the polymerization system at Al/Li = 1. *ht*-Poly(EMA)s with narrow MWD were obtained in high yields at Al/Li $\geq$ 2. Under these conditions, excess $MeAl(ODBP)_2$ existing in the polymerization system may activate the monomer through coordination. As mentioned in General Introduction, bulky aluminum phenoxides recognize the difference in steric hinderance around carbonyl groups in organic substrates.[15,16] The initiator, *t*-BuLi / $MeAl(ODBP)_2$, also could exhibit this feature in copolymerization of methacrylates, that is, the copolymerization of EMA and TMSMA with *t*-BuLi / $MeAl(ODBP)_2$ proceeds in a monomer-selective manner, giving a stereoregular block copolymer that comprises *ht*-poly(EMA) block and *st*-poly(TMSMA) block; the second block is easily converted to *st*-poly(methacrylic acid) block (Scheme 1-I).[17]

Scheme 1-I



These results suggests that the less reactive propagating species, stabilized by the coordination with $MeAl(ODBP)_2$, should react preferentially with the activated monomer (Scheme 1-II). The steric restriction due to the sterically bulky active end and also bulky monomer complex might be an important factor for the *ht*-propagation.

Scheme 1-II

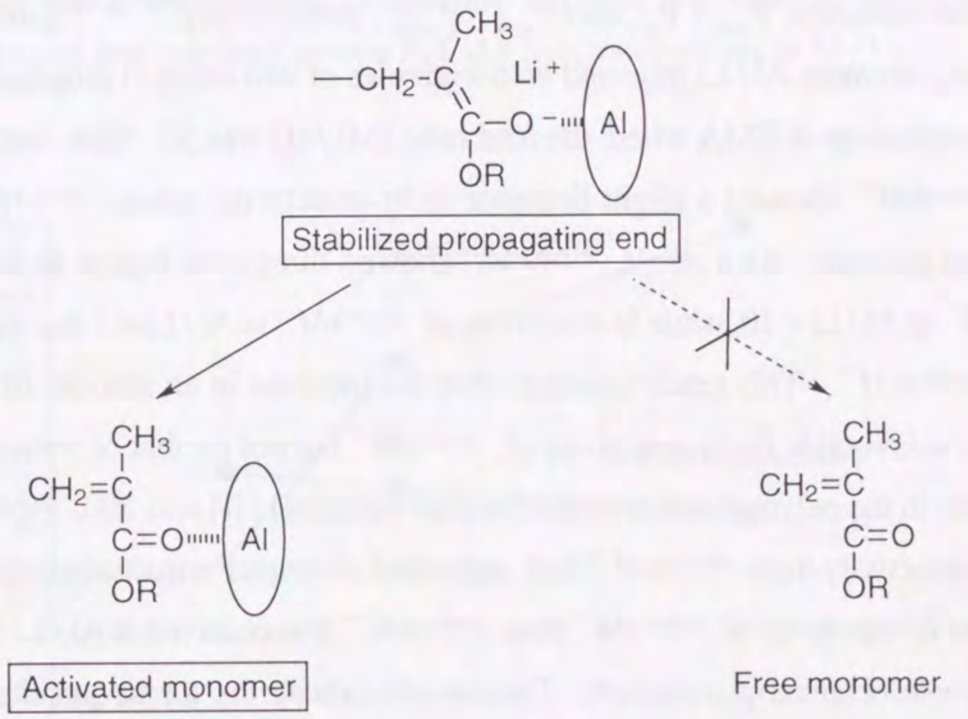


Table 1-II summarizes the results of the EMA polymerization at Al / Li $\geq$ 2. In the case of M/I = 50, heterotacticity of the obtained polymers increased with increasing Al / Li ratio and the highest heterotacticity was obtained at Al / Li = 5. *ht*-Selectivities of $\sim rM^{-}$ and $\sim mM^{-}$ can be expressed by the ratio of the conditional probabilities in first-order

Table 1-II. Polymerization of EMA with various ratios of *t*-BuLi / MeAl(ODBP)$_2$ in toluene at – 78° C for 24h[a]

Run	M / I	Al mmol	Al / Li	Yield %	Tacticity / %[b]			$\overline{M}_n$[c]	$\overline{M}_w / \overline{M}_n$[c]
					m m	*m r*	*r r*		
1	50	0.4	2	100	6.8	81.2	12.0	7080	1.16
2	50	0.6	3	100	7.3	87.6	5.1	7510	1.13
3	50	1.0	5	100	7.7	88.6	3.7	7010	1.07
4	50	2.0	10	100	8.6	88.4	2.8	7200	1.15
5	200	0.25	5	88	5.8	85.7	8.5	19170	1.16
6	200	0.5	10	100	6.4	89.3	4.3	26070	1.21
7	200	1.0	20	100	7.2	89.6	3.2	23060	1.18

a EMA 10mmol, toluene 10ml. b Determined by ^{13}C NMR.
c Determined by SEC.

Markovian statistics, $P_{r/m}$ / $P_{r/r}$ and $P_{m/r}$ / $P_{m/m}$, respectively.[12,18] Figure 1-IV shows relationship between Al / Li ratio and *ht*-selectivities of two kinds of propagating anions in the polymerization of EMA where the feed ratio [M] / [I] was 50. With increasing Al / Li ratio, $\sim\sim mM^-$ showed a slight decrease in *ht*-selectivity, while $\sim\sim rM^-$ showed a significant increase. As a result, $\sim\sim rM^-$ showed three time higher *ht*-selectivity than $\sim\sim mM^-$ at Al / Li = 10, while *ht*-selectivity of $\sim\sim rM^-$ at Al / Li = 2 was even lower than that of $\sim\sim mM^-$. This result indicates that the increase in an amount of the activated monomer is favorable for *ht*-selectivity of $\sim\sim rM^-$ but not for that of $\sim\sim mM^-$. On the other hand, in the polymerization where the feed ratio [M] / [I] was 200, $\sim\sim rM^-$ showed lower *ht*-selectivity than $\sim\sim mM^-$ and unreacted monomer remained even at Al / Li = 5. The higher *ht*-selectivity of $\sim\sim rM^-$ than $\sim\sim mM^-$ was observed at Al / Li ≥ 10 where the polymers were obtained quantitatively. These results indicate that for the quantitative formation of highly *ht*-polymers is required the appropriate Al/Li ratio against the feed ratio [M] / [I].

A similar phenomenon was observed in the experiments in which monomer concentration was varied. Table 1-III summarizes the results of the EMA polymerization carried out under various monomer concentrations, and Figure 1-VI shows the relationship between the monomer concentration and *ht*-selectivities of $\sim\sim rM^-$ and

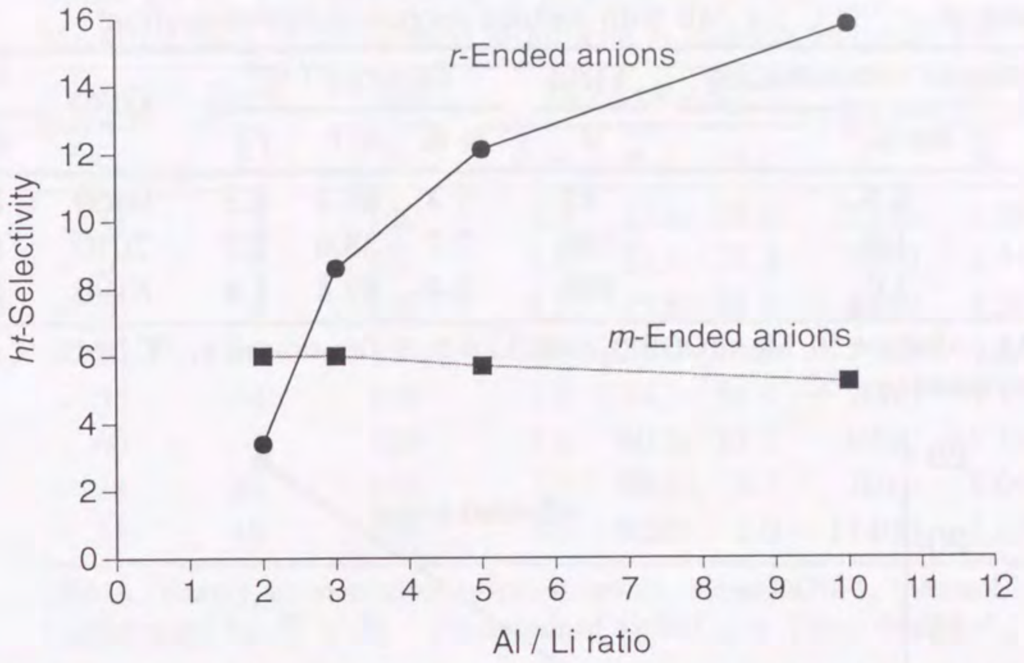


Figure 1-IV. Relationship between Al / Li ratio and *ht*-selectivities of *m*-ended and *r*-ended anions in EMA polymerizations at M / I = 50.

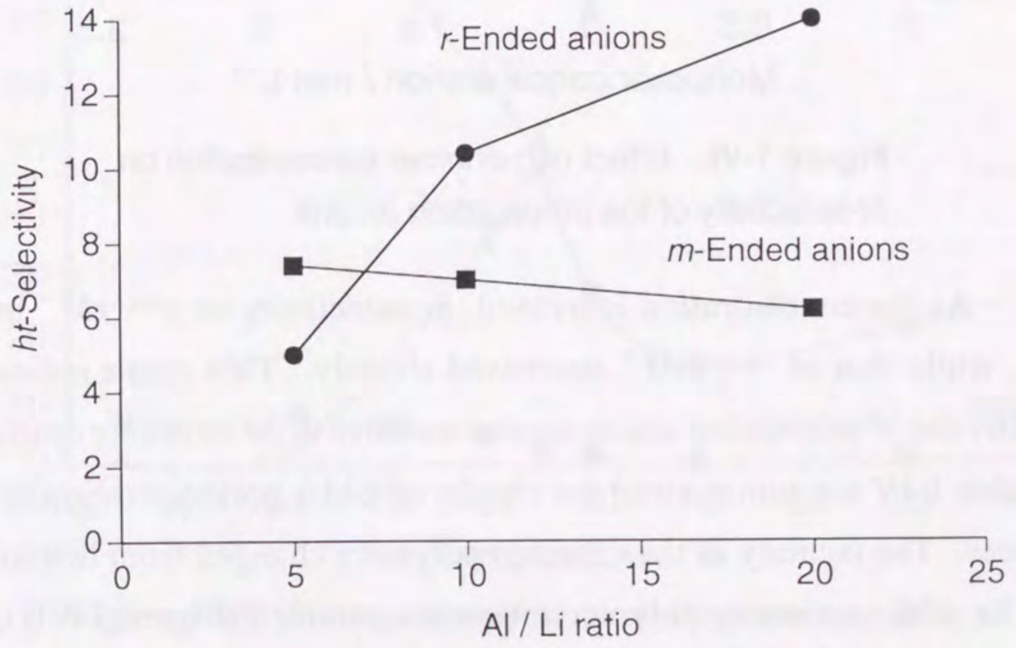


Figure 1-V. Relationship between Al / Li ratio and *ht*-selectivities of *m*-ended and *r*-ended anions in EMA polymerizations at M / I = 200.

Table 1-III. Polymerization of EMA with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at – 78° C for 24h with various monomer concentration[a]

Monomer concentration mol L^{-1}	Yield %	Tacticity / %[b]			$\bar{M}_n$[c]	$\bar{M}_w / \bar{M}_n$[c]
		m m	*m r*	*r r*		
0.5	83	7.4	86.3	6.3	9460	1.15
1.0	100	7.7	88.6	3.7	7010	1.07
2.0	100	8.4	89.8	1.8	8190	1.15

a EMA / *t*-BuLi = 50, MeAl(ODBP)$_2$ / *t*-BuLi = 5. b Determined by ^{13}C NMR.
c Determined by SEC.

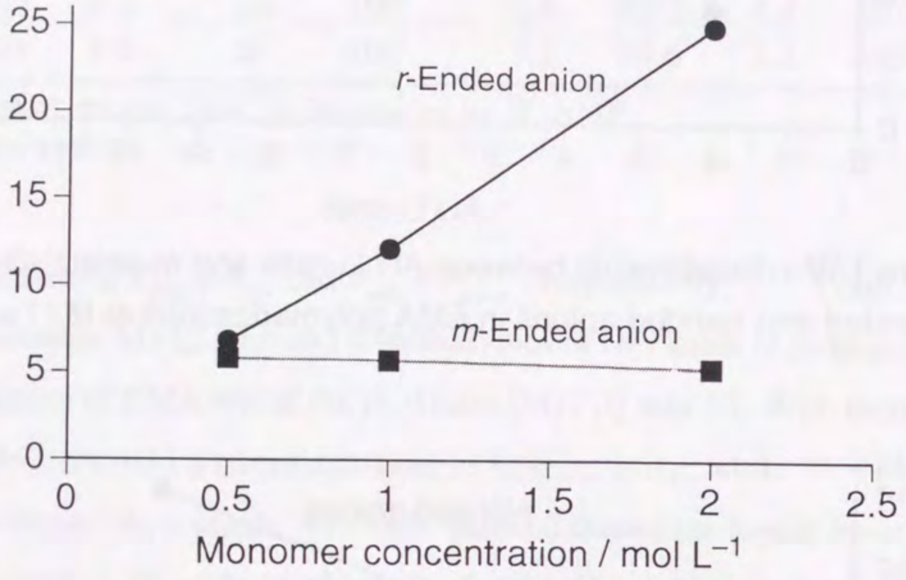


Figure 1-VI. Effect of monomer concentration on *ht*-selectivity of the propagating anions.

$\sim\sim mM^{-}$. As the concentration increased, *ht*-selectivity of $\sim\sim rM^{-}$ increased evidently, while that of $\sim\sim mM^{-}$ decreased slightly. This result indicates that stereoselectivities of propagating anions are also sensitive to the monomer concentration.

In Table 1-IV are summarized the results of EMA polymerization at various temperatures. The tacticity of the obtained polymers changed from heterotactic to syndiotactic with increasing polymerization temperature (Figure 1-VII). In the temperature range from –55°C to 0°C, predominantly *st*-poly(EMA)s were formed. The syndiotacticity was the highest at –40°C (*rr* = 84.1%).

The effect of permittivity in polymerization system on the stereoselectivities of

Table 1-IV. Polymerization of EMA with *t*-BuLi / MeAl(ODBP)$_2$ (1/5mol/mol) in toluene at various temperature[a]

Temp. ° C	Time h	Yield %	Tacticity / %[b]			$\bar{M}_n$[c]	$\bar{M}_w / \bar{M}_n$[c]
			m m	*m r*	*r r*		
0[d]	5	100	2.0	30.0	68.0	7730	1.59
– 20[d]	5	100	1.1	21.6	77.3	7690	1.54
– 40	4	100	0.1	15.8	84.1	8460	1.24
– 50	4	100	1.1	27.0	71.9	7550	1.18
– 55	4	100	2.5	46.5	51.0	7000	1.11
– 60	4	100	4.4	60.5	35.1	6950	1.14
– 78	24	100	7.7	88.6	3.7	7010	1.07
– 95	48	100	7.0	92.0	1.0	11100	1.07

a EMA 10mmol, toluene 10ml, *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol.
b Determined by ^{13}C NMR. c Determined by SEC. d Taken from Ref 1.

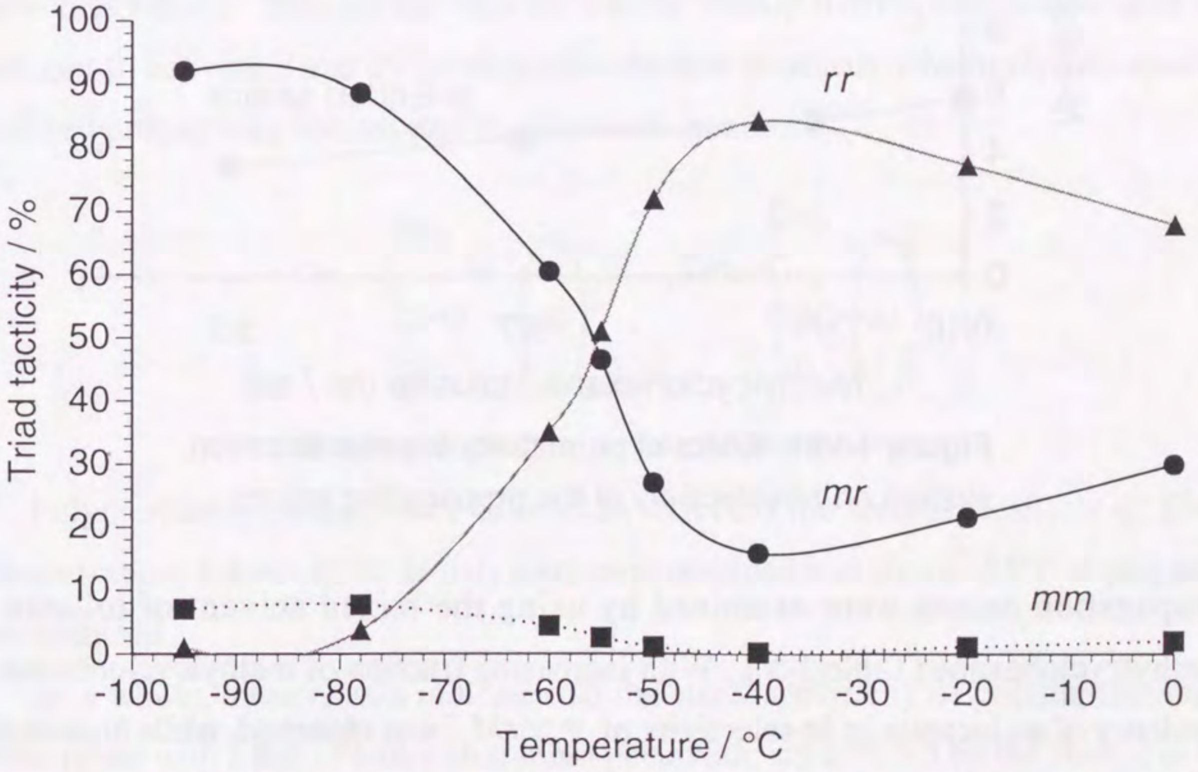


Figure 1-VII. Effect of temperature on the stereoregularity of the polymers formed in the polymerizations of EMA with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at Al/Li = 5.

Table 1-V. Polymerization of EMA with *t*-BuLi / MeAl(ODBP)$_2$ (1 / 5 mol / mol) in mixed solvent of toluene and Me *c*-Hex at – 78° C for 24h[a]

Methylcyclohexane / Toluene	Yield %	Tacticity / %[b] *m m*	*m r*	*r r*	$\bar{M}_n$[c]	$\bar{M}_w$[c] / $\bar{M}_n$
0 /10	100	7.7	88.6	3.7	5680	1.08
1 / 9	98	8.6	87.3	4.1	6790	1.14
3 / 7	97	6.9	86.8	3.6	7380	1.14
5 / 5	98	11.8	85.4	2.8	8010	1.14

a EMA 10mmol, *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol, solvent 10ml.
b Determined by ^{13}C NMR. c Determined by SEC.

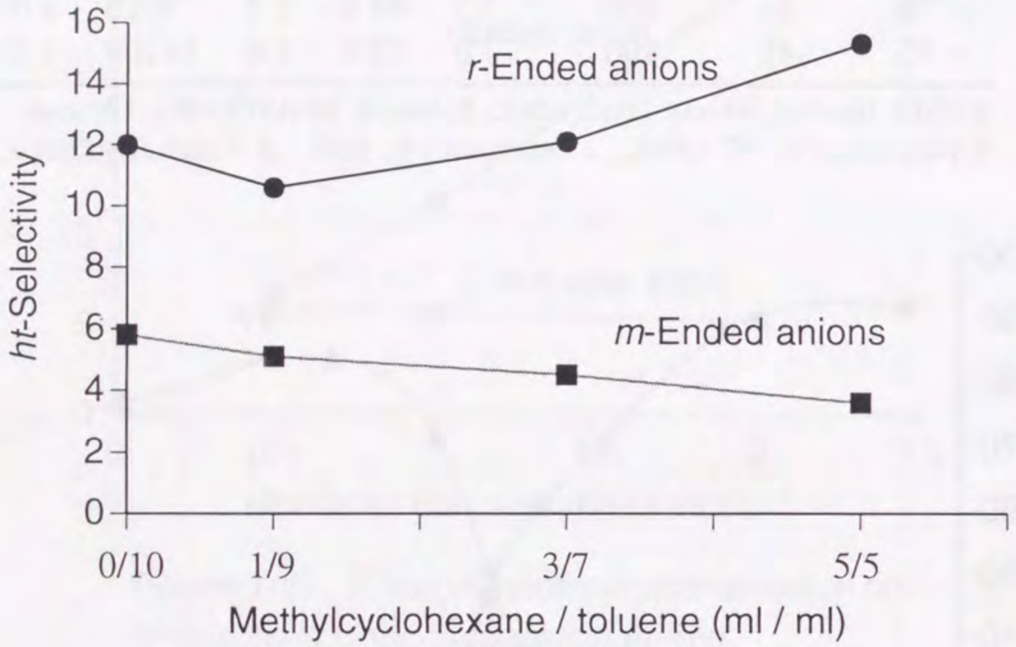


Figure 1-VIII Effect of permittivity in polymerization system on *ht*-selectivity of the propagating anions.

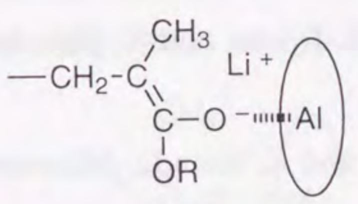
propagation anions were examined by using the mixed solvent of toluene and methylcyclohexane (Table 1-V). With increasing fraction of methylcyclohexane, the tendency of an increase in *ht*-selectivity of $\sim\sim rM^{-}$ was observed, while *ht*-selectivity of $\sim\sim mM^{-}$ decreased slightly (1-VIII). The result suggests that a decrease in permittivity of solvent makes the relative Lewis acidity of MeAl(ODBP)$_2$ stronger, and as a result the stereoselectivities of propagating anions behave as if Lewis acidity of MeAl(ODBP)$_2$ itself increases (*cf.* Chapter 2).

Conclusion

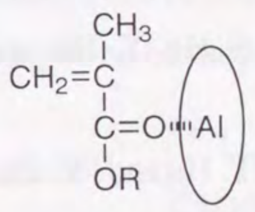
The polymerizations of methacrylates with *t*-BuLi / MeAl(ODBP)$_2$ was examined. Monomer structure affected evidently the stereospecificity in this polymerization system; primary and secondary alkyl methacrylates gave *ht*-polymers, while tertiary alkyl methacrylates gave *st*-polymers. In particular, at –95°C EMA gave the polymer with *mr* content of 92.0%.

The living nature was confirmed by a linear dependence of $\bar{M}_n$ on conversion and a monomer-repeated-addition experiment in EMA polymerizations.

The polymerization of EMA with *t*-BuLi / MeAl(ODBP)$_2$ (Al/Li = 1) gave *st*-polymer with low yield, suggesting that MeAl(ODBP)$_2$ coordinates with the propagating anion to stabilize it and the stabilized anion exhibits *st*-specificity. For the quantitative formation of highly *ht*-polymers was required MeAl(ODBP)$_2$ at least twice as much as *t*-BuLi. This implies that the excess MeAl(ODBP)$_2$ coordinates with the monomer to activate it and the propagation reaction proceeds selectively between the stabilized propagating species and the activated monomers.



Stabilized anion



Activated monomer

Polymerization temperature drastically affected the stereospecificity of EMA polymerization; below –60°C *ht*-polymers were obtained and above –55°C *st*-polymers were obtained.

As a whole, these results indicate that the stereospecificity of polymerization of methacrylate with *t*-BuLi / bulky aluminum phenoxide are affected by the change in the polymerization conditions, markedly such as steric factors and polymerization temperature and sufficiently such as Al/Li and [M]/[I] ratios. In the next Chapter are examined the effects of structure of bulky aluminum phenoxides on the stereospecificity.

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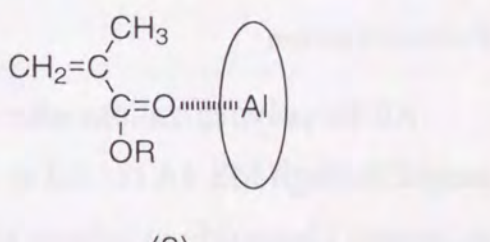
Chapter 2

Stereospecific Polymerization of Methacrylates with Bulky Aluminum Phenoxide

Introduction

In heterotactic (*ht*-) polymerization of methacrylates with *t*-BuLi / bis(2,6-di-*t*-butylphenoxy)methylaluminum [MeAl(ODBP)$_2$], the existence of an excess amount of MeAl(ODBP)$_2$ over *t*-BuLi is essential for the formation of the *ht*-sequence (*cf.* Chapter 1). In fact, at the ratio of Al / Li = 1, where most of the aluminum phenoxide might coordinate with the propagating species, a syndiotactic (*st*-) polymer forms in low yields[1]. The result suggests that the propagating species is stabilized by the coordination with the bulky aluminum phenoxide, becomes less reactive, and favors *r*-addition with the monomer free from the coordination by the aluminum phenoxide. At higher Al / Li ratios, the excess MeAl(ODBP)$_2$ may activate the monomer through coordination, and the less reactive propagating species preferentially add the activated monomer. In this process, the steric interaction between the sterically crowded active-end (1) and the bulky monomer–MeAl(ODBP)$_2$ complex (2) might be an important factor for the

(1)



(2)

ht-propagation. Thus MeAl(ODBP)$_2$ in this polymerization plays roles of the stabilization of the propagating species and of the activation of the monomer, thereby providing not only livingness but also the unique stereospecificity. In this Chapter, polymerizations of MMA and EMA with *t*-BuLi and several aluminum phenoxides are written and the effects of the structure of the aluminum compounds on the stereocontrol in the polymerization are discussed based on the stereochemical sequence analysis of the obtained polymers.[2]

Experimental

The experimental procedures except for these described below are the same as those described in detail in Chapter 1.

Materials

2,6-Di-*t*-butyl-4-methylphenol, 2,4,6-tri-*t*-butylphenol, and 4-bromo-2,6-di-*t*-butylphenol were recrystallized from heptane, dried over MS 4A, and used as toluene solutions.

Triethylaluminum and triisobutylaluminum (Nippon Aluminum Alkyls) were used as toluene solutions.

Preparation of alkylaluminum bisphenoxide[3]

A solution of substituted phenol (2,6-di-*t*-butyl-4-methylphenol, 2,4,6-tri-*t*-butylphenol, or 4-bromo-2,6-di-*t*-butylphenol) in toluene (2 equiv.) was added slowly to a toluene solution of trialkylaluminum (1 equiv.) at 0°C. The resulting mixture was stirred at room temperature for 20h and used for the polymerization reaction without further purification.

Polymerization

All the polymerizations were carried out in a glass ampoule filled with dried nitrogen passed through MS 4A cooled at –78°C. A heptane solution of *t*-BuLi was added to an aluminum phenoxide in toluene at –78°C. The polymerization reaction was initiated by adding the monomer slowly to this mixture at –78°C. The reaction was terminated by adding methanol containing HCl at the polymerization temperature. The reaction mixture was concentrated to dryness under reduced pressure, and the residue was dissolved in benzene. Insoluble materials were removed by centrifugation, and the polymer was recovered from the solution by freeze-drying and dried under vacuum.

Measurements

Tacticities of PMMAs were determined from α-methyl hydrogen signals in ^{1}H NMR spectra measured in $CDCl_3$ at 55°C on a JEOL JNM GX270 spectrometer operated at 270MHz. Tacticities of poly(EMA)s were determined from carbonyl carbon signals in ^{13}C NMR spectra measured in nitrobenzene-d_5 at 110°C or $CDCl_3$ at 55°C on a Varian Unity Inova 500 spectrometer operated at 125MHz. Molecular weight and its distribution of the polymers were determined by size exclusion chromatography (SEC) using a JASCO 880-PU chromatograph equipped with Shodex SEC columns KF-80M (30cm x 0.8cm) and KF-802.5 (30cm x 0.8cm) using tetrahydrofuran as an eluent at 40°C. The SEC chromatogram was calibrated against standard polystyrene samples.

Results

Polymerization with Combinations of t-BuLi and Several Methylaluminum Bisphenoxides

To examine the effects of the structure of aluminum phenoxides on the polymerization, MMA and EMA were polymerized in toluene at –78°C with *t*-BuLi in the presence of several methylaluminum bisphenoxides having *t*-butyl groups at 2- and 6-positions of the phenoxy groups.

When polymerizations of MMA and EMA were carried out with *t*-BuLi / $MeAl(ODBP)_2$, *ht*-polymers with narrow molecular weight distribution (MWD) were obtained (runs 1 and 5 in Table 2-I). When methylaluminum bisphenoxides with *p*-substituents such as *p*-methyl, *p*-*t*-butyl, and *p*-bromo groups were employed in the polymerization of MMA, *ht*-rich PMMAs with narrow MWD were also obtained almost quantitatively (runs 2, 3, and 4). The *ht*-triad (*mr*) contents were lower than that for the polymer obtained with $MeAl(ODBP)_2$. The decrease in *mr* content in runs 2 (*p*-methyl) and 3 (*p*-*t*-butyl) was accompanied by the increase in *mm* and *rr* contents. In run 4 (*p*-bromo), however, the *mm* content increased but the *rr* content decreased. The results indicate that these *p*-substituents of the aluminum bisphenoxide affect the stereospecificity of the polymerization in different ways.

Table 2-I. Polymerization of MMA and EMA with *t*-BuLi / methylaluminum bisphenoxide (1/3 mol/mol) in toluene at – 78° C for 24h[a]

Run	Monomer	*p*-Substituent	Yield %	Tacticity / %[b] *m m*	*m r*	*r r*	$\bar{M}_n$[c]	$\bar{M}_w / \bar{M}_n$[c]
1[d]	MMA	H	100	11.6	67.8	20.6	11640	1.14
2	MMA	Me	90	13.7	59.1	27.3	6010	1.27
3	MMA	*t*-Bu	99	14.7	60.9	24.4	6300	1.12
4	MMA	Br	100	19.4	65.1	15.5	6410	1.10
5	EMA	H	100	7.3	87.6	5.1	7510	1.13
6	EMA	Me	97	6.9	67.5	25.6	6040	1.12
7	EMA	*t*-Bu	100	6.2	84.3	9.5	8170	1.10
8	EMA	Br	100	13.2	82.7	4.1	6360	1.08

a Monomer 10mmol, toluene 10ml, *t*-BuLi 0.2mmol, methylaluminum bisphenoxide 0.6mmol. b Determined by ^1H NMR or ^{13}C NMR. c Determined by SEC.
d $MeAl(ODBP)_2$ 1.0mmol.

The effect of *p*-substituent on tacticity is more remarkable in the case of the polymerization of EMA. All the polymers obtained were heterotactic and had narrow MWDs (runs 5 - 8). The unsubstituted derivative, $MeAl(ODBP)_2$, gave the highest *mr* content (run 5) as in the case of the polymerization of MMA. It is evident that in the cases of *p*-methyl (run 6) and *p*-*t*-butyl (run 7) derivatives, the decrease in *mr* content was accompanied by the increase in *rr* content. Contrastingly, the introduction of *p*-bromo group (run 8) gave rise to the increase in *mm* content while *rr* content being almost unchanged from the case of $MeAl(ODBP)_2$ (run 5). Since the *p*-methyl and *p*-bromo groups are sterically almost identical, the results indicate that the main factor that governs the change of stereospecificity is not the steric but electronic features of the aluminum bisphenoxides. The most probable cause is the change in their Lewis acidity; the presence of the electron-withdrawing bromo group at *para* position of the aluminum phenoxide may increase the Lewis acidity of the aluminum center while the electron-donating alkyl groups may decrease it. Therefore, the structural change even at the position away from the aluminum center affected coordination ability of the aluminum compounds to the propagating chain-ends and thus altered the stereospecificity in the polymerization.

As described in the General Introduction, $\sim\!\sim\!\sim rM^-$ and $\sim\!\sim\!\sim mM^-$ anions coexist in the *ht*-polymerization, which should have opposite stereospecificity, *i.e.*, *m*-addition and *r*-addition, respectively. Thus it is reasonable to expect that the effect of the Lewis acidity of the aluminum phenoxides on stereospecificity differs in these two types of propagating anions. Stereochemical sequence in the main chain of *ht*-poly(EMA) prepared with *t*-BuLi/$MeAl(ODBP)_2$ almost obeys first-order Markovian statistics (*cf.* Chapter 6).[4,5] The conditional probability of *m*-addition by *r*-ended anion ($\sim\!\sim\!\sim rM^-$), $P_{r/m}$, and that of *r*-addition by *m*-ended anion ($\sim\!\sim\!\sim mM^-$), $P_{m/r}$, were determined from the triad values for the poly(EMA)s obtained with several aluminum phenoxides as shown in Table 2-II. In the polymerization with $MeAl(ODBP)_2$ (*p*-substituent = H), $P_{r/m}$ was greater than $P_{m/r}$, indicating the higher *ht*-selectivity of $\sim\!\sim\!\sim rM^-$ than that of $\sim\!\sim\!\sim mM^-$. In the polymerization with aluminum phenoxide having electron-donating

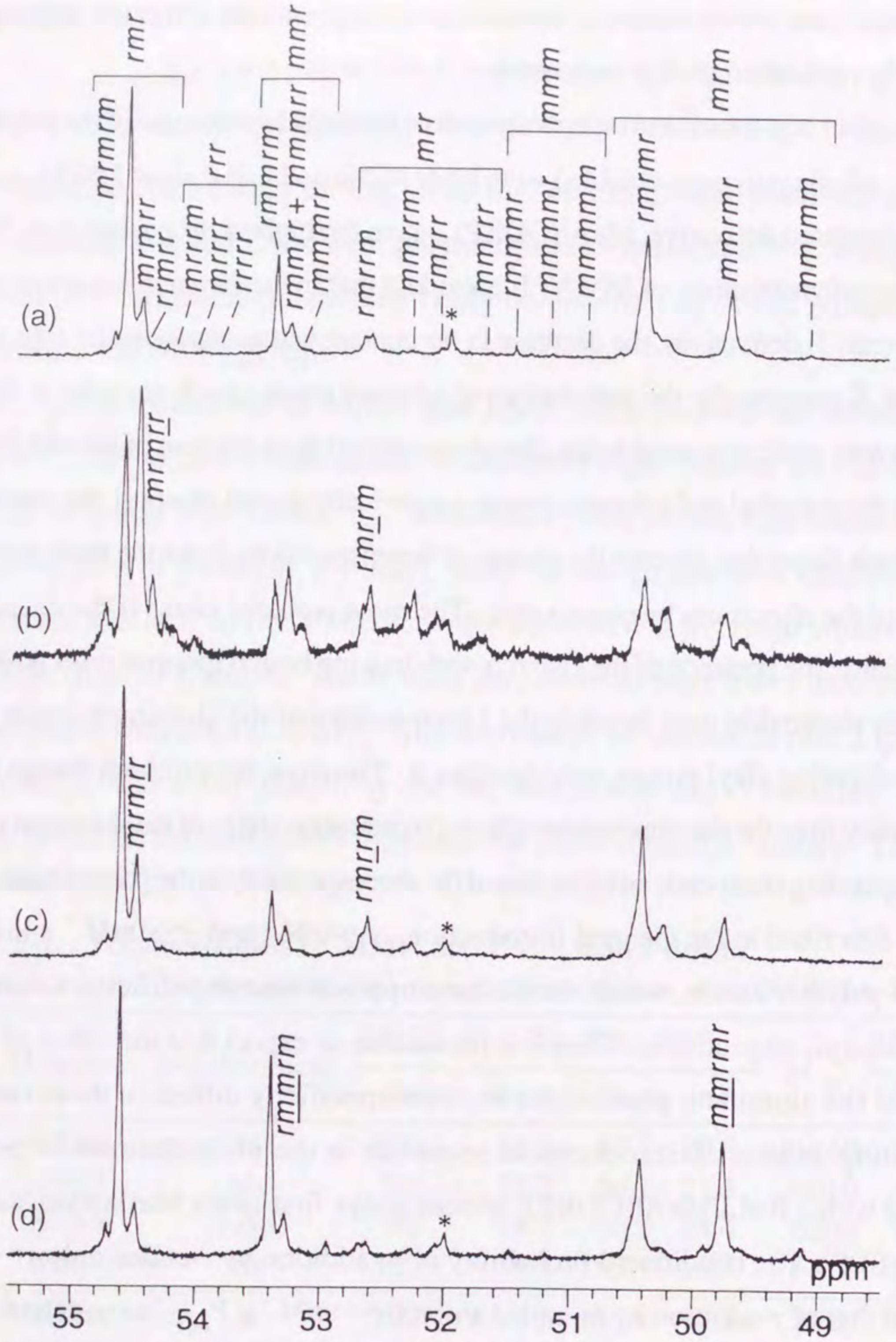


Figure 2-I. ^{13}C NMR spectra of methylene carbon in *ht*-poly(EMA)s prepared with *t*-BuLi / methylaluminum bisphenoxide; *p*-substituent (a) –H, (b) –Me, (c) –*t*-Bu, and (d) –Br.
* A signal due to α2 unit (cf. Chapter 6).

Table 2-II. Parameters of first-order and second-order Markovian statistics in *ht*-polymerization of EMA

Run[a]	*p*-Substituent	First-order parameter				Second-order parameter			
		$P_{m/r}$	$P_{r/m}$	$\frac{P_{m/r}}{P_{m/m}}$	$\frac{P_{r/m}}{P_{r/r}}$	$P_{mm/r}$	$P_{rm/r}$	$P_{mr/m}$	$P_{rr/m}$
5	H	0.86	0.90	$6._{0}$	$8._{6}$	0.86	0.91	0.90	0.91
6	Me	0.83	0.57	$4._{9}$	$1._{3}$	0.90	0.88	0.73	0.70
7	*t*-Bu	0.87	0.82	$6._{8}$	$4._{4}$	0.90	0.89	0.85	0.93
8	Br	0.76	0.91	$3._{1}$	$10._{1}$	0.90	0.73	0.94	(1.00)

a See Table 1-I. b Due to low content of *rrr* tetrad, the value could not be estimated in sufficient accuracy.

p-methyl (run 6) or *p*-*t*-butyl group (run7), $P_{r/m}$ decreased greatly and became smaller than $P_{m/r}$. On the other hand, in the case of *p*-bromo derivative (run 8), $P_{m/r}$ decreased drastically while $P_{r/m}$ was the same as that with MeAl(ODBP)$_2$. The ratios, $P_{m/r}$ / $P_{m/m}$ and $P_{r/m}$ / $P_{r/r}$, are shown in the table as the measure of the *ht*-selectivity of ~~~mM^- and ~~~rM^-, respectively, which express the effects of the *p*-substituent more evidently.

Table 2-II also includes second-order Markovian parameters estimated from tetrad fractions determined from methylene carbon NMR signals, which show hexad-level splittings as illustrated in Figure 2-I. In most cases except run 8, the difference in the second diad from the terminal (antepenultimate diad) of ~~~mM^- affected the parameters only slightly, *i.e.* $P_{mm/r} \doteqdot P_{rm/r}$. This seems to mean that the first-order Markovian treatment is adequate. However, the difference between $P_{mm/r}$ and $P_{rm/r}$ was quite evident for the case of *p*-bromo derivative (run 8). This implies that the antepenultimate diad configuration affects the stereoselectivity of ~~~mM^-, probably due to stronger penultimate coordination of *p*-bromo derivative.

The stereochemical defect in the *ht*-poly(EMA)s is either —*mm*— or —*rr*— sequence. In the ^{13}C NMR spectra of poly(EMA)s obtained with *p*-methyl derivative (Figure 2-Ib), *mrmrr* hexad peak was evidently strong, while in the spectrum of *ht*-poly(EMA) obtained with *p*-bromo derivative, the main defect was —*mm*— as in *rmmrm* and *mmrmr* hexads (Figure 2-Id). These reflect the lower *ht*-selectivity of ~~~rM^- anion formed with *p*-methyl derivative and lower *ht*-selectivity of ~~~mM^-

anion formed with *p*-bromo derivative.

The effects of *p*-substituent of the aluminum phenoxides were also observed on the stereoregularity at the initiating chain-ends of the poly(EMA)s. The ^{13}C NMR analysis of *ht*-poly(EMA) for the stereoregularity at and near the initiating chain-end provides the information on the stereospecificity of the dimer and trimer anions as described in Chapter 3.[5] Figure 2-II shows the ^{13}C NMR spectra of methyl carbons of *t*-butyl group at the initiating chain-end of the *ht*-poly(EMA)s obtained with several aluminum phenoxides. The methyl carbon resonances show splittings due to triad tacticity at the initiating chain-end as indicated in Figure 2-II.

The relative intensities of four peaks provides the *r* / *m* ratio of the first diad, as determined from the ratio [*r r*+ *r m*] / [*mm* + *mr*], and the *m* / *r* ratio at the second diad following the first *r* diad, as estimated from the triad ratio of *r m* / *r r*. The results of the analysis are shown in Table 2-III. In all the cases, the first diads were predominantly *r*. However, the second diad after the first *r*-diad strongly depended on the kind of aluminum phenoxide used; as compared with the case of MeAl(ODBP)$_2$ (*p*-substituent = H), *r m* / *r r* increased for the case of *p*-bromo derivative and decreased for the cases of *p*-methyl and *p*-*t*-butyl derivatives. The results are consistent with those obtained from the main-chain sequence analysis; that is, *ht*-selectivity of $\sim\!\sim\!\sim rM^-$ anion as represented by $P_{r/m}$ / $P_{r/r}$ is in the order of *p*-Br > *p*-H > *p*-*t*-Bu > *p*-Me. A similar analysis for $\sim\!\sim\!\sim mM^-$ anion was difficult due to the low content of *mm* triad at the initiating chain-end.

Table 2-III. Stereoselectivities of dimer and trimer anions in *ht*-EMA polymerization estimated from the first (*r* / *m*) and the second diads (*rm* / *rr*) at the initiating chain-end

Run[a]	*p*-Substituent	First diad *r* / *m*	Second diad *rm* / *rr*
5	H	92 / 8	72 / 28
6	Me	93 / 7	46 / 54
7	*t*-Bu	85 /15	68 / 32
8	Br	91 / 9	85 / 15

a See Table 2-I.

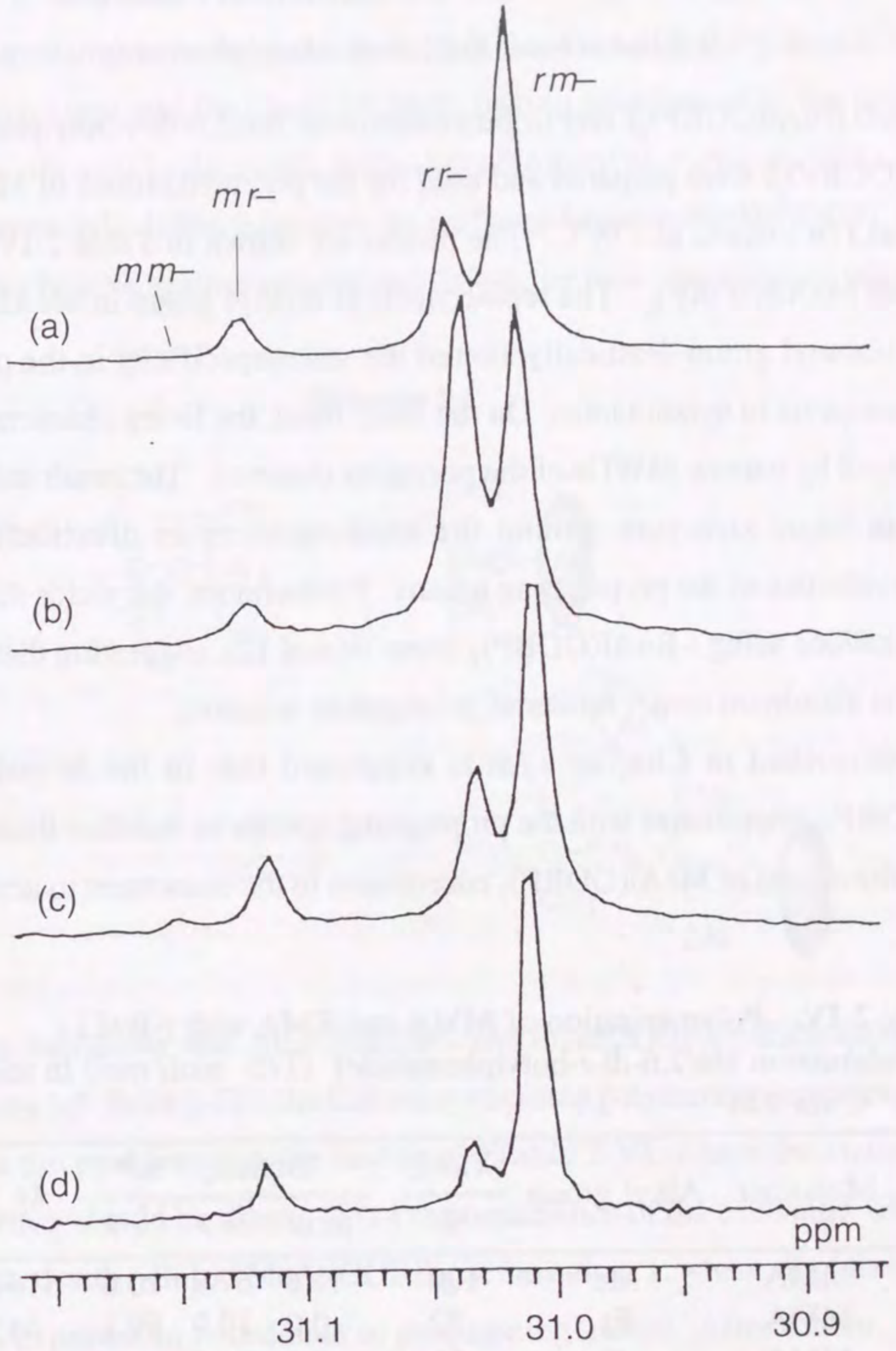


Figure 2-II. Expanded spectra of methyl carbon NMR signals of *t*-butyl group at the initiating chain-end of *ht*-poly(EMA)s obtained with four different methyl-aluminum phenoxides: *p*-substituent (a) –H, (b) –Me, (c) –*t*-Bu, and (d) –Br.

Polymerization with Combinations of t-BuLi and Alkylaluminum Bis(2,6-di-t-butylphenoxide)

Ethyl- [EtAl(ODBP)$_2$] and isobutylaluminum bis(2,6-di-*t*-butylphenoxide)s [*i*-BuAl(ODBP)$_2$] were prepared and used for the polymerizations of MMA and EMA with *t*-BuLi in toluene at –78°C. The results are shown in Table 2-IV together with those with MeAl(ODBP)$_2$. The replacement of methyl group in MeAl(ODBP)$_2$ with ethyl or isobutyl group drastically altered the stereospecificity in the polymerization from heterotactic to syndiotactic. On the other hand, the living character was retained as evidenced by narrow MWDs of the polymers obtained. The result indicates that the change in steric structure around the aluminum center drastically affects the stereospecificities of the propagating anions. Furthermore, the yields decreased in the polymerizations using *i*-BuAl(ODBP)$_2$ (runs 10 and 12), suggesting that the bulkiness around the aluminum center hindered propagation reaction.

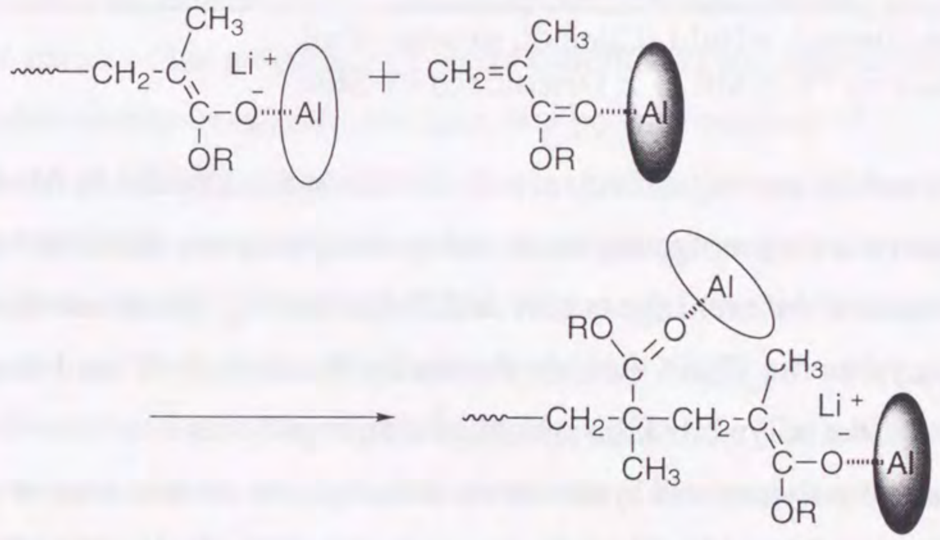
As described in Chapter 1, it is suggested that in the *ht*-polymerization, MeAl(ODBP)$_2$ coordinates with the propagating species to stabilize them [*cf.* structure (1)], and the excess of MeAl(ODBP)$_2$ coordinates to the monomers to activate them [*cf.* structure (2)]. In the process that the monomer coordinated with MeAl(ODBP)$_2$ reacts with the propagating species, there is a possibility that MeAl(ODBP)$_2$ stays at the newly formed chain-end unit and the MeAl(ODBP)$_2$ having coordinated to the propagating end is kept coordinated to the newly formed penultimate unit after the addition of the monomer (Scheme 2-I). If this is the case, an exchange between MeAl(ODBP)$_2$ molecule coordinating to the propagating species and that to the monomers should take place.

Table 2-IV. Polymerization of MMA and EMA with *t*-BuLi / alkylaluminum bis(2,6-di-*t*-butylphenoxide) (1/5 mol/mol) in toluene at – 78° C for 24h[a]

Run	Monomer	Alkyl group	Yield %	Tacticity / %[b] *m m*	*m r*	*r r*	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	MMA	Me	100	11.6	67.8	20.6	11640	1.14
9	MMA	Et	82	0.0	10.9	89.1	4450	1.10
10	MMA	*i*-Bu	20	0.0	16.2	83.8	1920	1.38
5	EMA	Me	100	7.7	88.6	3.7	7010	1.07
11	EMA	Et	100	0.0	8.1	91.9	6490	1.09
12	EMA	*i*-Bu	30	0.3	17.5	82.2	4990	1.14

a Monomer 10mmol, alkylaluminum bis(2,6-di-*t*-butylphenoxide) 1.0mmol, toluene 10ml, *t*-BuLi 0.2mmol. b Determined by ^{1}H NMR or ^{13}C NMR.
c Determined by SEC.

Scheme 2-I



Based on the finding that MeAl(ODBP)$_2$ and EtAl(ODBP)$_2$ exhibit quite different stereospecificity (*cf.* Table 2-IV), the following two-step polymerizations were examined to investigate the possibility of the exchange (Table 2-V), where the tacticity of the obtained polymer should be diagnostic of the occurrence of the exchange. First, EMA was polymerized with *t*-BuLi / MeAl(ODBP)$_2$ at the ratio = 1, where all of the aluminum compound is expected to coordinate to propagating anions. After 1 hour, two times EtAl(ODBP)$_2$ as much as *t*-BuLi was added to the polymerization mixture and the reaction was continued for further 23 hours. The yield for the first 1 hour was very low (run 13) because of the absence of activated monomers, and thus most of the polymer obtained in this two-step polymerization (run 14) should form after the second aluminum phenoxide, EtAl(ODBP)$_2$, was added. If the exchange of the aluminum compounds

Table 2-V. Polymerization of EMA with *t*-BuLi and two kinds of aluminum phenoxide in toluene at – 78° C for 24h[a]

Run	Aluminum phenoxide	Al / Li	Time / h	Yield / %	Tacticity / %[b]			$\bar{M}_n$[c]	$\bar{M}_w / \bar{M}_n$[c]
					m m	*m r*	*r r*		
13	$MeAl(ODBP)_2$	1	1	4	-	-	-	-	-
14	$MeAl(ODBP)_2$ $EtAl(ODBP)_2$	1 +2	1 +23	80	0.8	25.7	73.5	6220	1.16
15	$MeAl(ODBP)_2$ $MeAl(ODBP)_2$	1 +2	1 +23	100	7.0	74.6	18.4	7340	1.14

a Monomer 10mmol, *t*-BuLi 0.2mmol, toluene 10ml.
b Determined by ^{13}C NMR. c Determined by SEC.

does not occur and the stereospecificity of polymerization is controlled by $MeAl(ODBP)_2$ which coordinates to the propagating anion, the resulting polymer should be heterotactic. On the other hand, if the exchange occurs and $EtAl(ODBP)_2$, which coordinates to the monomer, stays at the chain end as shown in Scheme 2-IV and controls the stereospecificity, the polymerization should give an *st*-polymer.

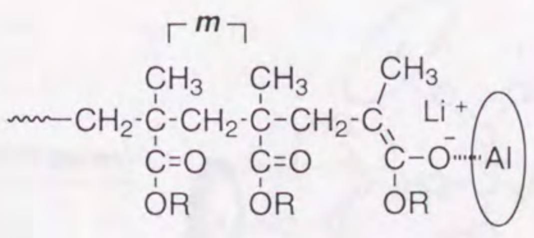
The obtained polymer was syndiotactic, although the *st*-triad content was lower than that of the polymer obtained by the polymerization with *t*-BuLi / $EtAl(ODBP)_2$ (*cf.* Table 2-IV, run 11). This results suggest the occurrence of the exchange of the aluminum compounds during the propagation process. When $MeAl(ODBP)_2$ was added in the second stage, the resulting polymer was heterotactic (run 15), though the heterotacticity was slightly lower than that of the polymer obtained by the usual polymerization (run 5 in Table 2-I).

Discussion

When the polymerization with *t*-BuLi / $MeAl(ODBP)_2$ is carried out at the Al/Li ratio = 1, an *st*-polymer forms in a low yield[1,4]. The result suggests the formation of *st*-specific species with low activity, which may be stabilized through the coordination by the bulky aluminum phenoxide as suggested by Ballard *et al.* for the polymerization of MMA with *t*-BuLi / *i*-$Bu_2Al(ODBP)$.[6] If all the $MeAl(ODBP)_2$ coordinates to the propagating chain-end, there exists no excess $MeAl(ODBP)_2$ in the polymerization system. Under these conditions where most of the incoming monomers are free from the coordination by $MeAl(ODBP)_2$, the *st*-polymer is formed probably due to the intrinsic *st*-specific nature of the propagating species coordinated with $MeAl(ODBP)_2$ as in the cases of other aluminum-assisted methacrylate polymerizations[7-13].

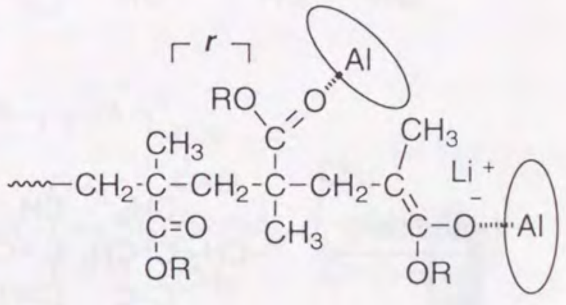
ht-Poly(EMA)s with narrow MWD are obtained in high yields at Al / Li 2, where excess $MeAl(ODBP)_2$ existing in the polymerization system may activate the monomer through coordination[14,15]. As depicted in Scheme 2-I, the less reactive propagating species, stabilized through the coordination by $MeAl(ODBP)_2$, should react preferentially with the activated monomer carrying the bulky $MeAl(ODBP)_2$. The mechanism implies the possibility that two aluminum phenoxides coordinate at the terminal and penultimate units.

In order to explain the different stereospecificity of ~~~mM^- and ~~~rM^- anions, it is assumed that the difference in the terminal diad configuration affects the stability of the coordination of the aluminum phenoxide to the penultimate unit. Based on this assumption, the structure models of the two types of propagating species are proposed



~~mM^-

(3)

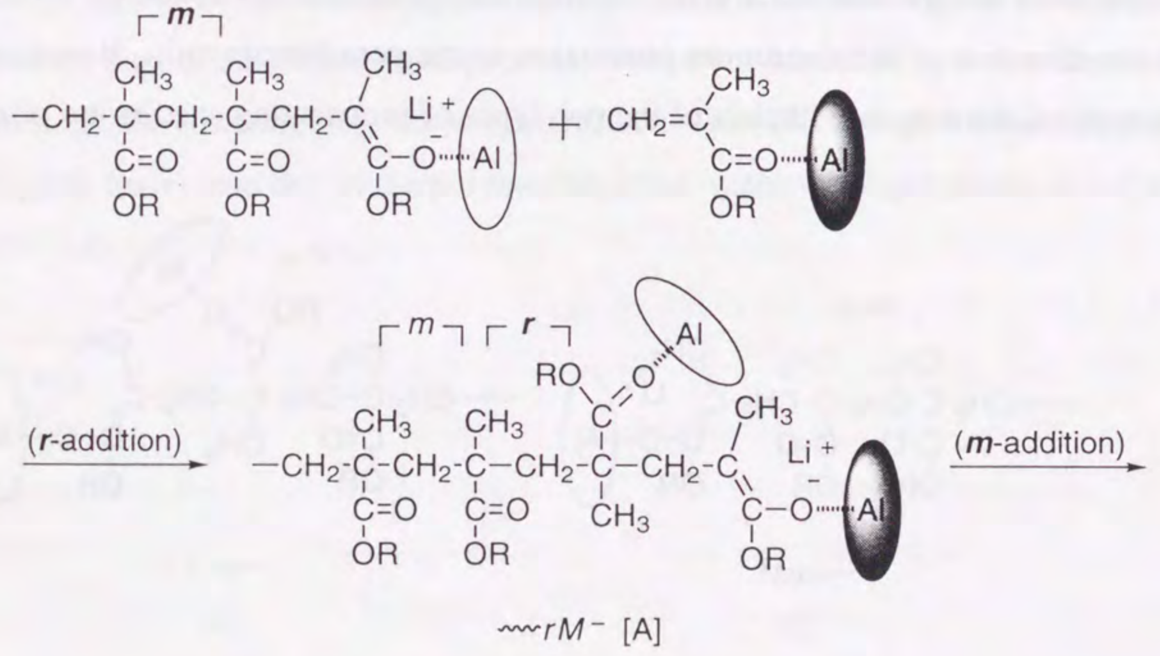


~~rM^-

(4)

as follows; $\sim\!\sim\!\sim mM^{-}$ anion coordinates one aluminum phenoxide at the terminal unit (3), and $\sim\!\sim\!\sim rM^{-}$ anion bears two phenoxides at the terminal unit and the penultimate ester group (4)[16]. The models explain the higher stability and higher stereospecificity of $\sim\!\sim\!\sim rM^{-}$ anion than $\sim\!\sim\!\sim mM^{-}$ anion.[5,16] The *r*-selectivity of $\sim\!\sim\!\sim mM^{-}$ anion seems consistent with *st*-specific nature of the species formed at *t*-BuLi / MeAl(ODBP)$_2$ = 1, which should carry one MeAl(ODBP)$_2$. The *m*-selectivity of $\sim\!\sim\!\sim rM^{-}$ anion can be explained as follows. When $\sim\!\sim\!\sim rM^{-}$ anion, bearing two bulky aluminum phenoxides, adds the monomer coordinated with the phenoxide, which can be regarded as a temporarily bulky monomer, the situation is similar to the polymerization of exceedingly bulky triarylmethyl methacrylates such as triphenylmethyl methacrylate, which undergoes in an *it*-specific manner regardless of polymerization conditions.[17] The result of two-step polymerization (run 14), where EtAl(ODBP)$_2$ was added to the polymerization mixture formed with *t*-BuLi / MeAl(ODBP)$_2$ = 1, suggests the exchange between the aluminum phenoxide coordinated to the propagating species and that to the monomer during the propagation. The exchange can occur through the mechanism shown in Scheme 2-I.

Scheme 2-II



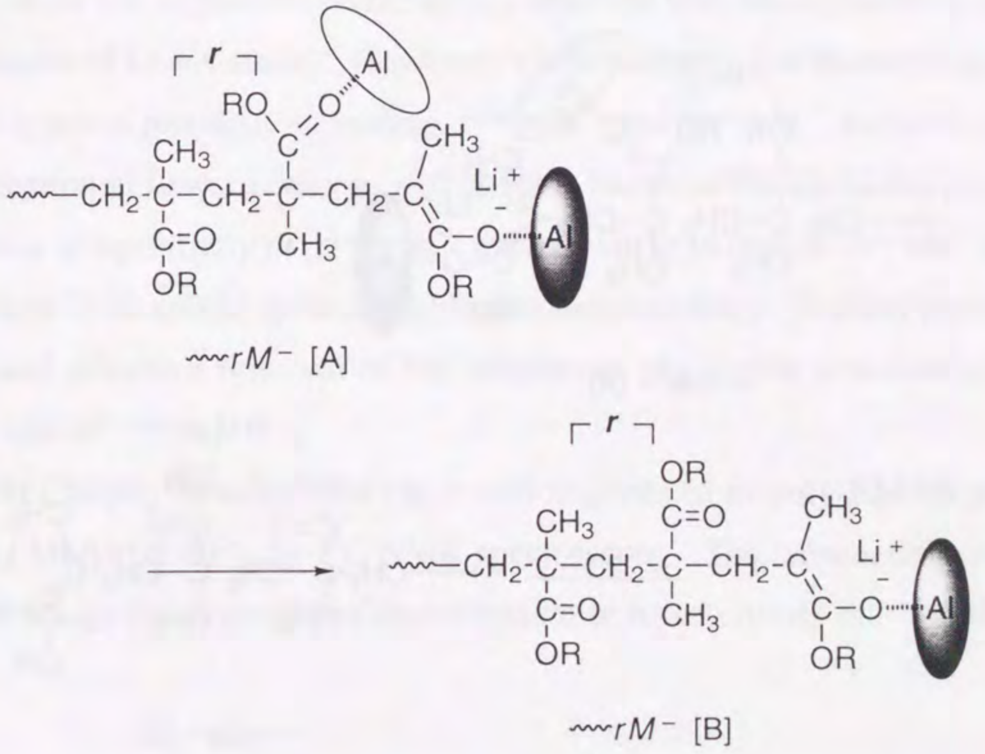
Starting from $\sim\!\sim\!\sim mM^{-}$ anion, which carries one aluminum phenoxide and favors *r*-addition, the addition of a monomer carrying MeAl(ODBP)$_2$ gives an intermediate species bearing two aluminum phenoxides, $\sim\!\sim\!\sim rM^{-}$ [A] (Scheme 2-II), which favors *m*-addition.

When the aluminum phenoxide of lower Lewis acidity such as *p*-methyl derivative is used, the coordination to the penultimate unit becomes weaker and the $\sim\!\sim\!\sim rM^{-}$ [A] tends to release the phenoxide at the penultimate unit and becomes the species having one aluminum phenoxide, $\sim\!\sim\!\sim rM^{-}$ [B] (Scheme 2-III). The released phenoxide may coordinate with the monomer, and be involved again in the process depicted in Scheme 2-I.

The structure of $\sim\!\sim\!\sim rM^{-}$ anion [B] is similar to $\sim\!\sim\!\sim mM^{-}$ anion and expected to exhibit *r*-selectivity. This explains the lower $P_{r/m}$ values for the polymerization with *p*-methyl and *p*-*t*-butyl derivatives (*cf.* Table 2-II, runs 6 and 7).

It is postulated that $\sim\!\sim\!\sim mM^{-}$ anion has one aluminum phenoxide. As depicted in Scheme 2-I, however, immediately after it is formed from $\sim\!\sim\!\sim rM^{-}$ anion, the aluminum

Scheme 2-III

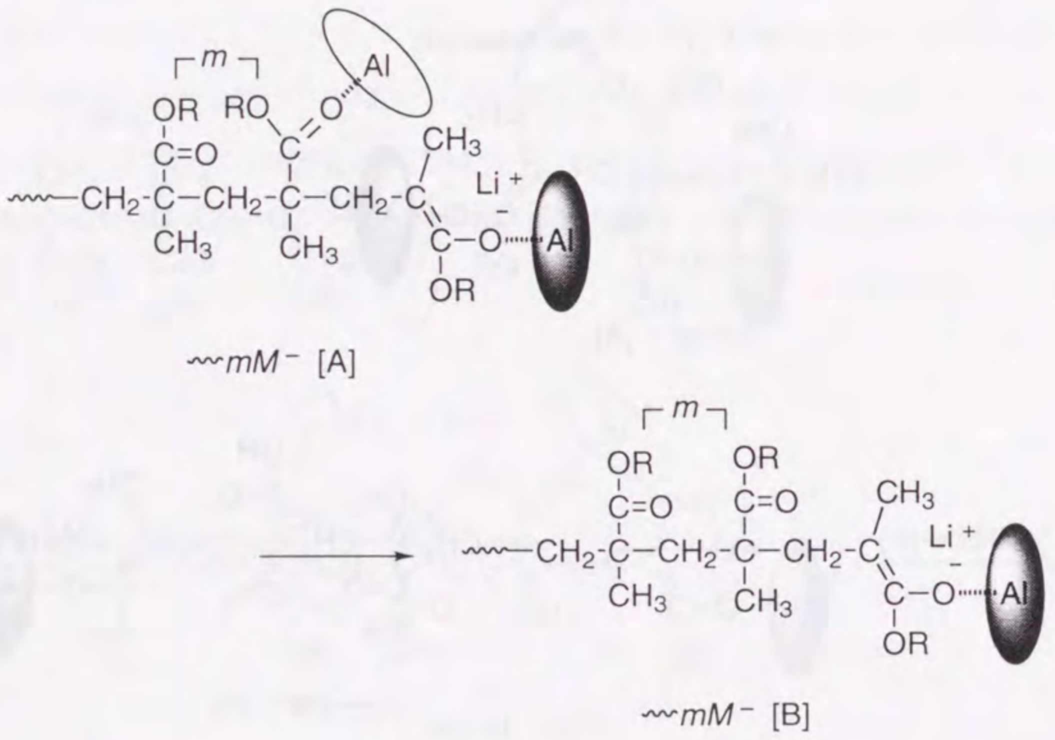


phenoxide having coordinated to the $\sim\sim rM^-$ anion may stay at the newly formed penultimate monomer unit to generate $\sim\sim mM^-$ [A] shown in Scheme 2-IV. The Lewis acidity of the aluminum phenoxide is again the key that determines whether the phenoxide coordinated the penultimate unit is released before or kept until the monomer addition takes place. In the case of $MeAl(ODBP)_2$ the phenoxide at the penultimate unit is expected to be removed easily to form $\sim\sim mM^-$ [B] as depicted in Scheme 2-IV, which exhibits *r*-selectivity to form *mr* sequence.

If an aluminum phenoxide with higher Lewis acidity such as *p*-bromo derivative is used, it tends to stay at the penultimate unit ($\sim\sim mM^-$ [A]) and makes the species *m*-selective as in the case of $\sim\sim rM^-$ [A] (*cf.* Scheme 2-II). Thus $P_{m/r}$ value for the polymerization with *p*-bromo derivative is smaller than other cases (*cf.* Table 2-II).

In the cases of $EtAl(ODBP)_2$ and *i*-$BuAl(ODBP)_2$, the coordination to the penultimate unit may be sterically unfavorable, leading to the formation of *st*-specific species like $\sim\sim rM^-$ [B] (Scheme 2-III).

Scheme 2-IV



Conclusion

The effects of the structure of bulky aluminum phenoxide on the stereospecificity of the polymerization of methacrylates with *t*-BuLi / bulky aluminum phenoxide was discussed. Bulky aluminum bisphenoxides, in which ethyl or isobutyl groups binds to aluminum atom instead of methyl group, give *st*-polymers. This result indicates that even the small change in the steric factor around the aluminum center affects markedly the stereospecificity of this polymerization system.

Para-substituted derivatives $[MeAl(OAr)_2]$ of $MeAl(ODBP)_2$ gave *ht*-polymers, though heterotacticity of the polymers decreased slightly as compared with that of the polymer prepared with $MeAl(ODBP)_2$. The analysis of stereochemical sequence distribution in the main chain of the obtained polymers revealed that weaker Lewis acidity of the aluminum phenoxides led to a decrease of *ht*-selectivity of $\sim\sim rM^-$ and an increase of *ht*-selectivity of $\sim\sim mM^-$, and *vice versa* in the cases of the stronger Lewis acid. Since an increase or a decrease of Lewis acidity affects the degree of stereospecificity of $\sim\sim mM^-$ and $\sim\sim rM^-$ anions in opposite ways, it seems difficult to increase heterotacticity of the polymer by changing the Lewis acidity of the aluminum phenoxide. So far the highest heterotacticity is obtained with $MeAl(ODBP)_2$, which is in a good balance of Lewis acidity. However, it is noteworthy that the stereospecificity of particular types of propagating anions, $\sim\sim mM^-$ and $\sim\sim rM^-$, could be changed by proper selection of Lewis acidity as well as steric factors of the aluminum phenoxide.

The lower *ht*-specificity of $\sim\sim mM^-$ anion relative to that of $\sim\sim rM^-$ anion is still the problem to be solved for attaining higher heterotacticity. The key process may be smooth and selective removal of the aluminum phenoxide coordinated to the penultimate unit of $\sim\sim mM^-$.

The next Chapter describes the chain-end analysis of *ht*-poly(EMA)s prepared with *t*-BuLi / $MeAl(ODBP)_2$ by ^{13}C NMR spectroscopy. The terminating chain-end analysis also brings the necessity of improvement in *ht*-selectivity of $\sim\sim mM^-$ into relief.

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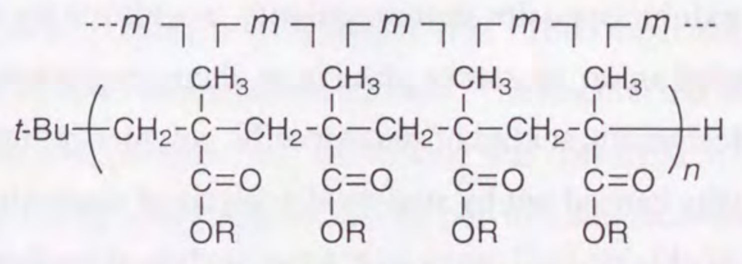
Chapter 3

Stereochemistry near the Chain Ends of Heterotactic Poly(ethyl methacrylate)

Introduction

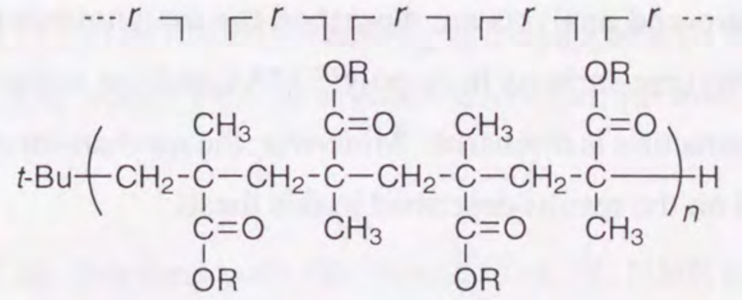
End-group analysis of polymers by NMR spectroscopy often provides important information for the understanding of polymerization mechanism.[1] In particular, stereochemical structures near the initiating and terminating chain-ends relate to stereospecificity of initiating and propagating species.

Methacrylate is one of the most intensively investigated monomers in regard of stereospecificity of polymerization.[2,3] During the last decade stereospecific living polymerization of methacrylate has become possible.[4-8] It have been reported that *t*-butylmagnesium bromide (*t*-BuMgBr)[4,5] and *t*-butyllithium (*t*-BuLi) / trialkylaluminum[6,7] give highly isotactic (*it*-) and syndiotactic (*st*-) polymethacrylates, respectively, with narrow molecular weight distributions. These stereoregular polymethacrylates have the same chemical structure from initiating chain-end (*t*-butyl group) to terminating chain-end (methine hydrogen). The diad tacticities of both the initiating and terminating chain-ends have been studied by ^{1}H NMR spectroscopy and by the analysis of the distribution of



$t\text{-Bu}\left(\mathrm{CH_2{-}C(CH_3)(C{=}O\,OR){-}CH_2{-}C(CH_3)(C{=}O\,OR){-}CH_2{-}C(CH_3)(C{=}O\,OR){-}CH_2{-}C(CH_3)(C{=}O\,OR)}\right)_n\mathrm{H}$

Isotactic polymer



$t\text{-Bu}\left(\mathrm{CH_2{-}C(CH_3)(C{=}O\,OR){-}CH_2{-}C(C{=}O\,OR)(CH_3){-}CH_2{-}C(CH_3)(C{=}O\,OR){-}CH_2{-}C(C{=}O\,OR)(CH_3)}\right)_n\mathrm{H}$

Syndiotactic polymer

stereoisomeric oligomers by means of chromatographic separation.[9-13]

Heterotactic (*ht*-) polymer prepared with *t*-BuLi / bis(2,6-di-*t*-butylphenoxy)-methylaluminum [MeAl(ODBP)$_2$] in toluene at low temperature has the same chemical structure with above-mentioned *it*- and *st*-polymers.[14,15] The structural feature of *ht*-polymer, *i.e.*, the alternation of meso (*m*) and (*r*) diads in the chain, ∿∿*mrmrmrmr*∿∿, raises the question whether the polymer chain starts with *m* or *r* diad and ends with *m* or *r* diad. Thus the end-group analysis of *ht*-polymer in regard of stereochemistry is particularly interesting.

In this Chapter, the stereostructure near the chain ends of *ht*-poly(ethyl methacrylate) [*ht*-poly(EMA)] was investigated by ^{13}C NMR spectroscopy. As mentioned above, the end-group structure of *ht*-poly(EMA) is identical to those of *it*- and *st*-poly(EMA)s obtained with the respective stereospecific living polymerizations. Thus ^{13}C NMR spectra of the *it*- and *st*-polymers could be used as good references for the spectral assignments of the chain-end signals of the *ht*-poly(EMA).

On the other hand, the mechanism of the *ht*-polymerization is very interesting for investigation on stereocontrol in polymerization reaction, because two types of monomer additions, which exhibit opposite stereoregularity, *r*-addition by *m*-ended anion and *m*-addition by *r*-ended anion, must take place in an alternating manner for the formation of *ht*-polymers. Mechanistic studies of stereospecific polymerization of vinyl monomers have been principally carried out by statistical analysis of stereostructural distribution in the main chain of obtained polymers with some analytical methods, mainly by NMR method,[16-21] since it is difficult to isolate active species themselves with few exception.[22] In addition to chain-end analysis are described the assignments of NMR spectra of carbonyl and methylene carbons in *ht*-poly(EMA), and the statistical analysis of the main chain stereostructure is discussed. Moreover, the mechanism of *ht*-polymerization is proposed based on the results described in this thesis.

Experimental

The experimental procedures except for these described below are the same as those described in detail in Chapters 1 and 2.

Materials

Methanol was fractionally distilled and dried over Molecular Sieves 4A. Phenol and *t*-butyl alcohol, obtained commercially, were fractionally distilled and dried over Molecular Sieves 4A and used as toluene solutions.

t-BuMgBr was prepared in diethyl ether from *t*-butyl bromide and magnesium.[5] The amounts of *t*-BuMg- group, total magnesium (Mg^{2+}) and total bromide (Br^-) ions were determined by acid-base titration, chelatometric titration and Fajans's method, respectively.

Polymerization

All the polymerizations were carried out in a glass ampoule filled with dried nitrogen. The polymerization reaction was initiated by adding the monomer slowly to the initiator solution in toluene at polymerization temperature. In the case of two component initiators, *t*-BuLi/*n*-Bu$_3$Al and *t*-BuLi/MeAl(ODBP)$_2$, each component was mixed at the polymerization temperature. The reaction was terminated by adding methanol, *t*-butyl alcohol or phenol at the polymerization temperature. Then methanol containing a small amount of HCl was added to neutralize this mixture. The reaction mixture was concentrated to dryness under reduced pressure, and the residue was dissolved in benzene. Insoluble materials were removed by centrifugation, and the polymer was recovered from the solution by freeze-drying and dried under vacuum. In the case of the *ht*-specific polymerization the product contained 2,6-di-*t*-butylphenol, which was removed by size exclusion chromatography (SEC) using a JASCO TRI ROTAR-II chromatograph equipped with Shodex SEC column K-2003 (30cm x 2.0cm) using CHCl$_3$ as an eluent at room temperature.

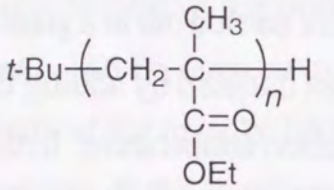
Measurement

Tacticities of the polymers were determined from ^{13}C NMR signals measured in CDCl$_3$ at 55°C or in nitrobenzene-d_5 at 110°C on a JEOL JNM GSX500 or a Varian Unity Inova 500 spectrometer operated at 125MHz.

Results and Discussion

Stereochemical Analysis near the Initiating Chain-End

The polymerization of EMA in toluene was carried out at –78°C and/or –95°C with three initiators, *t*-BuMgBr,[5,23] *t*-BuLi/*n*-Bu_3Al,[6] and *t*-BuLi / $MeAl(ODBP)_2$,[14,15] which are known to promote *it*-, *st*- and *ht*-polymerizations, respectively. Based on the knowledge that kinds of alcohol used as a terminating agent affect the stereospecificity in the terminating reaction, phenol, *t*-butyl alcohol and methanol were used as terminating agent depending on the polymerization system. The results are shown in Table 3-I. All the polymers have a *t*-butyl group at the initiating chain-end and methine carbon at the terminating chain-end.



$$t\text{-Bu}\left(CH_2-\overset{CH_3}{\underset{\underset{OEt}{C=O}}{C}}\right)_n H$$

Figure 3-I shows the resonances of *t*-butyl group at the initiating chain-end of the *it*-, *st*- and *ht*-poly(EMA)s. In all the spectra, the methyl carbon resonances split into

Table 3-I. Polymerization of ethyl methacryalte with several initiators in toluene at – 78° C for 24h, terminated with several alcohols

Initiator	Terminator	Yield	Tacticity / %[a]			$\overline{M}_n$ [b]	$\overline{M}_w$ [b] / $\overline{M}_n$
		%	*m m*	*m r*	*r r*		
t-BuMgBr[c]	MeOH	100	91.8	8.2	0.0	2400	1.82
	PhOH+dioxane	100	91.8	8.2	0.0	2560	1.20
t-BuLi / *n*-Bu_3Al[d] (1/3)	MeOH	100	0.0	10.4	89.6	3000	1.06
	t-BuOH	100	0.0	9.5	90.5	2900	1.05
t-BuLi / $MeAl(ODBP)_2$[e] (1/5)	MeOH	100	7.7	87.2	5.1	5680	1.08
	t-BuOH	100	7.6	87.6	4.8	6220	1.08
	PhOH	100	8.0	87.2	4.8	6230	1.08
	MeOH[f]	100	7.1	91.6	1.3	8100	1.11

a Determined by ^{13}C NMR signals due to carbonyl carbon. b Determined by SEC. c EMA 10mmol, *t*-BuMgBr 0.5mmol, toluene 10ml. d EMA 5mmol, *t*-BuLi 0.25mmol, *n*-Bu_3Al 0.75mmol, toluene 5ml. e EMA 10mmol, *t*-BuLi 0.2mmol, $MeAl(ODBP)_2$ 1.0mmol, toluene 10ml. f Polymerization temperature – 95° C, polymerization time 48h.

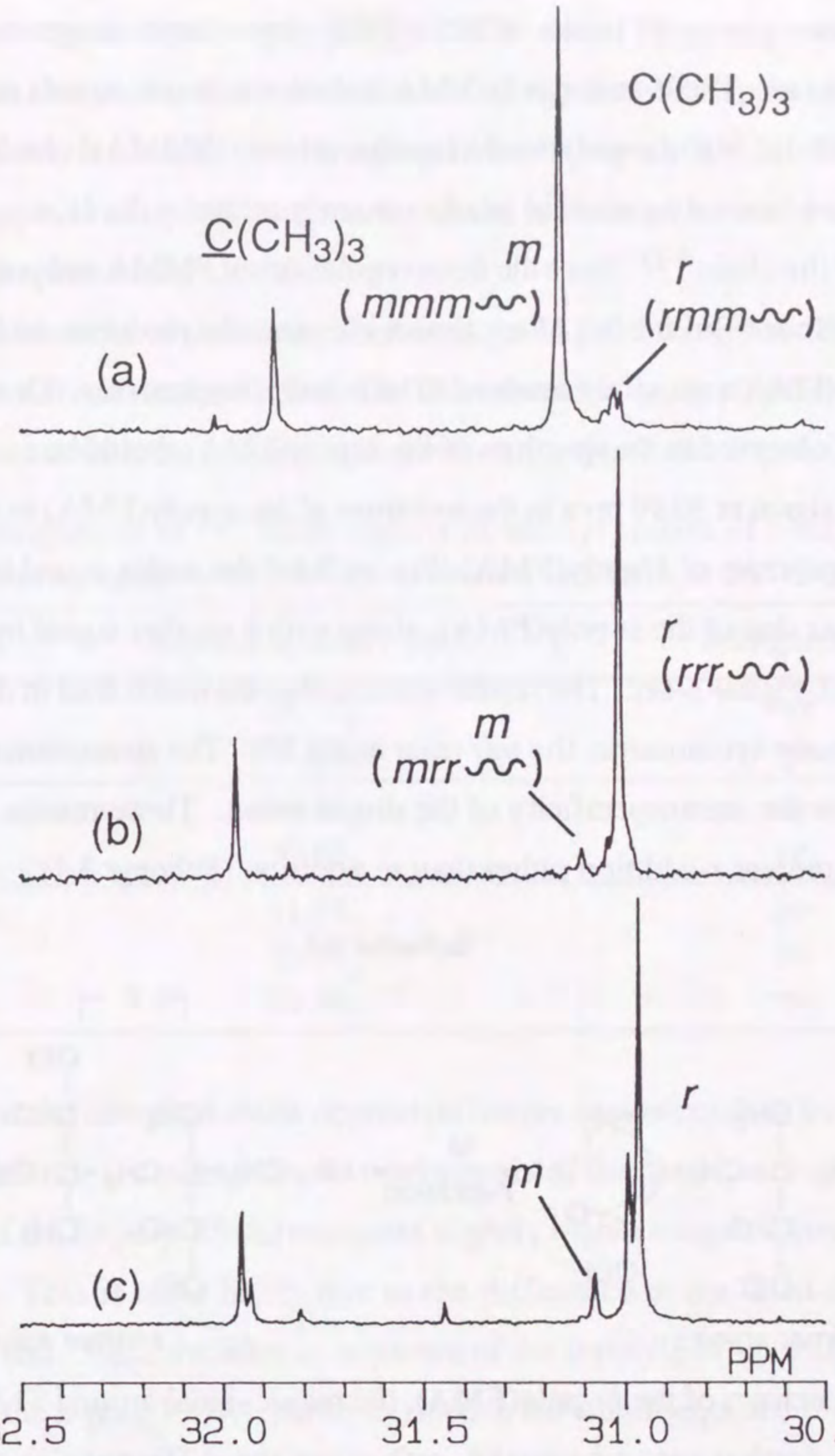
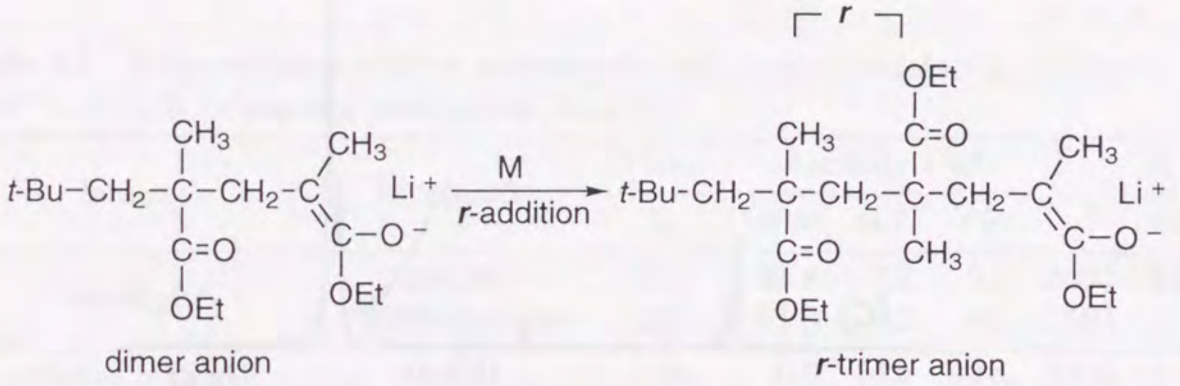


Figure 3-I. 125 MHz ^{13}C NMR spectra of *t*-butyl group at the initiating chain-end of three types of stereoregular poly(EMA)s prepared with (a) *t*-BuMgBr / $MgBr_2$, (b) *t*-BuLi / *n*-Bu_3Al, and (c) *t*-BuLi / $MeAl(ODBP)_2$ in toluene at –78°C, measured in $CDCl_3$ at 55°C.

principally two groups of peaks reflecting the stereochemical structure of the initial diad of the chains. The *it*-and *st*-poly(EMA)s show the major signals at 31.16 and 30.99 ppm, respectively. *it*-and *st*-poly(methyl methacrylate)s (PMMAs) obtained under similar conditions are known to contain predominantly *m* and *r* diads, respectively, at the beginning of the chain.[9-13] Since the stereoregularities of PMMA and poly(EMA) obtained with *t*-BuMgBr or *t*-BuLi/*n*-Bu_3Al are almost identical, the predominant initial diads of the *it*-and *st*-poly(EMA)s are safely assumed to be *m* and *r*, respectively. Thus the major signal at 31.16 ppm observed in the spectrum of the *it*-poly(EMA) should be assigned to initial *m* diad, and the signal at 30.99 ppm in the spectrum of the *st*-poly(EMA) to initial *r* diad.

In the spectrum of *ht*-poly(EMA) (Figure 3-Ic) the major signal is observed in the same region as that of the *st*-poly(EMA), along with a smaller signal in the region for *m* diad signal (*cf.* Figure 3-Ia). The results indicate that the initial diad in the *ht*-poly(EMA) is predominantly syndiotactic, the *m*/*r* ratio being 1/9. The stereostructure of the initial diad relates to the stereospecificity of the dimer anion. These results indicate that the dimer anion prefers *r*-addition rather than *m*-addition (Scheme 3-I).

Scheme 3-I



In the spectrum of the *ht*-poly(EMA), the major signal around 31.0 ppm due to the *r* diad splits further into two peaks, reflecting the difference in the second diad configuration following the initial *r* diad. Thus the chemical shift of *t*-butyl methyl signal is sensitive to the initial triad configuration. In this respect, the two methyl carbon signals of the *it*-poly(EMA) (31.16 and 31.02 ppm) should be assigned to *mm* and *rm* triads because the interior sequence of the polymer mostly comprises *m* diad.

Similarly, the two signals of the *st*-poly(EMA) (30.99 and 31.08 ppm) should be ascribed to the initial *rr* and *mr* triads. The minor shouldered signal at 30.99 ppm in the spectrum of the *ht*-poly(EMA) is close to the *rr* triad signal of the *st*-poly(EMA). Thus the major signal at 30.97 ppm is assignable to *rm* triad at the initiating chain-end and the minor one at 30.99 ppm to *rr* triad.

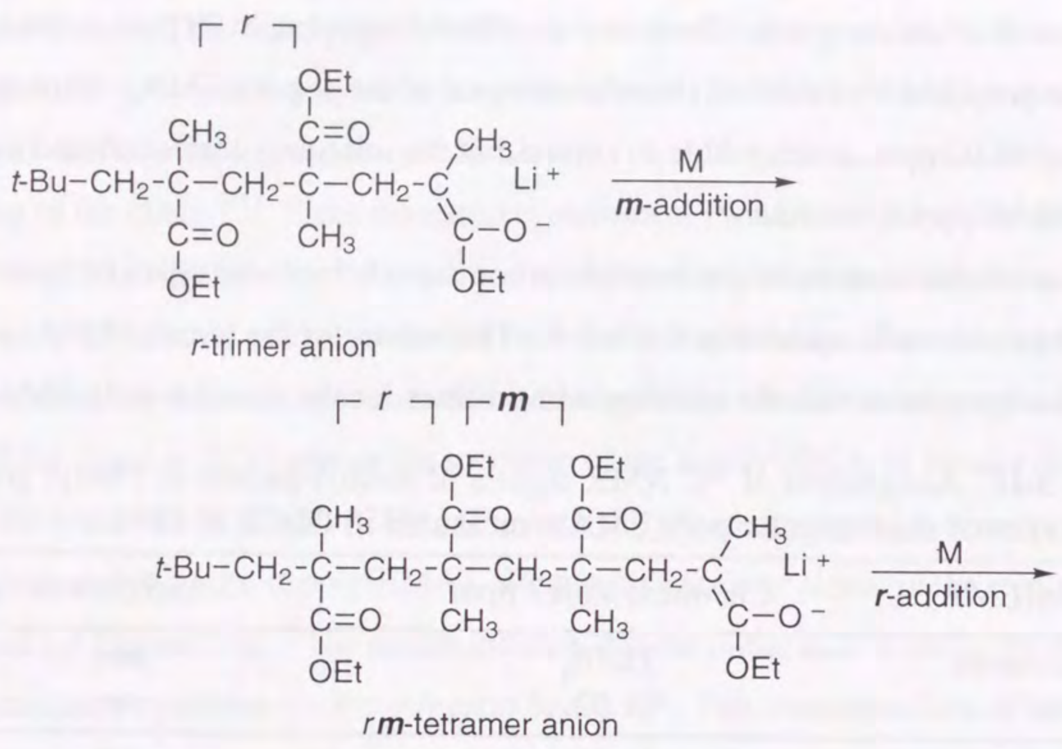
The chemical shifts of the methyl carbon signals for three types of stereoregular poly(EMA)s are summarized in Table 3-II. The values for the *ht*-poly(EMA) are not in complete agreement with the corresponding values for the *it*-and *st*-poly(EMA)s. The fact suggests that the chemical shifts depend on longer sequences than triad. The most remarkable difference is observed in *rm* triad signals of the *ht*-polymer and *it*-polymer. The *rm* signal of the *ht*-poly(EMA) resonates slightly higher magnetic field than that of the *it*-polymer. This is most likely due to the difference in the third diad from the initiating chain-end. Since the interior sequence of the *it*-poly(EMA) comprises *m* diad, the *rm* signal of the *it*-poly(EMA) can be ascribed to the tetrad sequence *rmm*. Therefore the *rm* signal of the *ht*-poly(EMA) is due to *rmr* tetrad, indicating the formation of *ht*-sequence at the beginning of the chain (Scheme 3-II).

Table 3-II. Assignment of ^{13}C NMR signals of methyl carbon of *t*-butyl group of three types of stereoregular poly(EMA)s measured in $CDCl_3$ at 55° C

poly(EMA)	Chemical shift / ppm	Assignment
Isotactic	31.16_4	*mm*
	31.02_5	*rm*
Syndiotactic	31.08_4	*mr*
	30.98_9	*rr*
Heterotactic	31.07_3	*mr*
	30.99_2	*rr*
	30.96_7	*rm*

Figure 3-II shows the methyl carbon signals of *t*-butyl group of poly(EMA)s prepared at –78 and –95°C, respectively. The *rr* triad signal at 30.99 ppm is much smaller for the polymer obtained at –95°C than for the polymer formed at –78°C. The

Scheme 3-II



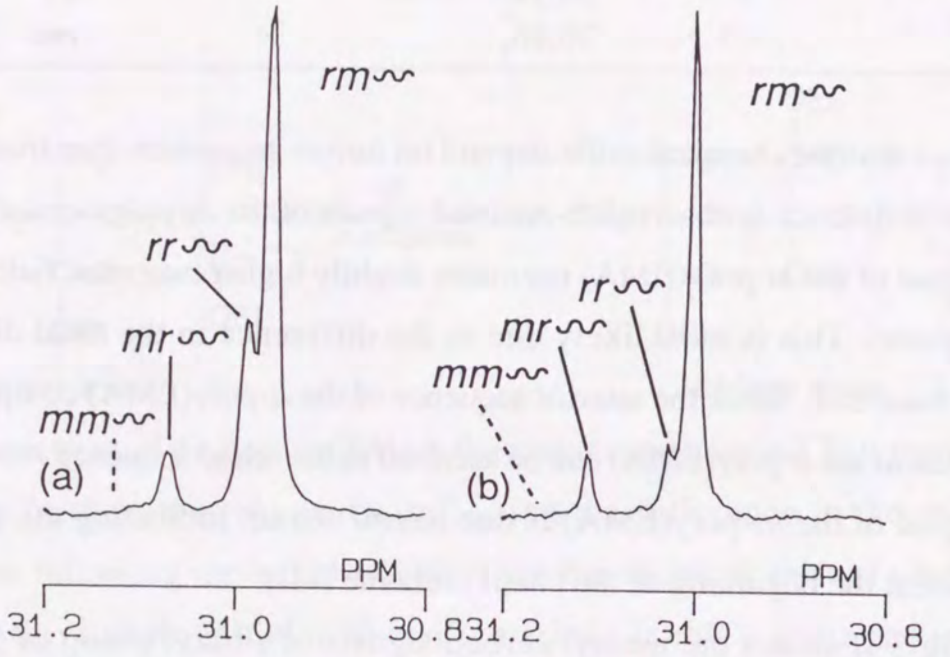


Figure 3-II. Expanded spectra of methyl carbons of *t*-butyl group in *ht*-poly(EMA)s prepared at (a) –78 and (b) –95°C.

polymer obtained at –95°C has higher heterotacticity (*mm* : *mr* : *rr* = 7.1 : 91.6 : 1.3) than that formed at –78°C (*mm* : *mr* : *rr* = 7.6 : 87.2 : 5.2). The fact that syndiotacticity is reduced and heterotacticity is enhanced by lowering the polymerization temperature seems consistent with the higher fraction of the initial *rm* triad in the polymer obtained at –95°C and thus supports the present assignments. Another signal due to initial *m* diad at 31.07 ppm is closer in its chemical shift to the signals of the *st*-poly(EMA) rather than that of the *it*-polymer, and thus can be assigned to *mr* triad. The *mm* triad signal expected to be observed at around 31.16 ppm (*cf.* Figure 3-Ia) is hardly observable. Though the lower intensity of the signal does not allow decisive conclusion, the initial *m* diad mostly follows *r* diad.

Table 3-III shows the triad sequence distribution at the initiating chain-end of *it*-, *st*- and *ht*-poly(EMA)s. The values for each set of tactic poly(EMA)s are expectedly in good agreement irrespective of terminating agent used. The fraction of the initial diad in the *ht*-poly(EMA) indicates that the dimer anion forms *r*-trimer anion as described before. For the *ht*-poly(EMA) obtained at –78°C, the fraction of the second diad following the initial *r* diad suggests that *r*-trimer favors *m*-addition about three times as much as *r*-addition, leading to the preferential formation of *ht*-triad even in the early stage of polymerization. The *m*-selectivity by the *r*-trimer anion is much enhanced at –95°C, the

Table 3-III. Triad sequence distribution near the initiating chain-end of stereoregular poly(EMA)s

Poly(EMA)	Terminating agent	Triad tacticity / %				[*mm*–] + [*mr*–] / [*rm*–] + [*rr*–]
		mm–	*mr*–	*rm*–	*rr*–	
Isotactic	MeOH	89	—	11	—	89 / 11
Isotactic	PhOH	90		10		90 / 10
Syndiotactic	MeOH	—	9	—	91	9 / 91
Syndiotactic	*t*-BuOH	—	13	—	87	13 / 87
Heterotactic	MeOH	—	8	66	26	8 / 92
Heterotactic	PhOH	—	9	66	25	9 / 91
Heterotactic	*t*-BuOH	—	8	62	30	8 / 92
Heterotactic[a]	MeOH	—	7	83	10	7 / 93

a Polymerization temperature – 95° C.

ratio *rm*/*rr* being 9/1. The signals due to initial *m*-diad does not change evidently with the polymerization temperature, suggesting that the stereospecificity of the *m* diad trimer anion is less sensitive to the polymerization temperature. Stereochemical sequence of the main chain tacticity obeys first-order Markovian statistics as described later.[14,15] The conditional probability of *m*-addition by *r*-ended anion ($\sim\!\sim rM^-$), $P_{r/m}$, and that of *r*-addition by *m*-ended anion ($\sim\!\sim mM^-$), $P_{m/r}$, were determined as follows;

$P_{r/m} = 0.972 \quad P_{m/r} = 0.866$ at –95°C

$P_{r/m} = 0.926 \quad P_{m/r} = 0.833$ at –78°C.

It is evident that *r*-ended propagating species has higher stereospecificity than the *m*-ended anion. Moreover, the *m*-selectivity of $\sim\!\sim rM^-$ ended anion, as expressed by the ratio, $P_{r/m} / P_{r/r}$, is improved by lowering the temperature with much greater extent than *r*-selectivity of $\sim\!\sim mM^-$ ($P_{m/r} / P_{m/m}$):

$P_{r/m} / P_{r/r} = 34.7$, $P_{m/r} / P_{m/m} = 6.5$ at –95°C

$P_{r/m} / P_{r/r} = 12.5$, $P_{m/r} / P_{m/m} = 5.0$ at –78°C

Table 3-IV shows stereoselectivity of dimer anion and *r*-trimer anion. Comparing the *m*-selectivity of the *r*-trimer anion and the *r*-ended polymer anion, one can find a similar tendency of temperature dependence, though the selectivity itself is much lower for the trimer anion. The selectivity of the dimer anion, which has no antepenultimate unit, was almost invariable at –78°C and –95°C. The results suggest the important role of penultimate and antepenultimate units in the *ht*-propagation step, *m*-addition by $\sim\!\sim rM^-$ as described in Chapter 2.

Table 3-IV. Stereoselectivity of dimer anion and *r*-ended trimer anion

Temp / ° C	Dimer anion			*r*-Ended trimer anion		
	P_r^*	P_m^*	$\frac{P_r^*}{P_m^*}$	$P_{r/m}^*$	$P_{r/r}^*$	$\frac{P_{r/m}^*}{P_{r/r}^*}$
– 95	0.93	0.07	13	0.90	0.10	9
– 78	0.92	0.08	11.5	0.75	0.25	3

Stereochemical Analysis near the Terminating Chain-End

Configuration of terminal methine carbon of the polymer is fixed upon protonation by the addition of alcohol as a terminating agent, forming a terminal diad. For the *it*-and *st*-living polymerizations of MMA, the terminal diad configuration is known to depend on the kind of alcohol used for termination.[13] In the *it*-specific polymerization of MMA with *t*-BuMgBr, the termination with phenol preferentially forms terminal *m* diad. On the other hand, *t*-butyl alcohol terminates the *st*-specific polymerization of MMA with *t*-BuLi / *n*-Bu_3Al to form terminal *r* diad preferentially.[13] In both systems, methanol was found to be a non-stereospecific terminator.[13]

The *ht*-living polymer may be either $\sim\!\sim rM^-$ or $\sim\!\sim mM^-$. By quenching the living anions with a terminating agent, the chain-end diad configurations are fixed to form the terminal triads as follows:

$$\sim\!\sim rM^- \longrightarrow \sim\!\sim rm + \sim\!\sim rr$$

$$\sim\!\sim mM^- \longrightarrow \sim\!\sim mm + \sim\!\sim mr\,.$$

Thus the information on the triad tacticity at the terminating chain-end is particularly important in the case of the end-group analysis of *ht*-polymers.

Figure 3-III shows ^{13}C NMR signals due to the terminal methine carbons of *it*-, *st*- and *ht*-poly(EMA)s formed by the termination with methanol. The assignments shown in the figure were made as follows, based on the knowledge about the stereospecificity of the alcohols in the termination reaction mentioned above.[13] The *it*-poly(EMA) obtained by the termination with methanol shows two signals, one at 36.88 ppm and the other at 36.05 ppm (Figure 3-IIIa). The polymer formed by protonation with phenol which is an *it*-specific terminator,[13] showed a strong signal at 36.93 ppm and very weak one at 36.05 ppm. Thus the peak at 36.88 ppm is assignable to *–mm* terminal and the other at 36.05 ppm to *–mr* terminal. Two major signals of *st*-poly(EMA) were also assigned similarly as shown in Figure 3-IIIb based on the fact that *t*-butyl alcohol preferentially forms *r* diad in the termination reaction of the *st*-living polymerization with *t*-BuLi / *n*-Bu_3Al[13]; the signal at 35.42 ppm (*–rr*) was the major

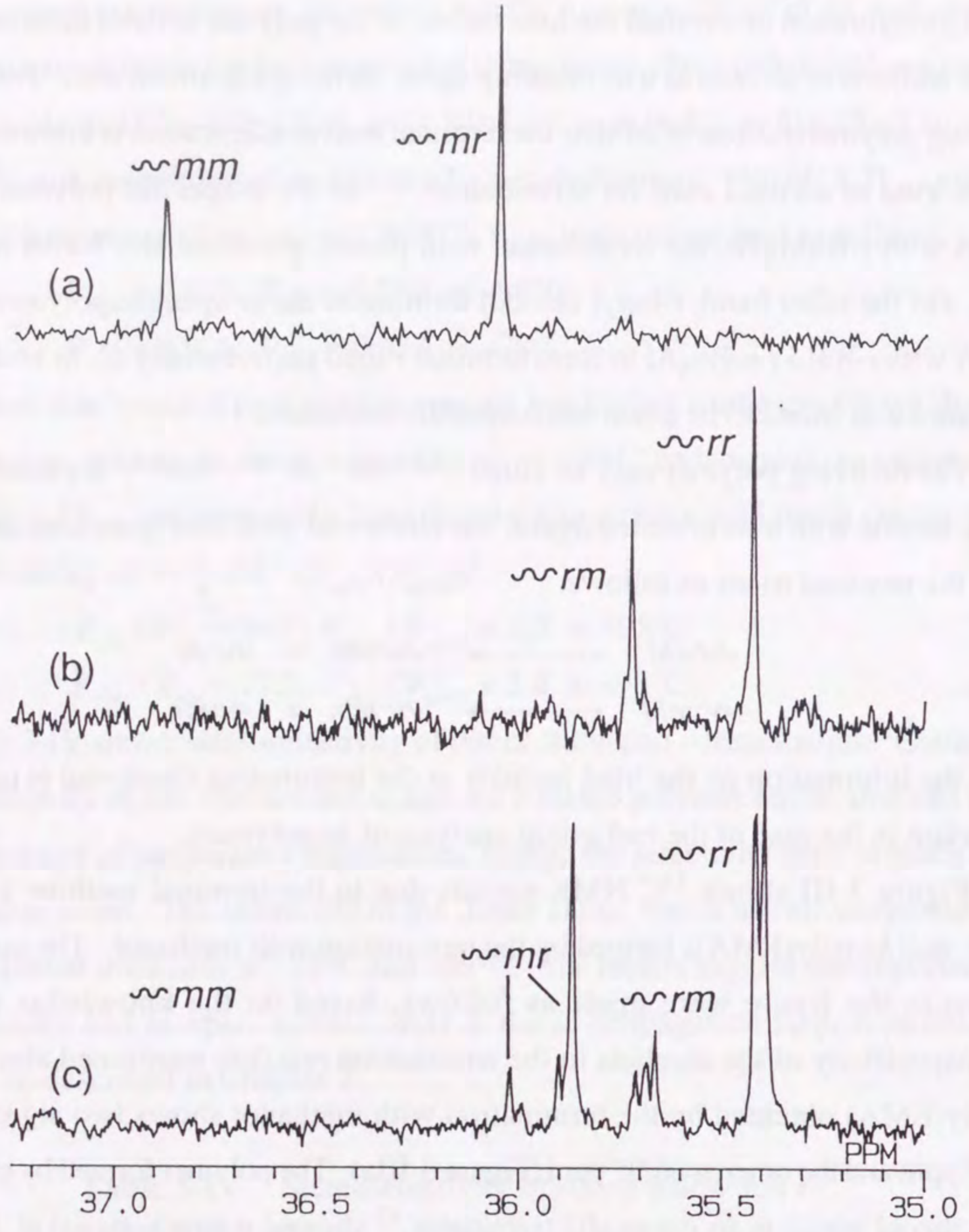


Figure 3-III. 125 MHz ^{13}C NMR spectra of methine carbon at the terminating chain-end of stereoregular poly(EMA)s prepared with (a) *t*-BuMgBr / $MgBr_2$, (b) *t*-BuLi / *n*-Bu_3Al, and (c) *t*-BuLi / $MeAl(ODBP)_2$, respectively, in toluene at –78°C terminated with methanol, measured in $CDCl_3$ at 55°C.

Table 3-V. Triad sequence distribution near the terminating chain-end of stereoregular poly(EMA)s

Poly(EMA)	Terminating agent	Triad tacticity / %				$\frac{[-mm]+[-mr]}{[-rm]+[-rr]}$
		– *mm*	– *mr*	– *rm*	– *rr*	
Isotactic	MeOH	36	64	—	—	100 / ~0
Isotactic	PhOH	90	10	—	—	100 / ~0
Syndiotactic	MeOH	—	—	44	56	~0 / 100
Syndiotactic	*t*-BuOH	—	—	—	100	~0 / 100
Heterotactic	MeOH	—	35	15	50	35 / 65
Heterotactic	PhOH	—	37	15	48	37 / 63
Heterotactic	*t*-BuOH	12	23	27	38	35 / 65
Heterotactic[a]	MeOH	10	22	22	46	32 / 68

a Polymerization temperature – 95° C.

signal and the signal at 35.72 ppm (–*rm*) the minor one in the spectrum of *st*-poly(EMA) obtained by termination with *t*-butyl alcohol. Based on these assignments the signals of methine carbons of *ht*-poly(EMA) were assigned in terms of triad as shown in Figure 3-IIIc, though the resonances show further splittings due to the longer tactic sequences near the terminating chain-end.

The triad sequence distribution at the terminating chain-end are shown in Table 3-V. The fractions of the second diad from the terminal corresponds to the fractions of two kinds of anions, $\sim\!\sim mM^-$ and $\sim\!\sim rM^-$ having existed in the polymerization system before the termination reaction. The ratio could be determined from the terminal triad fractions as $(-mm + -mr) / (-rm + -rr) = \sim\!\sim mM^- / \sim\!\sim rM^- = 1 / 2$. The values for the poly(EMA)s obtained by termination with different alcohols are quite consistent with each other, confirming the reproducibility of the *m*/*r* ratio at the second diad from the terminating chain-end. The ratio $\sim\!\sim mM^- / \sim\!\sim rM^- = 1 / 2$ means that $\sim\!\sim rM^-$ is more abundant than $\sim\!\sim mM^-$ in this polymerization system. The dominant population of $\sim\!\sim rM^-$ anion suggests its higher stability than $\sim\!\sim mM^-$ anion, which might bring about the higher stereoselectivity of $\sim\!\sim rM^-$.

The *m* / *r* ratios at the terminal diad of *ht*-poly(EMA)s were also analyzed to

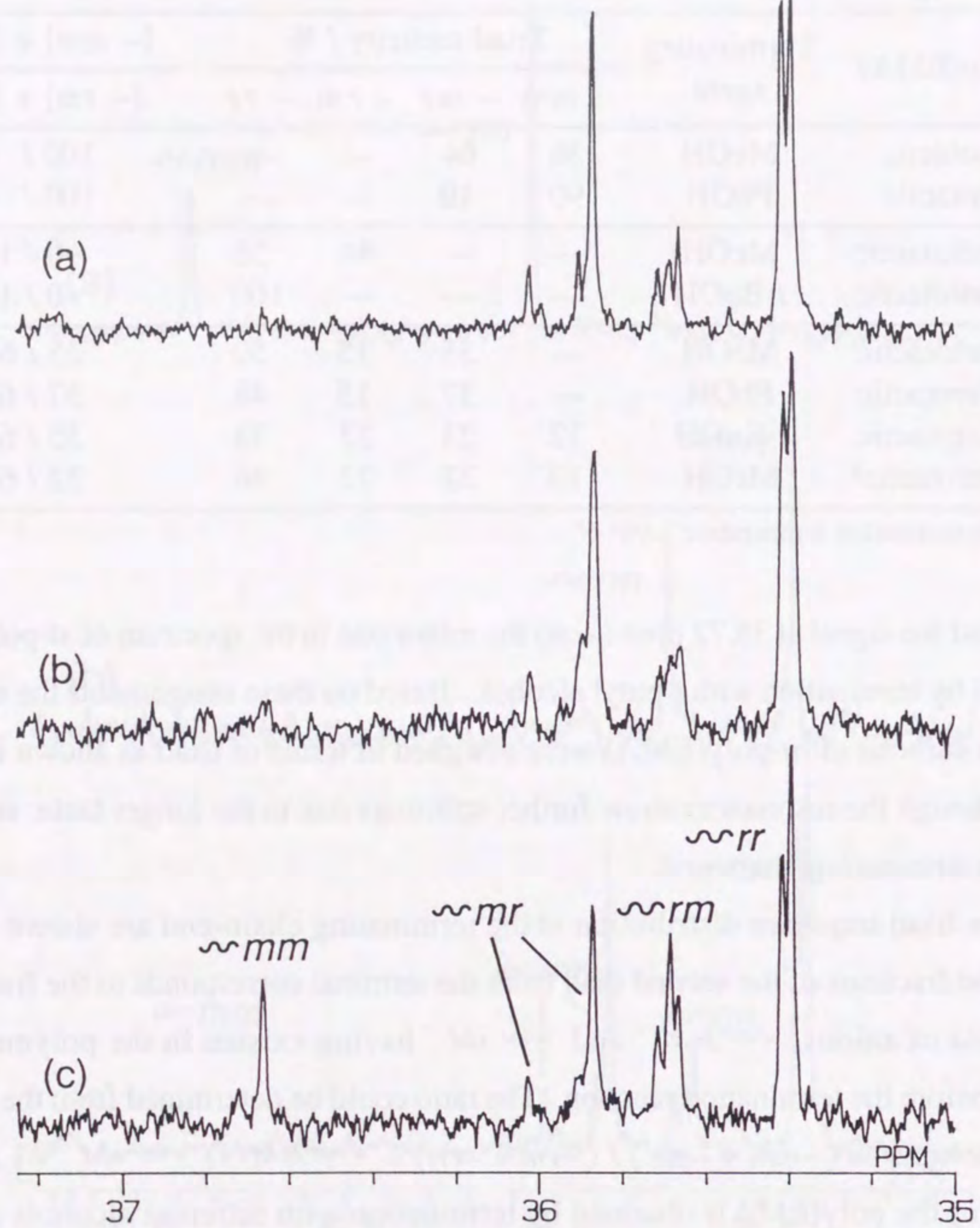


Figure 3-IV. 125 MHz ^{13}C NMR spectra of methine carbon at the terminating chain-end of *ht*-poly(EMA)s formed by termination with (a) methanol, (b) *t*-butyl alcohol, and (c) phenol, respectively, measured in $CDCl_3$ at 55°C.

Table 3-VI. Stereospecificity in protonation of heterotactic poly(EMA) anion with several alcohols

Alcohol	(*meso* Addition) / (*racemo* Addition) Poly(EMA) anion in average[a]	 $\sim mM^-$ ended anion[b]	 $\sim rM^-$ ended anion[c]
MeOH	15 / 85	~0 / 100	23 / 77
t-BuOH	15 / 85	~0 / 100	24 / 76
PhOH	39 / 61	34 / 66	41 / 59
MeOH[d]	32 / 68	31 / 69	32 / 68

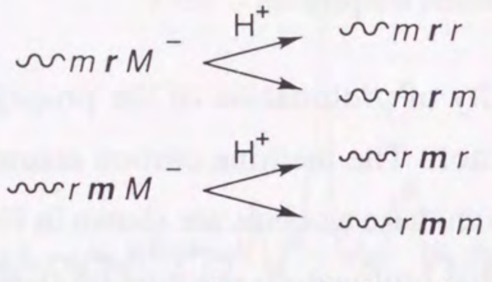
a Determined from the triad fractions at the terminating chain-end (see Table 3-IV) as ([– *mm*] + [– *rm*]) / ([– *mr*] + [– *rr*]).
b Determined by [– *mm*] / [– *mr*]. c Determined by [– *rm*] / [-*rr*].
d Polymerization temperature – 95° C.

examine stereospecificity of protonation of the propagating anion with methanol, *t*-butyl alcohol and phenol. The methine carbon resonances of the *ht*-poly(EMA)s formed by termination with these alcohols are shown in Figure 3-IV. Table 3-VI shows the stereoselectivity in the protonation reaction by these alcohols with the *ht*-living polymer. The chain-end diad of the *ht*-poly(EMA)s are predominantly *r*, when the polymerization was terminated with *t*-butyl alcohol or even with methanol which is known as a non-stereospecific terminator in both the *it*-and *st*-living polymerizations of MMA.[13] Even in the case of phenol, which has high *m*-selectivity in the *it*-specific polymerization and moderate *m*-selectivity in the *st*-specific polymerization,[13] exhibited moderate *r*-selectivity. The results suggest that both $\sim mM^-$ and $\sim rM^-$ anions in the *ht*-polymerization have intrinsically *st*-specific nature.

Monomer-Concentration Dependence of the Stereoselectivities of the Propagating Anions

Since the *mr* triad content in the main chain is close to 90%, *m* diad mostly follows *r* diad and *vice versa*. If such a high stereospecificity prevails throughout the whole process of the polymerization, most of ∿*rM*⁻ should be ∿*mrM*⁻, and most of ∿*mM*⁻ be ∿*rmM*⁻. Thus, the termination with protic compounds such as alcohol should produce mostly the following four types of tetrad sequences at the terminal end (Scheme 3-III):

Scheme 3-III



However, the methine carbon resonances show splittings due to longer stereosequence than triad level (*cf.* Figure 3-IV). In particular, the carbon due to –*rr* triad shows two signals with comparable intensity at 35.39 and 35.42ppm. This suggested the lower stereoregularity near the terminating chain-end than that in the main chain. The poly(EMA) analyzed above was obtained at 100% conversion and thus the chain-end structure should reflect the stereospecificity under such a condition that the monomer

Table 3-VII. Polymerization of EMA with *t*-BuLi / MeAl(ODBP)$_2$ (1/5 mol / mol) in toluene at– 78° C[a]

Time	Yield	Tacticity / %[b]			$\bar{M}_n$[c]	$\bar{M}_w / \bar{M}_n$[c]	[– *mm*] + [– *mr*] / [– *rm*] + [– *rr*][d]
h	%	*m m*	*m r*	*r r*			
0.3	28	6.8	90.0	3.2	2450	1.08	22 / 78
0.5	41	6.9	90.2	3.1	3240	1.09	22 / 78
24	100	7.7	88.6	3.7	7010	1.07	35 / 65

a EMA 10mmol, *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol, toluene 10ml.
b Determined by ^{13}C NMR signals due to carbonyl or methylene[24] carbon.
c Determined by SEC. d The *m* / *r* ratio of the second diad from the terminal.

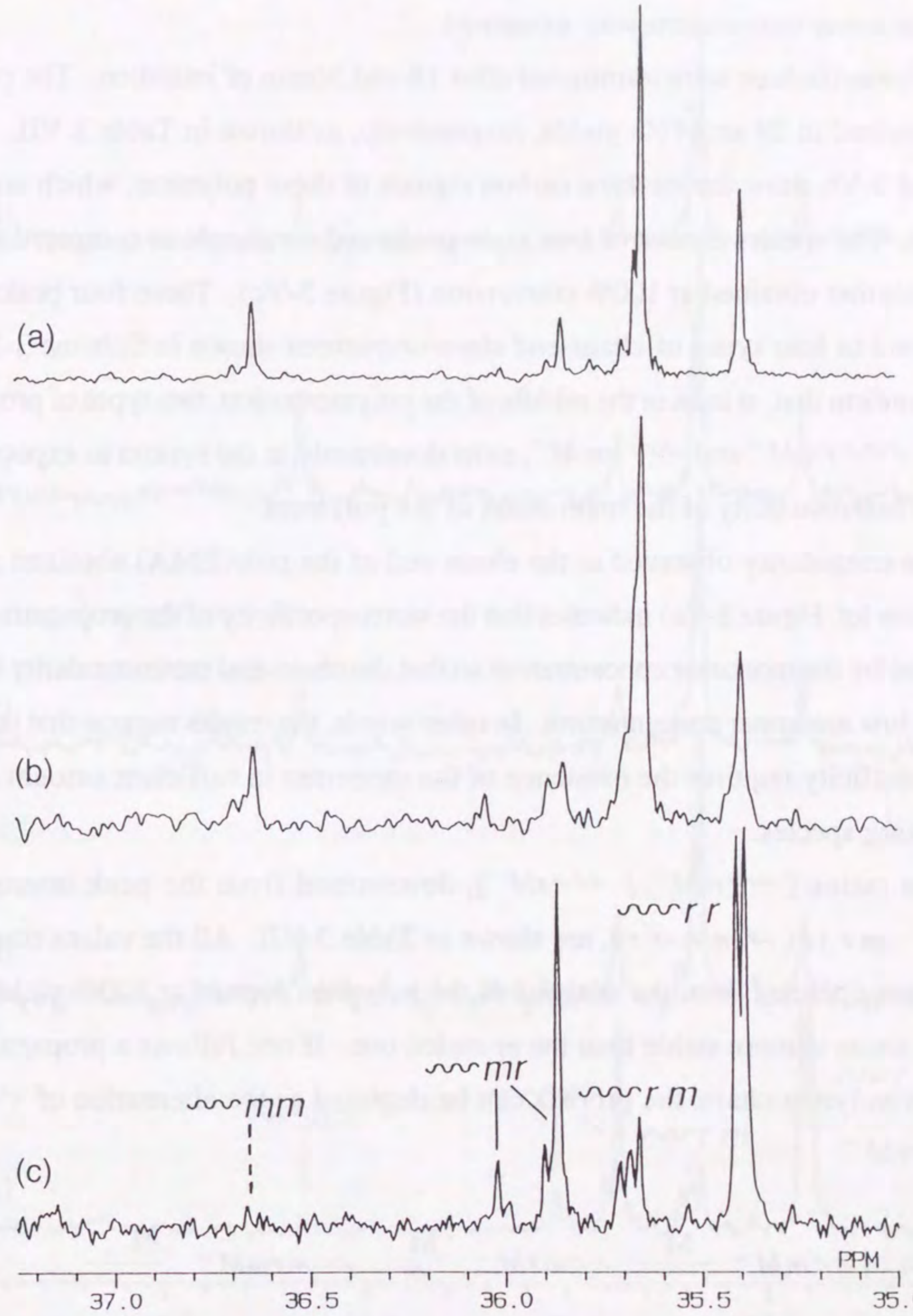


Figure 3-V. 125 MHz ^{13}C NMR spectra of methine carbon at the terminating chain-end of *ht*-poly(EMA)s formed at (a) 28, (b) 41, and (c) 100%, respectively.

concentration is close to zero. In this section, the chain-end structure of poly(EMA)s formed at lower conversions was examined.

Polymerizations were terminated after 18 and 30min of initiation. The polymers were obtained in 28 and 41% yields, respectively, as shown in Table 3-VII. Figures 3-Va and 3-Vb show the methine carbon signals of these polymers, which are almost identical. The spectra consist of four main peaks and are simple as compared with that of the polymer obtained at 100% conversion (Figure 3-Vc). These four peaks should correspond to four types of chain-end stereosequences shown in Scheme 3-III. The results confirm that, at least in the middle of the polymerization, two types of propagating species, $\sim\sim\sim rmM^-$ and $\sim\sim\sim mrM^-$, exist dominantly in the system as expected from the high heterotacticity of the main chain of the polymers.

The irregularity observed at the chain end of the poly(EMA) obtained at 100% conversion (*cf.* Figure 3-Vc) indicates that the stereospecificity of the propagating anions is affected by the monomer concentration so that the chain-end stereoregularity becomes lower at low monomer concentration. In other words, the results suggest that the higher stereospecificity requires the existence of the monomer in sufficient amount over the propagating species.

The ratios [$\sim\sim\sim mM^-$ / $\sim\sim\sim rM^-$], determined from the peak intensities as ($-m\,m + -m\,r$) / ($-r\,m + -r\,r$), are shown in Table 3-VII. All the values confirm the conclusion obtained from the analysis of the polymers formed at 100% yield that the *r*-ended anion is more stable than the *m*-ended one. If one follows a propagation of a single *ht*-polymer chain, the process can be depicted as the alternation of $\sim\sim\sim mM^-$ and $\sim\sim\sim rM^-$:

$$\sim\sim mM^- \xrightarrow{\text{M}} \sim\sim mrM^- \xrightarrow{\text{M}} \sim\sim mrmM^- \xrightarrow{\text{M}} .$$

The ratio [$\sim\sim\sim mM^-$] / [$\sim\sim\sim rM^-$] at low conversions is 22/78, while the ratio at 100% conversion is 35/65. The predominant existence of $\sim\sim\sim rM^-$ over $\sim\sim\sim mM^-$ in 22/78 and 35/65 ratios means that the propagating anion stays in $\sim\sim\sim rM^-$ state about four

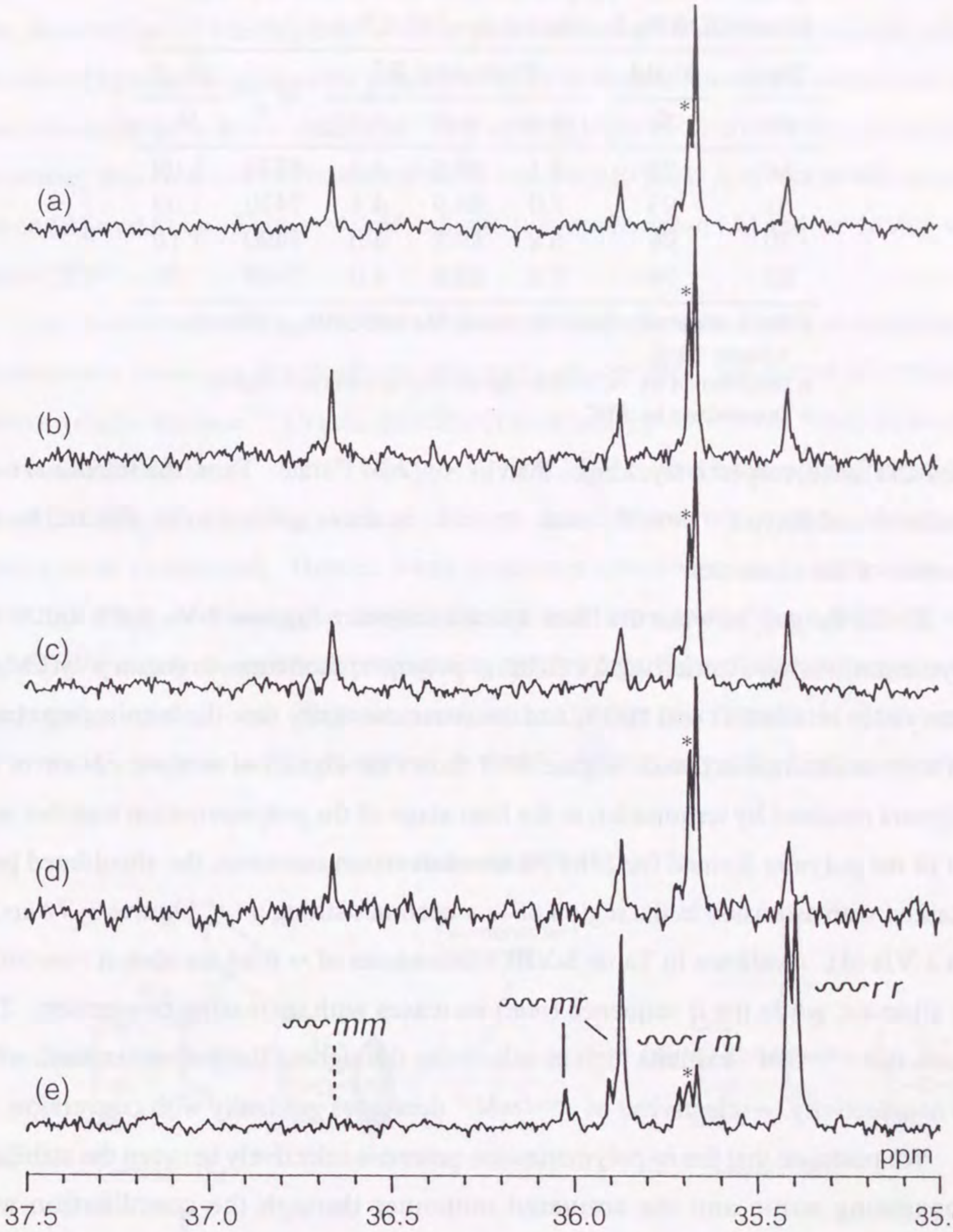


Figure 3-VI. 125 MHz ^{13}C NMR spectra of methine carbon at the terminating chain-end of *ht*-poly(EMA)s formed at (a) 75, (b) 93, (c) 96, (d) 99 and (e) 100%, respectively.

Table 3-VIII. Polymerization of EMA with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at– 78° C[a]

Time	Yield	Tacticity / %[b]			$\bar{M}_n$[c]	$\bar{M}_w$[c] / $\bar{M}_n$
min	%	*m m*	*m r*	*r r*		
54	75	6.1	89.8	4.1	6270	1.09
61	93	7.0	88.9	4.1	7420	1.09
70	96	6.8	89.2	4.0	7490	1.10
80	99	7.4	88.6	4.0	7900	1.09

a EMA 10mmol, *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol, toluene 10ml.
b Determined by ^{13}C NMR signals due to carbonyl carbon.
c Determined by SEC.

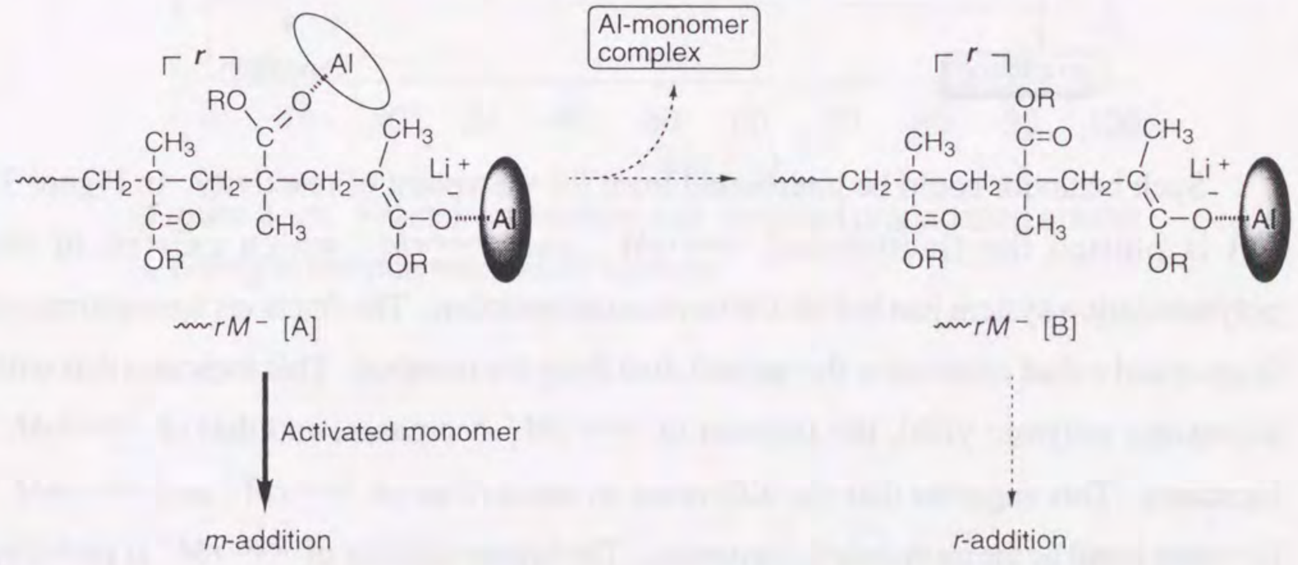
times and twice, respectively, longer than in $\sim\sim mM^-$ state. Thus, the fractional ratio or relative stability of $\sim\sim mM^-$ and $\sim\sim rM^-$ is also expected to be affected by the presence of the monomer.

To fill the gap between the three spectra shown in Figures 3-Va and b and 3-Vc, polymerizations were carried out for different polymerization times to obtain poly(EMA)s at the yields between 41 and 100%, and the stereochemistry near the terminating chain-end was reexamined in detail. Figure 3-VI shows the signals of methine carbon of the polymers obtained by termination at the later stage of the polymerization together with that of the polymer formed for 24h. As the conversion increases, the shouldered peak (marked with asterisks) in the region of –*rm* becomes stronger (*cf.* Figures 3-Va and b, and 3-VIa~d). As shown in Table 3-VIII, the contents of *rr* triad are almost constant in the all cases, while the *it*-sequence (*mm*) increases with increasing conversion. This means that $\sim\sim rM^-$ exhibits high *m*-selectivity throughout the polymerization, while the *ht*-selectivity (*r*-selectivity) of $\sim\sim mM^-$ decreases gradually with conversion.

We postulate that the *ht*-polymerization proceeds selectively between the stabilized propagating anion and the activated monomer through the coordination with MeAl(ODBP)$_2$.[14,15] To explain the unique stereocontrol in *ht*-polymerization, the author propose the mechanism shown in Scheme 3-IV. The propagating reaction between stabilized anion and activated monomers forms a new anion[A] which is coordinated with two MeAl(ODBP)$_2$ at the chain end and the penultimate monomeric unit. However, the coordination of MeAl(ODBP)$_2$ at the penultimate unit is not strong enough to keep the state [A] and it may leave the penultimate unit to form an anion [B] coordinated with one MeAl(ODBP)$_2$ at the chain end. The stereoselectivity of anions depends on their structure, that is, anion [A] coordinated by two MeAl(ODBP)$_2$ favors *m*-addition and anion [B] *r*-addition. Thus, $\sim\sim rM^-$ should favor to be anion [A] and $\sim\sim mM^-$ to be anion [B].[26]

As described in Chapter 4, the addition of less bulky esters such as acetates and isobutyrates decreases drastically *ht*-selectivity of $\sim\sim rM^-$, while that of $\sim\sim mM^-$ shows a slight decrease.[27] Drastic decrease of *m*-selectivity of $\sim\sim rM^-$ may be ascribed to the transformation of $\sim\sim rM^-$ [A] to $\sim\sim rM^-$ [B] caused by complex formation of MeAl(ODBP)$_2$ coordinating at the penultimate unit with ester compounds. Monomer is also a ester compound. Hence, when monomer concentration becomes low, the MeAl(ODBP)$_2$ coordinating at the penultimate unit favors to stay there, resulting in an increase of *m*-selectivity of the propagating species regardless of stereochemistry near the propagating chain-end. Thus, the decrease in monomer concentration is advantageous to $\sim\sim rM^-$ (Scheme 3-IV). However, $\sim\sim rM^-$ exhibits originally high *m*-selectivity

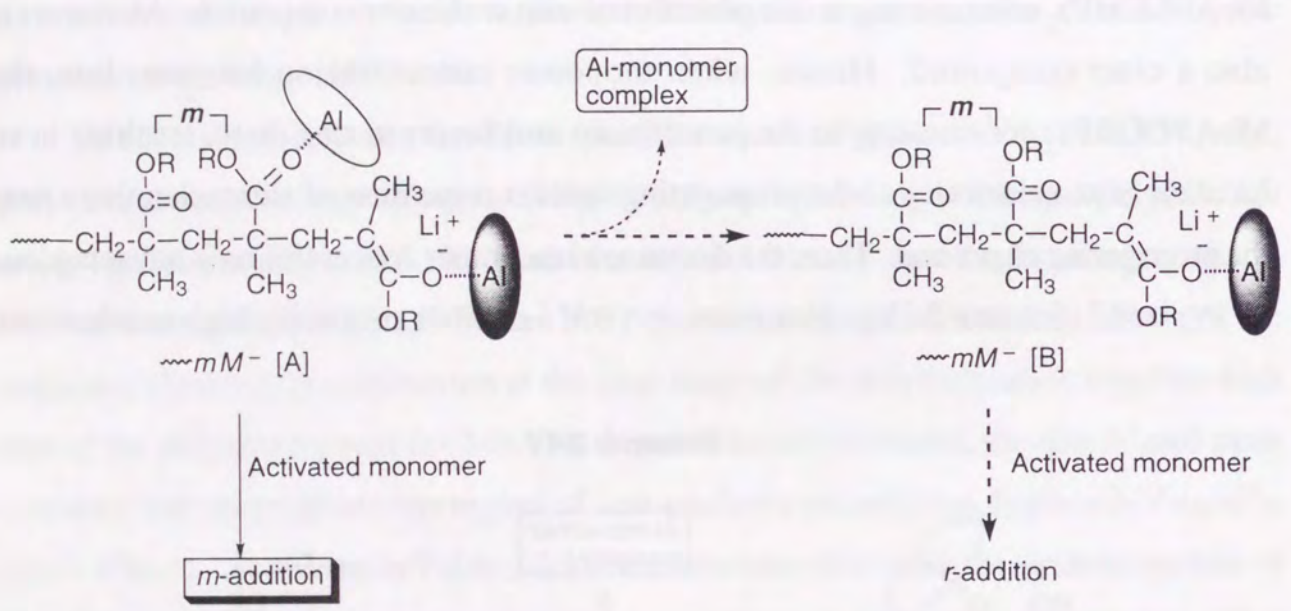
Scheme 3-IV



so that the improvement in *ht*-selectivity of $\sim\sim rM^-$ brought by the decrease in monomer concentration is hard to observe evidently.

In contrast, to undergo *r*-addition, $\sim\sim mM^-$ should release $MeAl(ODBP)_2$ coordinating at the penultimate unit before adding the activated monomer. In other words, the high monomer concentration is of importance for this process. Thus, the decrease in the monomer concentration with conversion increases the possibility of *m*-addition by $\sim\sim mM^-$ to introduce a stereochemical defect , –*mm*– (Scheme 3-V), and the resonances due to methine carbons at the terminating chain-end of the polymers formed at high conversion show complicated splittings as a result.

Scheme 3-V



Such behavior could be interpreted from the viewpoint of reactivity. In Figure 3-VII is plotted the fractions of $\sim\sim mM^-$ and $\sim\sim rM^-$ which existed in the polymerization system just before the termination reaction. The fractions were estimated from *m* and *r* diad contents at the second diad from the terminal. This indicates that with increasing polymer yield, the fraction of $\sim\sim rM^-$ decreases, and that of $\sim\sim mM^-$ increases. This suggests that the difference in reactivities of $\sim\sim rM^-$ and $\sim\sim mM^-$ becomes small as the monomer is consumed. The higher stability of $\sim\sim rM^-$ is probably

due to more shield of the active center of $\sim\sim rM^-$ than that of $\sim\sim mM^-$ by two bulky $MeAl(ODBP)_2$. This means that it becomes difficult for $\sim\sim mM^-$ [A], which has less reactivity, to transform into $\sim\sim mM^-$ [B], which has higher reactivity, due to the decrease in monomer concentration. Thus the amount of $\sim\sim mM^-$ [A], which exhibits *m*-selectivity, increases gradually, resulting in a decrease in *ht*-selectivity of $\sim\sim mM^-$.

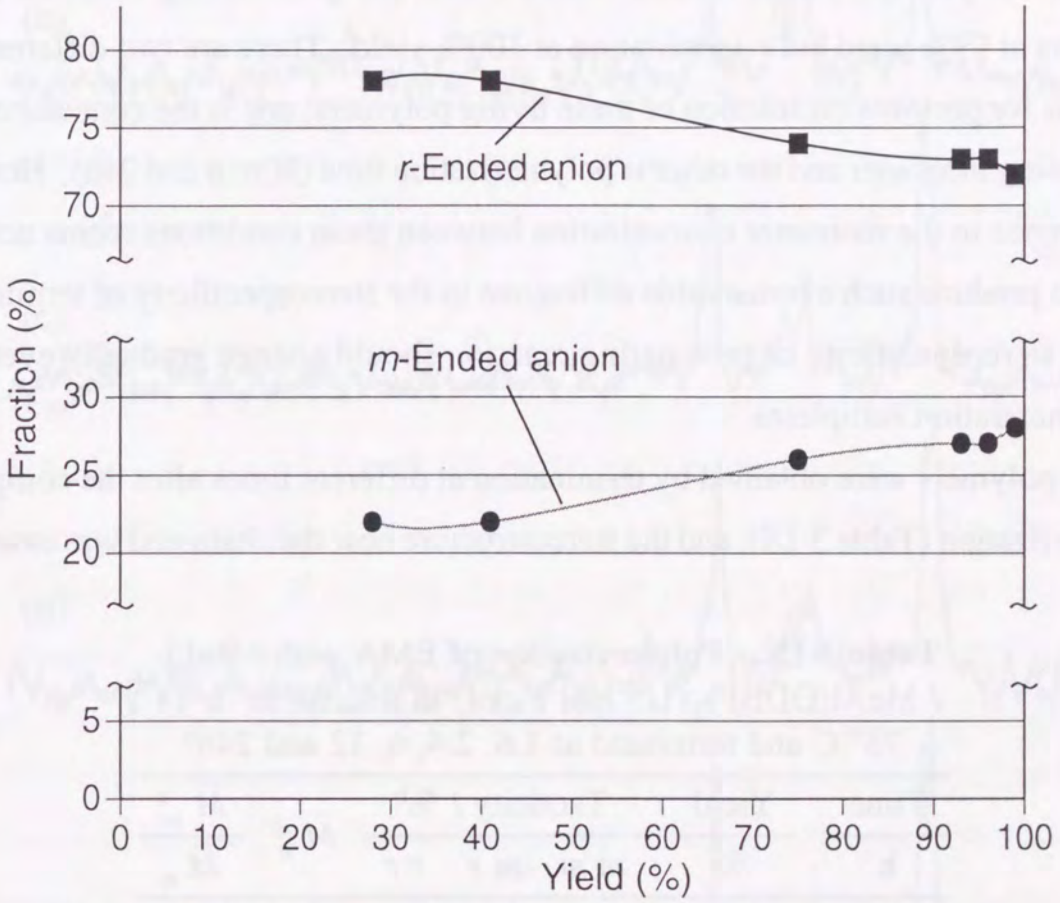


Figure 3-VII. Fraction of *r*-ended and *m*-ended propagating anions existing in the polymerization system.

Time Dependence of the Stereochemistry in the Terminating Reaction

The ^{13}C NMR spectra of the polymers formed at 99 and 100% yields (Figures 3-VId and e) are quite different in shape. The signals due to *–rm* terminal triad (35.66 and 35.68 ppm) has the strongest intensity in the spectrum of the polymer obtained at 99% yield (Figure 3-VId), while that due to *–rr* triad (35.39 and 35.41 ppm) is the strongest in the case of the polymer formed at 100% yield (Figure 3-VIe). The resonances of *–mm* appears in Figure 3-VId (99% yield), while that is not observable in Figure 3-VIe (100% yield). These results indicate that the protonating reaction favors *m*-addition at 99% yield but *r*-termination at 100% yield. There are two differences in conditions for protonation reaction of these living polymers; one is the concentration of the remaining monomer and the other is polymerization time (80min and 24h). However, the difference in the monomer concentration between these conditions seems not large enough to produce such a remarkable difference in the stereospecificity of termination. Thus the stereospecificity of protonating reaction should change gradually even after the polymerization completes.

The polymers were obtained by termination at different times after the completion of polymerization (Table 3-IX), and the stereostructure near the chain-end was examined.

Table 3-IX. Polymerization of EMA with *t*-BuLi / MeAl(ODBP)$_2$(1/5 mol / mol) in toluene at – 78° C and terminatd at 1.6, 2.4, 6, 12 and 24h[a]

Time	Yield	Tacticity / %[b]			$\bar{M}_n$[c]	$\bar{M}_w$[c] / $\bar{M}_n$
h	%	*m m*	*m r*	*r r*		
1.6	100	8.2	88.1	3.7	7820	1.10
2.4	100	7.8	87.6	4.1	7370	1.09
6.	100	7.8	89.1	3.1	9780	1.11
12.	100	7.8	88.7	3.5	9110	1.11
24.	100	7.7	88.6	3.7	7010	1.07

a EMA 10mmol, *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol, toluene 10ml.
b Determined by ^{13}C NMR signals due to carbonyl or methylene[24] carbons. c Determined by GPC.

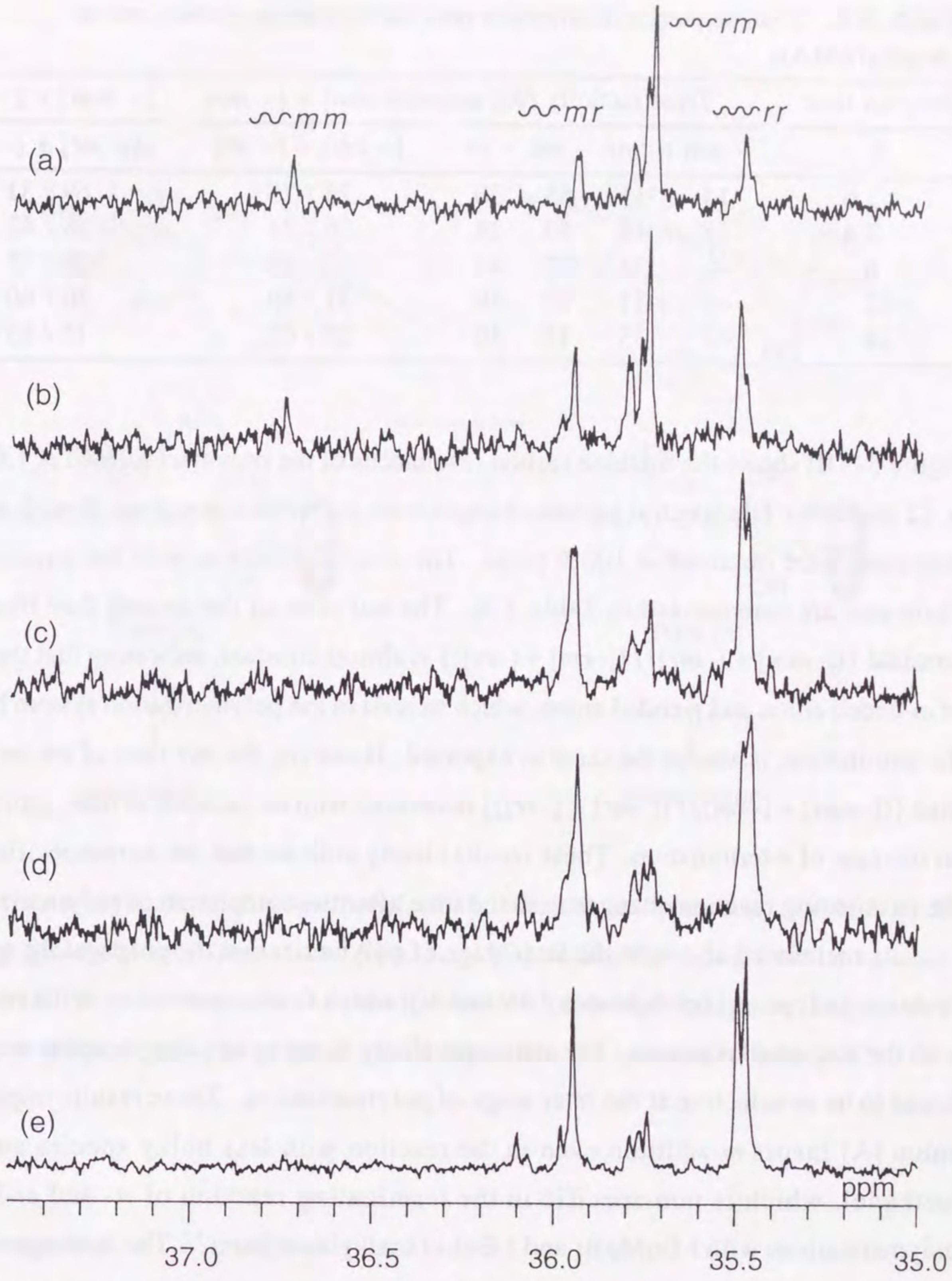


Figure 3-VIII. 125 MHz ^{13}C NMR spectra of methine carbon at the terminating chain-end of *ht*-poly(EMA)s formed at (a) 1.6, (b) 2.4, (c) 6, (d) 12, and (e) 24h, respectively.

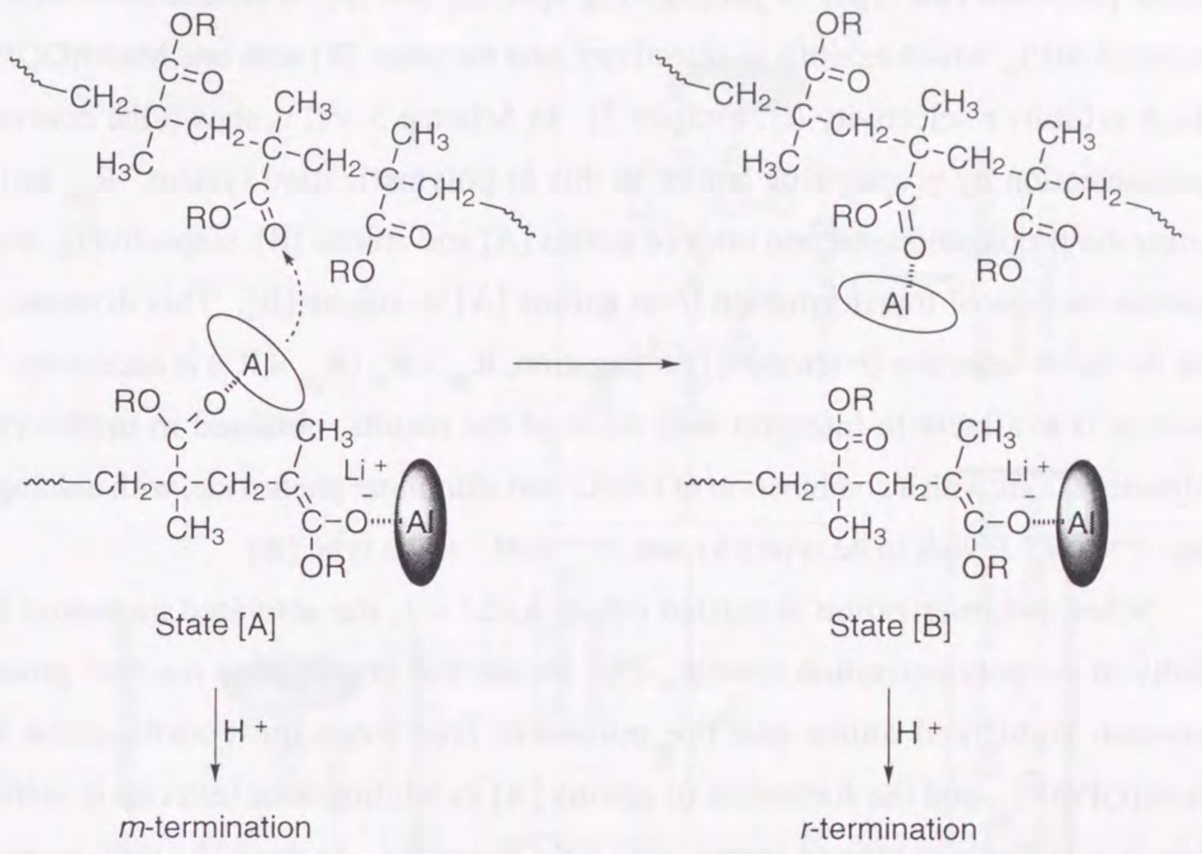
Table 3-X. Triad sequence distribution near the terminating chain-end of *ht*-poly(EMA)s

Polymn time	Triad tacticity /%				$[-mm] + [-mr]$	$[-mm] + [-rm]$
h	$-mm$	$-mr$	$-rm$	$-rr$	$[-rm] + [-rr]$	$[-mr] + [-rr]$
1.6	14	11	55	20	25 / 75	69 / 31
2.4	8	18	50	24	26 / 74	58 / 42
6	—	32	27	41	32 / 68	27 / 73
12	—	31	20	49	31 / 69	20 / 80
24	—	35	15	50	35 / 65	15 / 85

Figure 3-VIII shows the methine carbon resonances of the polymers formed at 1.6, 2.4, 6, 12 and 24h. The spectral pattern changes with polymerization time, though all the polymers were obtained at 100% yield. The triad distribution near the terminating chain-end are summarized in Table 3-X. The *m*/*r* ratio of the second diad from the terminal {([–*mm*] + [–*mr*]) / ([–*rm*] + [–*rr*])} is almost constant, indicating that the ratio of *m*-ended anion and *r*-ended anion, which existed in the polymerization system before the termination, is almost the same as expected. However, the *m*/*r* ratio of the terminal diad {([–*mm*] + [–*rm*]) / ([–*mr*] + [–*rr*])} decreased with an increase in time, indicating an increase of *r*-termination. These results clearly indicate that the stereospecificity of the terminating reaction changes with the time after the completion of polymerization.

As mentioned above, at the later stage of polymerization the propagating species favors to be type [A] (*cf.* Schemes 3-IV and V), which favors *m*-addition in the reaction with the activated monomer. The stereospecificity in the terminating reaction was also found to be *m*-selective at the later stage of polymerization. These results imply that anion [A] favors *m*-addition even in the reaction with less bulky species such as methanol, which is non-specific in the terminating reaction of *it*- and *st*-living polymerizations with *t*-BuMgBr and *t*-BuLi / trialkylaluminum.[13] The stereospecificity in termination reaction changes gradually from *m*-selective to *r*-selective with increasing the aging time after the completion of the polymerization. Based on the fact that propagating anions after 24h of initiation exhibit *r*-selectivity in termination reaction

Scheme 3-VI



with several alcohols, such as methanol, *t*-butyl alcohol, and phenol (*cf.* Table 3-V), the living anion changes from state [A] to state [B] during the aging time by releasing $MeAl(ODBP)_2$ coordinated at the penultimate unit, probably through exchange with in-chain monomeric units in polymer chains formed in the system (Scheme 3-VI).

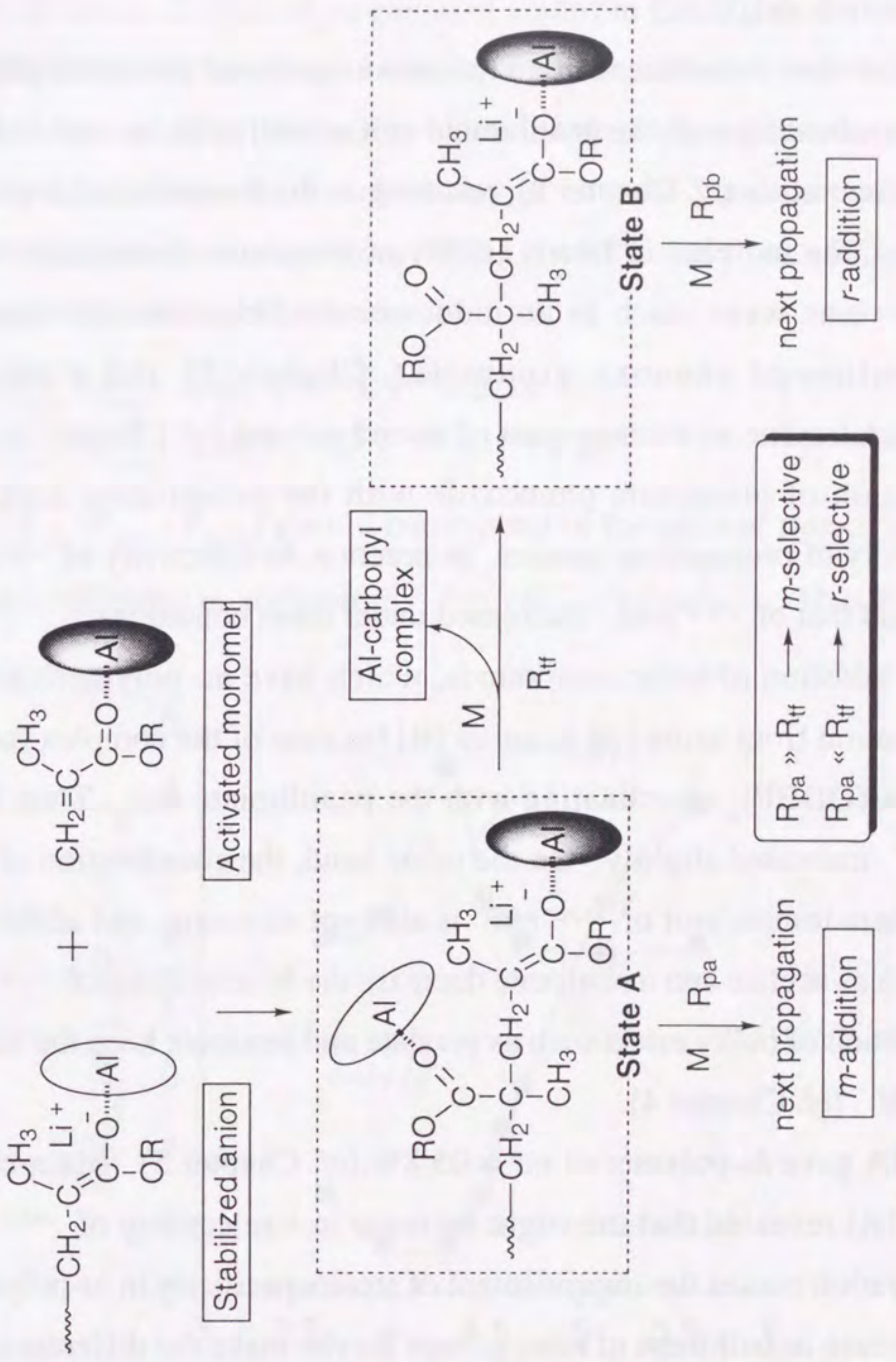
Mechanism of ht-Polymerization of Methacrylates

In order to explain the opposite stereospecificity of $\sim\sim\sim rM^{-}$ and $\sim\sim\sim mM^{-}$, the author proposed two types of propagating species; one [A] is coordinated with two MeAl(ODBP)$_2$, which exhibits *m*-selectivity, and the other [B] with one MeAl(ODBP)$_2$, which exhibits *r*-selectivity (*cf.* Chapter 2). In Scheme 3-VII is shown the concept of stereoselection by propagating anions in this *ht*-polymerization system. R_{pa} and R_{pb} denote the propagation reaction rates of anions [A] and anions [B], respectively, and R_{tf} denotes the rate of transformation from anions [A] to anions [B]. This demonstrates that for the *m*-selective (*r*-selective) propagation, $R_{pa} \gg R_{tf}$ ($R_{pa} \ll R_{tf}$) is necessary. The concept is available to interpret well most of the results, obtained in methacrylate polymerizations with a combination of *t*-BuLi and aluminum phenoxide, with assumption that $\sim\sim\sim rM^{-}$ favors to be type [A] and $\sim\sim\sim mM^{-}$ to be type [B].

When polymerization is carried out at Al/Li = 1, the activated monomer exist hardly in the polymerization system. This means that propagation reaction proceeds between stabilized anion and the monomer free from the coordination with MeAl(ODBP)$_2$, and the formation of anions [A] exhibiting *m*-selectivity is difficult. Thus *st*-polymer was formed in low yield (*cf.* Chapter 1). As the Al/Li ratio increases, the propagating species stabilized though the coordination with MeAl(ODBP)$_2$ become to react frequently with the monomer carrying MeAl(ODBP)$_2$ to form type [A] anions. Consequently, MeAl(ODBP)$_2$ twice more than *t*-BuLi induces the formation of highly *ht*-polymers quantitatively.

At high temperature, the transformation seems to be more significant than the propagation due to the weak coordination of MeAl(ODBP)$_2$ with the neutral penultimate unit, although high polymerization temperature promote both steps, propagation and transformation. This suggests the preferential formation of anions [B] which exhibit *r*-selectivity. In fact, *st*-polymers were obtained in polymerizations over –50°C (*cf.* Chapter 1). On the other hand, the lowered temperature makes the coordination of MeAl(ODBP)$_2$ with the penultimate unit stronger and the difference between the coordination with penultimate unit of $\sim\sim\sim mM^{-}$ and $\sim\sim\sim rM^{-}$ more significant. This

Scheme 3-VII



suggests an increase of *ht*-selectivity and relative stability of $\sim\sim rM^-$. Moreover, the propagation process is suppressed very much enough for $MeAl(ODBP)_2$ to leave from the penultimate unit of $\sim\sim mM^-$, resulting in an increase in *ht*-selectivity of $\sim\sim mM^-$ (*cf.* Chapters 1 and 3).

The increase in bulkiness around aluminum center of aluminum phenoxide prevents it from coordinating with the penultimate unit as well as in the cases of polymerization at high temperature (*cf.* Chapter 2), resulting in the formation of *st*-polymers. On the other hand, the increase in Lewis acidity of aluminum phenoxide which is brought about by some ways, such as an inducement of electron-withdrawing groups at *para*-position of phenoxy groups (*cf.* Chapter 2) and a use of less polar methylcyclohexane as a component of mixed solvent (*cf.* Chapter 1), strengthens the coordination of aluminum phenoxide with the penultimate unit, and enhances *m*-selectivity of propagating species. In practice, *ht*-selectivity of $\sim\sim rM^-$ increased slightly and that of $\sim\sim mM^-$ decreased under these conditions.

The addition of ester compounds, which have no polymerizability, promotes transformation from anion [A] to anion [B] because of the complex formation of them with $MeAl(ODBP)_2$ coordinating with the penultimate unit. Thus *ht*-selectivity of $\sim\sim mM^-$ increased slightly. On the other hand, the coordination of $MeAl(ODBP)_2$ with the penultimate unit of $\sim\sim rM^-$ is also not so strong, and addition of less bulky esters such as acetate and isobutyrate decrease the *ht*-selectivity of $\sim\sim rM^-$ evidently, while addition of bulky esters such as pivalate and benzoate keep the high *ht*-selectivity of $\sim\sim rM^-$ (*cf.* Chapter 4).

AlMA gave *ht*-polymer of $mr = 95.8\%$ (*cf.* Chapter 5). Main-chain analysis of poly(AlMA) revealed that the slight increase in *r*-selectivity of $\sim\sim mM^-$ in AlMA polymerization causes the improvement of stereospecificity in *ht*-polymerization. The slight increase in bulkiness of ester groups maybe make the difference in coordination of $MeAl(ODBP)_2$ with penultimate units of $\sim\sim mM^-$ and $\sim\sim rM^-$ more evident. Furthermore, it is suggested that the use of AlMA decreased the rate of propagation reaction, based on the result that unreacted AlMA remained in polymerization system under the conditions where EMA and PrMA gave polymers quantitatively. These lead sufficiently $\sim\sim mM^-$ into transformation from type [A] to type [B].

These assumptions are also explained from other viewpoint. Figure 3-IX shows Arrhenius plots of *ht*-selectivities of propagating anions in EMA polymerizations with *t*-BuLi / $MeAl(ODBP)_2$ (Al / Li = 5 mol / mol) (*cf.* Chapter 1, Table 1-IV). *ht*-Selectivity of both anions did not exhibit Arrhenius behavior throughout the polymerization temperature examined, however, *ht*-selectivity of $\sim\sim rM^-$ and that of $\sim\sim mM^-$ showed linear dependence in a range from –95°C to –40°C and from –60°C to –45°C, respectively, approximated as follows;

$$\ln(P_{r/m} / P_{r/r}) = 4.9 \times 10^3 \times T^{-1} - 2.3 \times 10 \qquad [1]$$

$$\ln(P_{m/r} / P_{m/m}) = -2.7 \times 10^3 \times T^{-1} + 1.5 \times 10 \qquad [2].$$

The ratio $P_{r/m} / P_{r/r}$ ($P_{m/r} / P_{m/m}$) should correspond to the ratio of rate of *m*-addition (*r*-addition) and *r*-addition (*m*-addition) by $\sim\sim rM^-$ ($\sim\sim mM^-$). Thus $P_{r/m} / P_{r/r}$ is

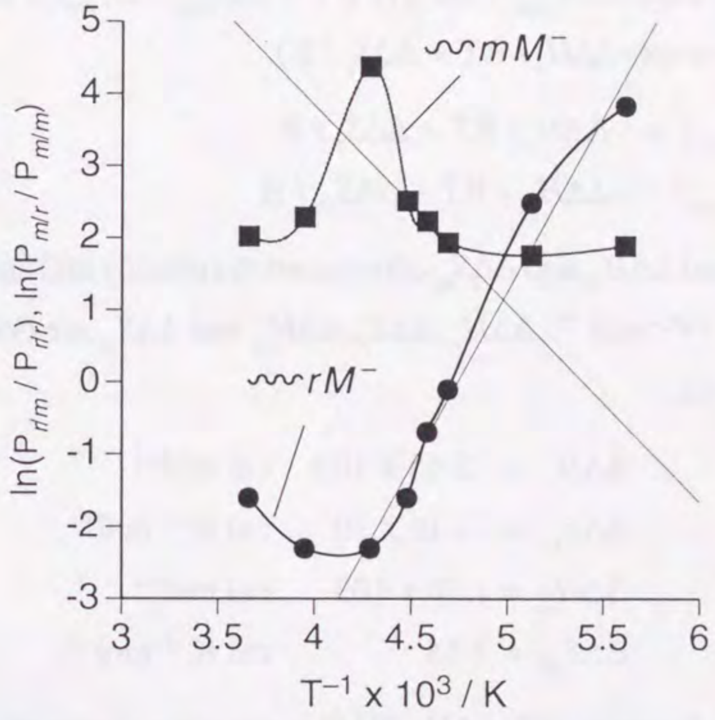


Figure 3-IX. Arrhenius plots of *ht*-selectivities of propagating anions in EMA polymerization with *t*-BuLi / $MeAl(ODBP)_2$ (1 / 5 mol / mol). (*cf.* Table 1-IV)

expressed as

$$P_{r/m} / P_{r/r} = (k_{r/m} [P_r^*][M^*]) / (k_{r/r} [P_r^*][M^*]) = k_{r/m} / k_{r/r} \qquad [3]$$

where $[P_r^*]$ and $[M^*]$ are the concentration of active species with *r* terminal diad and that of activated monomer, $k_{r/m}$ and $k_{r/r}$ the rate constant of *m*-addition by $\sim\sim\sim rM^-$ and that of *r*-addition by $\sim\sim\sim rM^-$. Similarly, $P_{m/r} / P_{m/m}$ is expressed as

$$P_{m/r} / P_{m/m} = k_{m/r} / k_{m/m} \qquad [4]$$

where $k_{m/r}$ and $k_{m/m}$ are the rate constant of *r*-addition by $\sim\sim\sim mM^-$ and that of *m*-addition by $\sim\sim\sim mM^-$.

If rate constants are expressed as Arrhenius equation, [3] and [4] are transformed into [5] and [6], respectively.

$$\begin{aligned} P_{r/m} / P_{r/r} &= k_{r/m} / k_{r/r} \\ &= \exp(-\Delta G_{r/m} / RT + \Delta G_{r/r} / RT) \\ &= \exp\{[-(\Delta H_{r/m} - T\Delta S_{r/m}) + (\Delta H_{r/r} - T\Delta S_{r/r})] / RT\} \\ &= \exp[-(\Delta H_{r/m} - \Delta H_{r/r}) / RT + (\Delta S_{r/m} - \Delta S_{r/r})] / R] \\ &= \exp(-\Delta\Delta H_r / RT + \Delta\Delta S_r / R). \end{aligned}$$

$$\ln(P_{r/m} / P_{r/r}) = -\Delta\Delta H_r / RT + \Delta\Delta S_r / R \qquad [5]$$

$$\ln(P_{m/r} / P_{m/m}) = -\Delta\Delta H_m / RT + \Delta\Delta S_m / R \qquad [6]$$

$\Delta\Delta H_r$ and $\Delta\Delta S_r$, and $\Delta\Delta H_m$ and $\Delta\Delta S_m$ correspond to enthalpy and entropy for *ht*-selectivity of $\sim\sim\sim rM^-$ and $\sim\sim\sim mM^-$. $\Delta\Delta H_r$, $\Delta\Delta S_r$, $\Delta\Delta H_m$ and $\Delta\Delta S_m$ are determined from [1] and [5], and [2] and [6].

$$\begin{aligned} \Delta\Delta H_r &= -2.45 \text{ x } 103 && \text{cal mol}^{-1} \\ \Delta\Delta S_r &= -1.16 \text{ x } 10 && \text{cal K}^{-1}\text{ mol}^{-1} \\ \Delta\Delta H_m &= 1.38 \text{ x } 103 && \text{cal mol}^{-1} \\ \Delta\Delta S_m &= 7.55 && \text{cal K}^{-1}\text{ mol}^{-1} \end{aligned}$$

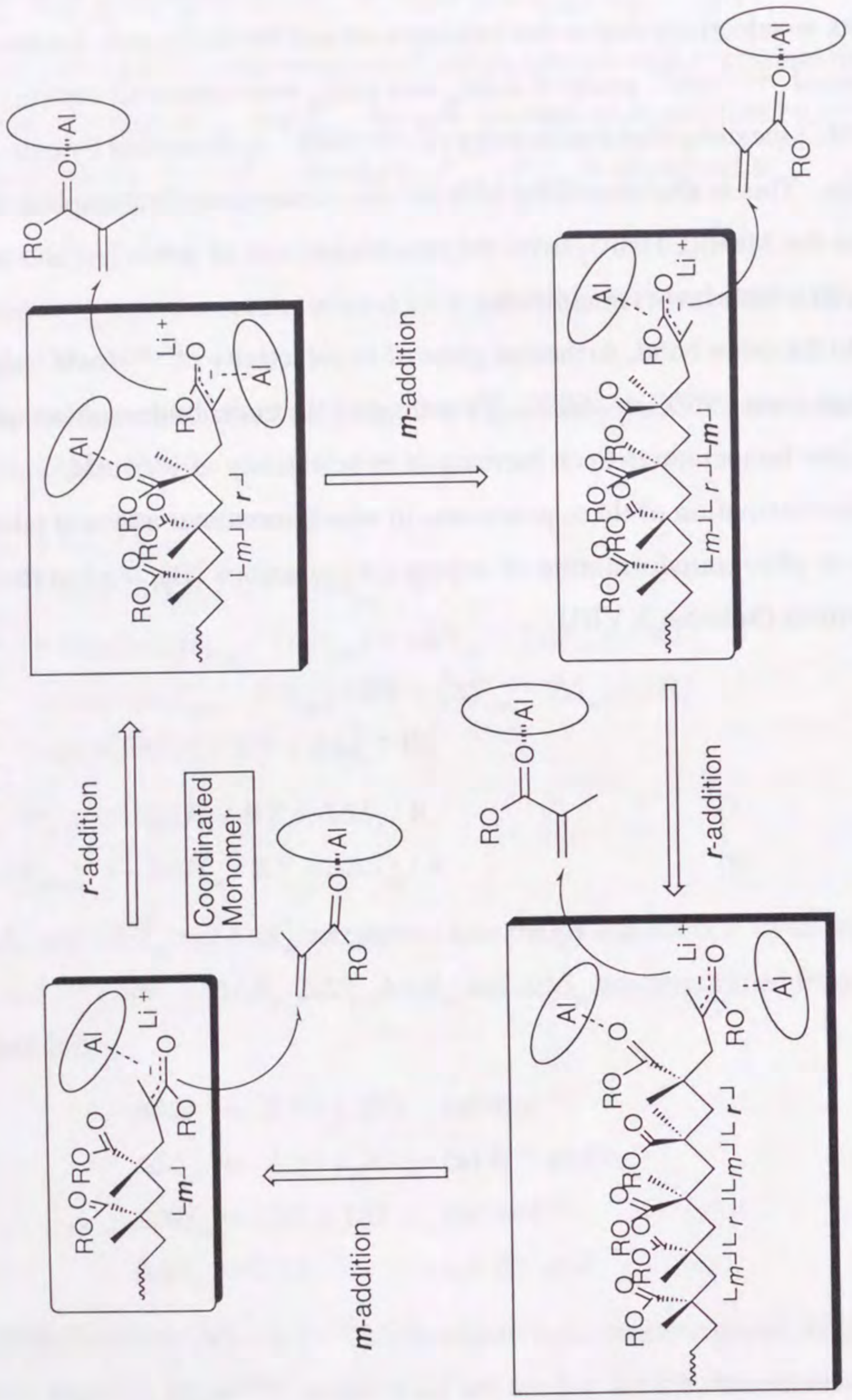
When Gibbs function ($\Delta G = \Delta H - T\Delta S$) is negative, the reaction proceeds smoothly. In other words, negative ΔH and/or positive ΔS are needed for the smooth reaction. In the case of $\sim\sim\sim rM^-$, both $\Delta\Delta H_r$ and $\Delta\Delta S_r$ are negative, meaning that $\sim\sim\sim rM^-$ exhibits

m-selectivity owing to enthalpy effect with sacrifice of entropy. This is consistent with the assumption that $\sim\sim\sim rM^-$ have two bulky MeAl(ODBP)$_2$ at the chain end and exhibits *m*-selectivity due to the bulkiness around the chain end. On the other hand, in the case of $\sim\sim\sim mM^-$ positive $\Delta\Delta H_m$ and $\Delta\Delta S_m$ were observed contrary to the case of $\sim\sim\sim rM^-$, meaning that *r*-selectivity of $\sim\sim\sim mM^-$ is controlled by entropy rather than enthalpy. This is also consistent with the above-mentioned assumption that $\sim\sim\sim mM^-$ releases the MeAl(ODBP)$_2$ from the penultimate unit of anion [A] and transforms into anion [B] which favors *r*-addition.

On the other hand, Arrhenius plots of *ht*-selectivity of $\sim\sim\sim mM^-$ showed a flat in the range from –95°C to –60°C. This suggest the contribution of low polymerization rate at low temperatures to an increase in *ht*-selectivity of $\sim\sim\sim mM^-$.

The alternation of these processes, in which monomer addition takes place either before or after transformation of anions [A] to anions [B], lead to the formation of *ht*-polymers (Scheme 3-VIII).

Scheme 3-VIII



Appendix 3-I

Assignment of Signals due to Terminal Methine Carbons Derived from $\sim\!\sim rM^{-}$

The chain-end analysis of poly(EMA)s formed at different times revealed that the stereospecificity in terminating reaction changed from *m*-selective to *r*-selective during the aging time after the polymerization completed. Moreover, the signal at 35.68ppm decreased more quickly than the signal at 35.66ppm with increasing time, although both signals were assigned as *–rm* at triad level (*cf.* Figure 3-VIII). Similarly, the intensities of two signals assignable to *–rr* increased in different ways as time passed. This behavior indicates that the rate of the change of stereospecificity in termination reaction depends on the stereochemistry near the propagating chain-end at longer sequence than at triad level. Then the author attempts to assign the signals derived from $\sim\!\sim rM^{-}$ at longer level.

The terminal *–rm* triad can be expressed as two stereosequence, *–mrm* and *–rrm*, at tetrad level. However, the resonances assignable to *–rm* split into three signals. This means that the splitting is at least due to pentad stereosequence. If this signals split at pentad level, possible stereosequences are four as follows;

–mmrm (α)	*–mrrm* (β)
–rmrm (γ)	*–rrrm* (δ) .

The pentad (γ) is the most probable stereosequence in *ht*-polymerization. The signal at 35.66ppm is strongest in spectra of the polymers obtained by termination in the middle of polymerization (*cf.* Figures 3-V and 3-VI). This suggests that this signal is assignable to *–rmrm* (γ). The *it*-triad, *–mm–*, increases with increasing polymer yield. The intensity of the signal at 36.68ppm also increase with an increase in yield (*cf.* Figure 3-VI). These results imply that the signal at 36.68ppm is concerned with *–mm–* sequence. Only *–mmrm* (α) pentad includes *it*-sequence among the series of pentad stereosequences, suggesting that the signal at 36.68ppm is due to *–mmrm* (α). The third signal at 36.71ppm is automatically assigned to minor sequences, *–mrrm* (β) and/or *–rrrm* (δ) (Figure 3-X). *st*-Polymer showed the signal due to terminal *–rm* at 36.71ppm (*cf.* Figure 3-III). This result supports the assignment.

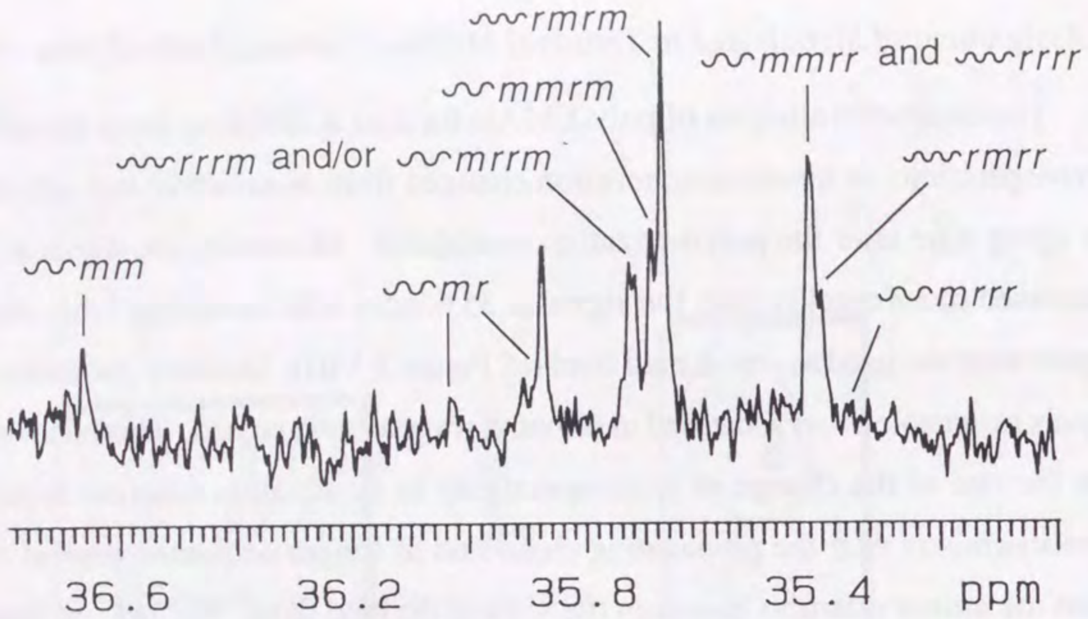


Figure 3-X. Assignments of the signals of methine carbons, derived from 〰rM^-, at the terminating chain-end of poly(EMA) at pentad level.

The resonances due to *–rr* is also assignable at pentad level in the same way. The signal at 35.39ppm appeared in spectra of all the polymers, suggesting that this is due to the most probable stereosequence, *–rmrr*, among the pentad sequences including terminal *–rr* triad. The intensity of the signal at 35.41ppm increases as that at 36.68ppm, which is assigned to *–mmrm*, decreases. This behavior implies that this is due to *–mmrr*. The signal due to *–rr* was observed at 35.41ppm in the spectrum of *st*-polymer (*cf.* Figure 3-III). This indicates that the signal at 35.41ppm is assigned to *–mmrr* and *–rrrr*. Thus the peak at 35.35ppm is assigned to *–mrrr* (Figure 3-X).

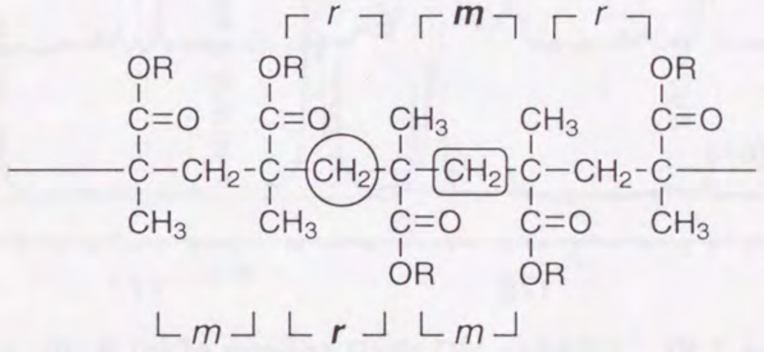
On the other hand, it was difficult to observe a similar phenomenon in the signals derived from 〰mM^- due to their weak intensities. Thus the assignment at pentad level for the peaks due to *–mm* and *–mr* was not performed.

Appendix 3-II

Assignment of NMR Spectra of Carbonyl and Methylene Carbons of ht-Poly(EMA) and Statistical Analysis of the Main Chain Stereostructure

Figure 3-XI shows carbonyl carbon region of ^{13}C NMR spectra of three types of stereoregular poly(EMA)s prepared in *it*-, *st*-, and *ht*-living polymerization systems with *t*-BuMgBr, *t*-BuLi / R_3Al, and *t*-BuLi / MeAl(ODBP)$_2$, respectively. One strong peak was observed in each spectrum at different chemical shift, which were assigned to *m mmm*, *rrrr*, and *mrmr* pentad sequences, respectively, although small peaks due to defective sequences were also observed. This indicates clearly that the polymer prepared with *t*-BuLi / MeAl(ODBP)$_2$ is one kind of stereoregular polymers different from *it*- and *st*-polymers.

Figure 3-XII shows methylene and carbonyl carbon NMR spectra of *ht*-poly(EMA) with detailed assignments. Resonances due to methylene groups showed two major signals, while those due to carbonyl carbons showed one major signal. The splitting in methylene carbon resonances reflect even-number stereosequences such as tetrad and hexad. This means that each major signal in the spectrum of methylene carbons is assigned to *m* and *r* diad-centered sequences, *rmr* and *mrm*, respectively, at tetrad levels. Such resonances are characteristic of the spectrum of methylene carbons of *ht*-polymers.



Tables 3-XI and XII summarize the observed and calculated values of stereosequence distribution in carbonyl and methylene carbon resonances at pentad and hexad levels, respectively. Statistical calculations were carried out in two ways of first-order and second-order Markov models.

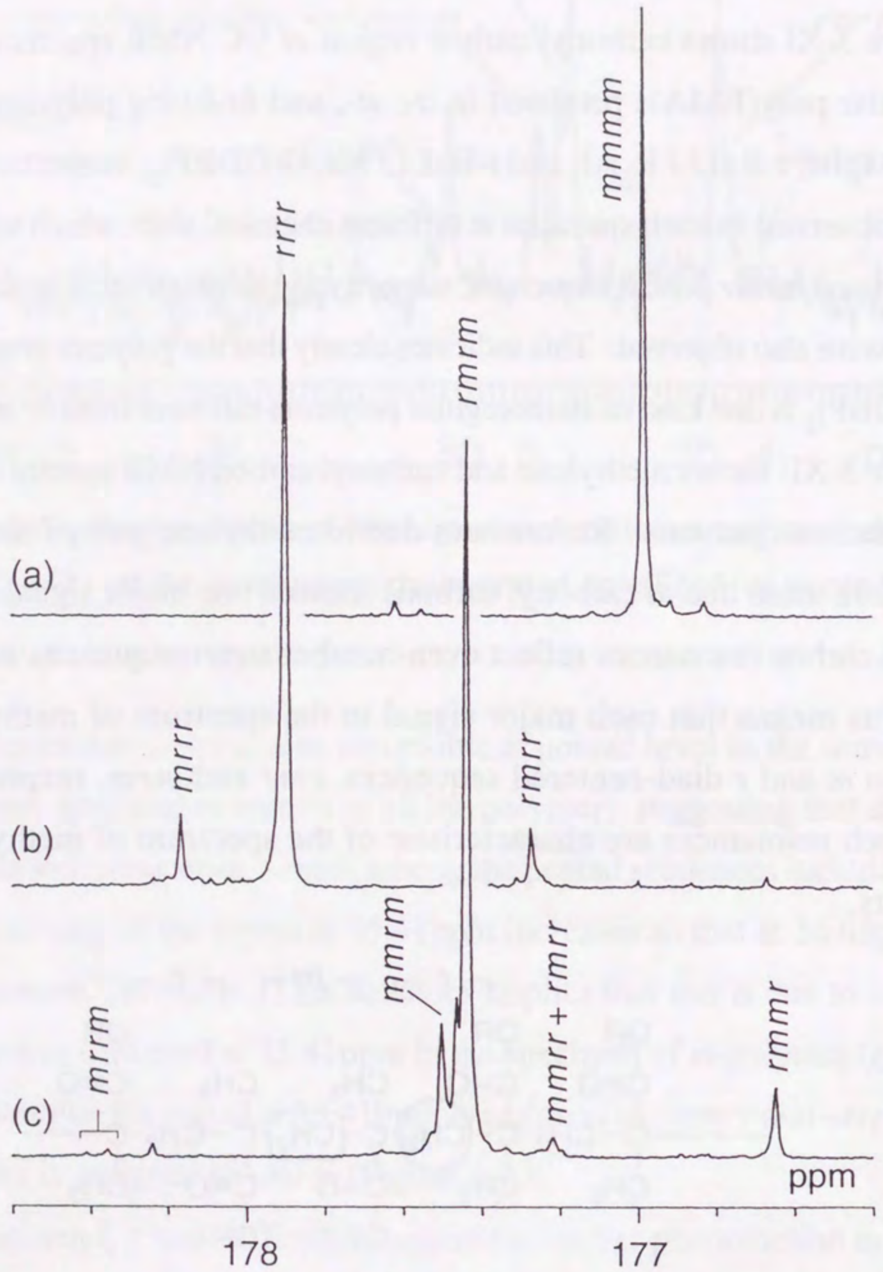


Figure 3-XI. 125MHz ^{13}C NMR spectra of (a) *it*-, (b) *st*-, and (c) *ht*-poly(EMA)s prepared with *t*-BuMgBr, *t*-BuLi / R_3Al, and *t*-BuLi / MeAl(ODBP)$_2$, respectively, measured in nitrobenzene-d_5 at 110°C.

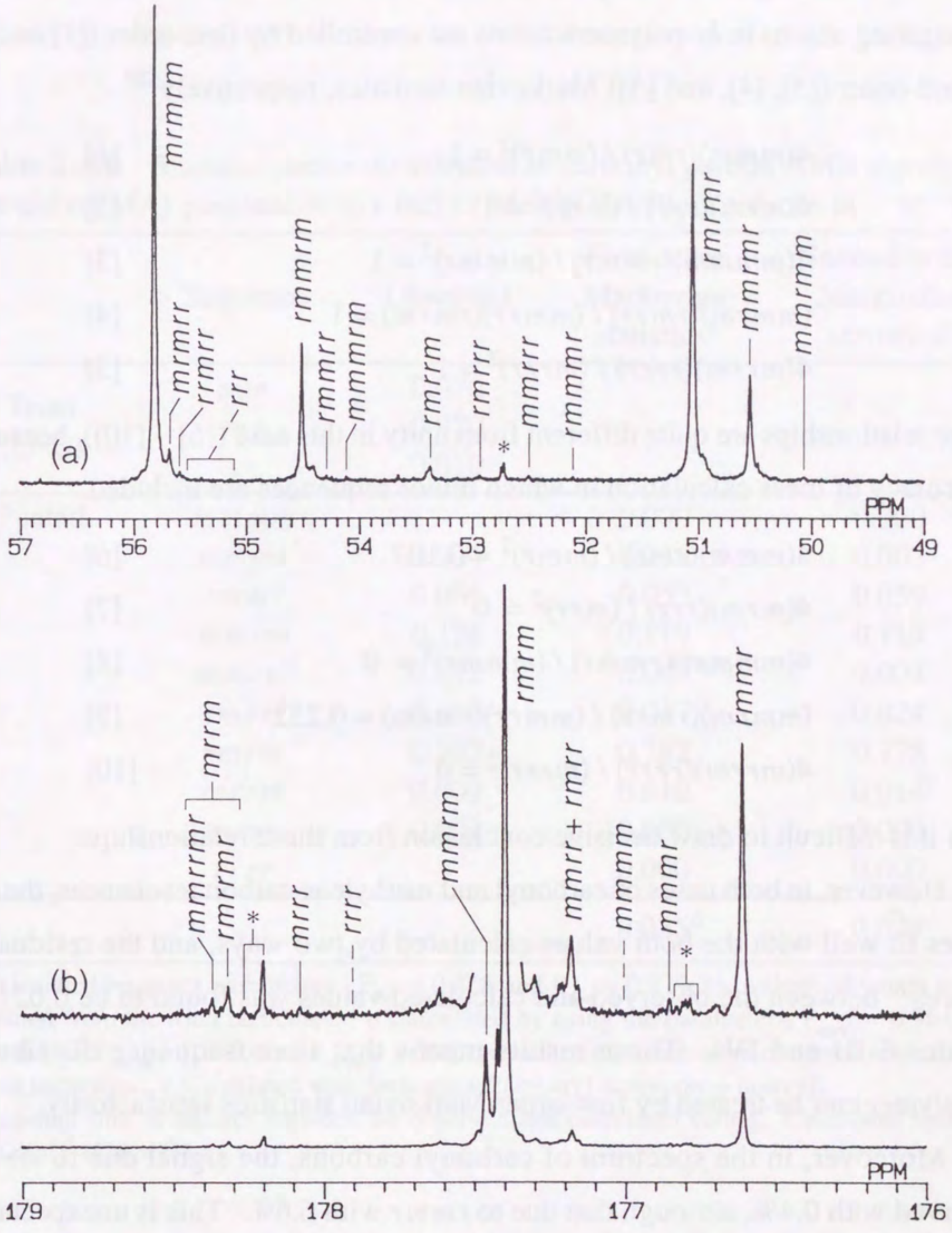


Figure 3-XII. ^{13}C NMR spectra of (a) methylene and (b) carbonyl carbons of *ht*-poly(EMA) prepared with *t*-BuLi / MeAl(ODBP)$_2$ (1/5 mol/mol) in toluene at –95°C for 48h, measured in nitrobenzene-d_5 at 110°C.
*; The signals due to chain-end units.

The following relationships ([1] ~ [5]) must fold, if the stereoselectivities of the propagating anions in *ht*-polymerizations are controlled by first-order ([1] and [2]) and second-order ([3], [4], and [5]) Markovian statistics, respectively.[28]

$$4(mmm)(rmr) / (mmr)^2 = 1 \qquad [1]$$

$$4(mrm)(rrr) / (mrr)^2 = 1 \qquad [2]$$

$$4(mmmm)(rmmr) / (mmmr)^2 = 1 \qquad [3]$$

$$(mmrm)(rmrr) / (mmrr)(rmrm) = 1 \qquad [4]$$

$$4(mrrm)(rrrr) / (mrrr)^2 = 1 \qquad [5]$$

These relationships are quite different from unity in this case ([6] ~ [10]), because of the inaccuracy of these calculation in which minor sequences are included.

$$4(mmm)(rmr) / (mmr)^2 = 0.107 \qquad [6]$$

$$4(mrm)(rrr) / (mrr)^2 = 0 \qquad [7]$$

$$4(mmmm)(rmmr) / (mmmr)^2 = 0 \qquad [8]$$

$$(mmrm)(rmrr) / (mmrr)(rmrm) = 0.252 \qquad [9]$$

$$4(mrrm)(rrrr) / (mrrr)^2 = 0 \qquad [10]$$

Thus it is difficult to draw decisive conclusion from these relationships.

However, in both cases of carbonyl and methylene carbon resonances, the obtained values fit well with the both values calculated by two ways, and the residual sum of squares[29] between the observed and calculated values was found to be 0.021 ~ 0.035 (Tables 6-III and IV). These results means that stereosequence distributions in *ht*-polymer can be treated by first-order Markovian statistics satisfactorily.

Moreover, in the spectrum of carbonyl carbons, the signal due to *mmmr* was observed with 0.4%, although that due to *rmmr* with 6.6%. This is unexpectable from first-order Markov model, suggesting an existence of antepenultimate unit effect. Similarly, the methylene carbon signals, which reflect longer stereosequences than carbonyl carbon signals, showed such an unexpected phenomenon more evidently; *mmmrm* 0.1%, *rmmrm* 12.1%. These results imply that the sequence distribution involving *mm* triad is better explained by second-order Markov model.

Table 3-XI. Stereosequence distribution in carbonyl carbon NMR signals of *ht*-poly(EMA) prepared with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at – 95° C

	Sequence	Observed	First-order Markovian statistics[a]	Second-order Markovian statistics[b]
Triad (C=O)	*mm*	0.070		
	mr	0.920		
	rr	0.010		
Pentad	*mmmm*	-	0.000	0.000
	mmmr	0.004	0.016	0.002
	rmmr	0.066	0.053	0.059
	mmrm	0.128	0.119	0.119
	mmrr[c]	0.012	0.003	0.004
	rmrr[c]	0.018	0.017	0.024
	rmrm	0.762	0.782	0.778
	mrrm	0.009	0.010	0.014
	mrrr	0.001	0.000	0.000
	rrrr	-	0.000	0.000
			0.035[d]	0.028[d]

a Calculated by using parameters, $P_{m/r} = 0.868$ and $P_{r/m} = 0.979$, the values of which were obtained from the triad tacticities. b Calculated by using the parameters, $P_{mm/r} = 0.984$, $P_{rm/r} = 0.869$, $P_{mr/m} = 0.970$, and $P_{rr/m} = 1.000$, the values of which were obtained from the tetrad tacticities. c Calculated with [*mmmr* + 2(*rmmr*) = *mmrm* + *mmrr*].
d Residual sum of squares between the observed and calculated values. Calculated with $[\Sigma|(\mathrm{Obsd})^2 - (\mathrm{Calcd})^2|]$.

Table 3-XII. Stereosequence distribution in methylene carbon NMR signals of *ht*-poly(EMA) prepared with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at – 95° C

	Sequence	Observed	First-order Markovian statistics[a]	Second-order Markovian statistics[b]
Tetrad	*mmm*	0.003		
	mmr	0.124		
	rmr	0.412		
	mrm	0.436		
	mrr	0.025		
	rrr	0.000		
Hexad	*mmmmm*	-	0.000	0.000
	mmmmr	-	0.002	0.000
	rmmmr	0.003	0.007	0.001
	mmmrm	0.001	0.016	0.002
	mmmrr	0.000	0.000	0.000
	rmmrm	0.121	0.103	0.115
	rmmrr	0.002	0.002	0.004
	mrmrm	0.389	0.383	0.377
	mrmrr	0.021	0.017	0.023
	rrmrr	0.002	0.000	0.000
	mmrmm	0.003	0.008	0.008
	mmrmr	0.110	0.103	0.103
	rmrmr	0.323	0.339	0.338
	mmrrm	0.003	0.003	0.004
	mmrrr	0.000	0.000	0.001
	rmrrm	0.019	0.017	0.024
	rmrrr	0.003	0.000	0.000
	mrrrm	-	0.000	0.000
	mrrrr	-	0.000	0.000
	rrrrr	-	0.000	0.000
			0.020[c]	0.021[c]

a Calculated by using parameters, $P_{m/r} = 0.868$ and $P_{r/m} = 0.979$, the values of which were obtained from the triad tacticities. b Calculated by using the parameters, $P_{mm/r} = 0.984$, $P_{rm/r} = 0.869$, $P_{mr/m} = 0.970$, and $P_{rr/m} = 1.000$, the values of which were obtained from the tetrad tacticities. c Residual sum of squares between the observed and calculated values. Calculated with [$\Sigma|(Obsd)^2-(Calcd)^2|$].

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24. In the carbonyl carbon spectra, carbonyl carbon of the terminal unit resonates in the region from *mm* to *rr* depending on the stereochemistry in terminal diad, thus triad tacticities were determined from methylene carbon resonances using triad-tetrad relationships as follows;[25]

$$mm = mmm + 1/2\, mmr$$
$$mr = rmr + mrm + 1/2\, mmr + 1/2\, mrr$$
$$rr = rrr + 1/2\, mrr.$$

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Chapter 4

Control of Stereospecificity in Methacrylate Polymerization by Added Esters

Introduction

Internal and external aromatic esters, such as ethyl benzoate or methyl *p*-toluate, are known to increase the stereospecificity in olefin polymerization with heterogeneous Ziegler-Natta catalysts such as $MgCl_2$-supported Ti catalysts. The internal electron donors suppress the formation of non-stereospecific sites,[1] and the external electron donors convert the non-stereospecific sites to the high isotactic- (*it*-) specific ones, and the low *it*-specific sites to an inactive ones.[2,3]

Ester compounds, as weak Lewis bases, have also been used in ionic polymerization systems as the third initiator component. Cationic polymerization of isobutyl vinyl ether (IBVE) with IBVE-acetic acid adduct / $EtAlCl_2$ in the presence of ester additive, such as ethyl acetate and ethyl benzoate, proceeds in a living manner, while in the absence of the Lewis base neither living nor long-lived propagating species are formed under the same conditions.[4,5]

Anionic polymerization of methacrylates with *t*-butyllithium (*t*-BuLi) / trialkylaluminum in toluene at low temperatures gives syndiotactic (*st*-) polymers with narrow molecular weight distribution (MWD).[6] However, Müller and his coworkers found that this polymerization of methyl methacrylate (MMA) at –78°C deviated significantly from conventional first-order kinetics due to the formation of a coordinative polymer network as gel in which the living chain ends are coordinated with carbonyl groups in the chain.[7] They claim that the addition of ester compounds such as methyl pivalate and methyl benzoate prevents the formation of the coordinative network of living polymer chains, giving first-order time-conversion plots in the temperature range of –78 to 0°C.[7,8]

Stereochemical analysis of heterotactic (*ht*-) poly(ethyl methacrylate) [poly(EMA)], prepared with *t*-BuLi / bis(2,6-di-*t*-butylphenyl)methylaluminum [$MeAl(ODBP)_2$] in toluene at low temperature,[9,10] by ^{13}C NMR revealed that *ht*-

selectivity [*meso*- (*m*-) selectivity] of *r*-ended anions was higher than *ht*-selectivity [*racemo*- (*r*-) selectivity] of *m*-ended anions (*cf.* Chapter 1). The chain-end analysis showed that (1) dimer anion favored *r*-addition, (2) the resultant *r*-trimer anion favored *m*-addition and (3) *r*-ended anion was more abundant than *m*-ended anion in this polymerization system (*cf.* Chapter 3).[11] Moreover, the NMR analysis at the terminating chain-end revealed that stereoregularity near the terminating chain-end decreased with increasing polymer yield (Chapter 3).[12,13] This means that stereoselectivity of the propagating anions is affected by the monomer concentration. Since the monomer, ethyl methacrylate (EMA), is also an ester compound, the results imply the possibility that certain ester compounds may affect the stereospecificity of this polymerization. In this Chapter, the author attempted to control the stereoselectivities of the propagating anions by adding non-polymerizable ester compounds (as the third initiator component), with the aim of improving *ht*-selectivity.[14]

Experimental

The experimental procedures except for these described below are the same as those described in detail in Chapters 1-3.

Materials

Ester compounds were purified by fractional distillation under dry nitrogen or under reduced nitrogen pressure, dried over MS 4A, and used for polymerization reactions. Ethyl pivalate was dried over calcium dihydride and vacuum-distilled just before use.

Preparation of MeAl(ODBP)$_2$[15]

A solution of 2,6-di-*t*-butylphenol in heptane (2 equiv.) was added slowly to a toluene solution of trimethylaluminum (1 equiv.) at 0°C. The resulting mixture was stirred at room temperature for 20h. The solvent was removed under vacuum to leave a yellowish solid. The product was recrystallized three times by dissolving it in hot heptane and cooling to –30°C. After most of heptane was removed by a syringe and the residual heptane was evaporated under vacuum to dryness, the solid residue was dissolved in toluene and used for the polymerization reactions.

Polymerization

All the polymerization were carried out in a glass ampoule filled with dried nitrogen passed through MS 4A cooled at –78°C. A heptane solution of *t*-BuLi was added to an aluminum phenoxide in toluene at polymerization temperature. The polymerization reaction was initiated by adding the monomer slowly to this mixture at polymerization temperature. Every ester compound was added into the polymerization mixture at 10min after initiation.[16,17] The last polymerizations summarized in Table 4-IV were initiated by adding a heptane solution of *t*-BuLi to the mixture of monomer, ethyl pivalate, toluene, and MeAl(ODBP)$_2$ to suppress the possible reaction of *t*-BuLi with ethyl pivalate prior to start of polymerization.[16] The reaction was terminated by adding methanol containing HCl at the polymerization temperature. The reaction mixture was poured into a large amount of hexane to precipitate the polymeric product. In the case of MMA polymerization, the precipitate was collected by filtration, washed with hexane, dilute HCl and water, successively, and dried under vacuum. In the case of EMA polymerization, the polymeric product was precipitated by cooling the hexane to –78°C and organic impurities such as monomer and 2,6-di-*t*-butylphenol derived from MeAl(ODBP)$_2$ were removed by repeated decantation. The product was redissolved in acetone and the solution was poured into a large amount of water to reprecipitate the polymeric product. The precipitate was collected by filtration, washed with dilute HCl and water, successively, and dried under vacuum.

Measurements

^{13}C NMR spectra of ethyl isobutyrate, ethyl pivalate, and the mixture of them with EMA in the absence or presence of MeAl(ODBP)$_2$ were measured in toluene-d_8 at –78°C on a JEOL JNM GX270 spectrometer operated at 67.8 MHz. Tacticities of PMMAs were determined from α-methyl signals in ^{1}H NMR spectra measured in CDCl$_3$

at 55°C on a JEOL JNM GX270 spectrometer operated at 270MHz or on a JEOL AL400 spectrometer operated at 400MHz. Tacticities of poly(EMA)s and several PMMAs were determined from integration intensity of carbonyl carbon signals, measured in $CDCl_3$ at 55°C or in nitrobenzene-d_5 at 110°C on a Varian Unity Inova 500 spectrometer operated at 125MHz. However, the signals due to chain-end units were observed in the region of *rr* triad (*cf.* Chapter 6),[18] thus tacticities were calculated with removal of peak intensity of the resonances due to chain-end units. The standard deviations of tacticity were within 0.44% for five runs. Molecular weight and its distribution of the polymers were determined by size exclusion chromatography (SEC) using a JASCO 880-PU chromatograph equipped with two Shodex SEC columns [KF-806L (30cm x 0.8cm) x2] using tetrahydrofuran as an eluent at 40°C. The SEC chromatogram was calibrated against standard PMMA samples.

Results and Discussion

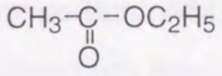
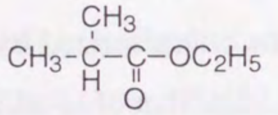
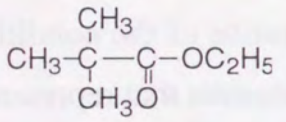
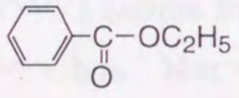
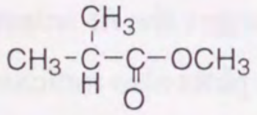
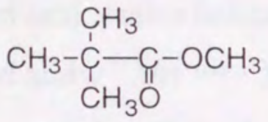
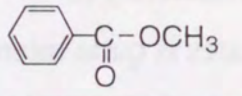
In Table 4-I are summarized the results of polymerizations of MMA with *t*-BuLi / MeAl(ODBP)$_2$ / ester compound (1 / 5 / 5 mol / mol / mol) in toluene at –78°C. In all the cases *ht*-polymers were obtained. Variation of the tacticity of the polymers obtained is relatively small ($mr = 64.0 \sim 69.2\%$) irrespective of the bulkiness of the esters.

The polymerizations of EMA were also carried out under the same conditions. The results are summarized in Table 4-II. *ht*-Polymers were obtained with narrow MWDs. Stereoregularities of polymers obtained were affected significantly by the addition of ester compounds as compared with the cases of MMA, and *mr* content varies from 63.0% (ethyl acetate) to 89.2% (ethyl pivalate).

Stereochemical processes in the *ht*-polymerization may be characterized by two parameters; the probability of *r*-addition by *m*-ended anion ($P_{m/r}$) and that of *m*-addition by *r*-addition ($P_{r/m}$) in first-order Markovian statistics. The ratios of the conditional probabilities, $P_{m/r} / P_{m/m}$ and $P_{r/m} / P_{r/r}$, can be regarded as parameters that represent *ht*-selectivity of *m*-ended anions ($\sim\!\sim\!\sim mM^{-}$)and that of *r*-ended anions ($\sim\!\sim\!\sim rM^{-}$), respectively. In Figure 4-I are plotted the *ht*-selectivities of $\sim\!\sim\!\sim mM^{-}$ and $\sim\!\sim\!\sim rM^{-}$. The plots clearly demonstrate that the addition of the esters changes the *ht*-selectivity of $\sim\!\sim\!\sim rM^{-}$ drastically but only slightly that of $\sim\!\sim\!\sim mM^{-}$. The plots also indicate that the *ht*-selectivity of $\sim\!\sim\!\sim rM^{-}$ depends on the bulkiness of the added esters; less bulky esters such as acetates and isobutyrates decrease the selectivity of $\sim\!\sim\!\sim rM^{-}$ while bulky esters such as pivalates and benzoates do not sacrifice the high selectivity of $\sim\!\sim\!\sim rM^{-}$.

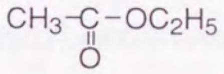
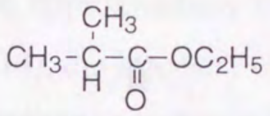
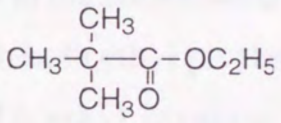
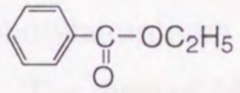
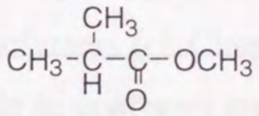
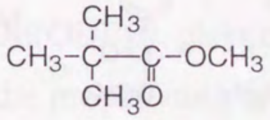
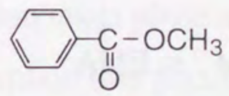
The remarkable difference between isobutyrates and pivalates is quite interesting. To examine this, coordination ability of ethyl isobutyrate and ethyl pivalate with MeAl(ODBP)$_2$ was studied by ^{13}C NMR spectroscopy. Figure 4-II shows ^{13}C NMR signals of carbonyl carbons of ethyl isobutyrate and ethyl pivalate in the presence or absence of an equimolar amount of MeAl(ODBP)$_2$. In both cases, the carbonyl carbon signals showed downfield shift by the addition of MeAl(ODBP)$_2$, indicating that both the ester compounds have the ability to form complexes with MeAl(ODBP)$_2$. The results imply the possibility that these esters existing in the polymerization system may

Table 4-I. Polymerization of MMA with *t*-BuLi /MeAl(ODBP)$_2$/ester compound in toluene at –78°C for 24h[a]

Ester	Yield	$\overline{M}_n$ [b]	$\overline{M}_w$ [b]	Tacticity / %[c]			$P_{m/r}$ [e]	$P_{r/m}$ [e]
	%		$\overline{M}_n$	*mm*	*mr*	*rr*		
None	100	8330	1.18	11.6[d]	67.8[d]	20.6[d]	0.745	0.622
 $CH_3-\underset{\underset{O}{\Vert}}{C}-OC_2H_5$	44	4290	1.14	11.5	64.0	24.5	0.736	0.566
 $CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{\underset{O}{\Vert}}{C}-OC_2H_5$	80	6190	1.26	11.4	67.2	21.4	0.747	0.611
 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\underset{O}{\Vert}}{C}-OC_2H_5$	99	8620	1.38	12.2	69.2	18.6	0.739	0.650
	99	8010	1.29	14.2	68.9	16.9	0.708	0.671
 $CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{\underset{O}{\Vert}}{C}-OCH_3$	92	7010	1.24	11.8	66.7	21.5	0.739	0.608
 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\underset{O}{\Vert}}{C}-OCH_3$	99	6420	1.31	11.2[d]	67.3[d]	21.5[d]	0.750	0.610
	100	8170	1.12	11.5[d]	66.9[d]	21.6[d]	0.744	0.608

a *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol, ester compound 1.0mmol, EMA 10mmol, toluene 10ml. Ester compounds were added at 10min after initiation. b Determined by SEC. c Determined by ^{1}H NMR. d Determined by ^{13}C NMR. e The conditional probabilities in the first-order Markovian statistics.

Table 4-II. Polymerization of EMA with *t*-BuLi /MeAl(ODBP)$_2$/ester compound in toluene at –78°C for 24h[a]

Ester	Yield	$\overline{M}_n$ [b]	$\overline{M}_w$ [b]	Tacticity / %[c]			$P_{m/r}$ [d]	$P_{r/m}$ [d]
	%		$\overline{M}_n$	*mm*	*mr*	*rr*		
None	100	7010	1.07	7.7	88.6	3.7	0.852	0.924
 $CH_3-\underset{\underset{O}{\Vert}}{C}-OC_2H_5$	68	5180	1.07	3.2	63.0	33.8	0.908	0.482
 $CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{\underset{O}{\Vert}}{C}-OC_2H_5$	100	7700	1.06	5.9	77.2	16.9	0.867	0.695
 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\underset{O}{\Vert}}{C}-OC_2H_5$	100	8240	1.06	6.5	89.2	4.3	0.873	0.912
	99	8170	1.12	7.5	88.9	3.6	0.856	0.925
 $CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{\underset{O}{\Vert}}{C}-OCH_3$	100	7190	1.08	6.2	80.9	12.9	0.867	0.758
 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\underset{O}{\Vert}}{C}-OCH_3$	97	8540	1.06	6.6	89.0	4.4	0.871	0.910
	100	8710	1.07	6.8	89.0	4.2	0.867	0.914

a *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol, ester compound 1.0mmol, EMA 10mmol, toluene 10ml. Ester compounds were added at 10min after initiation.

b Determined by SEC. c Determined by ^{13}C NMR.

d The conditional probabilities in the first-order Markovian statistics.

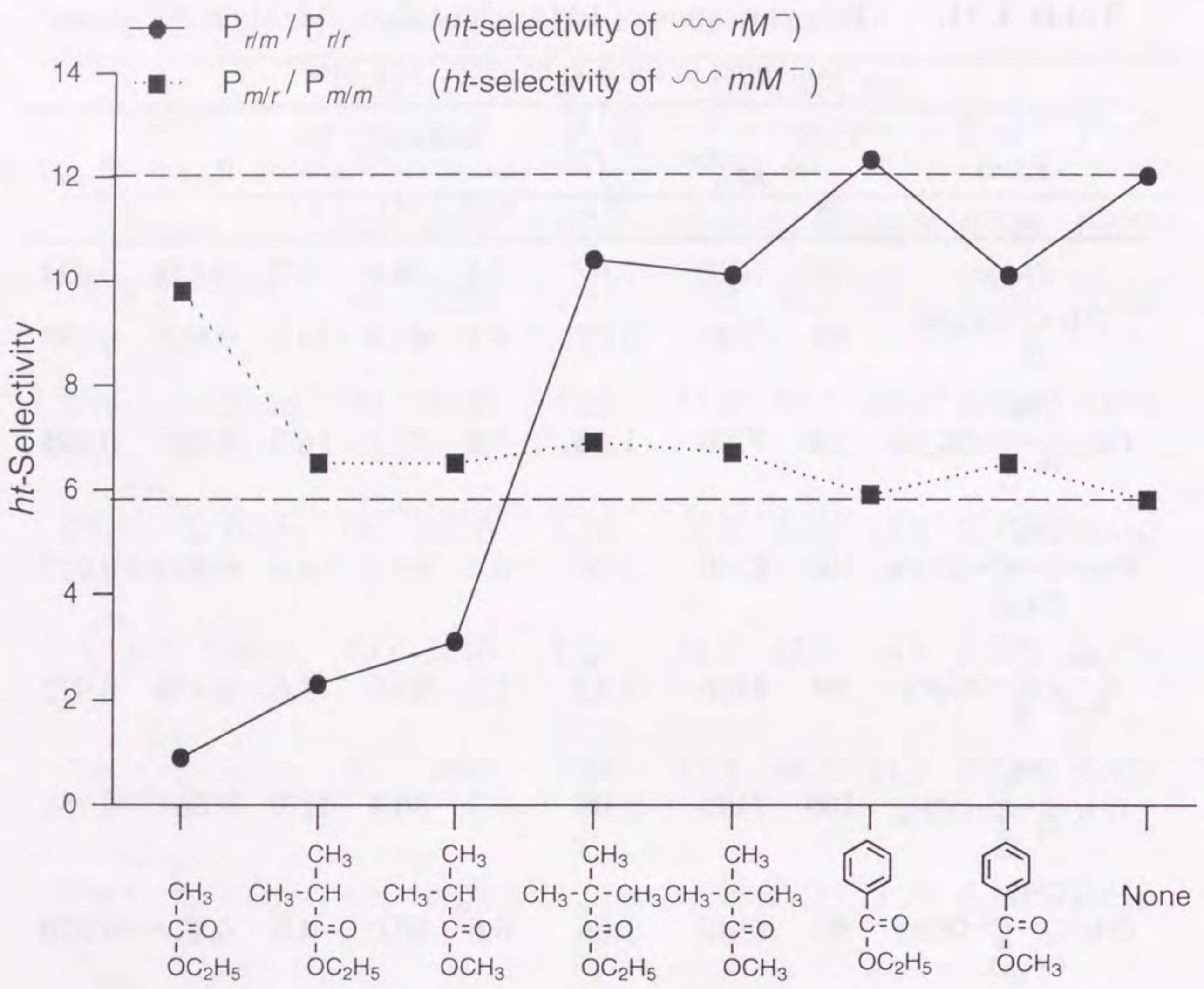


Figure 4-I. *ht*-Selectivities of $\sim\!\sim mM^-$ and $\sim\!\sim rM^-$ in EMA polymerizations with *t*-BuLi / MeAl(ODBP)$_2$ in the absence or presence of ester compounds.

compete with EMA monomer in the coordination with MeAl(ODBP)$_2$. Thus the NMR spectroscopic coordination experiments were also carried out for the mixtures of EMA and ester compounds. Figure 4-III shows the ^{13}C NMR signals of the equimolar mixtures of EMA and the ester in the presence or absence of MeAl(ODBP)$_2$. The ternary mixtures of EMA, ethyl isobutyrate or pivalate, and MeAl(ODBP)$_2$ showed four carbonyl carbon signals, indicating that EMA and the ester compounds competitively coordinate to MeAl(ODBP)$_2$. In the case of ethyl isobutyrate (Fig. 4-IIIb), the intensity of the signal at 173.1ppm due to the coordinated EMA is much weaker than that at 187.3ppm due to the coordinated isobutyrate. The results mean that MeAl(ODBP)$_2$ mainly coordinates with ethyl isobutyrate rather than EMA. The selectivity of coordination was determined to be approximately EMA:ethyl isobutyrate = 2:8.[19] In the case of ethyl pivalate (Fig. 3-IIId), the intensity of the signal at 173.1ppm is a little stronger than that at 185.5ppm due to the coordinated pivalate, indicating that MeAl(ODBP)$_2$ comparably coordinates with both ethyl pivalate and EMA; the selectivity of coordination was approximately EMA:ethyl pivalate = 6:4.[19] The latter result is consistent with the fact that triisobutylaluminum coordinates comparably to both methyl pivalate and MMA.[20]

The ratio of MeAl(ODBP)$_2$ and *t*-BuLi (Al / Li) is also important to obtain the *ht*-polymers (*cf.* Chapter 1). When Al / Li = 1, an *st*-polymer is obtained in low yield, while *ht*-polymers are obtained quantitatively at Al / Li ≥ 2.[9] This result suggests that MeAl(ODBP)$_2$ plays two significant roles in heterotactic polymerization; the stabilization of the propagating anions and the activation of the monomer. And the propagation reaction takes place selectively between the stabilized anion and the activated monomer. To explain this peculiar stereoregulation, the author has postulated a mechanism, where the presence or absence of MeAl(ODBP)$_2$ at the penultimate ester group is the key (*cf.* Chapter 2); (1) there exist two types of propagating anions, one is coordinated by two MeAl(ODBP)$_2$ molecules at the chain end and the carbonyl group of the penultimate monomeric unit [A], and the other by one aluminum phenoxide at the chain end [B], and (2) $\sim\!\sim rM^-$, which should undergo *m*-addition, favor to be the former [A] and $\sim\!\sim mM^-$, which should undergo *r*-addition, to be the latter [B].[21,22] Just after monomer

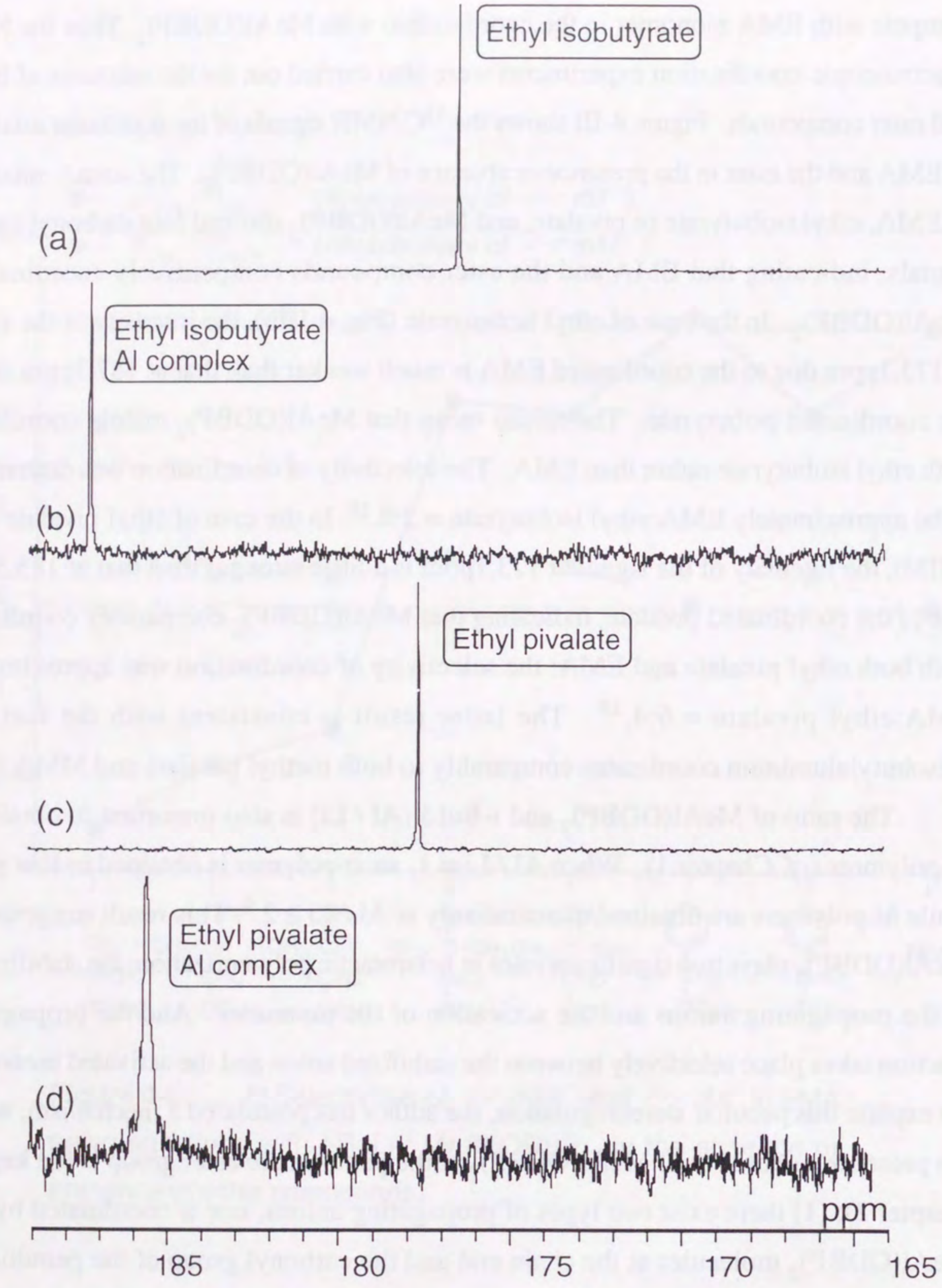


Figure 4-II. 67.8 MHz ^{13}C NMR spectra, measured in toluene-d_8 at –78°C, of carbonyl carbons of (a) ethyl isobutyrate, (b) ethyl isobutyrate / MeAl(ODBP)$_2$, (c) ethyl pivalate, and (d) ethyl pivalate / MeAl(ODBP)$_2$.

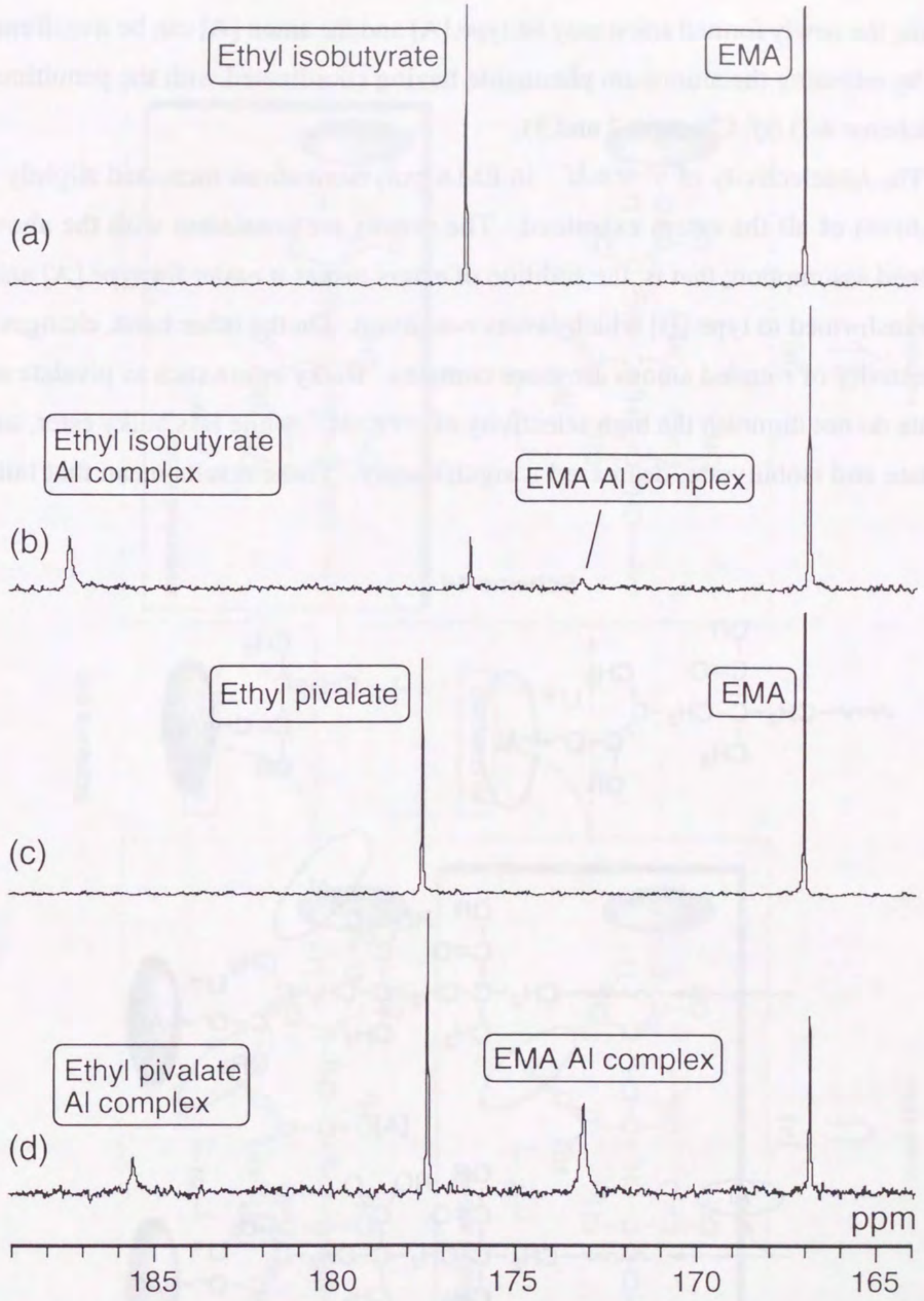
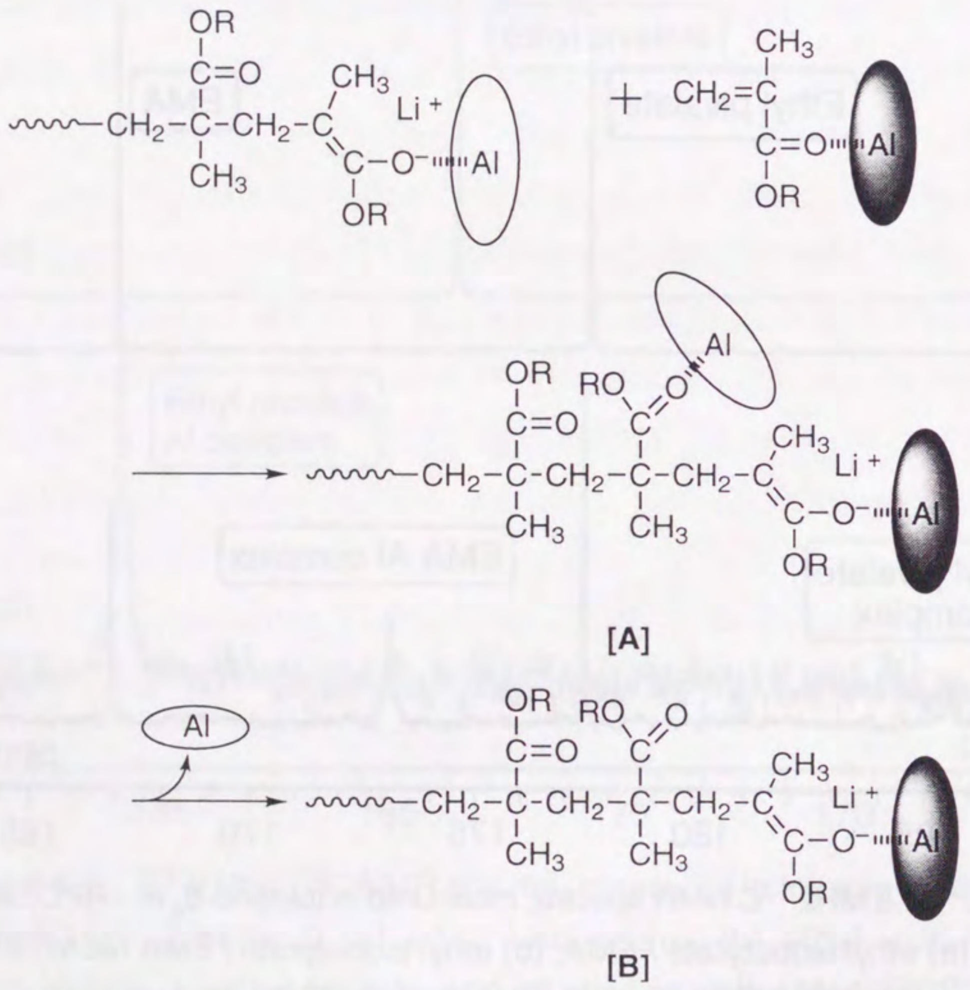


Figure 4-III. 67.8 MHz ^{13}C NMR spectra, measured in toluene-d_8 at –78°C, of carbonyl carbons of (a) ethyl isobutyrate / EMA, (b) ethyl isobutyrate / EMA MeAl(ODBP)$_2$, (c) ethyl pivalate / MeAl(ODBP)$_2$, and (d) ethyl pivalate / EMA MeAl(ODBP)$_2$.

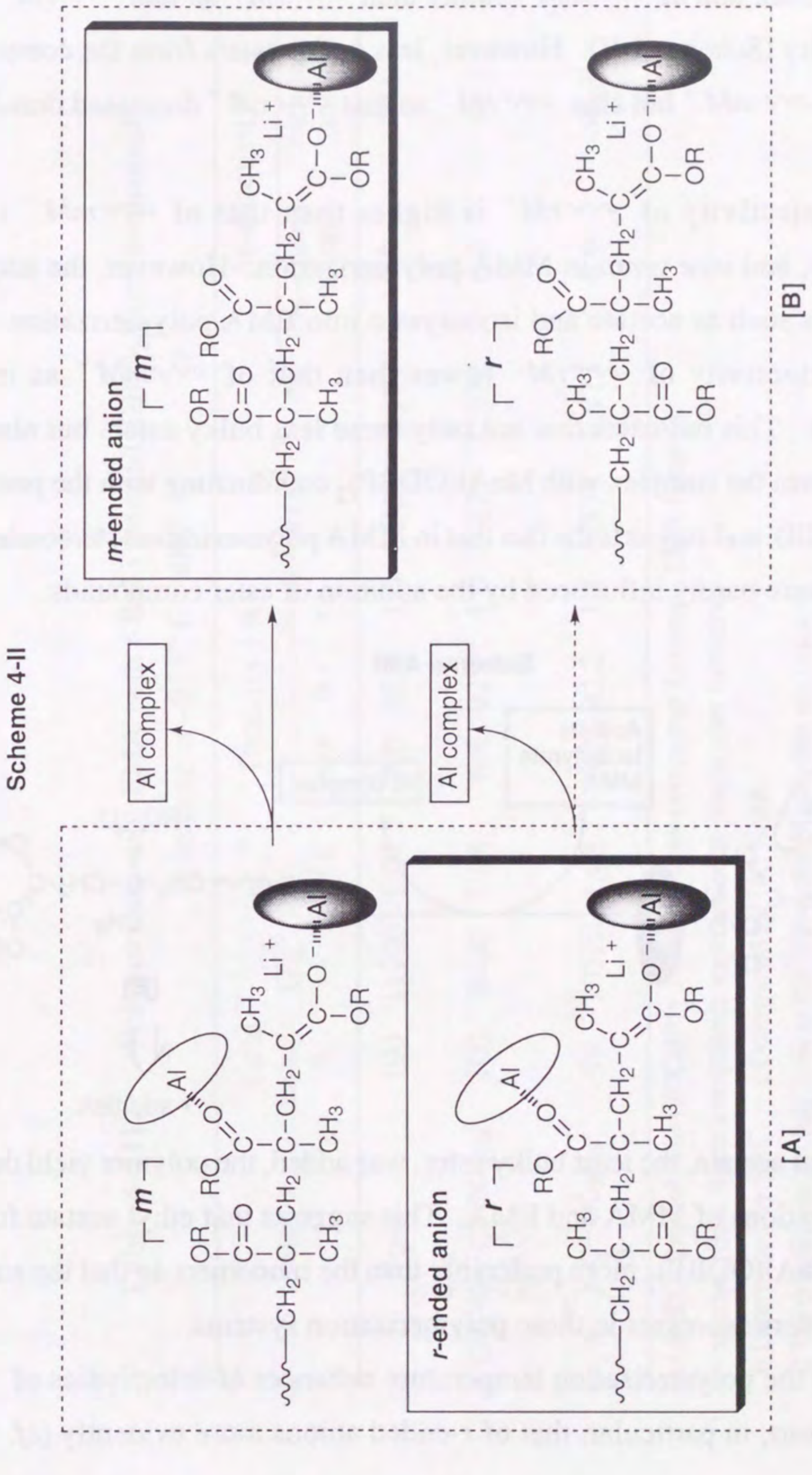
insertion, the newly formed anion may be type [A] and the anion [A] can be transformed to [B] by releasing the aluminum phenoxide having coordinated with the penultimate unit (Scheme 4-I) (*cf.* Chapters 2 and 3).

The *ht*-selectivity of ~~~*mM*$^-$ in EMA polymerizations increased slightly by the addition of all the esters examined. The results are consistent with the above-mentioned assumption; that is, the addition of esters makes it easier for type [A] anion to be transformed to type [B] which favors *r*-addition. On the other hand, changes of the selectivity of *r*-ended anions are more complex. Bulky esters such as pivalate and benzoate do not diminish the high selectivity of ~~~*rM*$^-$, while less bulky ester, such as acetate and isobutyrate, decreased it significantly. These results mean that bulky

Scheme 4-I



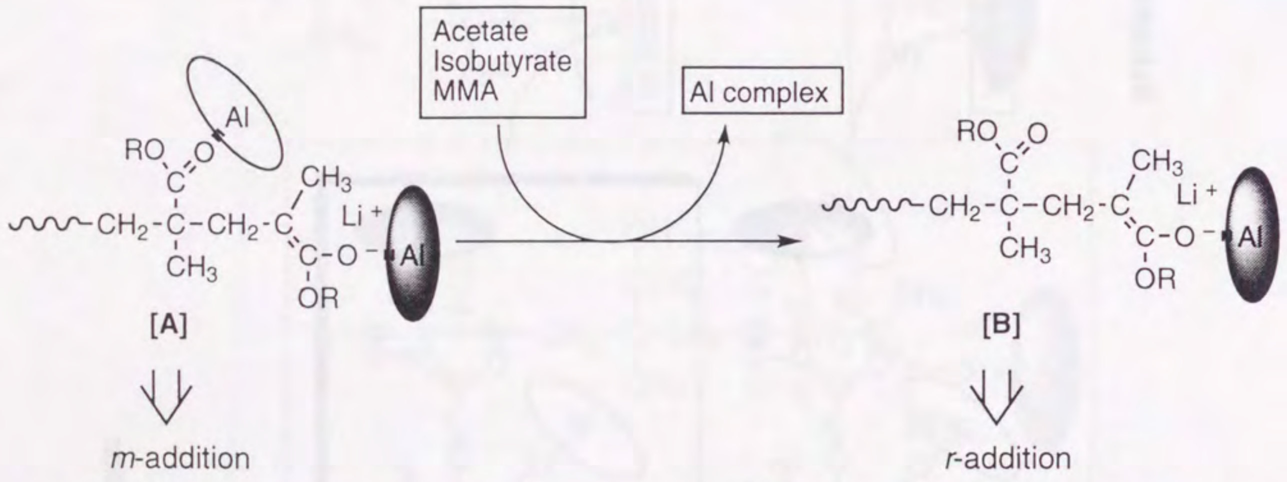
Scheme 4-II



esters form the complex selectively with the aluminum phenoxide which has coordinated with the penultimate unit of ~~~mM^- rather than ~~~rM^- so that ~~~rM^- kept its high *ht*-selectivity (Scheme 4-II). However, less bulky esters form the complex with that of not only ~~~mM^- but also ~~~rM^- so that ~~~rM^- decreased drastically its *ht*-selectivity.

The *ht*-selectivity of ~~~rM^- is higher than that of ~~~mM^- in EMA polymerizations, and *vice versa* in MMA polymerization. However, the addition of less bulky esters such as acetate and isobutyrate into EMA polymerization systems made the *ht*-selectivity of ~~~rM^- lower than that of ~~~mM^- as in MMA polymerizations. This indicates that not only these less bulky esters but also MMA itself prefer to form the complex with MeAl(ODBP)$_2$ coordinating with the penultimate unit (Scheme 4-III), and supports the fact that in MMA polymerization stereoselectivities of both anions were hardly influenced by the addition of ester compounds.

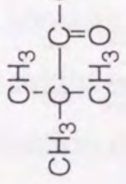
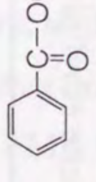
Scheme 4-III



When ethyl acetate, the least bulky ester, was added, the polymer yield decreased in the polymerizations of MMA and EMA. This suggests that ethyl acetate forms the complex with MeAl(ODBP)$_2$ more preferably than the monomers so that the amount of activated monomers decreases in these polymerization systems.

Lowering the polymerization temperature enhances *ht*-selectivities of both *m*- and *r*-ended anions, in particular, that of *r*-ended anions more evidently (*cf.* Chapter

Table 4-III. Polymerization of EMA with *t*-BuLi /MeAl(ODBP)$_2$/ester compound in toluene at –95°C for 48h[a]

Ester	Yield	$\overline{M}_n$ [b]	$\overline{M}_w / \overline{M}_n$ [b]	Tacticity / %[c]			$P_{m/r}$ [d]	$P_{r/m}$ [d]	*ht*-selectivity[e]	
	%			*mm*	*mr*	*rr*			*m*-ended anion	*r*-ended anion
None	100	11100	1.07	7.0	92.0	1.0	0.868	0.979	6.6	46.0
 $CH_3-C(CH_3)_2-C(=O)-OC_2H_5$	100	9430	1.08	6.8	92.2	1.0	0.871	0.979	6.8	46.1
	99	10520	1.08	6.7	92.2	1.1	0.873	0.977	6.9	41.9

a *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol, ester compound 1.0mmol, EMA 10mmol, toluene 10ml. Ester compounds were added at 10min after initiation.

b Determined by SEC. c Determined by ^{13}C NMR.

d The conditional probabilities in the first-order Markovian statistics.

e Calculated from $P_{m/r} / P_{m/m}$ and $P_{r/m} / P_{r/r}$.

Table 4-IV. Polymerization of EMA with *t*-BuLi /MeAl(ODBP)$_2$ in toluene/ethyl pivalate at various ratio at –95°C for 48h^a

Solvent toluene:ethyl pivalate	Yield %	$\overline{M}_n$ ^{b}	$\overline{M}_w/\overline{M}_n$ ^{b}	Tacticity / %^{c} *mm*	*mr*	*rr*	$P_{m/r}$ ^{d}	$P_{r/m}$ ^{d}	*ht*-selectivity^e *m*-ended anion	*r*-ended anion
10 : 0	100	11100	1.07	7.0	92.0	1.0	0.868	0.979	6.6	46.0
9 : 1	81	7670	1.08	5.9	93.5	0.6	0.888	0.987	7.9	77.9
7 : 3	51	9220	1.08	5.2	94.3	0.5	0.901	0.990	9.1	94.3
5 : 5	27	4630	1.07	7.4	92.4	0.2	0.862	0.996	6.2	231.0

a *t*-BuLi 0.2mmol, MeAl(ODBP)$_2$ 1.0mmol, EMA 10mmol, solvent 10ml.
Polymerization was started by adding *t*-BuLi.
b Determined by SEC. c Determined by ^{13}C NMR.
d The conditional probabilities in the first-order Markovian statistics.
e Calculated from $P_{m/r} / P_{m/m}$ and $P_{r/m} / P_{r/r}$.

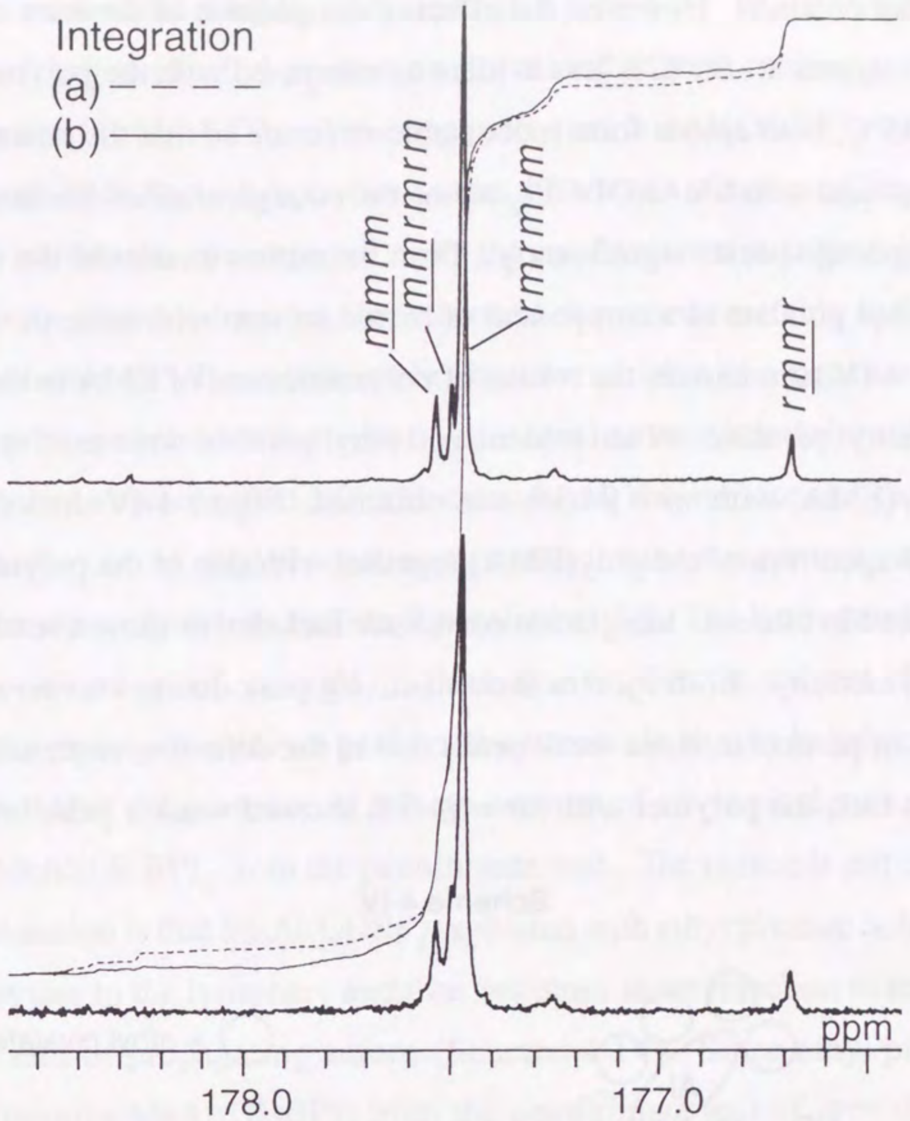
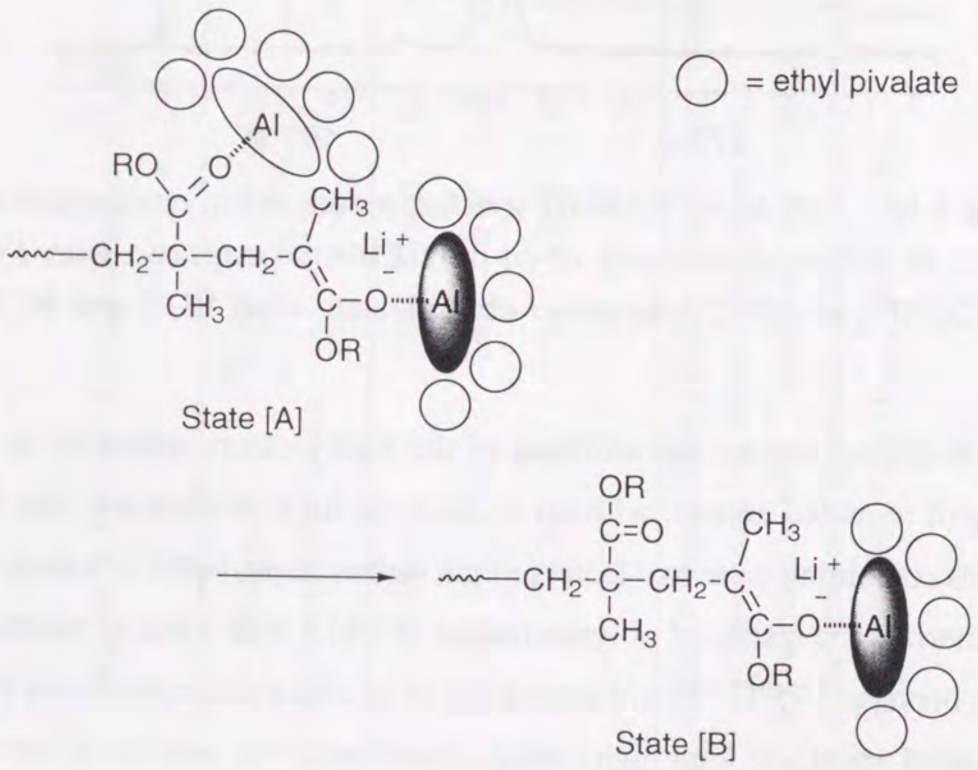


Figure 4-IV. 125 MHz ^{13}C NMR spectra, measured in nitrobenzene-d_5 at 110°C, of carbonyl carbons of *ht*-poly(EMA)s prepared with *t*-BuLi / MeAl(ODBP)$_2$ at –95°C in toluene / ethyl pivalate = (a) 10 / 0 and (b) 7/3.

3).[11] As described above, the addition of the bulky esters enhances heterotactic-selectivity of *m*-ended anions, without loosing the high stereoselectivity of *r*-ended anion. Thus combining these two factors might further improve the *ht*-selectivity. Table 4-III summarizes the results of polymerization of EMA with *t*-BuLi / MeAl(ODBP)$_2$ / ester compounds at –95°C. The *ht*-selectivity of *m*-ended anion increased slightly and that of *r*-ended anion was kept high enough, resulting in the increase of heterotacticity of the polymer obtained. However, the effect of the addition of the ester compounds in the polymerizations at –95°C is less evident as compared with the polymerization at –78°C. At –95°C, both anions form more stable structure so that the equimolar amount of ester compound with $MeAl(ODBP)_2$ seems not enough to affect the stereoselectivity of the propagating species significantly. Then the author examined the use of a large amount of ethyl pivalate as a component of mixed solvent with toluene.

Table 4-IV summarizes the results of polymerization of EMA in the mixtures of toluene and ethyl pivalate. When toluene and ethyl pivalate were used at 7/3 (vol/vol) ratio, *ht*-poly(EMA) with $mr = 94.3\%$ was obtained. Figure 4-IV shows the carbonyl carbon NMR spectrum of the poly(EMA) together with that of the polymer with $mr = 92.0\%$ prepared in toluene. Integration curves are included to show a small but evident difference in tacticity. Both spectra showed strong peak due to *rmrmrm* heptad and small peaks, in particular, three weak peaks due to the defective sequences containing *mm* triad. In fact, the polymer with $mr = 94.3\%$ showed weaker peak intensity in the region due to *rmmr* than the polymer prepared in toluene.

Scheme 4-IV



As the fraction of ethyl pivalate in the mixed solvent increased, the polymer yield decreased (Table 4-IV). This suggests that $MeAl(ODBP)_2$ competitively coordinates with EMA and ethyl pivalate so that the amount of activated EMA decreases. Although the added esters are expected, from the results shown in Table 4-II, to decrease the *ht*-selectivity of *r*-ended anions, the *rr* content decreased smoothly as the fraction of ethyl pivalate increased. This result implies that the addition of a large amount of ethyl pivalate brings about not the effect in molecular level as mentioned above but the effect in bulk level, *i.e.*, solvent effect. On the other hand, the *mm* content decreased with increasing the fraction of ethyl pivalate as expected, but the *mm* content increased again to 7.4% at the ratio of toluene and ethyl pivalate of 5/5. The latter result reflects the decrease of *r*-selectivity of $\sim\!\sim\!\sim mM^-$, which also implies the solvent effect by ethyl pivalate. If the propagating anions perform the stereoselection as in Scheme 4-II, these results suggest that the presence of a large amount of ethyl pivalate suppresses the removal of $MeAl(ODBP)_2$ from the penultimate unit. The reason is not clear, but one possible explanation is that $MeAl(ODBP)_2$ solvated with ethyl pivalate behaves as more bulky species due to the lyosphere and thus becomes more reluctant to leave from the penultimate unit of propagating anions (Scheme 4-IV). Since ethyl pivalate is not effective to remove $MeAl(ODBP)_2$ from the penultimate unit of $\sim\!\sim\!\sim rM^-$ at –95°C (the effect in molecular level) (see Table 4-III), the increase in the fraction of ethyl pivalate seems to be reflected directly on the *m*-selectivity of $\sim\!\sim\!\sim rM^-$ (solvation effect). On the other hand, ethyl pivalate might remove $MeAl(ODBP)_2$ from the penultimate unit of $\sim\!\sim\!\sim mM^-$, where the molecular level effect is still operative. Thus the *r*-selectivity of $\sim\!\sim\!\sim mM^-$ increased smoothly as expected. However, as the fraction of ethyl pivalate increases further, the solvation effect becomes more important than the effect in molecular level. Consequently, *r*-selectivity of $\sim\!\sim\!\sim mM^-$ shows a maximum ($mr = 94.3\%$) at the ratio of toluene and ethyl pivalate of 7/3.

Conclusion

The effect of the addition of ester compounds on the stereospecificity was examined. The addition of ester compound into the MMA polymerization system affected slightly the stereospecificity of polymerization irrespective of the bulkiness of ester compounds. This suggested that the coordination of $MeAl(ODBP)_2$ with MMA monomer itself was very strong so that the effect of the addition of ester compounds was not observed evidently.

The addition of bulky esters, such as ethyl benzoate and ethyl pivalate, to the polymerization system of EMA led to the slight increase in heterotacticity of the obtained polymer. In contrast, less bulky carbonyl compounds, such as ethyl acetate and ethyl isobutyrate, lowered heterotacticity. NMR analysis of obtained polymers revealed that the addition of bulky esters into the polymerization system increased *ht*-selectivity of $\sim\sim\sim mM^-$ slightly, keeping high *ht*-selectivity of $\sim\sim\sim rM^-$, while the addition of less bulky esters decreased *ht*-selectivity of $\sim\sim\sim rM^-$ drastically with a slight increase in *ht*-selectivity of $\sim\sim\sim mM^-$. These results suggest that the addition of ester compound with appropriate bulkiness could increase selectively *ht*-selectivity of $\sim\sim\sim mM^-$, resulting in a slight increase in heterotacticity of the obtained polymers.

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16. When ester compounds, even bulky ester such as ethyl pivalate, were added before the addition of monomer, the initiator efficiency decreased to 0.38 from 0.87 for the opposite case described in the experimental section, probably because *t*-BuLi reacts with carbonyl group of esters.
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19. ^{13}C NMR spectra, obtained under complete-decoupling condition, usually do not

allow quantitative analysis. Since the peak intensity ratios of EMA and esters, ethyl isobutyrate and ethyl pivalate, in the equimolar mixtures were 1:0.9 and 1:1.2, respectively. Though the values deviate 10~20% from the theoretical one, the results support that the difference of the isobutyrate and pivalate (*cf.* Figures 4-IIIb and 4-IIId) is meaningful enough to discuss the selectivity of coordination from ^{13}C NMR spectra.

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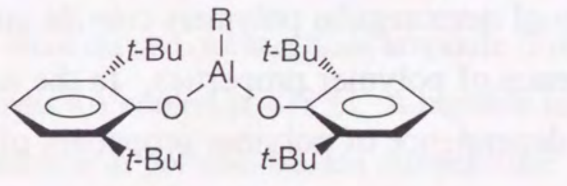
Chapter 5

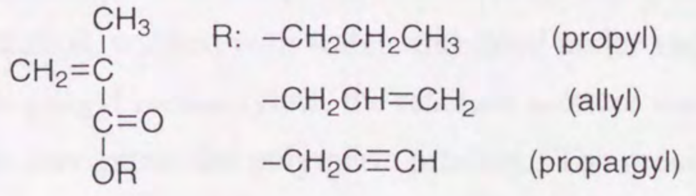
Polymerization of Methacrylates Having Linear C-3 Ester Group

Introduction

In the polymerization of methacrylates with a combination of *t*-BuLi and bulky aluminum bisphenoxides, the stereospecificity of the polymerization strongly depends on the structure of the aluminum phenoxides. For instance, use of bis(2,6-di-*t*-butylphenoxy)ethylaluminum or bis(2,6-di-*t*-butylphenoxy)isobutylaluminum, instead of bis(2,6-di-*t*-butylphenoxy)methylaluminum [MeAl(ODBP)$_2$] which exhibits heterotactic- (*ht*-) specificity,[1,2] changes the stereospecificity from heterotactic to syndiotactic, while the living character of the polymerization is retained (*cf.* Chapter 2).[3] The bulkiness of the ester group also affects drastically the stereospecificity of the polymerization with *t*-BuLi / MeAl(ODBP)$_2$ (*cf.* Chapter 1); both primary and secondary alkyl methacrylates give *ht*-polymers,[1] and, in sharp contrast, tertiary alkyl methacrylates such as *t*-butyl[1] and trimethylsilyl methacrylates[4] give *st*-polymers. Moreover, even in the polymerization of a series of primary alkyl methacrylates, the length of alkyl group slightly affects the stereoregularities of the obtained polymers (*cf.* Table 5-I). These results mean that the stereospecificity in the polymerization with *t*-BuLi / MeAl(ODBP)$_2$ is very sensitive to steric factors, implying the possibility that even a small change in steric bulkiness of the monomer may improve the stereospecificity in the *ht*-polymerization. In the first part of this Chapter are described the polymerizations of

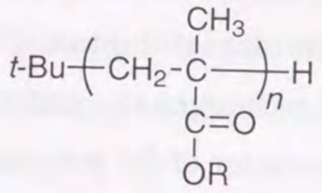


R = Me, Et, *i*-Bu



propyl (PrMA), allyl (AlMA), and propargyl methacrylate, which have linear C-3 ester group.[5]

The chemical structure of *ht*-polymethacrylates prepared with *t*-BuLi / $MeAl(ODBP)_2$ is identical with those of isotactic (*it*-) and syndiotactic (*st*-) polymethacrylates prepared with *t*-butylmagnesium bromide (*t*-BuMgBr)[6,7] and *t*-BuLi / trialkylaluminum (R_3Al),[8,9] respectively, in a living manner; *t*-butyl groups at the initiating chain-end and methine hydrogens at the terminating chain-end. This means that these three types of stereoregular polymers provide great profit for the investigation of tacticity dependence of polymer properties. In the second part of this Chapter is described tacticity dependence of polymer properties of three types of stereoregular polymethacrylates.



$t\text{-Bu}-\left(CH_2-C(CH_3)(C{=}O)(OR)\right)_n-H$

Experimental

The experimental procedures except for these described below are the same as those described in detail in Chapters 1-4.

Materials

PrMA was prepared from methyl methacrylate (MMA) and propan-1-ol by transesterification with tetrabutyl titanoate as a catalyst.[10] Propargyl methacrylate was prepared by the reaction of methacryloyl chloride and propargyl alcohol in the presence of triethylamine. PrMA, AlMA which was obtained commercially, and propargyl methacrylate were purified by fractional distillation under reduced nitrogen pressure, dried over calcium dihydride and vacuum-distilled just before use.

Polymerization

All the polymerizations were carried out in a glass ampoule filled with dried nitrogen passed through molecular sieves 4A cooled at –78°C. A heptane solution of *t*-BuLi was added to $MeAl(ODBP)_2$ in toluene at polymerization temperature. The polymerization reaction was initiated by adding the monomer slowly to this mixture at polymerization temperature. The reaction was terminated by adding methanol containing HCl at polymerization temperature. In the cases of PrMA polymerization, the reaction mixture was concentrated to dryness under reduced pressure, and the residue was dissolved in benzene. Insoluble materials were removed by centrifugation, and the polymeric products were recovered from the solution by freeze-drying and dried under vacuum. When AlMA was used as a monomer for the polymerization, the reaction mixture was poured into a large amount of methanol to precipitate the polymeric product. The polymeric product was precipitated by cooling the methanol to 0°C and organic impurities such as the monomer and 2,6-di-*t*-butylphenol derived from $MeAl(ODBP)_2$ were removed by repeated decantation. The product was redissolved in acetone and the solution was poured into a large amount of water to reprecipitate the polymeric product. The precipitate was collected by filtration, washed with water, and dried under vacuum. In the case of polymerization of propargyl methacrylate, the reaction mixture was poured into a large amount of hexane to precipitate the polymeric product. The precipitate was collected by filtration, washed with hexane and water, successively, and dried under vacuum.

Transformation from ht-poly(allyl methacrylate) to ht-poly(methyl methacrylate)[11]

To an ice-cooled solution of $Pd(PPh_3)_4$ (0.04mmol), PPh_3 (0.08mmol), and pyrrolidine (2mmol) in acetonitrile (2.5ml) was added a solution of poly(allyl methacrylate) [poly(AlMA)] (180mg, 1.5mmol of monomeric units) in acetonitrile (2.5ml). After stirring at 60°C for 24h, the mixture was poured into acetone and insoluble materials were isolated by centrifugation. The resulting precipitate was reacted with CH_2N_2 to convert it into poly(methyl methacrylate) (PMMA).[12] The conversion of allyl ester units into carboxylic acid units was approximately 90%, and it was necessary to repeat the reaction twice for the complete conversion.

Measurements

^{13}C NMR spectra of *ht*-polymers were measured in $CDCl_3$ at 55°C on a JEOL JNM GSX500 spectrometer or on a Varian Unity Inova 500 spectrometer operated at 125MHz. ^1H NMR spectra of stereoregular PMMAs were measured in nitrobenzene-d_5 at 110°C on a JEOL JNM GSX500 spectrometer or a Varian Unity Inova 500 spectrometer operated at 500MHz.

Differential scanning calorimetry (DSC) was performed on a RIGAKU DSC-8230 apparatus under nitrogen flow (100 mL/min) at a heating rate of 10°C/min. The weight of the samples was ~10mg.

Termogravimetry (TG) was performed on a RIGAKU TG-8110 apparatus under nitrogen flow (100 mL/min) or in air at a heating rate of 10°C/min. The weight of samples was ~ 5mg. A base line run without a sample was conducted, and resulting data was used to correct the observed TG curves for polymer samples. The degradation temperature (T_d) is defined as the temperature at which the weight loss reaches 50% of the total weight loss in each degradation step.

X–ray powder patterns of three types of stereoregular PMMAs were obtained with a RIGAKU RAD-ROC X–ray diffractometer using Cu-Kα radiation (λ = 1.5418 Å).

Results and Discussion

Polymerization of Methacrylates Having Linear C-3 Ester Group

In Table 5-I are summarized the results of the polymerizations of several primary alkyl methacrylates with *t*-BuLi / $MeAl(ODBP)_2$ in toluene at –78°C and/or –95°C. When the simplest ester, MMA, is used as a monomer, the polymer with *mr* = 67.8% is obtained at –78°C (run 1), while the *mr* content of poly(ethyl methacrylate) [poly(EMA)] prepared under the same conditions is 88.6% (run 2) and reaches 92.0% by lowering polymerization temperature to –95°C (run 3). *n*-Butyl methacrylate, a C-4 ester, gave a *ht*-polymer with almost the same *mr* value, *mr* = 87.1% (run 10), as in the case of EMA, and hexyl methacrylate, a C-6 ester, gave the polymer whose *mr* content decreases to 83.7% (run 11). These results imply the possibility that the stereospecificity in *ht*-polymerization reaches the maximum between C-2 and C-4 esters. Thus the author examined the polymerizations of PrMA, AlMA, and propargyl methacrylate, which have linear C-3 ester group.[5]

The polymerizations of PrMA at –78°C and –95°C gave *ht*-polymers whose *mr* contents were 91.2 and 93.3%, respectively, with narrow molecular weight distributions (MWDs) (runs 4 and 5). The polymerizations of AlMA gave the polymers with narrow MWDs, which

Table 5-I. Polymerization of primary alkyl methacrylate with *t*-BuLi / $MeAl(ODBP)_2$ in toluene at – 78° C and/or – 95° C[a]

Run	Alkyl	Temp.	Time	Yield	Tacticity / %[b]			$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
		° C	h	%	*m m*	*m r*	*r r*		
1[d]	$-CH_3$	– 78	24	100	11.6	67.8	20.6	8330	1.18
2	$-CH_2CH_3$	– 78	24	100	7.7	88.6	3.7	7010	1.07
3		– 95	48	100	7.0	92.0	1.0	11100	1.07
4	$-CH_2CH_2CH_3$	– 78	24	100	6.1	91.2	2.7	7650	1.07
5		– 95	48	100	5.7	93.3	1.0	7680	1.09
6	$-CH_2CH{=}CH_2$	– 78	24	94	5.8	89.8	4.4	8070	1.06
7		– 95	48	85	3.1	95.8	1.1	11200	1.08
8	$-CH_2C{\equiv}CH$	– 78	24	26	8.4	52.0	39.6	4170	1.15
9		– 95	48	18	10.4	79.4	10.2	3410	1.18
10[d]	$-(CH_2)_3CH_3$	– 78	24	98	8.4	87.1	4.5	9300	1.07
11	$-(CH_2)_5CH_3$	– 78	24	100	12.0	83.7	4.3	13460	1.41

a Monomer 10mmol, toluene 10ml, *t*-BuLi 0.2mmol, $MeAl(ODBP)_2$ 1.0mmol.
b Determined by ^{13}C NMR. c Determined by SEC. d Taken from Ref. 1.

are soluble in common organic solvents such as toluene and chloroform (runs 6 and 7). ^{1}H NMR spectra of the polymers confirm that all the allyl groups are retained without being involved in any side reactions. The heterotacticities of the polymers obtained at –78°C and –95°C were 89.8 and 95.8%, respectively. The heterotacticity of the latter is the highest among those of the *ht*-polymers so far reported.

On the other hand, propargyl methacrylate also gave polymers soluble in common organic solvents with narrow MWD, though the initiator efficiencies were lower than 0.4 probably due to partial quenching of the highly basic *t*-BuLi with the acetylenic hydrogen (runs 8 and 9). The peak intensity ratios in ^{1}H NMR spectra of the poly(propargyl methacrylate) agree well with the values expected from the structures. In addition to the narrow MWD, the result indicates that no side reaction involving the acetylenic groups takes place during the propagating reaction. However, the polymer yield and heterotacticity of the polymers obtained were much lower than those for PrMA and AlMA.

Figure 5-1 shows carbonyl carbon region of ^{13}C NMR spectra of poly(EMA), poly(PrMA), and poly(AlMA). All the spectra show strong peaks due to *rmrmrm* heptad and small peaks due to several defective sequences including *mm* triad, such as ***rmmr***, ***mmrm*** and ***mm****rmrm*. The peak intensity in the *rmmr* region decreases in the order of poly(EMA), poly(PrMA), and poly(AlMA), while that of the *mrrm* region are kept almost constant.

In Table 5-II are summarized the *ht*-selectivities of $\sim\sim mM^{-}$ and $\sim\sim rM^{-}$, calculated by the ratios of the conditional probabilities in first-order Markovian statistics, $P_{m/r}$ / $P_{m/m}$ and $P_{r/m}$ / $P_{r/r}$,[13] in the polymerizations of EMA, PrMA, and AlMA at –95°C. These results indicate that the slight increase in the stereoselectivity of *m*-ended anions in AlMA polymerization causes the improvement of stereospecificity in *ht*-polymerization.

Table 5-II. *ht*-Selectivity of propagating anions in *ht*-polymerization of methacrylates at – 95° C

Alkyl	*ht*-Selectivity^a	
	m-Ended anion	*r*-Ended anion
$-\ CH_2CH_3$	6.6	46.0
$-\ CH_2CH_2CH_3$	8.2	46.7
$-\ CH_2CH{=}CH_2$	15.5	43.5

a Calculated from $P_{m/r}$ / $P_{m/m}$ and $P_{r/m}$ / $P_{r/r}$

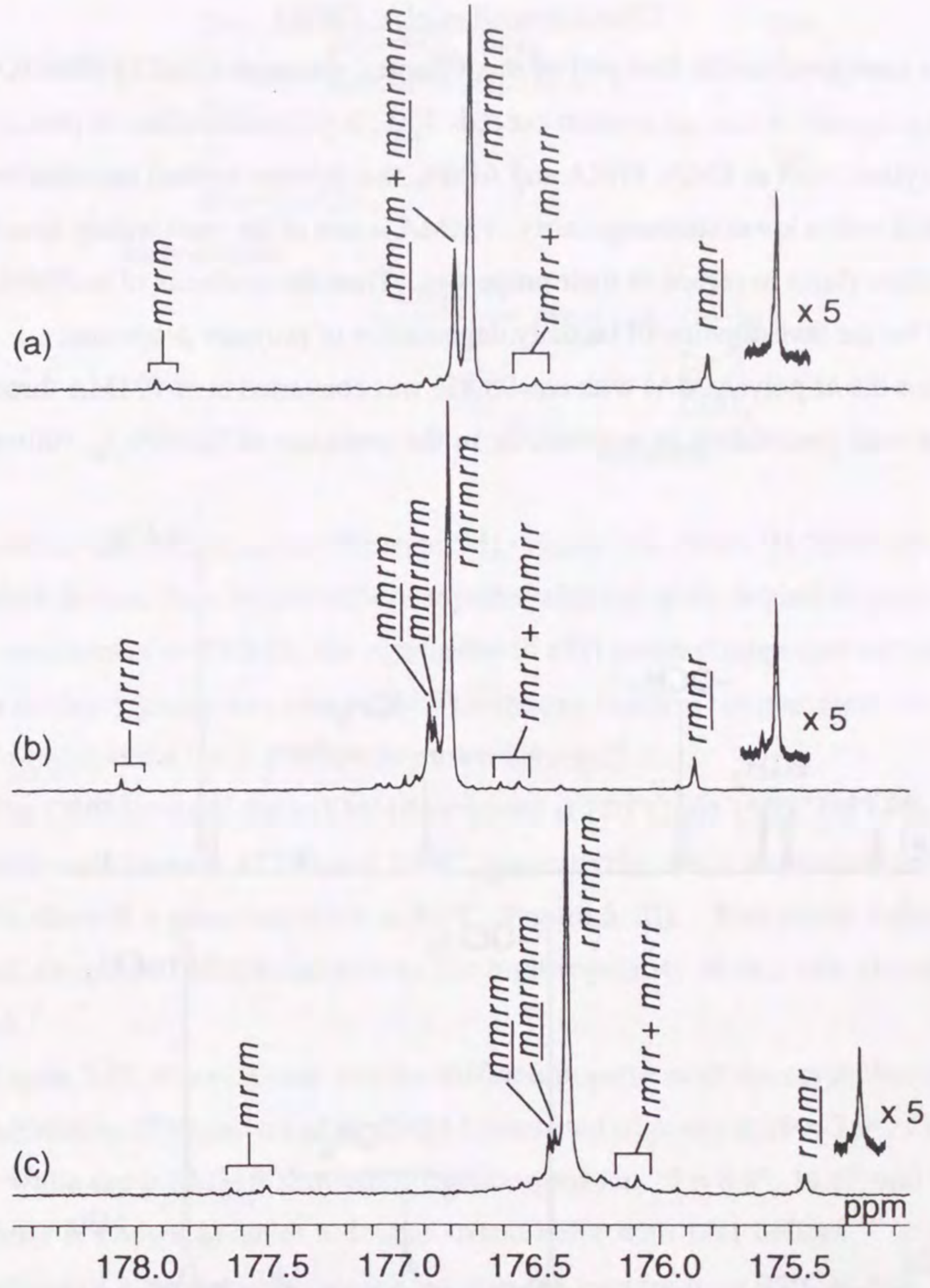


Figure 5-I. 125 MHz carbonyl carbon NMR signals of *ht*-polymers of (a) EMA, (b) PrMA, (c) AlMA prepared with *t*-BuLi / MeAl(ODBP)$_2$ (1/5 mol/mol) in toluene at –95°C, measured in CDCl$_3$ at 55°C.

Tacticity Dependence of Polymer Properties

Characterization of *ht*-PMMA

As mentioned in the first part of this Chapter, although *t*-BuLi / MeAl(ODBP)$_2$ gave *ht*-polymers, whose *mr* content exceeds 90%, in polymerizations of primary alkyl methacrylates such as EMA, PrMA and AlMA, this initiator system nevertheless gave *ht*-PMMA with a lower stereoregularity. PMMA is one of the most widely investigated polymethacrylates in regard to their properties. Thus the synthesis of *ht*-PMMA is of interest for the investigation of tacticity dependence of polymer properties.

Thus the *ht*-poly(AlMA) with *mr*=95.8% was converted to *ht*-PMMA through the reaction with pyrrolidine in acetonitrile in the presence of Pd(PPh$_3$)$_4$, followed by methylation with diazomethane (Scheme 5-I). Figure 5-II shows ^{1}H NMR spectrum of *ht*-PMMA derived from *ht*-poly(AlMA) together with that of the original *ht*-poly(AlMA). In the spectrum of *ht*-PMMA, the signals due to allyl group disappeared and the signal due to methoxy group was observed. The spectra confirm the complete conversion from *ht*-poly(AlMA) to *ht*-PMMA as shown Scheme 5-I.

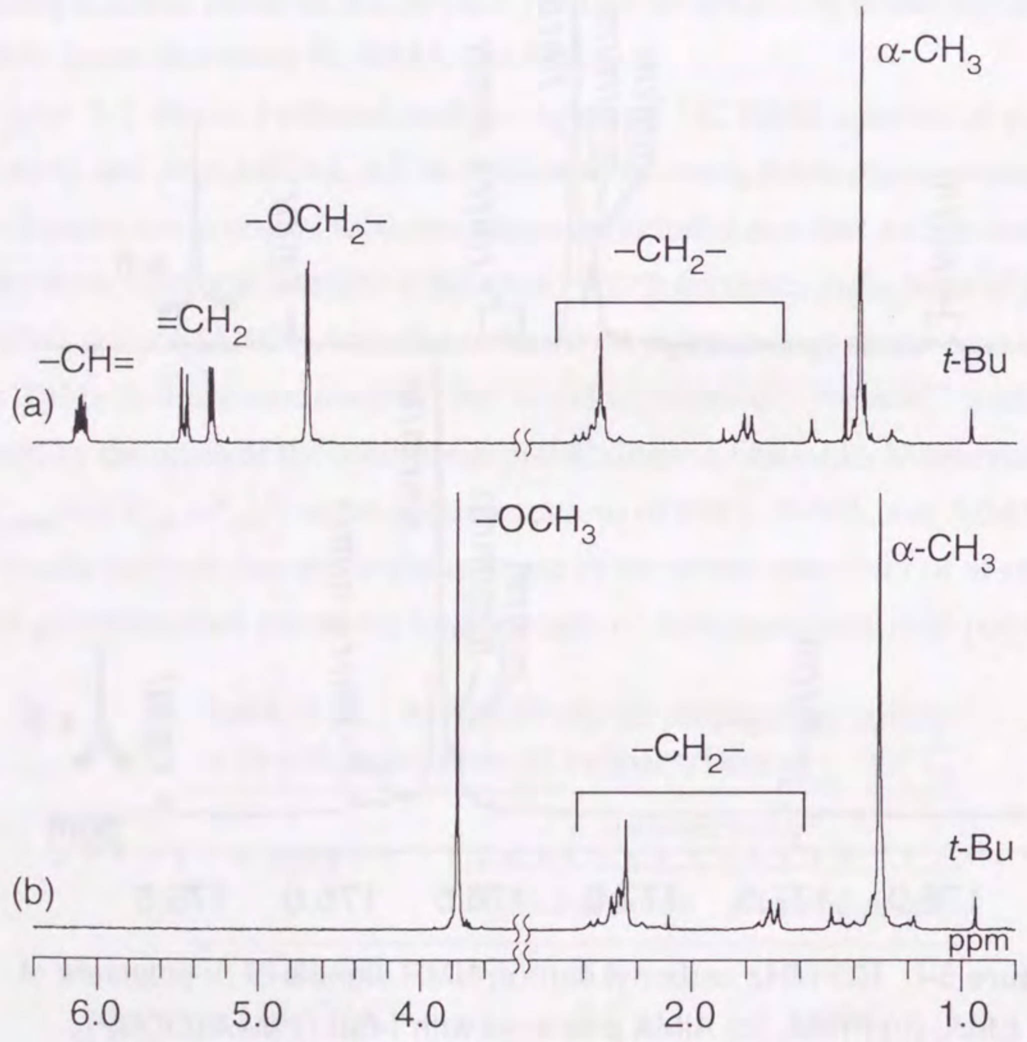
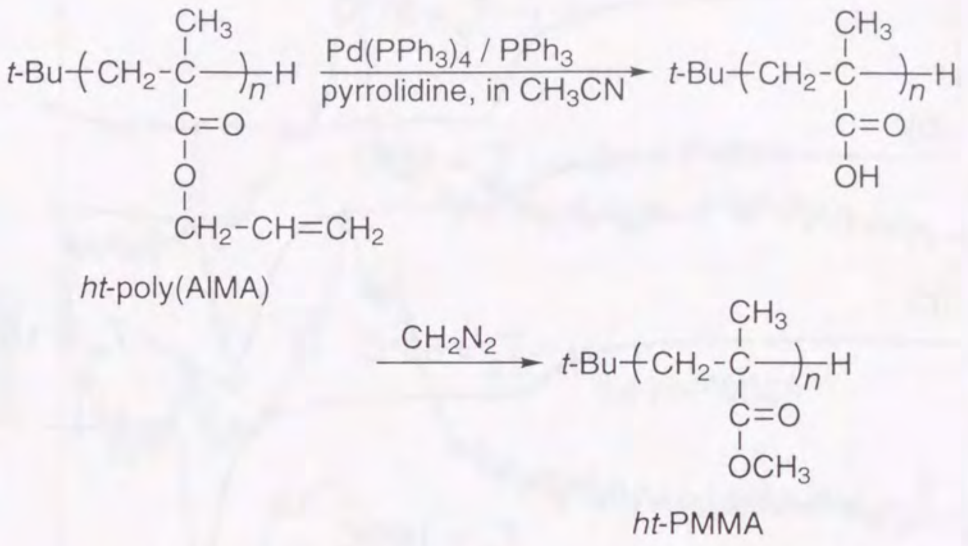


Figure 5-II. 500MHz ^{1}H NMR spectra of (a) *ht*-poly(AlMA) prepared with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at –95°C and (b) *ht*-PMMA derived from *ht*-poly(AlMA).

Scheme 5-I



The DSC curves of the *ht*-PMMA annealed at 120°C and 130°C for 144h showed a melting endotherm at 157°C and 166°C, respectively, while the melt-quenched *ht*-PMMA showed a glass transition at 91°C (Figure 5-III). This result indicates the crystallinity of *ht*-PMMA and proves the high regularity of this new stereoregular PMMA.[5]

Figure 5-IV shows X–ray powder diffraction patterns of the crystallized *it*-, *ht*-, and *st*-PMMAs. The pattern of *ht*-PMMA consisted of peaks at 2θ = 7.9°, 13.9°, and 15.9°, while the *it*-PMMA showed diffraction peaks at 2θ = 8.4°, 14.2°, and 16.8°.[14] The latter is known to adopt a double-strand helix with 10/1 helices.[15] *st*-PMMA crystallized in 3-heptanone by slowly cooling the mixture from 95°C to 55°C for 72h showed reflection peaks at 2θ = 4.5°, 11.4°, and 13.4° in its powder pattern. *st*-PMMA forms crystalline inclusion complexes with ketones, in which the PMMA chains takes a helical structure with a larger radius than that of *it*-PMMA.[16] In this regard, the structure

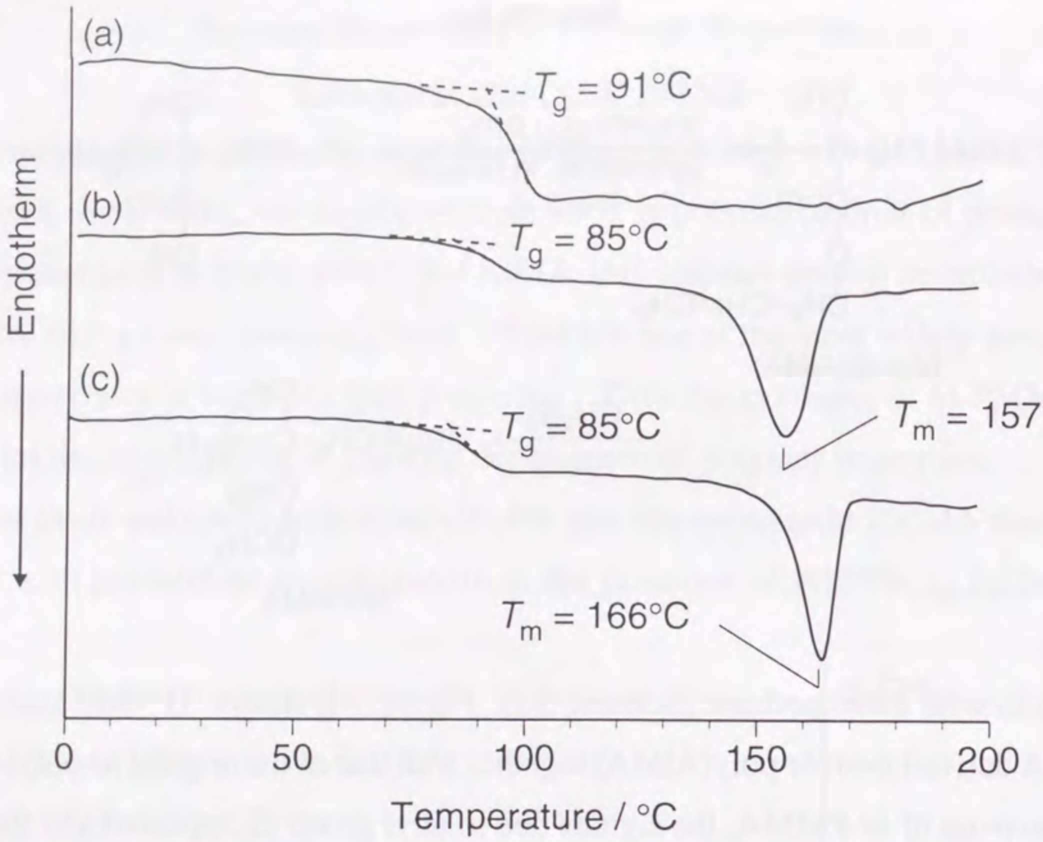


Figure 5-III. DSC curves of *ht*-PMMA derived from *ht*-poly(AlMA), recorded at a heating rate of 10°Cmin^{-1}. (a) melt-quenched; annealed at (b) 120°C and (c) 130°C for 144h.

of crystalline of *ht*-PMMA is rather similar to that of *it*-PMMA.

Table 5-III summarizes some thermal properties of three types of stereoregular PMMAs. Glass transition temperatures (T_g) increased in the order of *it*- < *ht*- < *st*-PMMAs. Though the higher $\overline{M}_n$ of the *st*-PMMA may give higher T_g, the contribution of the difference in $\overline{M}_n$ of *st*- and *ht*-PMMAs was estimated to be less than 3°C based on the Fox-Flory's equation on T_g [1][17] with assumption that K values for both PMMAs are in the order of 10^5;

$$T_g = T_{g\infty} - K / M \qquad [1]$$

where M and $T_{g\infty}$ denote molecular weight and T_g at infinite M, respectively. The melting temperature is in the order of isotactic < syndiotactic < heterotactic. Even though T_m is also affected by $\overline{M}_n$,[18] the fact that the *ht*-PMMA has the highest T_m

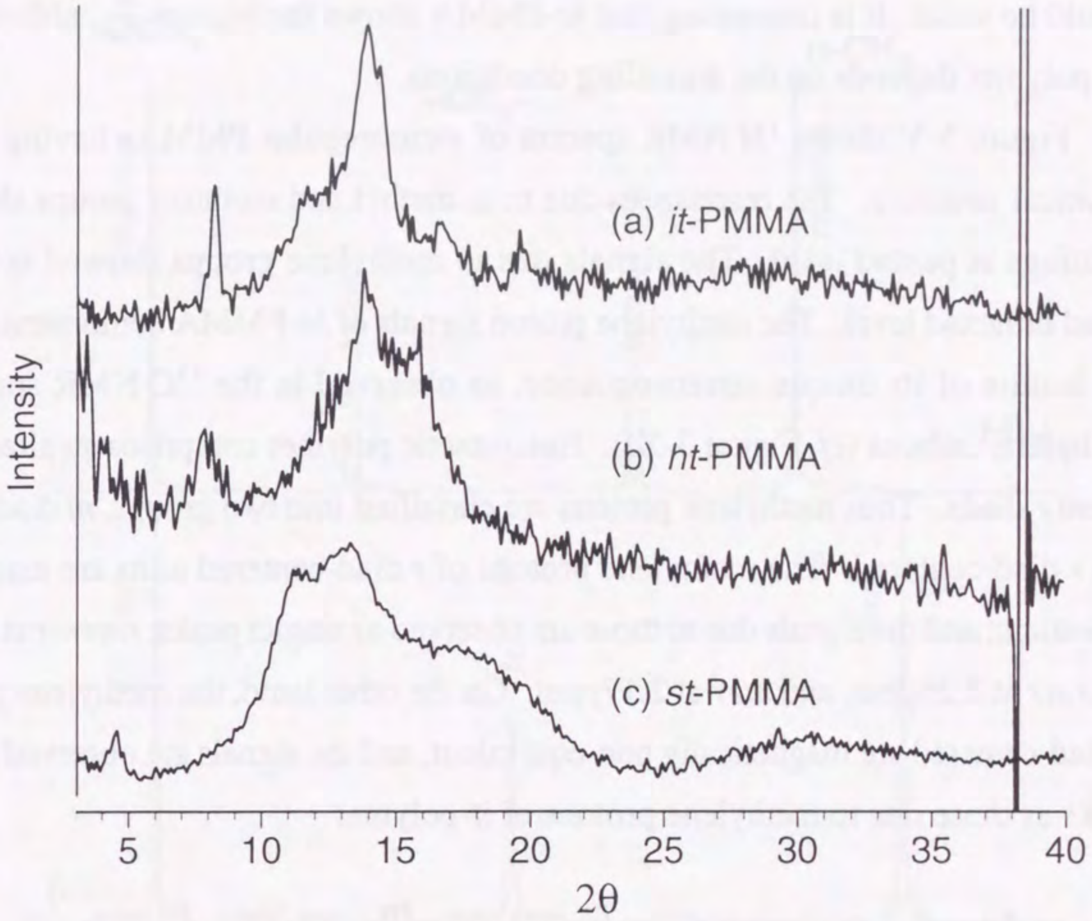


Figure 5-IV. X-ray powder patterns of *it*-PMMA annealed at 80°C for 72h (a), *ht*-PMMA annealed at 130°C for 144h (b), and *st*-PMMA crystallized in 3-heptanone by slowly cooling the mixture from 95°C to 55°C for 72h.

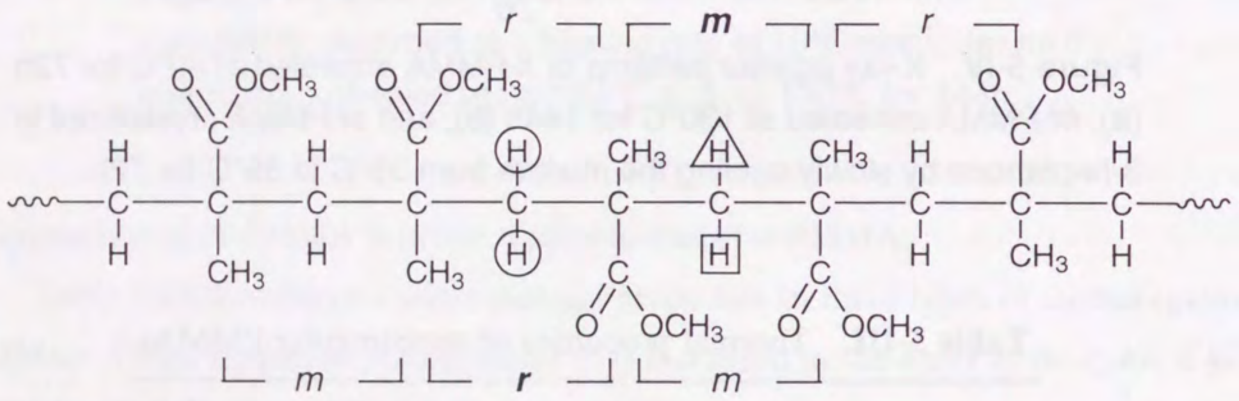
Table 5-III. Thermal properties of stereoregular PMMAs

Stereoregularity	$\overline{M}_n$	T_g [a] °C	T_m [a] °C
Isotactic (*mm* = 100%)[b]	7190	49	150
Syndiotactic (*rr* = 98%)[c]	13070	108	159
Heterotactic (*mr* = 96%)	9680	91	166

a Determined by DSC analysis. b Derived from the polymer obtained in polymerization of triphenylmethyl methacrylate with *t*-BuLi in tetrahydrofuran at – 78° C. c Derived from the polymer obtained in polymerization of trimethylsilyl methacrylate with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at – 95° C.

should be valid. It is interesting that *ht*-PMMA shows the highest T_m, although T_m of the polymer depends on the annealing conditions.

Figure 5-V shows ^{1}H NMR spectra of stereoregular PMMAs having the same chemical structure. The resonances due to α-methyl and methoxy groups showed the splittings at pentad level. The signals due to methylene groups showed splittings at tetrad or hexad level. The methylene proton signals of *ht*-PMMA demonstrated clearly the feature of its unique stereosequence, as observed in the ^{13}C NMR spectrum of methylene carbons (*cf.* Figure 3-XI). Heterotactic polymer comprises an alternation of *m* and *r* diads. Thus methylene protons are classified into two groups, *m* diad-centered and *r* diad-centered. The methylene protons of *r* diad-centered units are magnetically equivalent, and the signals due to those are observed as singlet peaks; *rmrmr* at 2.23ppm, *mmrmr* at 2.26ppm, and *mrr* at 2.17ppm. On the other hand, the methylene protons of *m* diad-centered are magnetically non-equivalent, and the signals are observed as quartet peaks as those due to methylene protons of *it*-polymer.



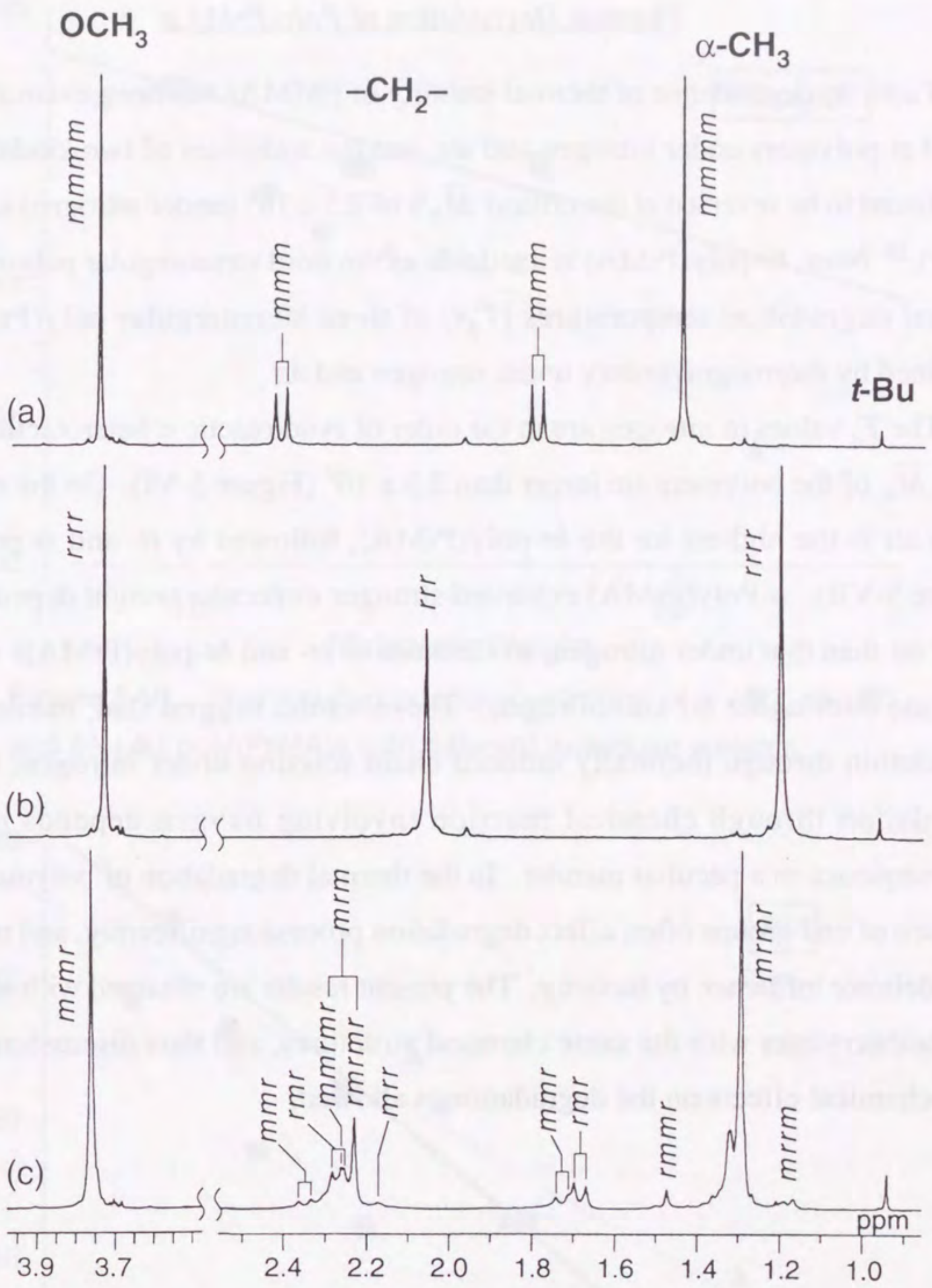


Figure 5-V. 500 MHz ^{1}H NMR spectra of (a) *it*-, (b) *st*-, and (c) *ht*-PMMAs, measured in nitrobenzene-d_5 at 110°C.

(a) Obtained by the polymerization of MMA with *t*-BuMgBr in toluene at –78°C

(b) Derived from poly(trimethylsilyl methacrylate) obtained with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at –95°C

(c) Derived from poly(AlMA) obtained with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at –95°C

Thermal Degradation of Poly(PrMA)s

Tacticity dependence of thermal stability of PMMAs has been examined by using *it*- and *st*-polymers under nitrogen and air, and the stabilities of two kinds of PMMAs were found to be reversed at the critical $\overline{M}_n$'s of 2.5 x 10^4 (under nitrogen) and 1.0 x 10^4 (in air).[19] Now, *ht*-poly(PrMA) is available as the third stereoregular polymer, and thus thermal degradation temperatures (T_ds) of three stereoregular poly(PrMA)s were examined by thermogravimetry under nitrogen and air.

The T_d values in nitrogen are in the order of syndiotactic < heterotactic < isotactic, when $\overline{M}_n$ of the polymers are larger than 2.0 x 10^4 (Figure 5-VI). On the contrary, the T_ds in air is the highest for the *ht*-poly(PrMA), followed by *it*- and *st*-poly(PrMA)s (Figure 5-VII). *it*-Poly(PrMA) exhibited stronger molecular weight dependence of T_d under air than that under nitrogen, while those of *st*- and *ht*-poly(PrMA)s were almost the same both under air and nitrogen. These results suggest that, in contrast to the degradation through thermally induced chain scission under nitrogen, the thermal degradation through chemical reaction involving oxygen depends on a longer stereosequence in a peculiar manner. In the thermal degradation of polymers chemical structure of end groups often affect degradation process significantly, and may hide the more delicate influence by tacticity. The present results are obtained with stereoregular polymethacrylates with the same chemical structures, and thus discussion about only stereochemical effects on the degradation is allowed.

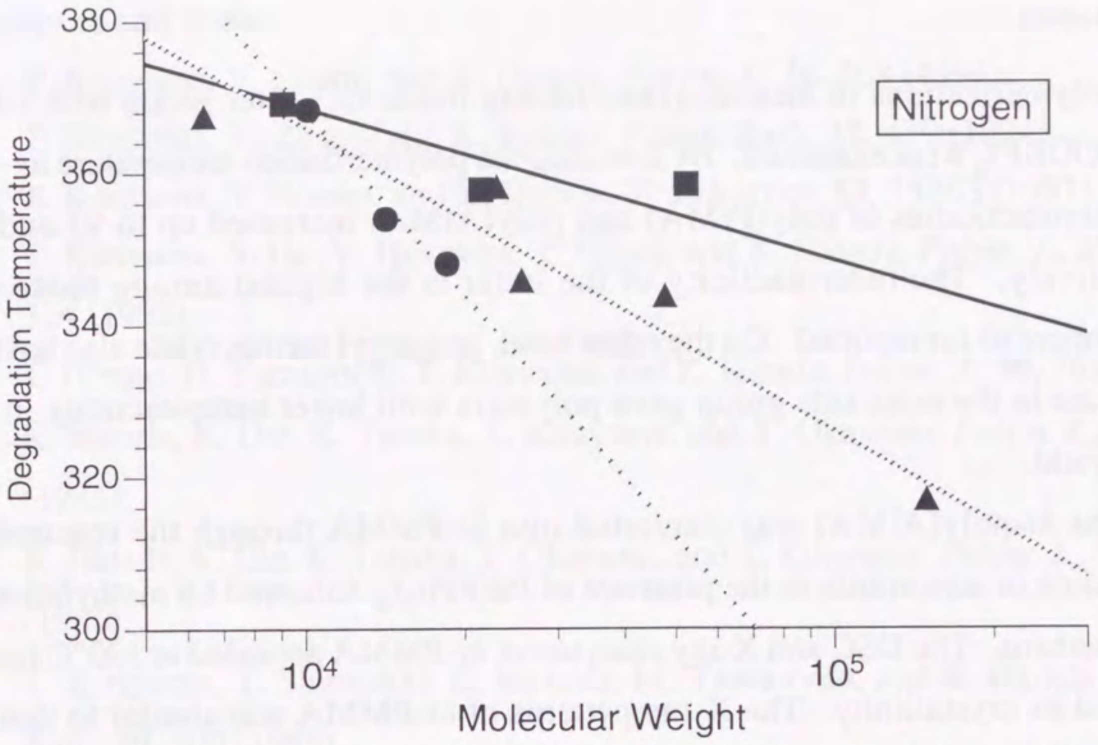


Figure 5-VI. Thermal degradation in nitrogen of *it*- (■), *st*- (●) and *ht*- (▲) poly(PrMA)s with different molecular weights.

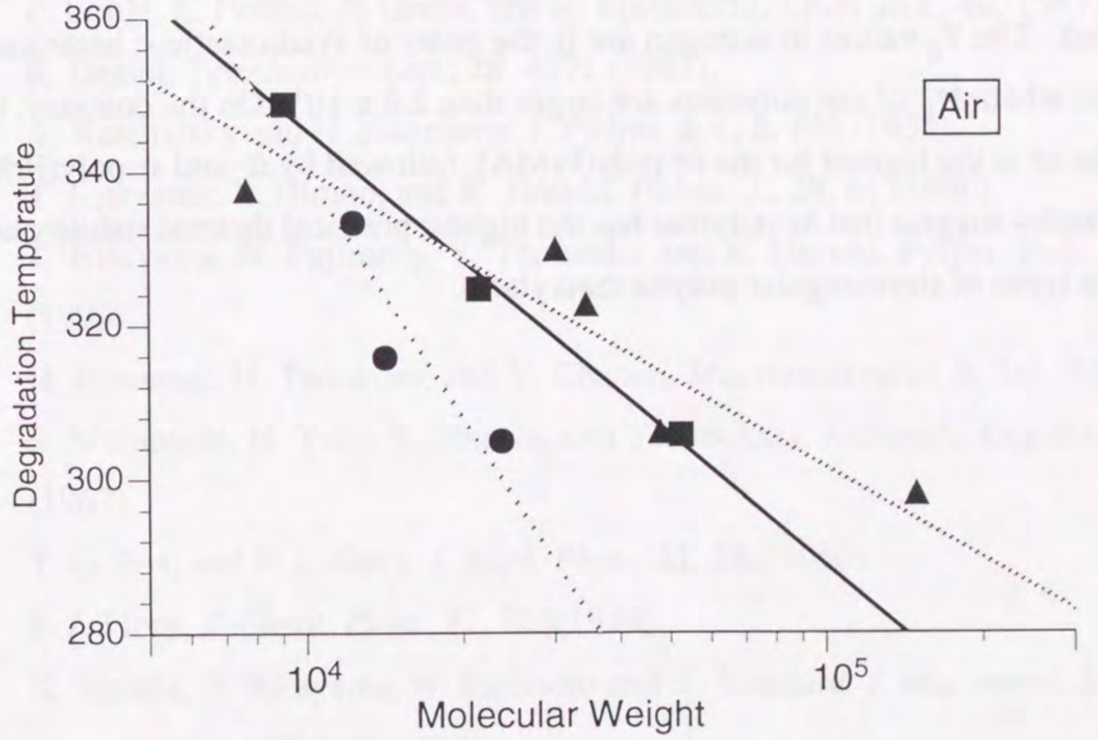


Figure 5-VII. Thermal degradation in air of *it*- (■), *st*- (●) and *ht*- (▲) poly(PrMA)s with different molecular weights.

Conclusion

Polymerizations of methacrylates having linear C-3 ester group with *t*-BuLi / MeAl(ODBP)$_2$ were examined. By lowering the polymerization temperature to –95°C, the heterotacticities of poly(PrMA) and poly(AlMA) increased up to 93 and 96%, respectively. The heterotacticity of the latter is the highest among those of the *ht*-polymers so far reported. On the other hand, propargyl methacrylate also having C-3 carbons in the ester side group gave polymers with lower heterotacticity in much lower yield.

The *ht*-poly(AlMA) was converted into *ht*-PMMA through the reaction with pyrrolidine in acetonitrile in the presence of Pd(PPh$_3$)$_4$, followed by methylation with diazomethane. The DSC and X-ray analyses of *ht*-PMMA annealed at 130°C for 144h revealed its crystallinity. The X-ray patterns of *ht*-PMMA was similar to that of *it*-PMMA which is known to adopt a double-strand helix with 10/1 helices. These results imply the possibility that *ht*-PMMA also takes a double-strand helix in the crystal state.

Thermal degradation behaviors of three types of stereoregular poly(PrMA) were examined. The T_d values in nitrogen are in the order of syndiotactic < heterotactic < isotactic, when $\overline{M}_n$ of the polymers are larger than 2.0 x 10^4. On the contrary, the T_d values in air is the highest for the *ht*-poly(PrMA), followed by *it*- and *st*-poly(PrMA)s. These results suggest that *ht*-polymer has the highest practical thermal stability among the three types of stereoregular polymethacrylates.

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Chapter 6

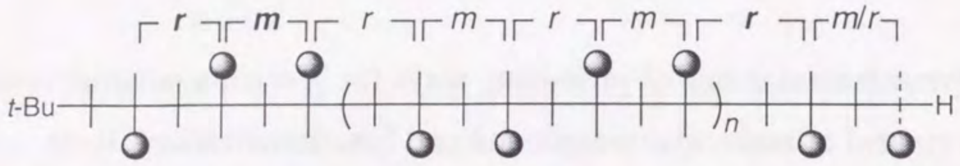
Even-Odd Alternation in Distribution of Degree of Polymerization Observed for *ht*-Poly(allyl methacrylate)

Introduction

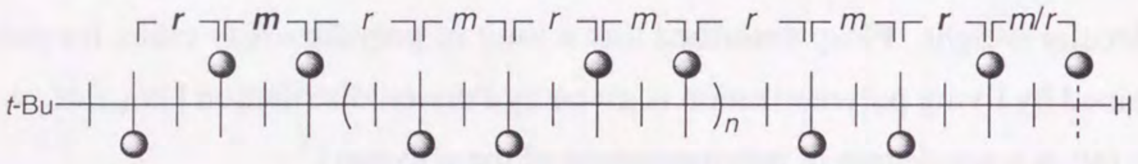
Living polymerization is one of promising ways for precision polymer synthesis, which provides control of molecular weight and end functionalization. Even in living polymerization, however, monomer addition by propagating species takes place at random, and the obtained polymers do not show uniformity but distribution in their molecular weight. Flory described that a limit of polydispersity index for polymers obtained by living polymerization is given by Poisson distribution [$\overline{M}_w / \overline{M}_n = 1 + 1/DP$; *DP* denotes degree of polymerization of the polymer].[1]

The nonuniformity with respect to *DP* of synthetic polymers even with narrow molecular weight distribution (MWD) has recently been revealed by several analytical means such as matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry[2-4] and supercritical fluid chromatography (SFC).[5-18] SFC is a powerful technique not only for analysis and but also for separation of polymers or oligomers with high *DP*. Preparative-scale SFC with packed columns has been used to obtain uniform polymers with respect to *DP*,[5,6] including PMMA,[7-11] polystyrene,[12-14] poly(lactide),[15] polyisocyanate,[16,17] and poly(oxymethylene).[18]

As described in Chapter 3, the stereochemical analysis near the chain ends of *ht*-poly(ethyl methacrylate) [*ht*-poly(EMA)] prepared with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at –78°C gave us sufficient information on initiating and propagating species. For example, dimer anion favors *r*-addition to form *r*-trimer anion, and the resultant *r*-trimer anion favors *m*-addition to form *rm*-tetramer anion. These suggest that propagating reaction proceeds in a heterotactic manner even in the early stage of polymerization. On the other hand, the analysis of terminating chain-end revealed that $\sim\sim rM^{-}$ is more abundant than $\sim\sim mM^{-}$, although active species switch from $\sim\sim rM^{-}$ to $\sim\sim mM^{-}$ and *vice versa* at each propagating step. This suggests that propagating anions stay in $\sim\sim rM^-$ state longer than in $\sim\sim mM^-$. If the in-chain stereosequence is completely heterotactic, consisting of *rm* repetition, the predominant structure of obtained *ht*-polymers could be depicted as follows;[19]



or



These structures represent the polymers with odd-number *DP*, but not the polymers with even-number *DP*. This implies that *ht*-polymers with odd-number *DP* is preferentially formed than those with even-number *DP*.

Recently, *ht*-specificity was found to be improved by using allyl methacrylate (AlMA) as a monomer, which gave an *ht*-polymer with *mr* triad content of 95.8%,[20] which is the highest among those of *ht*-polymers so far reported.[21-28] This Chapter describes chromatographic analysis of *ht*-oligo(AlMA)[29] and NMR analysis of uniform oligo(AlMA) obtained by chromatographic separation with respect to *DP*.[30] The results reveal the unique feature of stereoregularity of the *ht*-polymer and shed light on the mechanism of the polymerization.

Experimental

The experimental procedures except for these described below are the same as those described in detail in Chapters 1-5.

Measurement

^{13}C NMR spectra of oligomers were measured in benzene-d_6 at 35°C on a Varian Unity Inova 500 spectrometer operated at 125MHz. Molecular weight of the uniform 8mer and 13mer of *ht*-oligo(AlMA) was confirmed using a JEOL JMS-DX303HF spectrometer operated at the field-desorption (FD) mode. MALDI-TOF mass spectrum was recorded with Kratos Kompact MALDI IV using a nitrogen laser source ($\lambda = 337$ nm) and 2,5-dihydroxybenzoic acid as matrix. SFC was performed on a JASCO SUPER-200 chromatograph equipped with a Hewlett-Packard 589 column oven. A 10 mm i.d. x 250 mm column packed with non-bonded silica gel (Develosil 100-5, Nomura Chemical Co.,Ltd., particle size 5µm) was used. The system consists of two pumps, one is for the delivery of liquefied CO_2 as mobile phase, and the other for methanol as entrainer. The conditions for SFC measurements of *ht*-oligomers are summarized in Table 6-I. Chromatograms were recorded using a UV detector operated at a wave length of 220 nm.

Table 6-I. SFC conditions for analysis of *ht*-oligomers

	Oven temp.	Eluent	
		CO_2	MeOH
A	95 → 75 ° C for 20 min	9.2 → 8.7 ml/min for 20min	1.6 → 2.1 ml/min for 20min
B	90 → 70 ° C for 20 min	9.0 ml/min	1.8 ml/min
C	90 → 60 ° C for 30 min	9.2 → 8.7 ml/min for 20 min	1.6 → 2.1 ml/min for 20 min

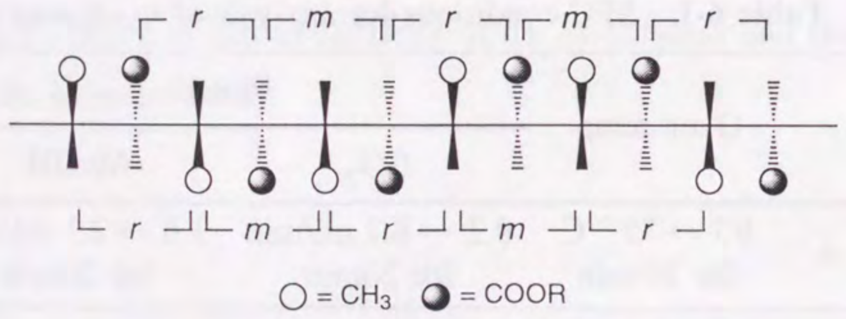
Results and Discussion

ht-Oligomers of AlMA were prepared with *t*-BuLi / MeAl(ODBP)$_2$ (1/5 mol/mol) at –95°C. The results are shown in Table 6-II. Figure 6-I shows an SFC trace for *ht*-oligo(AlMA) (I), whose number average *DP* and $\overline{M}_w/\overline{M}_n$ value are 13.8 and 1.13, respectively. The *DP*s of the fractions marked with asterisks were determined by FD mass spectrometry. The population of the oligomers with respect to *DP* showed even-odd alternation, the oligomers with odd-number *DP* being formed preferentially except for 8mer. Such even-odd alternation in *DP* distribution of vinyl polymers has scarcely been reported. The only exception is the polymerization of *t*-butyl crotonate with diphenylmagnesium in toluene at –78°C,[31] which gives a diheterotactic polymer.

Table 6-II. Oligomerization of AlMA with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at – 95° C

	AlMA	*t*-BuLi	Al	Tol.	Time	Yield	Tacticity / %^{a}			$\overline{M}_n$ ^{b}	$\overline{M}_w/\overline{M}_n$ ^{c}
	mmol	mmol	Li	ml	h	%	*m m*	*m r*	*r r*		
I	10	0.2	5	10	2	19	3.3	95.6	1.1	1800	1.13
II	50	1.0	3	50	4	22	2.6	94.7	2.7	1490	1.14
III	10	0.2	3	10	8	31	3.1	95.2	1.7	2390	1.22

a Determined by ^{13}C NMR. b Determined by ^{1}H NMR. c Determined by SEC.



Diheterotactic polymer

In this case, the oligomers with even-number *DP* are more abundant than those with odd-number *DP*. These suggest that this phenomenon of even-odd alternation in *DP* distribution is deeply concerned with the mechanism of *ht*-specific polymerization.

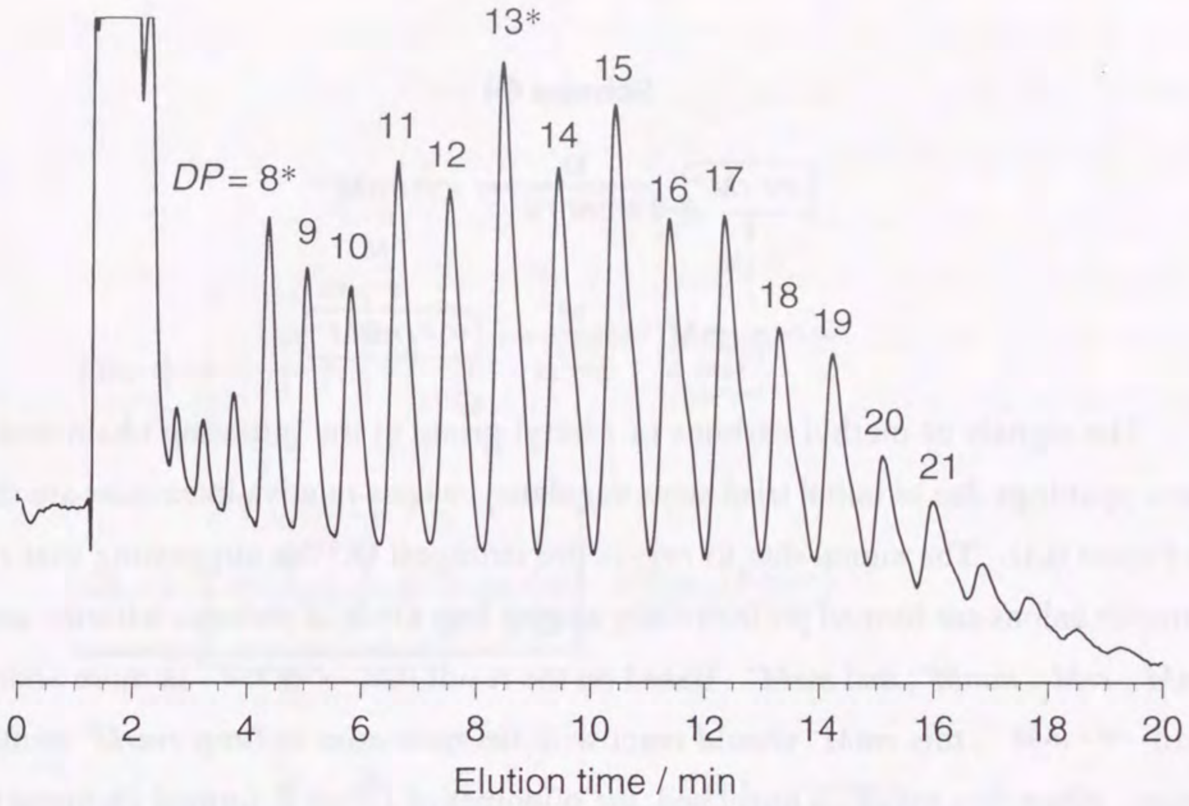
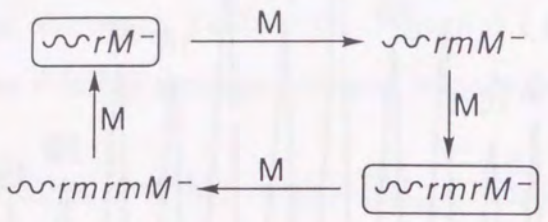


Figure 6-I. SFC trace of *ht*-oligo(AlMA) (I) prepared with *t*-BuLi / MeAl(ODBP)$_2$ (1/5 mol/mol) in toluene at –95°C for 2h.
(*: The *DP*s of the fractions were determined by FD mass spectrometry.)
SFC conditions : A. (*cf.* Table 6-II)

Figure 6-II shows the ^{13}C NMR signals of end groups of the oligomer. The resonances of methine carbons at the terminating chain-end split into four peaks due to terminal triad stereosequence. The *m*/*r* ratio of the second diad from the terminal corresponds with the ratio of $\sim mM^-$ and $\sim rM^-$ which had existed in the polymerization system before the polymerization reaction was quenched. The value ($\sim mM^-$ / $\sim rM^-$ = 13 / 87) indicates the predominance of $\sim rM^-$ as in the case of the EMA polymerization (*cf.* Chapter 3).[19] In other words, the propagating anions stay in $\sim rM^-$ state about 6.7 times longer than in $\sim mM^-$ state (Scheme 6-I).

Scheme 6-I



The signals of methyl carbons of *t*-butyl group at the initiating chain-end also show splittings due to initial triad stereoregularity, whose relative intensities are shown in Figure 6-II. The signal due to *rm*– is the strongest (83%), suggesting that rmM^- tetramer anions are formed preferentially among four kinds of possible tetramer anions, rmM^-, rrM^-, mmM^-, and mrM^-. Based on the result that ∼∼rM^- is more abundant than ∼∼mM^-, this rmM^- should react with the monomer to form $rmrM^-$ pentamer anion. When this $rmrM^-$ is quenched, the oligomer of *DP*=5 is formed (Scheme 6-II). Suppose that the propagation step proceeds completely *ht*-specific, the odd-number

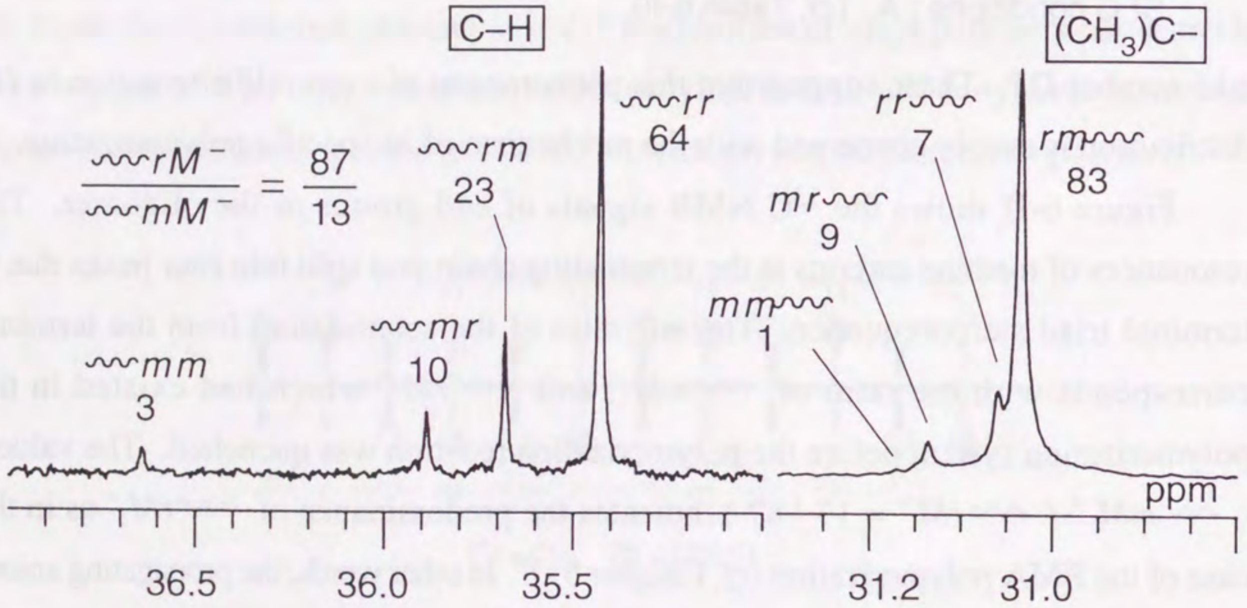
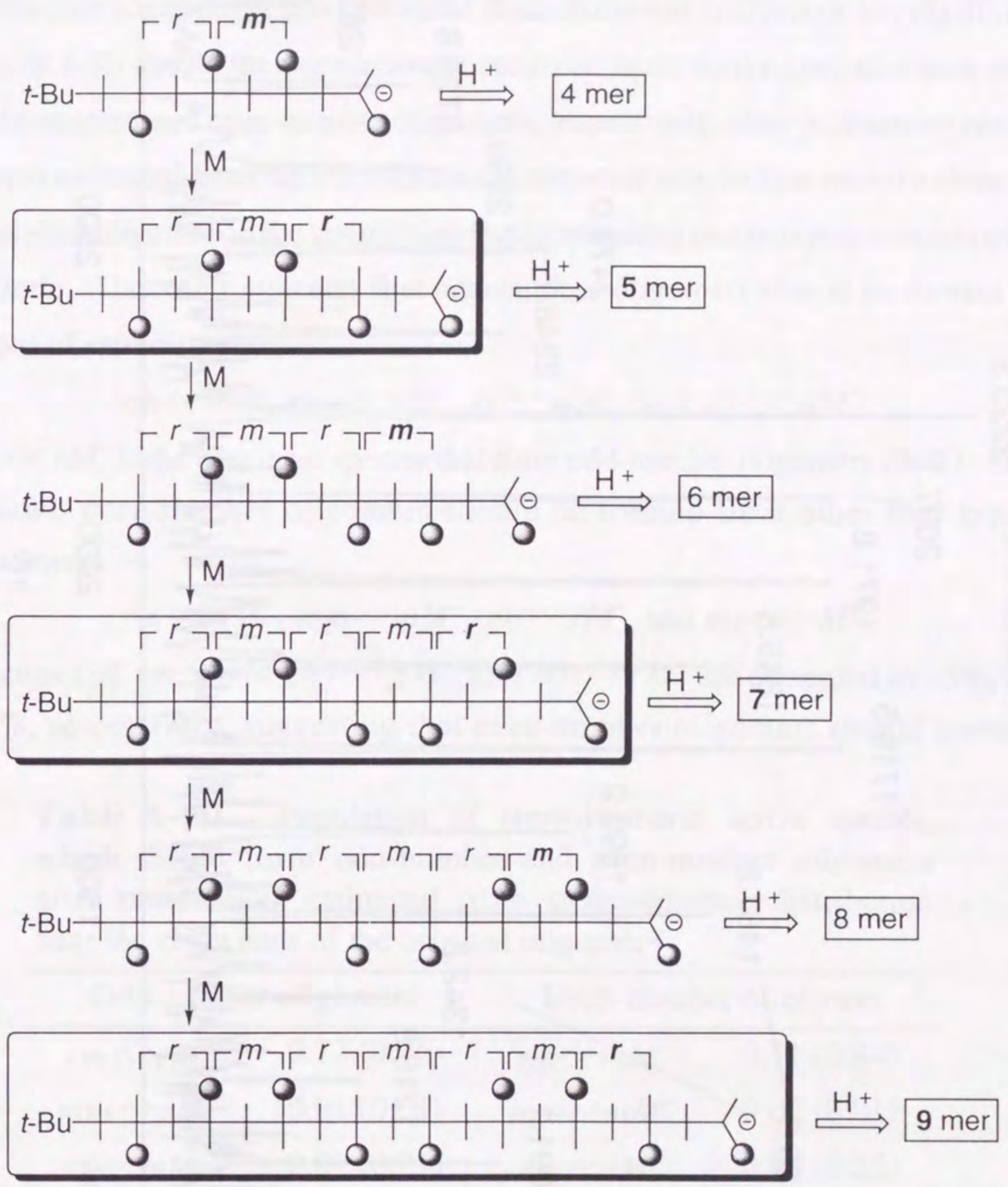


Figure 6-II. 125 MHz ^{13}C NMR spectra of methine carbon at the terminating chain-end and methyl carbon of *t*-butyl group at the initiating chain-end of the *ht*-oligo(AlMA), measured in $CDCl_3$ at 55°C.

Scheme 6-II



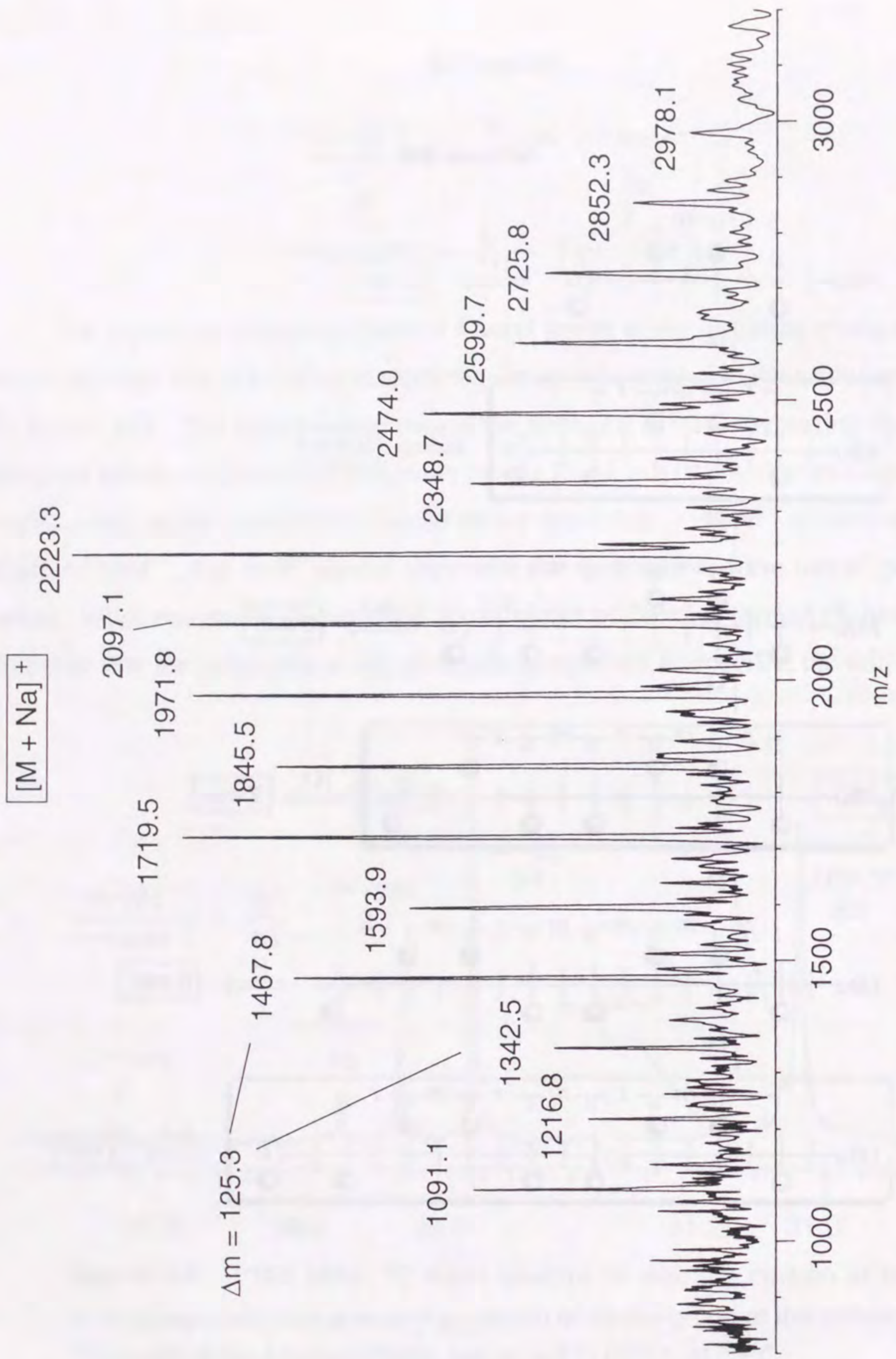


Figure 6-III. MALDI-TOF mass spectrum of oligo(AlMA). The masses correspond to sodium adducts, [M + Na]$^+$. 2,5-Dihydroxybenzoic acid was used as matrix.

oligomers are formed predominantly due to the stereochemical repetition of two consecutive diads (*m* and *r*) in *ht*-polymers (Scheme 6-II). MALDI-TOF mass spectrometric analysis (Figure 6-III) in addition to SFC analysis (Figure 6-I) showed the predominant formation of the oligomers with odd-number *DP*. These results confirm the above-mentioned suggestion obtained from chain-end analysis of *ht*-poly(EMA).

Table 6-III shows the population of stereoisomeric active species which should form odd-number and even-number oligomers, respectively, after protonation reaction, which was estimated from the stereochemical sequence distribution near the chain ends of the original oligomer on the assumption that propagating reaction proceeds completely heterotactic. The result indicates that odd-number oligomers should be formed from four types of stereoisomers;

$rm\sim\sim rM^-$, $mm\sim\sim rM^-$, $rr\sim\sim mM^-$, and $mr\sim\sim mM^-$,

and $rm\sim\sim rM^-$ is the dominant species that form odd-number oligomers (96%). On the other hand, even-number oligomers should be formed from other four types of stereoisomers;

$rm\sim\sim mM^-$, $mm\sim\sim mM^-$, $rr\sim\sim\sim rM^-$, and $mr\sim\sim\sim rM^-$.

The fractions of $rm\sim\sim mM^-$, $rr\sim\sim\sim rM^-$, and $mr\sim\sim\sim rM^-$ are estimated as 43%, 25%, and 32%, respectively, suggesting that even-number oligomers should consist of

Table 6-III. Population of stereoisomeric active species, which should form odd-number and even-number oligomers after protonation, estimated from stereosequence distribution near the chain ends of the original oligomer[a]

Odd-number oligomers		Even-number oligomers	
$rm\sim\sim rM^-$	0.72 (0.96)	$rm\sim\sim mM^-$	0.11 (0.44)
$mm\sim\sim rM^-$	0.01 (0.01)	$mm\sim\sim mM^-$	0.00 (0.01)
$rr\sim\sim mM^-$	0.01 (0.01)	$rr\sim\sim\sim rM^-$	0.06 (0.25)
$mr\sim\sim mM^-$	0.01 (0.01)	$mr\sim\sim\sim rM^-$	0.08 (0.32)
total	0.75 (1.00)	total	0.25 (1.00)

[a] Estimated on the assumption that propagating reaction proceeds completely heterotactic

oligomers, formed from these three stereoisomers, with comparable amounts.

Figure 6-IV shows ^{13}C NMR spectra of chain ends of uniform 12mer and 13mer separated by SFC. In the spectra of 13mer, the signal due to *rm*– triad at the initiating chain-end was observed with a fraction of 91%, and the signals due to –*rm* and –*rr* triads, derived from ∿rM^-, with a fraction of 95%. This indicates that almost all the oligomers with *DP*=13 are formed from *rm*∿rM^- anions. This result agrees well with the estimation from the stereosequence distribution near the chain ends of the original oligomer (*cf.* Table 6-III). On the other hand, in the spectra of 12mer the signals due to *rr*– (17%) and *mr*– (6%) at the initiating chain-end and the signals due to –*mr* (6%) and –*mm* (3%) at the terminating chain-end are observed more clearly than in the spectra of 13mer. This indicates that 12mer contains stereoisomers having different stereosequence at the chain ends more than 13mer. However, the signal intensities in the spectra of 12mer deviate from the estimation. For example, ∿mM^- is expected to form even-number *DP* oligomers with a fraction of 43%, but the signals derived from ∿mM^-, –*mr* and –*mm,* were observed with 9%. Similarly, the signals due to *rr*– and *mr*– at the initiating chain-end are expected to be observed with fractions of 32% and 25%, respectively, but the observed intensities correspond only to 17% and 6%. These results suggest that the assumption that propagation reaction proceeds in a complete heterotactic manner is inappropriate.

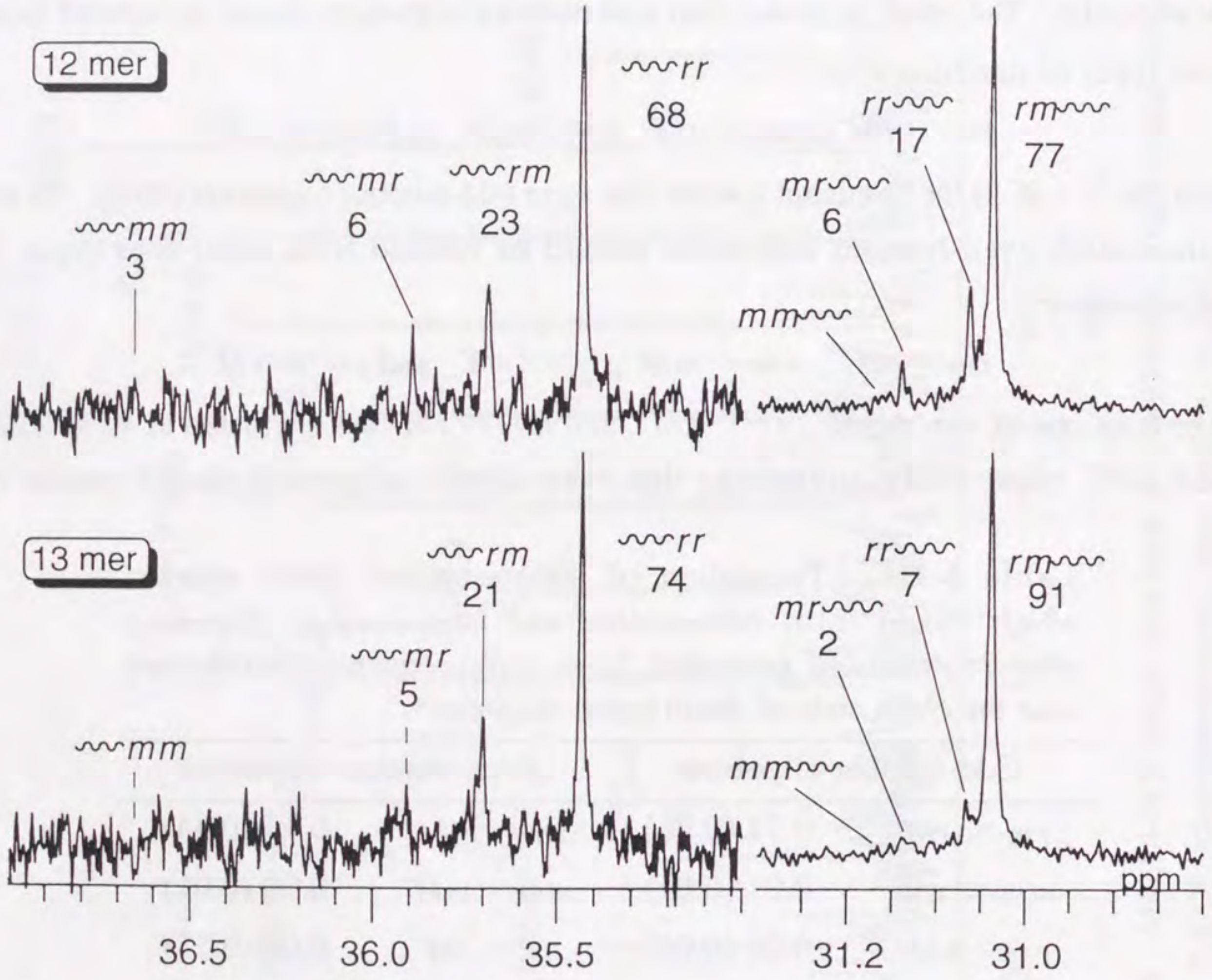


Figure 6-IV. 125 MHz ^{13}C NMR spectra of methine carbons at the terminating chain-end and methyl carbons of *t*-butyl group at the initiating chain-end of 12mer and 13mer, measured in $CDCl_3$ at 55°C.

The ratios of odd-number and even-number oligomers in the oligomers formed at Al / Li = 3 and at Al / Li = 5 were found to be 55 : 45 and 53 : 47, respectively. Odd-even alternation in *DP* distribution is more evident for the oligomer formed at Al/Li = 3 than at Al/Li = 5. Thus further investigation was made by using the oligomer formed at Al/Li = 3.

Figure 6-V (a) shows an SFC chromatogram of *ht*-oligo(AlMA) (II) with an average *DP* of 11.2 prepared with *t*-BuLi / MeAl(ODBP)$_2$ (Al / Li = 3) in toluene at –95°C for 4h. Uniform oligomers were obtained by repeated fractionation with SFC. Each fractionated oligomer exhibited a single peak in SFC chromatogram. As an example, the chromatogram of 9 mer is shown in Figure 6-V (b). The *DP* for each peak in the chromatogram [Figure 6-V(a)] was determined from the intensity ratios of the signals due to the side-chain –OCH_2– and the terminal *t*-butyl groups in ^{1}H NMR spectra of uniform oligomers.

Figure 6-VI shows the resonances due to methyl carbons of *t*-butyl group at the initiating chain-end and the signals due to methine carbons at the terminating chain-end of 5mer to 11mer and the original oligomer. Both signals split principally into four peaks due to triad stereosequence near the chain ends in all the cases. In Figure 6-VII are plotted the triad tacticity at the initiating chain-ends of 5mer to 11mer and the original oligomer. This indicates clearly even-odd alternation in stereosequence

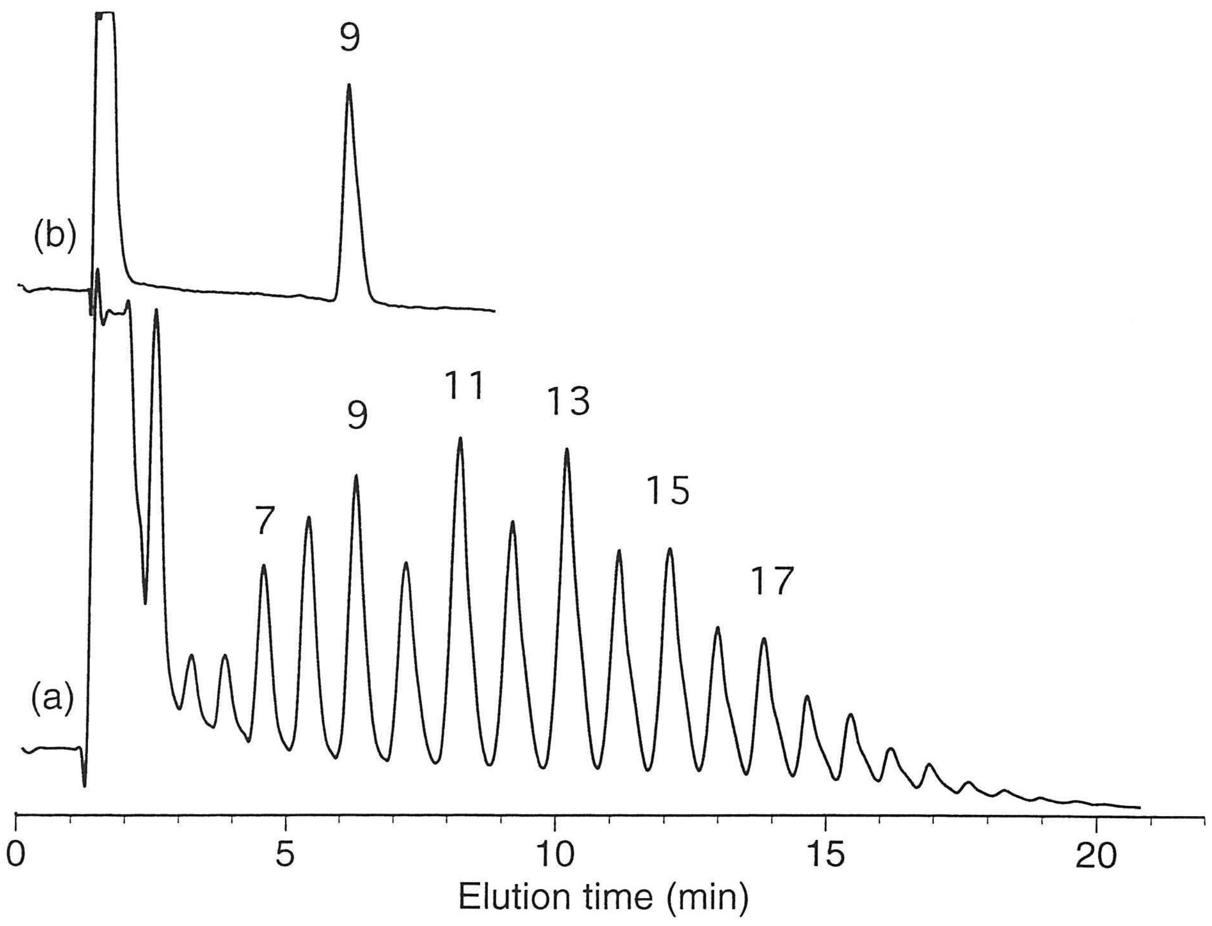


Figure 6-V. SFC traces of (a) *ht*-oligo(AlMA) (II), prepared with *t*-BuLi / MeAl(ODBP)$_2$ (1/3 mol/mol) in toluene at –95°C for 4h, of *DP* = 11.2 and (b) the 9mer isolated therefrom. SFC conditions: B. (*cf.* Table 6-II)

distribution at the initiating chain-end, although the signal due to *rm–* triad is observed with the strongest intensity in both cases of even- and odd-number oligomers. On the other hand, stereosequence distribution at the terminating chain-end scarcely showed even-odd alternation, suggesting that the predominance of $\sim\!\sim\!\sim rM^{-}$ has no connection with the *DP* of living anions (Figure 6-VIII). These results suggest that the stereoselection at the beginning of the polymerization is the important cause for the even-odd alternation in *DP* distribution of the oligomer obtained.

Figures 6-IX to 6-XII show ^{13}C NMR spectra of carbonyl and methylene carbons of 5mer to 11mer and the original oligomer. The notations (α1, ······ , ω1) of monomeric units are shown in Figures 6-XIII and 6-XIV. All the odd-number oligomers showed

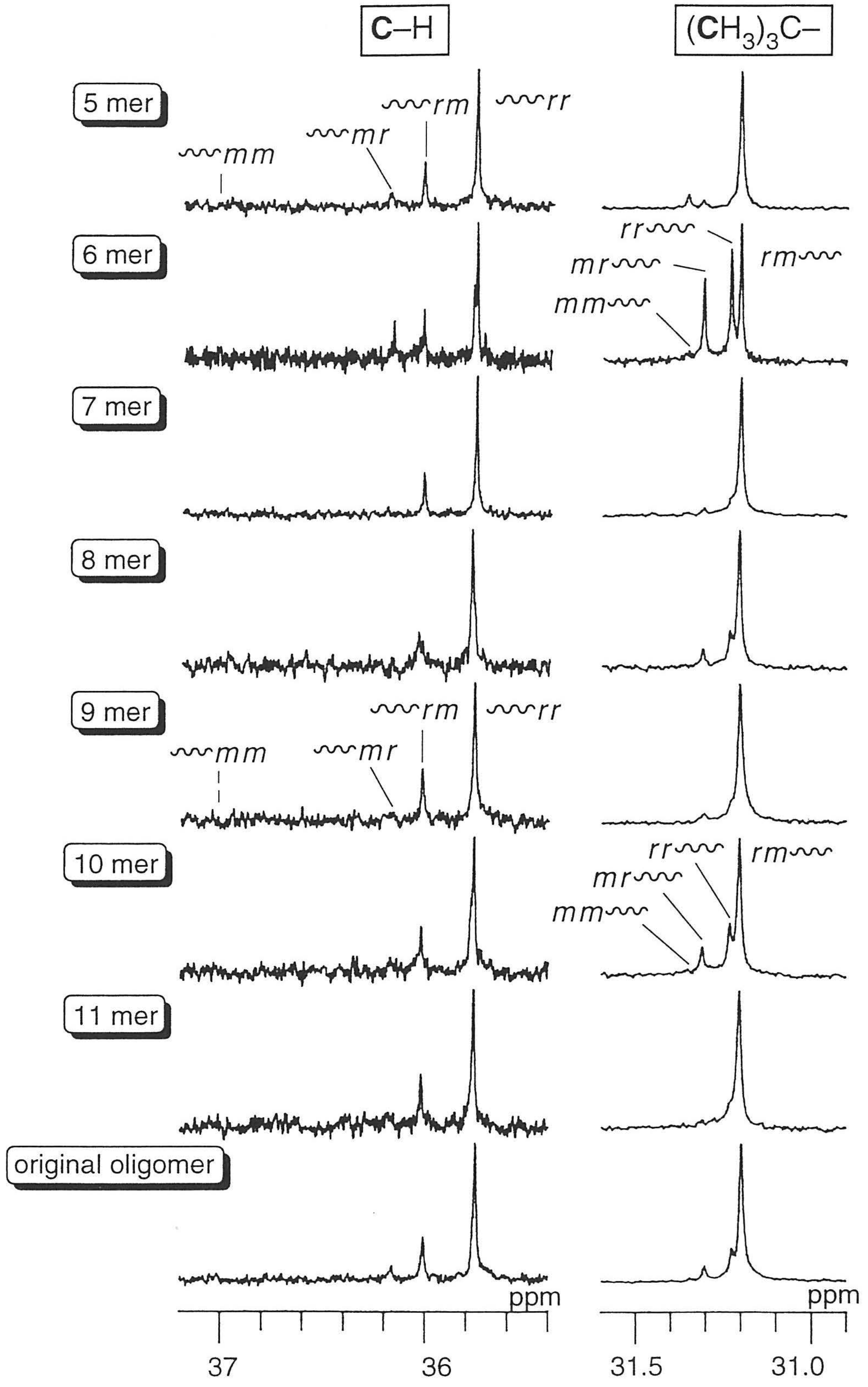


Figure 6-VI. 125 MHz ^{13}C NMR spectra of methine carbons at the terminating chain-end and methyl carbons of *t*-butyl group at the initiating chain-end of 5mer to 11mer and the original oligomer (benzene-d_6, 35°C).

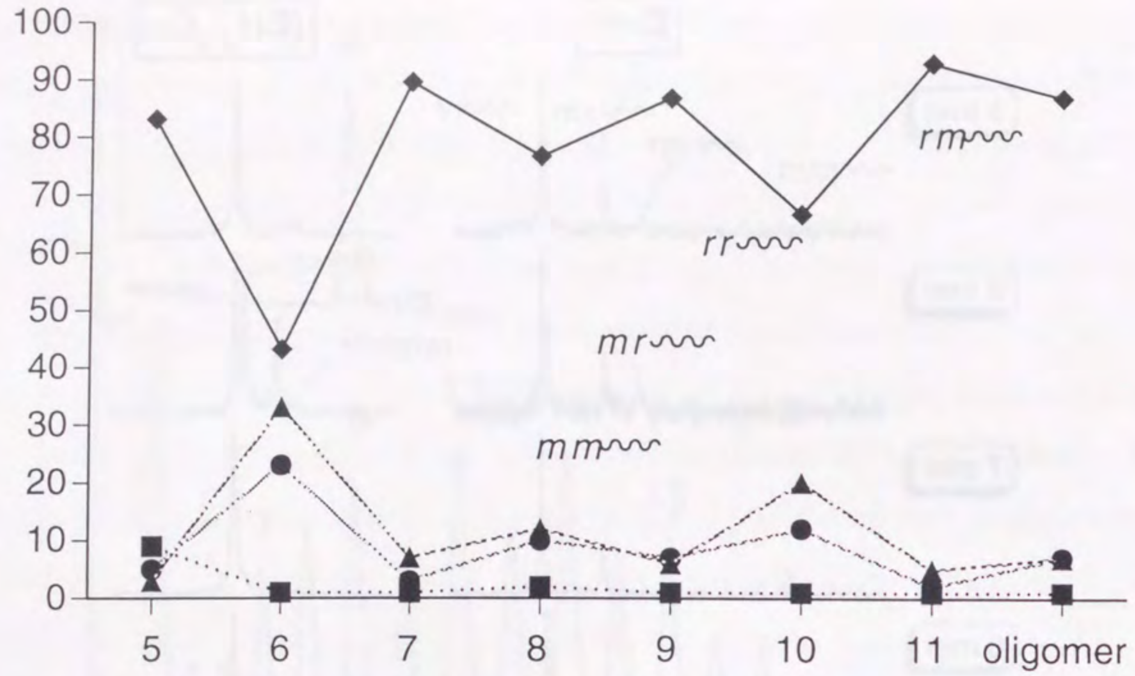


Figure 6-VII. Triad tacticity distribution at the initiating chain-end of 5mer to 11mer and the original oligomer.

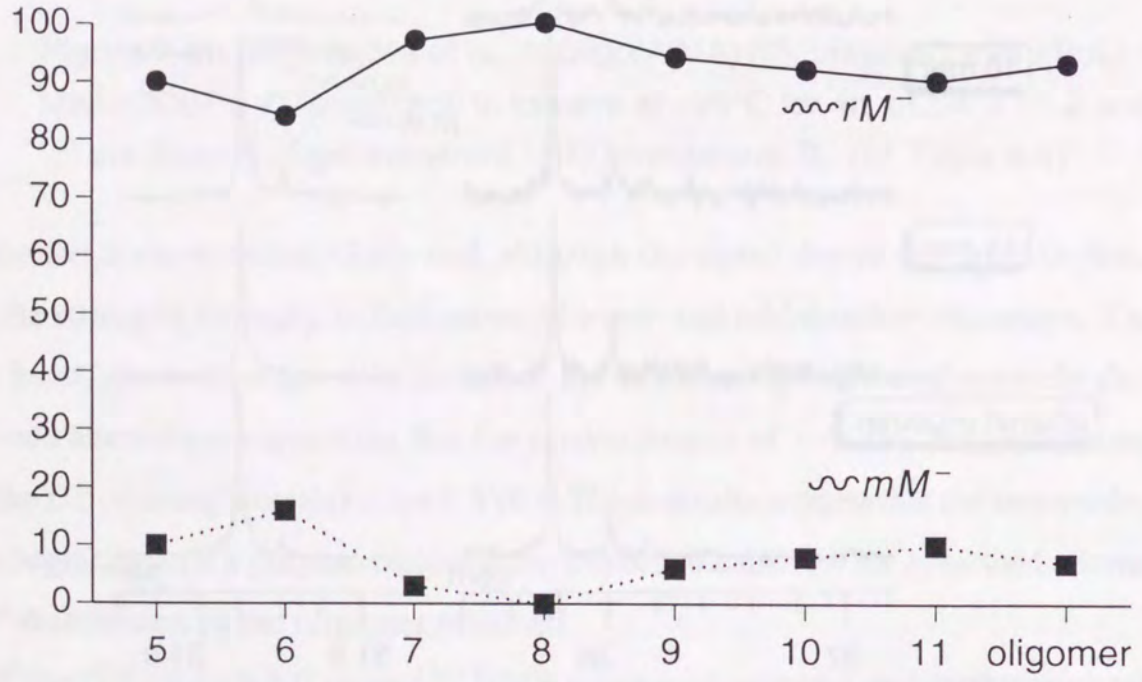


Figure 6-VIII. Fraction of ∿∿∿rM^- and ∿∿∿mM^- which formed 5mer to 11mer and the original oligomer.

simpler resonances than even-number oligomers in both series of the spectra. This indicates that stereostructures of odd-number oligomers, which are formed preferentially, are better controlled than those of even-number oligomers. The carbonyl carbon spectrum of 5mer showed two signals and three pairs of signals which should be assignable to the individual carbons of 5mer. In the spectrum of 5mer, however, the signal at 176.37 ppm was not observed, while the intensity of the signal increased without any changes in shape of other signals as the *DP* of odd-number oligomers increased. This suggests that the signal at 176.37 ppm is assignable to in-chain *ht*-sequence and the predominant structures of odd-number oligomers are expressed as shown in Figure 6-XIII, based on the results obtained from chain-end analysis. Triad tacticity near the chain ends of each odd-number oligomers was obtained from chain-end analysis of the individual oligomers

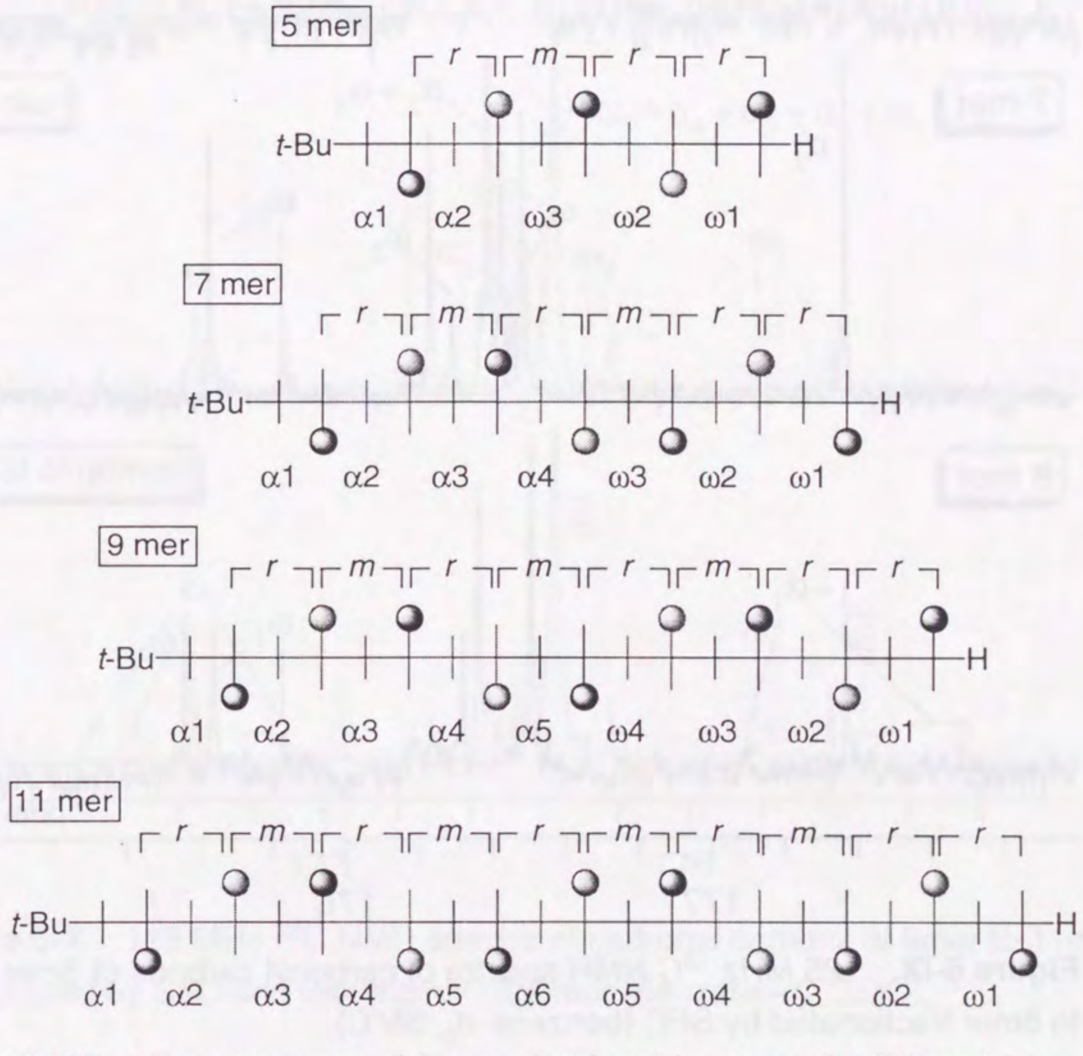


Figure 6-XIII. The structures of the predominant isomers of 5,7,9,and 11mers.[32]

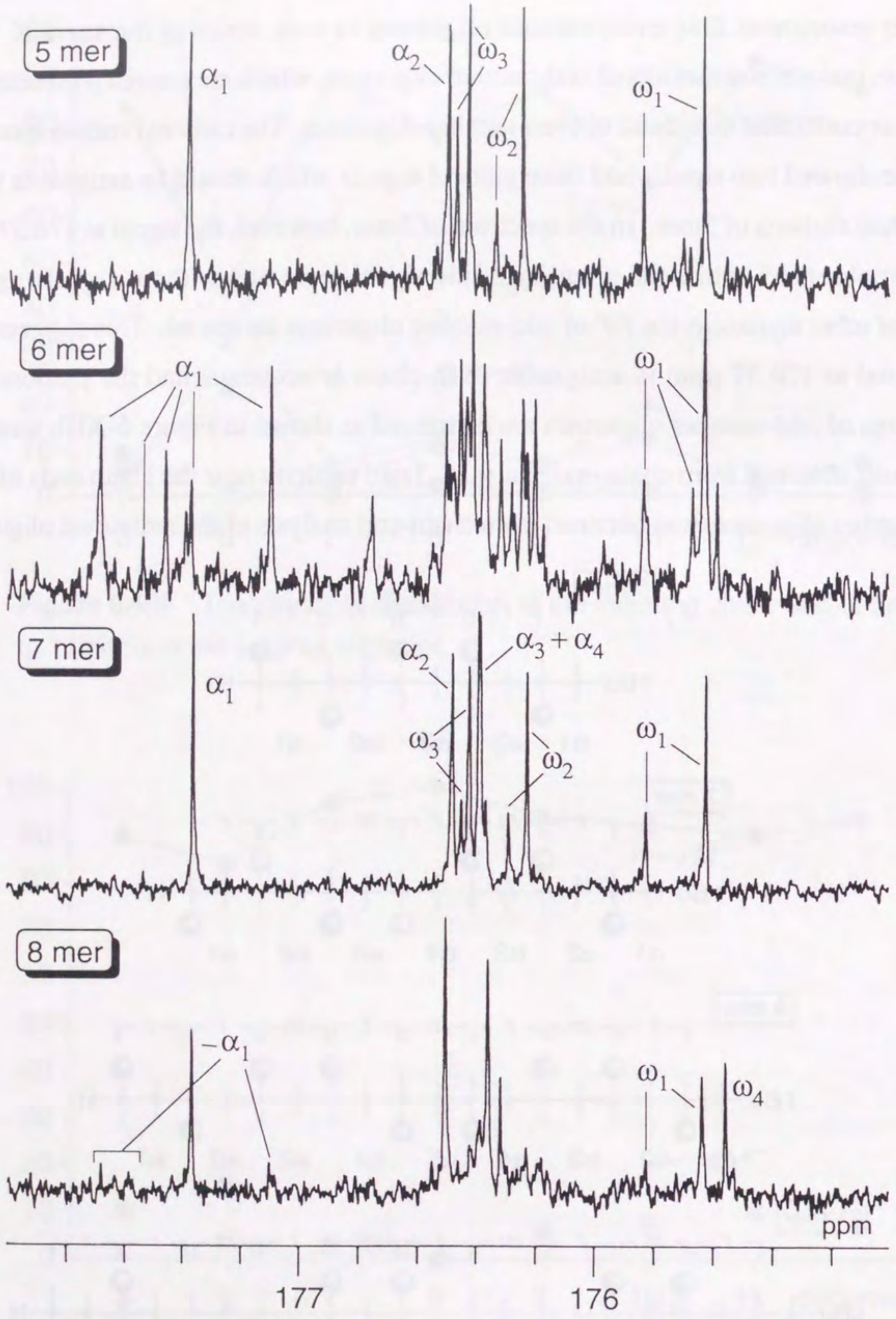


Figure 6-IX. 125 MHz ^{13}C NMR spectra of carbonyl carbons of 5mer to 8mer fractionated by SFC (benzene-d_6, 35°C).

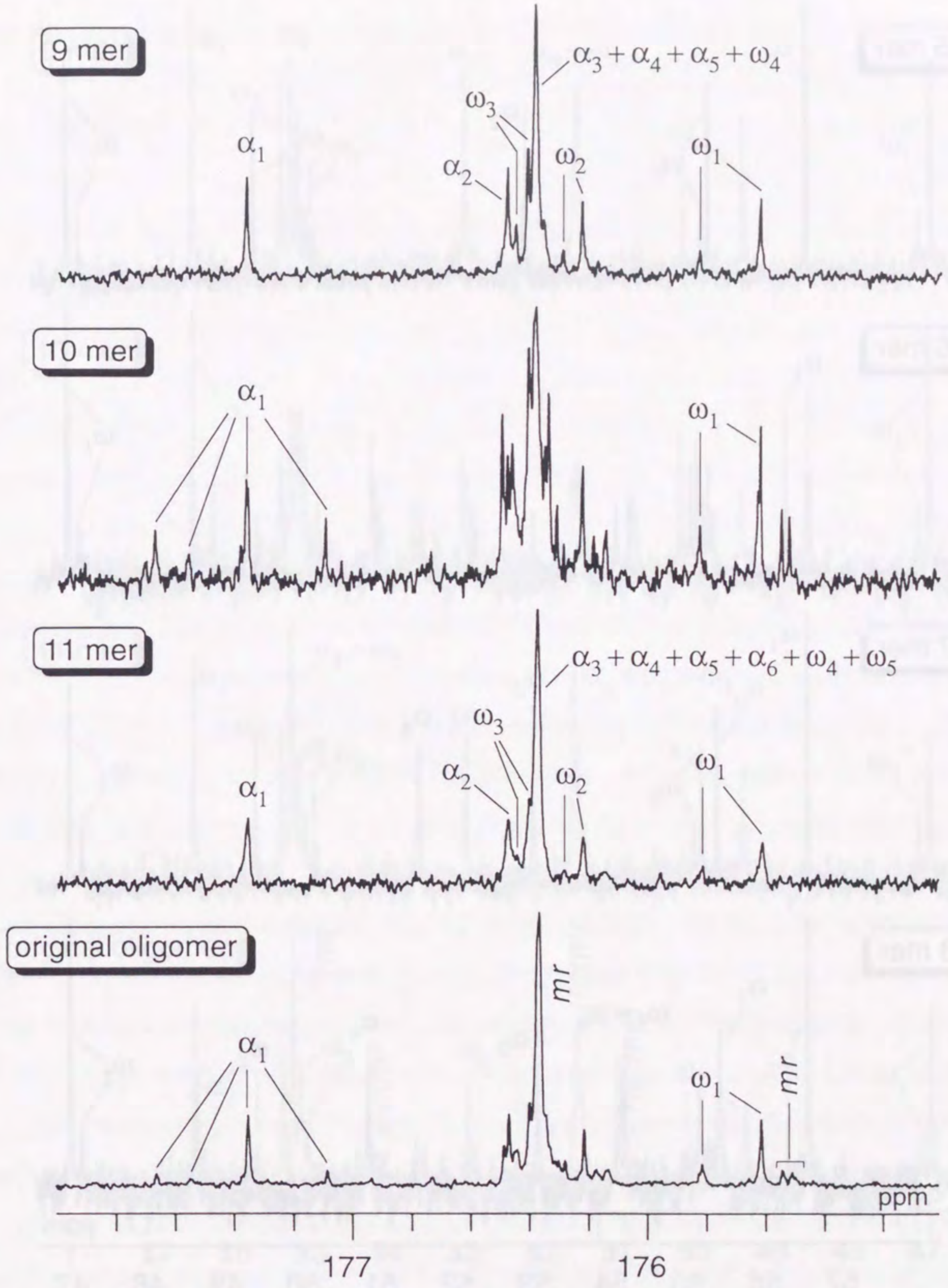


Figure 6-X. 125 MHz ^{13}C NMR spectra of carbonyl carbons of 9mer to 11mer fractionated by SFC and the original oligomer (benzene-d_6, 35°C).

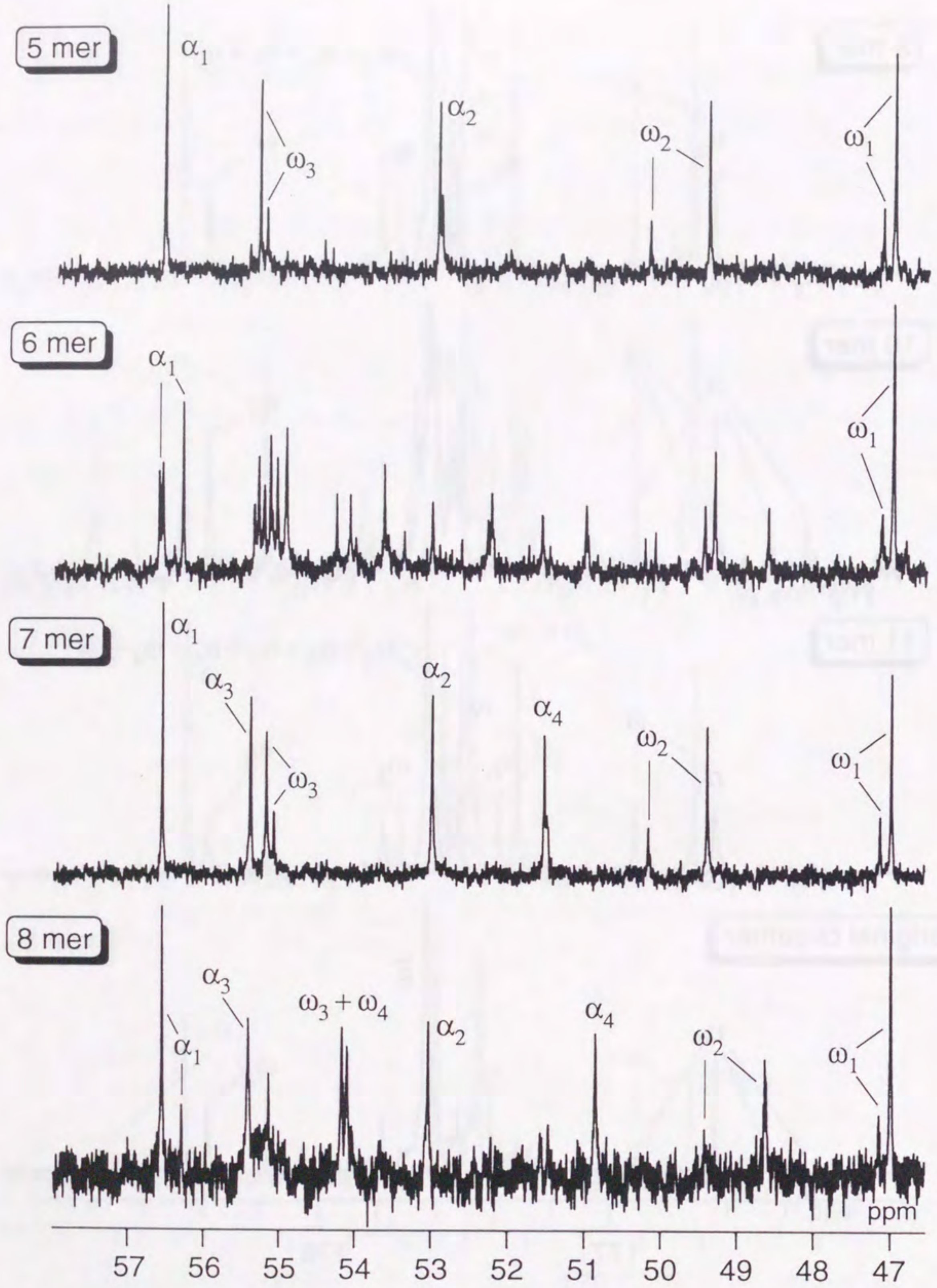


Figure 6-XI. 125 MHz ^{13}C NMR spectra of methylene carbons of 5mer to 8mer fractionated by SFC (benzene-d_6, 35°C).

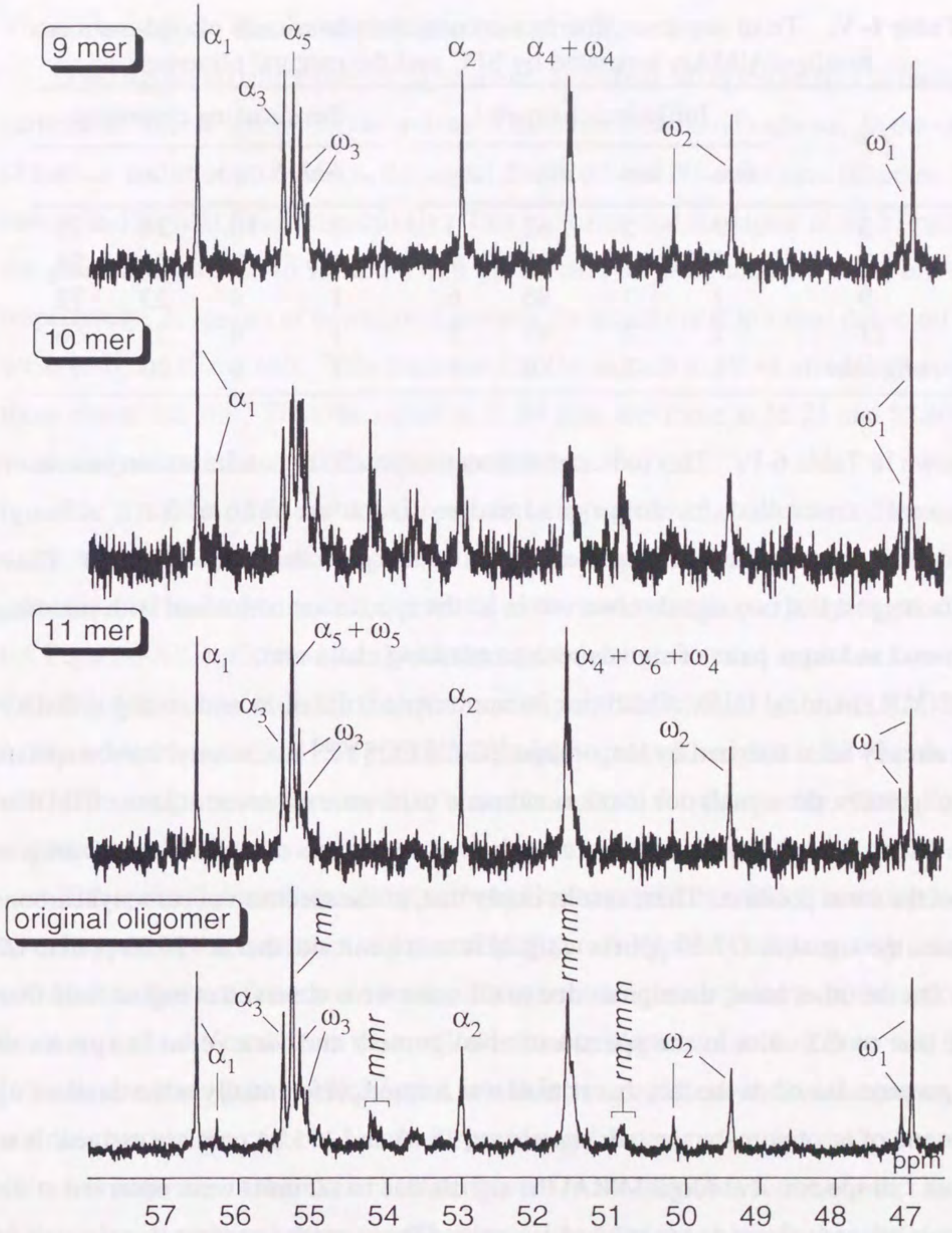


Figure 6-XII. 125 MHz ^{13}C NMR spectra of methylene carbons of 9mer to 11mer fractionated by SFC and the original oligomer (benzene-d_6, 35°C).

Table 6-V. Triad sequence distribution near the chain-ends of odd-number *ht*-oligo(AlMA)s separated by SFC and the original oligomer

DP	Initiating chain-end				Terminating chain-end			
	mm–	*mr*–	*rm*–	*rr*–	– *mm*	– *mr*	– *rm*	– *rr*
5	9	5	83	3	0	10	18	72
7	1	3	89	7	1	2	23	74
9	1	7	86	6	1	4	23	72
11	1	2	92	5	1	8	25	66
oligomer	1	7	86	7	1	6	20	73

as shown in Table 6-IV. This indicates that stereospecificity in termination reaction is not so well controlled, forming *r*-diad and *m*-diad at the ratio of 3 : 1, although stereochemistry near the initiating chain-end is better controlled (*rm* = 83-92%). These results suggest that two signals observed in all the spectra are concerned with initiating chain-end and three pairs of signals with terminating chain-end.

NMR chemical shifts of carbons in monomeric units of *it*- and *st*-oligo(MMA)s have already been assigned by long–range ^{13}C-^{1}H COSY.[33] In carbonyl carbon spectra of *it*-oligomers, the signals due to $\alpha1$ monomeric units were observed at lower field than those due to $\alpha2$ units, while *st*-oligomers showed the signals due to $\alpha1$ and $\alpha2$ units at almost the same position. These results imply that, in the spectrum of carbonyl carbons of 5mer, the signal at 177.39 ppm is assignable to $\alpha1$ unit and that at 176.50 ppm to $\alpha2$ unit. On the other hand, the signals due to $\omega1$ units were observed at higher field than those due to $\omega2$ units in the spectra of *st*-oligomers and *vice versa* in spectra of *it*-oligomers. Based on the fact that *rr* triad was formed preferentially at the terminating chain-end of *ht*-oligomers, the pair signals at 175.63 and 175.84 ppm are assignable to $\omega1$ unit. In spectra of *st*-oligo(MMA) the signals due to $\omega2$ units were observed at the position between those due to $\omega1$ and $\omega3$ units. These results suggest that the pair of signals at 176.25 and 176.34 ppm is due to $\omega2$ unit and those at 176.43 and 176.47 ppm due to $\omega3$ unit,[34] respectively. The differences in resonance frequencies between each signals of pairs were 25.4, 11.2, 6.0 Hz, respectively, in the order from higher field.

These also support the above-mentioned assignment.

Two signals and three pairs of signals were also observed in resonances of methylene carbons of 5mer (Figure 6-XI) as well as in the case of carbonyl carbons. In the spectra of both *it*- and *st*-oligo(MMA)s, the signal due to $\alpha1$ and $\omega1$ units were observed at the lowest and highest field, respectively. This indicates that the signal at 56.57 ppm and the pair of signals at 46.99 and 47.13 ppm could be assigned to $\alpha1$ and $\omega1$ units, respectively. In spectra of *it*- and *st*-oligomers, the signals next to signal due to $\omega1$ units were assigned to $\omega2$ unit. This suggests that the signals at 49.41 and 50.19 ppm are those due to $\omega2$ unit. Thus the signal at 52.94 ppm and those at 55.21 and 55.30 ppm were assigned to $\alpha2$ and $\omega3$[34] units, respectively.

The signals at 51.54 and 55.40 ppm newly appeared in the spectrum of 7mer. This suggests that these peaks are assignable to in-chain units. The stereostructure at methylene carbons of $\alpha3$ and $\alpha4$ units are represented as *rmr* and *mrm*, respectively, at tetrad level (*cf.* Figure 6-XIII). On the other hand, the signal due to *rmr* tetrad appear at lower field than that due to *mrm* tetrad in the spectrum of poly(EMA) (*cf.* Figure 3-XI).[35] These indicate that the signal at 51.54 ppm is assignable to $\alpha4$ unit and that at 55.40 ppm to $\alpha3$ unit. The assignments were made in a similar manner for the spectra of odd-number oligomers with $DP \geq 9$.

The spectra of methylene and carbonyl carbons of 8mer which is exceptionally abundant among even-number oligomers (*cf.* Figure 6-V) show comparatively a simpler pattern than those of 6mer and 10mer, although the resonance patterns in the spectra of 8mer are quite different from those of odd-number oligomers such as 7mer and 9mer. In particular, the signal at 176.37 ppm, which is assigned to in-chain *ht*-sequence, was not observed in the carbonyl carbon spectrum of 8mer, indicating the existence of defective sequence in the main chain of 8mer. On the other hand, one of other evident differences in carbonyl resonances between 7mer and 8mer is whether the signal at 175.56 ppm is observed or not. Based on the fact that the signal due to *mm* triad was observed at the highest field in spectra of poly(AlMA)s,[20] the signal at 175.56 ppm are considered to the signal due to the sequence involving *mm* triad. The structures of

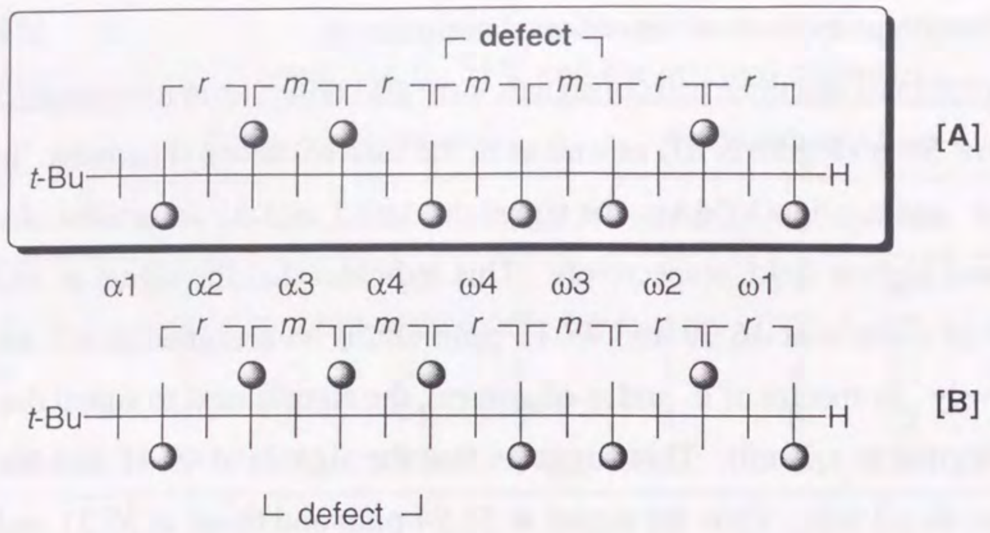


Figure 6-XIV. Two possible structures of the predominant isomers of 8mer.

8mers which contain *mm* sequence can be expressed by only two ways (Figure 6-XIV). The predominant structure of 8mer was assigned to the upper structure [A] based on the differences in methylene carbon spectra between 7mer and 8mer.

[1] The signals due to α_2 and α_3 methylene carbons are observed at the same positions in both spectra.

[2] The signal due to α_4 of 7mer is observed at the position due to *rmrmr* hexad sequence observed in the spectrum of the original oligomer (Figure 6-XII), while the corresponding signal of 8mer is observed at the position due to *rmr**mm*** hexad.

[3] In the spectrum of 8mer the ω_3 signal is observed at almost the same position as the ω_4 signal, and these signals are assignable to ***mm**r* tetrad in the spectrum of the original oligomer (Figure 6-XII).

[4] The signal due to ω_2 of 8mer is observed at higher field than that of 7mer.

The structure [B] in Figure 6-XIV does not explain anything for the difference described above. The upper structure indicates that 8mer was predominantly formed by termination reaction of $\sim\sim\sim \boldsymbol{mm}rM^{-}$. Therefore, the peculiar population of 8mer suggests the peculiar stability of $\sim\sim\sim \boldsymbol{mm}rM^{-}$.

Table 6-V shows the populations of stereoisomeric active species for each oligomer estimated from the distribution of stereostructures near the chain ends, together with for

Table 6-V. Population of stereoisomeric active species, estimated from stereosequence distribution near the chain ends[a]

	5mer	7mer	9mer	11mer	Odd-number oligomer
$rm\sim\sim rM^{-}$	0.76	0.87	0.82	0.83	(0.96)
$mm\sim\sim rM^{-}$	0.08	0.01	0.01	0.01	(0.02)
$rr\sim\sim mM^{-}$	0.00	0.00	0.00	0.01	(0.01)
$mr\sim\sim mM^{-}$	0.00	0.00	0.01	0.00	(0.01)
$rm\sim\sim mM^{-}$	0.09	0.03	0.05	0.09	
$mm\sim\sim mM^{-}$	0.01	0.00	0.00	0.00	
$rr\sim\sim rM^{-}$	0.02	0.06	0.05	0.04	
$mr\sim\sim rM^{-}$	0.04	0.03	0.06	0.02	
	6mer	8mer	10mer		Even-number oligomer
$rm\sim\sim rM^{-}$	0.36	0.74	0.61		
$mm\sim\sim rM^{-}$	0.01	0.02	0.01		
$rr\sim\sim mM^{-}$	0.05	0.00	0.02		
$mr\sim\sim mM^{-}$	0.04	0.00	0.01		
$rm\sim\sim mM^{-}$	0.07	0.02	0.06		(0.20)
$mm\sim\sim mM^{-}$	0.00	0.00	0.00		(0.00)
$rr\sim\sim rM^{-}$	0.28	0.13	0.19		(0.51)
$mr\sim\sim rM^{-}$	0.19	0.09	0.11		(0.29)

[a] Estimated on the assumption that propagating reaction proceeds in a complete heterotactic manner.

odd-number and even-number oligomers unfractionated. The populations of stereoisomers for odd-number oligomers, 5, 7, 9, and 11mers fit well with that for unfractionated odd-number oligomers as well as the case of 13mer fractionated from oligomer prepared with *t*-BuLi / $MeAl(ODBP)_2$ (Al/Li = 5) (*cf.* Figure 6-IV and Table 6-III). This also confirms the high stereoregularity of these odd-number oligomers. On the other hand, the populations for 6, 8, and 10mers deviate from the estimation for even-number oligomers. In particular, $rm\sim\sim rM^-$,which is unlikely to form even-number oligomers as far as the propagating step proceeds in a complete heterotactic manner, is estimated to be a main fraction in all the even-number oligomers.

The ratio of odd-number and even-number oligomers formed was estimated to be 76 : 24 from the stereoregularity distribution near the chain ends of the original oligomer on the assumption that tacticity of the oligomer is perfectly heterotactic. However, the observed ratio of odd-number and even-number oligomers formed was 55 : 45 from the peak intensities of 6-21mers in SFC chromatogram. The tacticity of the original oligomer was determined from ^{13}C NMR spectrum of carbonyl carbons with neglect of the resonances due to $\alpha 1$ and $\omega 1$ units; $mm : mr : rr = 2.7 : 96.4 : 0.9$. The high stereoregularity of the oligomer seems inconsistent with the the difference of 21% between the observed and expected fractions of odd-number and even-number oligomers.

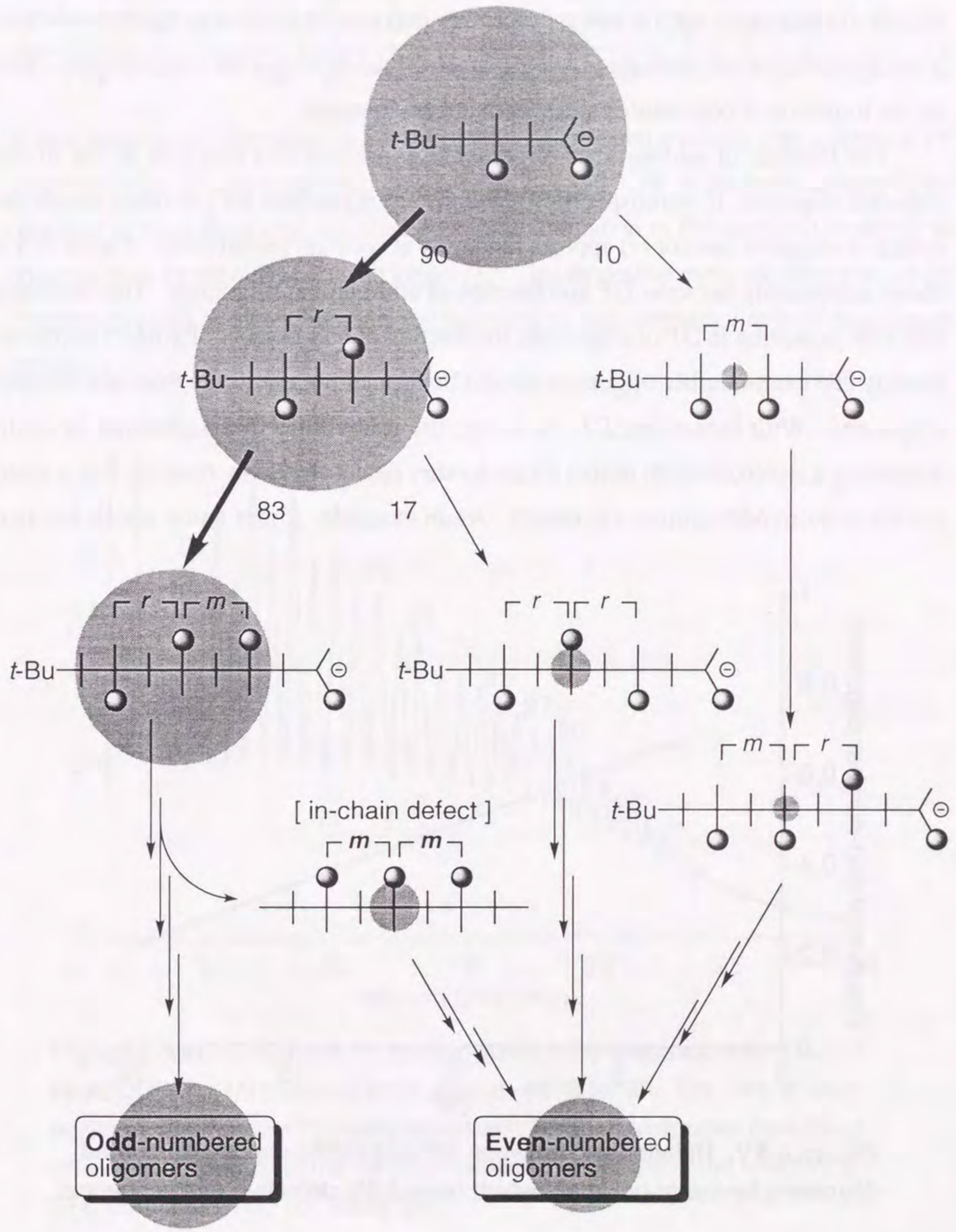
The expression of 100 triads using the macromolecules of $DP = 11.2$ requires 8.9 macromolecules in rough. If one macromolecule never contain more than one defective sequence, 3.6 macromolecules, which corresponds to 40% of 8.9 macromolecules, have one defective sequence, *mm* or *rr*. This stereostructural fault leads an increase of one degree of polymerization. Moreover, if this mistake occurs at random regardless the stereosequence at the initiating chain-end, the populations of odd-number and even-number oligomers are calculated as follows;

Odd-number oligomer $= 0.76 \times 0.60 + 0.24 \times 0.40 = 0.46 + 0.10 = 0.56$

Even-number oligomer $= 0.24 \times 0.60 + 0.76 \times 0.40 = 0.14 + 0.30 = 0.44.$

The difference between the fraction of odd-number oligomer transformed from even-number oligomer and *vise versa* was found to be 20 %. The roughly calculated values agree well with

Scheme 6-III



the observed value obtained from peak intensities in SFC chromatogram. This means that for even-odd alternation in *DP* distribution to be observed clearly, the suppression of the formation of defective sequences, such as *mm* and *rr*, is very important in addition to the stereoselection at the beginning of polymerization. In Scheme 6-III are described the simplified flowchart for the formation of odd-number and even-number oligomers.

The fraction of odd-number oligomer is expressed as a function of *DP* of the obtained oligomer, if stereospecificity is constant regardless *DP*; in other words the defective sequence (*mm* or *rr*) appears randomly at constant probabilities. Figure 6-XV shows relationship between *DP* and fraction of odd-number oligomers. This indicates that with increasing in *DP* of oligomers, the fraction of odd-number oligomers decreases linearly and even-number oligomers should be formed preferentially than odd-number oligomers. With increasing *DP*, however, the probability that a growing *ht*-chain containing a stereochemical defect forms another defect should increase so that it again prefers to form odd-number oligomers. As an example, 15mer anion which has two

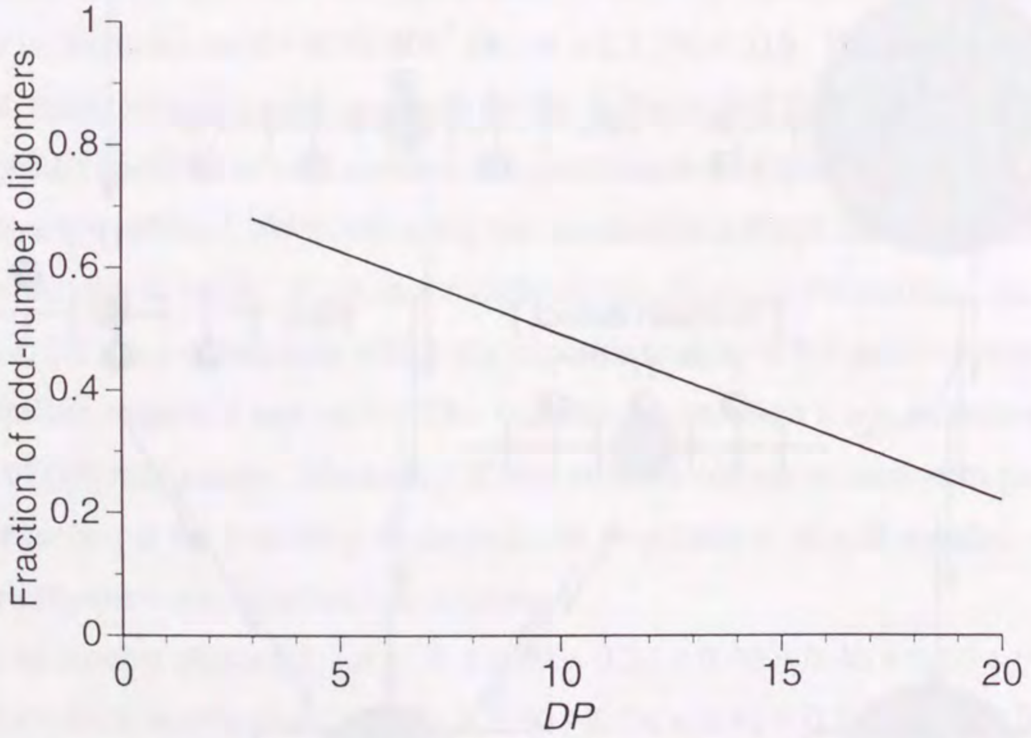
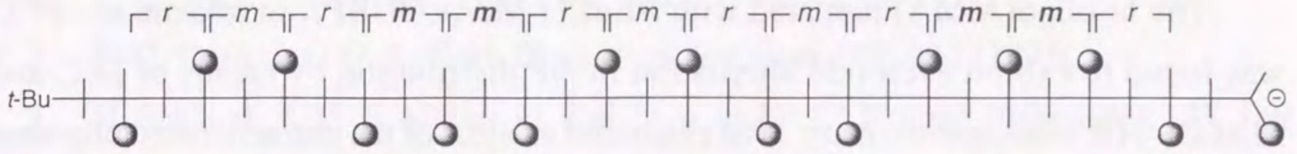


Figure 6-XV. Relationship between *DP* and fraction of odd-numbered oligomers for the *ht*-polymers which have 3,6% defective *mm* sequence.

defective *mm* sequence is shown below.



In fact, the even-odd alternation in *DP* distribution disappeared gradually with increasing *DP* observed in the SFC chromatogram as shown in Figure 6-XVI. If the heterotacticity of the oligomer is more improved, the clear even-odd alternation in *DP* distribution should be observed even for the oligomers with longer *DP*. This means that even-odd alternation in *DP* distribution could be a good measure for judgment of high stereoregularity of *ht*-polymers obtained.

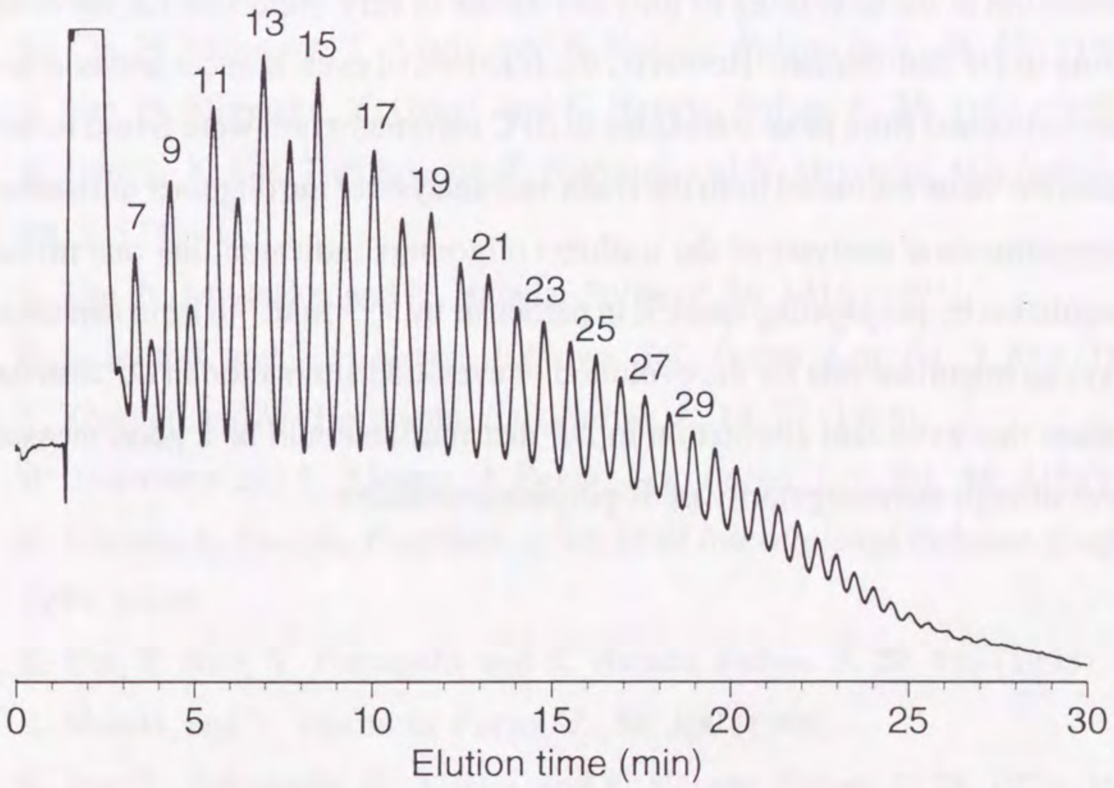


Figure 6-XVI. SFC trace of *ht*-oligo(AlMA) (III) prepared with *t*-BuLi / MeAl(ODBP)$_2$ (1/3 mol/mol) in toluene at –95°C for 8h. The *DP*s of each peaks were determined by comparison with that for the oligomer containing an authentic sample of the 19 mer measured under the same conditions. SFC conditions : C. (*cf.* Table 6-II)

Conclusion

The *ht*-oligo(AlMA) prepared with *t*-BuLi / MeAl(ODBP)$_2$ in toluene at –95°C was found to exhibit even-odd alternation in *DP* distribution by means of SFC and MALDI-TOF mass spectrometry. The chain-end analysis of the unfractionated oligomer suggested that the oligomers with odd-number *DP* should be formed preferentially than those with even-number *DP*. In fact, the SFC and MALDI-TOF mass spectrometric analyses demonstrated the preferential formation of the oligomer with odd-number *DP* except for 8mer.

The oligomers were fractionated into uniform oligomers with respect to *DP* by SFC, and the stereostructure of uniform oligomers were investigated by ^{13}C NMR spectroscopy. The chain-end analysis of uniform oligomers suggested that the stereoselection at the beginning of polymerization is very important for the even-odd alternation in *DP* distribution. However, the fractions of even-number and odd-number oligomers obtained from peak intensities in SFC chromatogram were found to be quite lower than the value estimated from the chain-end analysis of the oligomer unfractionated. The stereostructural analysis of the uniform oligomers indicated that one mistake in stereoregulation by propagating species, in particular by $\sim\sim\sim mM^-$ to form *mm* sequence, also plays an important role for the evolution of even-odd alternation in *DP* distribution. This means that even-odd alternation in *DP* distribution could be a good measure for judgment of high stereoregularity of *ht*-polymers obtained.

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List of Publications

Papers

1. "Chain-End Stereostructure of Heterotactic Poly(ethyl methacrylate) Prepared with *t*-Butyllithium / Bis(2,6-di-*t*-butylphenoxy)methylaluminum as Studied by ^{13}C NMR Spectroscopy"
Tatsuki KITAYAMA, Tomohiro HIRANO, and Koichi HATADA, *Polym. J.*, **28**, 61 (1996).

2. "Remarkable Change of Stereochemistry near the Terminating Chain-End of Heterotactic Poly(ethyl methacrylate) with Conversion. Importance in Mechanistic Study of Stereospecific Polymerization with the Aid of Chain-End Analysis"
Tatsuki KITAYAMA, Tomohiro HIRANO, and Koichi HATADA, *Polym. J.*, **28**, 1110 (1996).

3. "Highly Heterotactic Polymerization of Methacrylates — Higher Order Stereoregulation and Stereochemical Significance"
Tatsuki KITAYAMA, Tomohiro HIRANO, Yajun ZHANG, and Koichi HATADA, *Macromo. Symp.*, **107**, 297 (1996).

4. "Remarkable Effect of Structure of Bulky Aluminum Phenoxides on Stereospecificity of Methacrylate Polymerization"
Tatsuki KITAYAMA, Tomohiro HIRANO, and Koichi HATADA, *Tetrahedron*, **53**, 15263 (1997).

5. "Heterotactic Polymerization of Methacrylates Having C-3 Ester Group"
Tomohiro HIRANO, Hiroko YAMAGUCHI, Tatsuki KITAYAMA, and Koichi HATADA, *Polym. J.*, **30**, 767 (1998).

6. "Effect of Ester Compounds on Stereospecificity in Methacrylate Polymerization with *t*-BuLi / Bis(2,6-di-*t*-butylphenoxy)methylaluminum"
Tomohiro HIRANO, Tatsuki KITAYAMA, and Koichi HATADA, *Polym. J.* **30**, 736 (1998).

7. "Chain-End Analysis of Heterotactic Poly(ethyl methacryalte) — Monomer-Concentration Dependence of Stereoselectivity of Propagating Anions and Time Dependence of Stereospecificity in Termination Reaction"
   Tomohiro HIRANO, Tatsuki KITAYAMA, and Koichi HATADA, in preparation.

8. "Even-Odd Alternation in Distribution of Degree of Polymerization Observed for Heterotactic Poly(allyl methacrylate)"
   Tomohiro HIRANO, Tatsuki KITAYAMA, Jingzhe CAO, and Koichi HATADA, in preparation.

9. "^{13}C NMR Analysis of Uniform Heterotactic Oligo(allyl methacrylate) Aiming at Understanding of Polymerization Mechanism"
   Tomohiro HIRANO, Jingzhe CAO, Tatsuki KITAYAMA, and Koichi HATADA, in preparation.

Other Related Papers and Reviews

1. "Methacrylate Polymerization with Binary Initiators for Multiple Control of Polymer Structures — Molecular weight, Stereoregularity, End-functionality, and Monomer Sequence —"
   Tatsuki KITAYAMA, Tomohiro HIRANO, Takatsune YANAGIDA, Masato TABUCHI, Megumi SATOH, and Koichi HATADA, *Macromo. Symp.*, in press.

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