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Tamaki Nakano

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かさ高いメタクリル酸エステルの不斉重合とらせん状ポリマーのコンホメーション変化

Tamaki Nakano
中 野 環
1991

TO MY FAMILY AND FRIENDS

Asymmetric Polymerization of Bulky Methacrylates and Stereomutation of Helical Polymers

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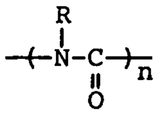
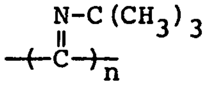
General Introduction

Conformation of a polymer has been of great interest because it is deeply concerned with physical and chemical properties of the polymer. As far as concerned with a linear polymer, helix is one of the simplest conformations in numerous numbers of geometrically possible structures. Helical conformation is often seen in naturally occurring polymers such as nucleic acids, polypeptides, and polysuccharides. As for synthetic polymers, many stereoregular vinyl polymers take the helical conformation in the solid state. However, only a few polymers are known to maintain the helical conformation in solution if the polymers have no optically active side group. Polyisocyanates, polyisocyanides, and poly(triarylmethyl methacrylate)s are the examples of such type of polymers. These polymers often show high optical activity in solution when the helix is of single screw sense. Optically active polyisocyanates are prepared by anionic polymerization of isocyanates having an optically active pendant group or by anionic copolymerization of an achiral isocyanate and a small amount



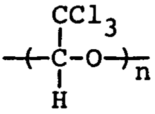
$-\!(\mathrm{N(R)}-\mathrm{C(=O)})_n-$

polyisocyanate



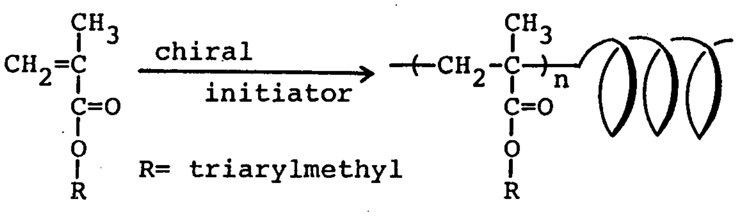
$-\!(\mathrm{C}(=\mathrm{N-C(CH_3)_3}))_n-$

poly(t-butyl isocyanide)



$-\!(\mathrm{C(CCl_3)(H)}-\mathrm{O})_n-$

polychloral

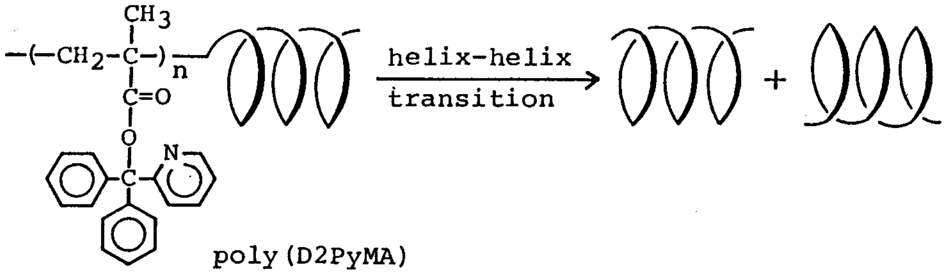


$CH_2=C(CH_3)-C(=O)-O-R \xrightarrow[\text{initiator}]{\text{chiral}} -\!(CH_2-C(CH_3)(C(=O)-O-R))_n-$

polymethacrylate

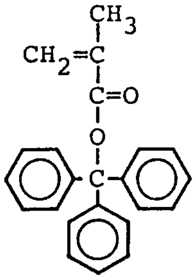
of an optically active isocyanate.[1] *t*-Butyl isocyanide directly affords an optically active polymer by polymerization with optically active nickel (II) complexes.[2] Optically active poly(triarylmethyl methacrylate)s are also directly obtained by asymmetric (helix-sense-selective) anionic polymerization.[3] Although, polychloral prepared with a chiral initiator is considered to belong to this category of an optically active polymer, the optical activity of the polymer has been confirmed only in film because the polymer is insoluble.[4] However, recently oligochloral was found to take helical conformation not only in the solid state but also in solution by ^{1}H NMR conformational analyses.[5] The helices of poly(triarylmethyl methacrylate)s and polychloral are considered to be maintained by the steric repulsion between the bulky side groups.

Conformational transition of a helical polymer has extensively been investigated for poly(α-amino acid)s, which can stereomutate among the α-helix, β-sheet, and random coil by changing external factors such as pH of a solution and temperature. However, as for the stereomutation of helical synthetic vinyl polymers, only a few studies have been done. The optically active poly(diphenyl-2-pyridylmethyl methacrylate) [poly(D2PyMA)] which can be directly produced by helix-sense-selective polymerization is the first example of the vinyl polymer which undergoes the helix-helix transition in solution.[6] The optically active, one-handed helical poly(D2PyMA) loses its optical activity in solution through the transition (racemization), and the polymers which lost its optical activity can be optically resolved into (+)- and (-)-polymers by chiral high-performance liquid chromatography (HPLC). In this transition, the final content of the right- and left-handed helices is dependent on the end groups, that is, the chirality of the asymmetric centers of the main chain in the vicinity of the chain end.[6b]

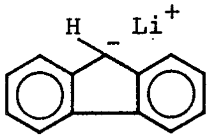


In this thesis, the author describes the asymmetric synthesis and stereomutation of optically active polymethacrylates with one-handed helical conformation. The first half (Part A) of the thesis mainly deals with the mechanism of formation of optically active, highly isotactic poly(triphenylmethyl methacrylate) [poly(TrMA)] which is the first example of an optically active vinyl polymer with chirality due to only helicity and also the first example of an optically active polymer directly obtained by helix-sense-selective polymerization.[7a]

Optically active poly(TrMA) can be directly prepared by anionic polymerization of TrMA monomer with chiral initiators.[7] However, in the polymerization, small amounts of oligomers with low optical activity are always produced in addition to the optically active polymer, and the amounts of the oligomers depend on the initiator system. It has been pointed out that the oligomers with certain specific structures may propagate to the one-handed helical polymer and the others may remain as oligomers until the completion of the polymerization.[7b] In order to get information on this point, the author carried out the asymmetric oligomerization of TrMA with the complexes of fluorenyllithium (FlLi) or its derivatives with chiral ligands at several different ratios of TrMA to initiator ([TrMA]/[Li]). The



TrMA



FlLi

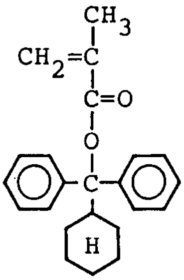
resulting oligomers were separated in terms of degree of polymerization (DP), diastereomers, and optical isomers. The absolute configuration of the oligomers was determined on the basis of an optically active dimer containing 9-fluorenyl moiety derived from (-)-(*R*,*R*)-2,4-dimethylglutaric acid. The results of the oligomerization provided the detailed information on the relative activity of stereoisomeric oligomer anions produced in the helix-sense-selective polymerization. The activity of the oligomer anions depended on thier DP and stereostructure. Moreover, by reference to the results of oligomerization, the absolute configuration of the main chain of the isotactic polymer was determined. There exist only a few examples of such a stereochemical analysis of polymerization mechanism including the absolute configuration of main chain.[8] The present study may be the first example of determination of the absolute configuration of a polymethacrylate produced from a prochiral monomer. Such a detailed study on the stereostructure of the oligomer and the polymer made it possible to discuss precisely about the mechanism of the polymerization leading to the one-handed helix. Wulff and coworkers reported on a similar oligomerization reaction of TrMA. However, they did not separate the oligomers into optical isomers.[9]

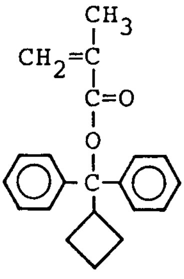
The stereochemistry of protonation and methylation of the oligo(TrMA) anions was also investigated. The activity of oligomer anions in the propagation reaction showed close relation with the stereochemistry of the termination reaction.

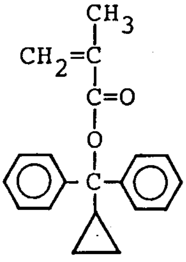
The latter half (Part B) of the thesis deals with the synthesis and conformation, particularly change of conformation, of helical polymers and oligomers.

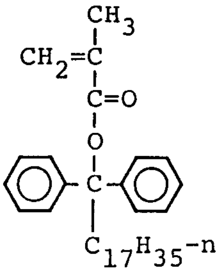
In contrast to the formation of one-handed helical, highly isotactic poly(TrMA) and poly(D2PyMA) in the polymerization of TrMA and D2PyMA with chiral anionic initiators, less bulky 1,1-diphenylethyl methacrylate affords an optically inactive, atactic polymer by polymerization under similar conditions.[10] This indicates that the replacement of a phenyl group of TrMA with a methyl group is not adequate to construct a helical polymethacrylate. The methyl group may be too small. In order to know critical bulkiness of the ester group to maintain helical conformation of polymethacrylates, four bulky methacrylates having 1,1-diphenylalkyl ester group, cyclohexyldiphenylmethyl, cyclobutyldiphenylmethyl, cyclopropyldiphenylmethyl, and 1,1-

diphenyloctadecyl methacrylates (CHDPMA, CBDPMA, CPDPMA, and DPODMA) were synthesized and polymerized. CHDPMA and CBDPMA afforded optically active, isotactic polymers and CPDPMA and DPODMA optically inactive, atactic polymers. Though the helix of poly(CHDPMA) was stable even at 60°C, that of poly(CBDPMA) changed into random-coil conformation at about -40°C. Cyclohexyldiphenylmethyl group is bulky enough, cyclopropyldiphenylmethyl group may be too small, and 1,1-diphenyloctadecyl group too flexible as an ester group, to form and to maintain a helical conformation. Cyclobutyldiphenylmethyl group is considered to be of critical bulkiness for the formation of helix. The optically active poly(CHDPMA) showed helix-helix transition similarly to the poly(D2PyMA).[6] Prevailing helical structure produced kinetically in the process of the polymerization irreversibly changed to thermodynamically stable one in solution at 60°C.

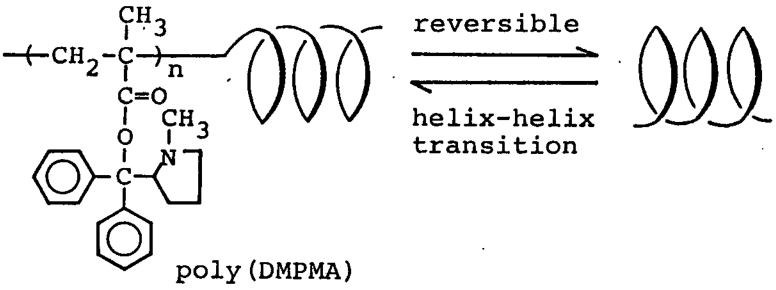

CHDPMA


CBDPMA


CPDPMA

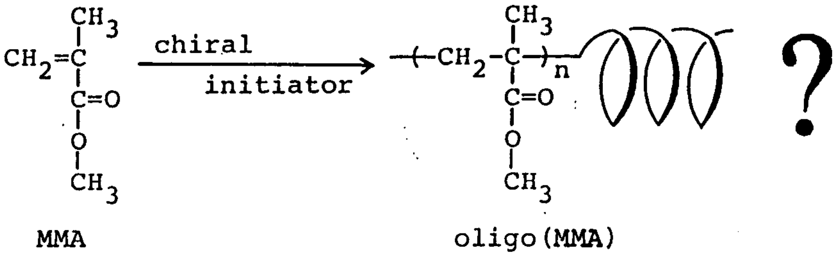

DPODMA

A helical polymethacrylate having an amino moiety in the ester group is interesting because the amino group is protonated with acids and the protonation may affect the conformation of the polymer. On this stand point, (-)-(*S*)-diphenyl(1-methylpyrrolidin-2-yl)methyl methacrylate (DMPMA) was synthesized and polymerized to obtain an optically active polymer of single screw sense. The polymer obtained was insoluble in usual nonpolar solvents such as toluene and chloroform but soluble in polar solvents such as methanol and water containing acids. This polymer showed reversible transition from one helix to the other in methanol containing a small amount of an acid such as methanesulfonic acid depending on the acidity of the solvent. This may be the first example of the reversible helix-helix transition of a vinyl polymer.



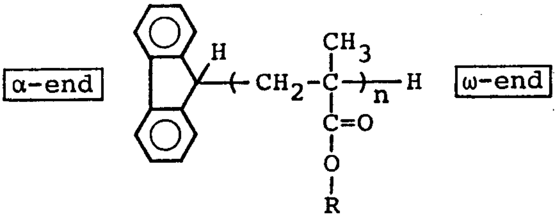
As described before, optically active poly(D2PyMA) undergoes a helix-helix transition similar to racemization.[6] The degree of polymerization (DP) of the polymers so far used was in the range of 27~81. In order to know the critical DP of poly(D2PyMA) at which helical conformation is maintained, oligo(D2PyMA)s of DP = 4~12 were prepared and their conformation was studied by means of ^{1}H NMR spectroscopy. The oligo(D2PyMA) was prepared under similar conditions to those of the polymerization in which an one-handed helical poly(D2PyMA) is produced. The oligomer mixture of DP = 6~12 partly hold helical conformation and underwent a reversible helix-coil transition by changing the temperature. Therefore, it became clear that the critical DP exists between 6~12.

Cram and Sogah carried out the asymmetric anionic polymerization of methyl methacrylate (MMA) by using chiral crown ethers and reported that the oligo(MMA)s obtained in their systems were highly isotactic and showed high optical activity.[11] The optical rotation of the oligomers decreased slowly in solution. They attributed the optical activity to the one-handed helical conformation of the oligomers and its decrease to helix-coil transition of the oligomers. In order to confirm the possibility of existence of the helical conformation of poly(MMA) in solution, isotactic oligo(MMA)s were prepared with 1-naphthylmagnesium bromide (1-NpMgBr) and optically resolved into optical isomers by chiral HPLC. The isotactic isomers showed very small optical rotation. This suggests that the oligomers probably do not possess the helical conformation.

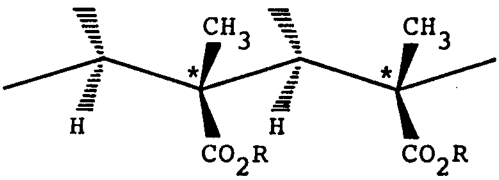


Part A is divided into three chapters dealing with the asymmetric oligomerization of TrMA and Part B four chapters dealing with the synthesis and conformational change of optically active, helical poly- and oligomethacrylates.

In this thesis, the following nomenclature of polymers is used. As an example, the structure of the polymethacrylate prepared with the complex of fluorenyllithium and terminated with methanol is shown below. According to the IUPAC structure-based nomenclature for the polymer, this polymer is named *α*-hydro-*ω*-9-fluorenyl-polymethacrylate in which the process of the formation of polymer chain is irrespective. However, in the present thesis, the *α*- and *ω*-ends are designated as the prefixes for the beginning and terminal of the polymer chain, respectively, on the basis of the process of the formation of the polymer. In the notation of absolute configuration, meso sequence is represented as *RR* or *SS*. Therefore, isotactic sequence is represented as *RRR*--- or *SSS*---.

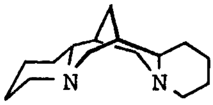


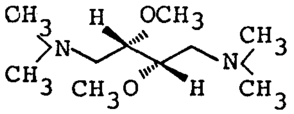
polymethacrylate having a 9-fluorenyl group at the α-end and a hydrogen at the ω-end.

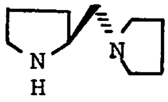


meso dyad of polymethacrylate (RR or SS)

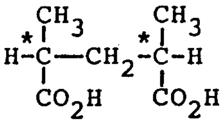
Chapter 1 of Part A describes the asymmetric oligomerization of TrMA with the complexes of 9-fluorenyllithium (FlLi) with (-)-sparteine (Sp), (+)-(2*S*,3*S*)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB), and (+)-(*S*)-2-(1-pyrrolidinylmethyl)pyrrolidine (PMP). These initiators gave highly isotactic,


Sp


DDB

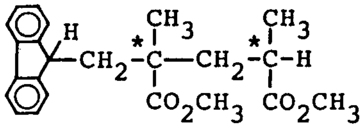

PMP

dextrorotatory polymers with high optical activity of similar degree, indicating that the polymers possess the helical conformation of the same screw sense. The oligo(MMA) derived from the obtained oligo(TrMA) was first fractionated by gel permeation chromatography (GPC) in terms of DP and further separated into diastereomers and optical isomers by HPLC. The assignment of the diasteromers of MMA-dimer derived from TrMA-dimer was accomplished by X-ray crystal structure analysis and the assignments of diasteromers of higher oligomers were done by ^{1}H NMR spectroscopic and field-desorption mass spectorscopic analyses of oligo(MMA)s derived from oligo(TrMA)s. The *meso/racemo* assignment of the in-chain dyad of oligo(MMA) was done on the basis of the fact that difference in ^{1}H NMR chemical shifts of the nonequivalent methylene protons of the main chain of oligo(MMA) having a *t*-butyl group at the α-end is larger for *meso* sequence than for *racemo* sequence.[12] However, as for the ω-end dyad, the difference of chemical shifts of the methylene protons was larger for *racemo* dyad. The absolute configuration of dimer was determined by the synthesis of *RR* and *RS* MMA-dimers from (-)-(2*R*, 4*R*)-2,4-dimethylglutaric acid; (-)-*meso* and (-)-*racemo* dimers possess (*R*,*R*) and (*S*,*R*) configurations, respectively. The oligomer distribution and the content of optical isomers

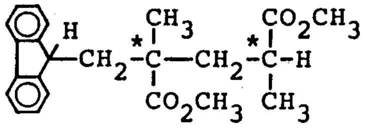


$H-\overset{*}{C}(CH_3)(CO_2H)-CH_2-\overset{*}{C}(CH_3)(CO_2H)-H$

2,4-dimethylglutaric acid

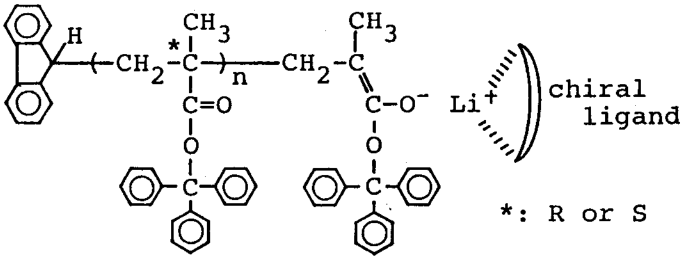


meso MMA-dimer



racemo MMA-dimer

in each oligomer obtained at several [TrMA]/[Li] gave important information on the mechanism of asymmetric polymerization. A stable helix starts at DP ~9 in the system with Sp and at DP ~7 in the systems with DDB and PMP. In these systems, one turn of the helix may consist of three or four monomeric units. With the CPK molecular model, only isotactic 3/1 or 4/1 helix can be built up. Theoretical analysis of conformation also supported this.[13] In the system with Sp, the oligomer anions whose asymmetric centers of the main chain have *R* configuration predominantly propagate to the one-handed helical polymer, while in the systems with DDB and PMP, the oligomer anions with *S* configuration predominantly propagate to the one-handed helical polymer. As the result of this predominant propagation, the polymer obtained with Sp-FlLi has *RRR*--- configuration and the polymers

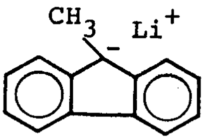


oligo(TrMA) anion

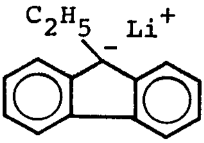
obtained with other two initiators *SSS*--- configuration, although the three polymers have the same screw sense. Therefore, it is concluded that the helicity of poly(TrMA) has no direct correlation with the configuration of the main chain. The helicity may be more influenced by the ligands. With the CPK model, both right- and left-handed helices can be built up for isotactic oligo(TrMA) (DP = 9) regardless of the configuration of the main chain. Thus, it is also concluded that in the polymerization of TrMA with a chiral anionic initiator, three kinds of stereoregulation have been achieved; regulation of conformation, regulation of tacticity, and regulation of the absolute configuration of the main chain.

Chapter 2 of Part A describes the stereochemistry of termination reaction of the oligomer anions of TrMA prepared with Sp-FlLi complex. Methylation was studied by terminating the oligomer anions with methyl iodide and methyl iodide-d_3. ^{1}H NMR analyses of dimers revealed that the methylation of the anion occurred selectively in *meso* fashion for dimer anion. In order to investigate the stereochemistry of protonation, the oligomer anions were terminated by four kinds of alcohols; methanol, butanol, 2-propanol, and *t*-butanol. The termination of the *S*-$^-$ dimer anion, *SS*-$^-$ trimer anion, and *SR*-$^-$ trimer anion which were found to be less active species in chapter 1 was strongly influenced by the bulkiness of the terminating alcohols. Termination generating *S* configuration at the ω-end increased with the increasing bulkiness of the alcohol for all the oligomer anions.

Chapter 3 of Part A describes the asymmetric oligomerization of TrMA with the complexes of 9-methyl and 9-ethyl derivatives of fluorenyllithium (MeFlLi and EtFlLi) and Sp. The effect of bulkiness of the initiating alkyllithium compounds on the stereochemistry of propagation was investigated. In the present systems, the predominantly propagating dimer anion was *S*-$^-$ which is the opposite one to the active dimer anion in the system with Sp-FlLi described in chapter 1. Tetramer in the present systems consisted of mainly two components which were considered to be the isotactic ones, while that in the system with Sp-FlLi consisted of many components, indicating that the stereospecificity in the step of trimer anion to tetramer anion in the present systems is much higher than that in the system with Sp-FlLi. These differences are attributable to the difference of the conformation of the oligomer anions caused by the steric effect



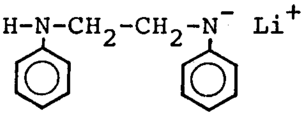
MeFlLi



EtFlLi

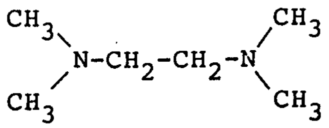
of the substituent at 9-position of the fluorenyl group.

Chapter 1 of Part B describes the polymerization of CHDPMA, CBDPMA, CPDPMA, and DPODMA. In the asymmetric polymerization with the complexes of *N,N'*-diphenylethylenediamine monolithium amide (DPEDA-Li) and chiral ligands, CHDPMA afforded a highly isotactic, optically active polymer, and CPDPMA and DPODMA atactic, optically inatctive ones. Though CBDPMA gave an isotactic polymer by polymerization at -78°C, the isolated polymer did not show significant optical activity at 25°C. The polymerization systems of CBDPMA at -78°C showed high optical activity ($[\alpha]_{435}^{-78}$ +676°, +359°), indicating the formation of an optically active, helical polymer. However, the optical activity decreased to zero when the polymerization system was warmed to -40°C. Helix of poly(CBDPMA) is considered to be unstable at the temperature higher than -40°C and to change into random-coil. The poly(CHDPMA) of DP = 34 prepared with PMP-DPEDA-Li complex showed a remarkable change of optical activity from $[\alpha]_{365}^{60}$ +770° to $[\alpha]_{365}^{60}$ -480° in solution. This is attributable to the helix-helix transition slightly different from that of the poly(D2PyMA) which undergoes a transition similar to racemization of helices.



DPEDA-Li

Chapter 2 of Part B describes the synthesis and reversible helix-helix transition of optically active poly(DMPMA). DMPMA afforded polymers of large positive optical rotation in the polymerization with the complexes of DPEDA-Li and chiral ligands regardless of the chirality of the ligands. Moreover, DMPMA afforded a polymer of similar positive optical rotation in the polymerization with the achiral complex of DPEDA-Li and *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The optical activity of the polymer reversibly changed in a mixture of methanol and a small amount of methanesulfonic acid or trifluoroacetic acid depending on the acid strength of the solution. Circular dichroism and ^{1}H NMR spectral analyses of the polymer in the course of the change of the optical rotation revealed that this change is attributable to the reversible helix-helix transition of the polymer.



TMEDA

Chapter 3 of Part B deals with the conformational change of oligomers of D2PyMA. Oligomerization of D2PyMA was done with the complex of DPEDA-Li and PMP. The obtained oligomer was fractionated by GPC. ^{1}H NMR spectrum of the fraction containing the oligomers of DP = 6~12 revealed that the oligomers consist of a mixture of helical conformation and random-coil conformation. The oligomers of helical conformation showed a reversible helix-coil transition in a temperature range of 30~60°C.

Chapter 4 of Part B deals with the investigation on the possibility of helical conformation of oligomers of MMA.

Oligomerization of MMA was carried out with 1-NpMgBr at -78°C in toluene and the isotactic oligomers were obtained. Isotactic pentamer and octamer were separated and optically resolved by HPLC using UV and polarimetric detectors immediately after the reaction. In the chromatographic analysis, the isotactic oligomers did not show significant optical activity.

The conclusions drawn in this thesis are summarized as follows:

1. In the asymmetric oligomerization of TrMA, complete analysis of the oligomer structures including absolute configuration was done. This made it possible to understand the detailed mechanism of the helix-sense-selective polymerization of TrMA with chiral anionic initiators.
2. Through the studies on the polymerization of 1,1-diphenylalkyl methacrylates, important information on critical bulkiness of ester group for the formation of a helical polymethacrylate was obtained. Cyclobutyldiphenylmethyl group possesses the critical bulkiness. The ester group must be more bulky than cyclopropyldiphenylmethyl and 1,1-diphenyloctadecyl groups to form a helical conformation in the polymerization process at low temperature and must be more bulky than cyclobutyldiphenylmethyl group to maintain the helical conformation at higher temperature.
3. CHDPMA afforded an optically active, helical polymer which underwent helix-helix transition slightly different from that of poly(D2PyMA).
4. DMPMA afforded the polymers with similar optical activity regardless of initiator systems. The optically active

poly(DMPMA) showed a reversible helix-helix transition in solution by changing the acidity of the solution. This may be the first example of reversible helix-helix transition of a vinyl polymer in which the content of right- and left-handed helices can be controlled by the property of solvent.

5. Oligo(D2PyMA)s of DP = 6~12 were isolated. The oligomer showed the reversible helix-coil transition in solution depending on temperature. This indicates that a stable helical structure starts at DP = 6~12.

6. Optical isomers of isotactic MMA-pentamer and -octamer were separated. These oligomers did not show significant optical activity, indicating that the isotactic oligo(MMA) can not maintain the helical conformation.

These findings are considered to contribute to an understanding of the stereochemistry of the formation process and the conformational stability of helical vinyl polymers.

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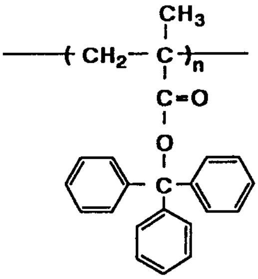
Part A: Chapter 1

Asymmetric Oligomerization of Triphenylmethyl Methacrylate. I. Mechanism of Helix-Sense-Selective Polymerization with the Complexes of Fluorenyllithium and Chiral Ligands

A-1-1 Introduction

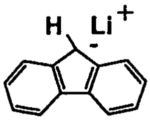
Several optically active poly(triarylmethyl methacrylate)s have been directly synthesized by asymmetric (helix-sense-selective) anionic polymerization.[1] Triphenylmethyl methacrylate (TrMA) is the first example of a vinyl monomer which directly affords an optically active, highly isotactic polymer by polymerization with chiral initiators.[1a,b,c] The optical activity of the polymer arises mainly from a stable one-handed helical conformation because poly(methyl methacrylate) [poly(MMA)] derived from the poly(triphenylmethyl methacrylate) [poly(TrMA)] shows a very low optical activity. Optically active poly(TrMA) shows high chiral recognition ability as a chiral stationary phase for optical resolution by high-performance liquid chromatography (HPLC) and many racemic compounds have been resolved on the phase.[2] Therefore, clarification of the detailed mechanism of this unique asymmetric polymerization is an attractive and chal-



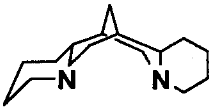
poly(TrMA)

lenging problem. TrMA gives an optically active polymer with several chiral initiators such as the complexes of Sp and butyllithium (*n*-BuLi),[1a,b] Sp and 1,1-diphenylhexyllithium (DPHLi),[3a] and (+)-*(2S,3S)*- or (−)-*(2R,3R)*-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB) and *N,N'*-diphenylethylenediamine monolithium amide (DPEDA-Li).[1c] However, in most cases, the products of the polymerization were a mixture of a polymer (80~90wt%) of high optical activity and an oligomer (10~20wt%) of low optical activity. The oligomer of low optical activity was considered to be produced from the species with lower activity than the species for the one-handed helical polymer; that is, the oligomer anions of certain specific stereostructure would propagate to the polymer and the others would remain as oligomers until the completion of the polymerization.[1b] Therefore, the composition of stereoisomers in the oligomer anions should change in the process of polymerization.

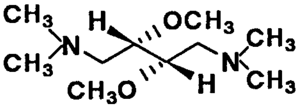
In this chapter, the author describes the detailed results of the asymmetric oligomerization of TrMA and the complete separation and assignment of resulting oligomers. With the obtained results, the mechanism of the asymmetric polymerization of TrMA was discussed in detail. Oligomerization of TrMA was carried out with the complexes of 9-fluorenyllithium (FlLi) and three chiral ligands in toluene at −78 °C at the several [TrMA]/[Li] ratios and terminated by protonation with CH_3OH to give the oligomers having a fluorenyl group at the initiation end (α-end) and a hydrogen at the termination end (ω-end).[4] The chiral ligands employed were Sp, DDB, and (+)-(*S*)-1-(2-pyrrolidinylmethyl)pyrrolidine[1d] (PMP). The resulting oligo(TrMA)s were



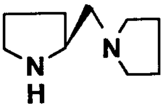
FlLi



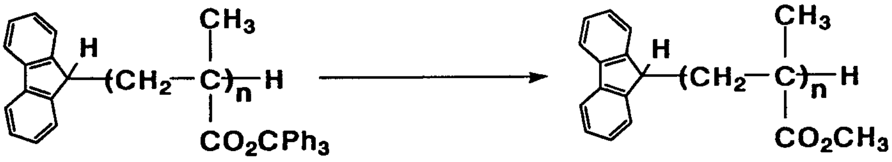
Sp



DDB



PMP



oligo(TrMA) **oligo(MMA)**

converted into methyl ester [oligo(MMA)] and fractionated by gel permeation chromatography (GPC) in terms of DP. Each oligomer was further separated into diastereomers and optical isomers by HPLC using columns packed with silica gel and polysaccharide derivatives-coated silica gel, respectively. The assignments of diastereomers were accomplished by means of ^{1}H NMR spectroscopy, field-desorption (FD) mass spectroscopy, and X-ray crystal structure analysis. Absolute configuration of oligomers was determined on the basis of an optically active MMA-dimer having an fluorenyl group at the α-end derived from (2*R*,4*R*)-2,4-dimethylglutaric acid. Wulff and coworkers also reported on similar oligomerization of TrMA with Sp-DPHLi[3a] and Sp-diphenylmethyllithium (DPMLi) complexes.[3b] They separated the oligomers in terms of degree of polymerization (DP) and analyzed the oligomers (DP = 1, 2, 3, and 4) by ^{1}H and ^{13}C NMR spectroscopies as a mixture of diastereomers.

A-1-2 Experimental Section

Materials. Toluene was purified in the usual manner, mixed with a small amount of *n*-BuLi and distilled under high vacuum just before use. Tetrahydrofuran (THF) was refluxed over CaH_2 and distilled over $LiAlH_4$.

n-BuLi was synthesized from butyl chloride (BuCl) and Li powder in heptane under argon atmosphere[5] and was used as a 0.756 M solution for preparation of an initiator solution.

Fluorene (Nacalai Tesque) was first recrystallized from ethanol and then from hexane: mp 104.5-105.0 °C.

Chiral ligands, Sp (Sigma), (+)-DDB (Aldrich), and PMP (Aldrich) were dried over CaH_2 and distilled under reduced pressure.

TrMA was synthesized from methacrylic acid and triphenylmethyl chloride in the presence of triethylamine[6] and was first recrystallized from diethyl ether and then from hexane; mp 101.9~102.9 °C (lit.[7] 102~103 °C).

Oligomerization and polymerization procedure. FlLi was prepared by adding one equivalent of *n*-BuLi to the solution of fluorene in toluene at room temperature. This was mixed with 1.2 equivalent of a chiral ligand. The mixture was left for 10 min at room temperature for the formation of a complex.

The oligomerization was carried out in a dry glass ampule under dry nitrogen atmosphere. TrMA (1.0 g, 3.15 mmol) was placed in a glass ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this procedure was repeated three times, a three-way stopcock was attached to the ampule and toluene or THF (20 ml) was added with a hypodermic syringe to dissolve TrMA. Then the monomer solution was cooled to -78 °C and a prescribed amount of an initiator solution was added to the monomer solution with a syringe. The reaction was terminated by the addition of a small amount of CH_3OH. After termination, the solvent was evaporated and a part of resulting oligomer was solvolyzed by refluxing in CH_3OH containing a small amount of hydrochloric acid. The resulting oligo(methacrylic acid) was suspended in benzene and methylated by CH_2N_2 in ether solution to give oligo(MMA).[8]

Polymerization was carried out in the same way as the oligomerization described above. The polymerization was also done in a quartz optical cell to monitor the optical activity of the reaction system.[1c] In the case of polymerization, the products were poured into a large amount of CH_3OH after termination and collected by centrifugation as quickly as possible. The polymer was dried under high vacuum at 60 °C for 3 h. The polymer was once dissolved in THF or in a mixture of THF and CH_2Br_2, and poured into a large amount of a mixture of benzene and hexane (1/1 v/v). The insoluble part was collected by centrifugation and the soluble part by evaporation under high vacuum. Conversion of the poly(TrMA) into poly(MMA)) was done in the same way as applied for the oligomers.

Preparation of MMA-dimer having a 9-fluorenyl group at the α-end from 2,4-dimethylglutaric acid. 9-Iodomethylfluorene was synthesized from 9-fluorenylmethanol. 9-Fluorenylmethanol (Aldrich, 4.98 g, 25.4 mmol) and aqueous HI (Nacalai Tesque, 55 v/v %, 16.0 ml) were mixed in a round bottomed flask and heated to 90 °C with vigorous stirring for 26 h. A deep red colored mixture was extracted with diethyl ether. The ethereal layer was washed with water, dried over magnesium sulfate, and evaporated under high vacuum. The crude product was a mixture of the iodide and the unreacted alcohol at a molar ratio 52:48 by ^1H NMR analysis. The alcohol was removed by silica gel column chromatography with a mixture of diethyl ether and hexane (1/1 v/v) as an eluent to give red-colored crystal. The obtained crystal was dissolved in diethyl ether. The solution was washed with a saturated water solution of Na_2SO_3 to remove iodine, and dried over $MgSO_4$ to give 2.48 g (31.9%) of the iodide free from alcohol and iodine. Further purification was done by recrystallization twice from diethyl ether and once from hexane to give 0.61 g (7.9%) of white crystal: mp 89.7-90.7 °C, ^1H NMR (270 MHz, $CDCl_3$, TMS) δ 7.30-7.75 (m, 8H, aromatic), 4.17 (t, 1H, CH), 3.71 (d, 2H, CH_2). Anal. Calcd for $C_{14}H_{11}I$: C, 54.93%; H, 3.62%; I, 41.45%. Found: C, 54.97%; H, 3.67%; I, 41.26%.

2,4-Dimethylglutaric acid (Aldrich, a mixture of (±)- and *meso*-isomers) was methylated with CH_2N_2. The resulting dimethyl 2,4-dimethylglutarate was reacted with one equivalent of lithium diisopropylamide (LDA) in dry THF at 0 °C for 0.5 h under dry nitrogen atmosphere in a round-bottomed flask equipped with a three-way stopcock. Then one equivalent of 9-iodomethylfluorene in dry THF was added with a syringe. The solution was stirred for 3 h at 0 °C. Then a large excess of hydrochloric acid in CH_3OH was added to the solution. After the solvent was evaporated, the crude product was extracted with diethyl ether. The ethereal layer was washed with water and dried over $MgSO_4$. HPLC separation of the product was done by using an HPLC column (50 x 0.72 (i.d.) cm) packed with silica gel (Nomura Chem., Develosil 100-5). A mixture of BuCl and CH_3CN (97/3 v/v, flow rate 2.4 ml/min) was used as an eluent.[9]

Preparation of optically active MMA-dimer having a 9-fluorenyl group at the α-end from (-)-(*2R,4R*)-2,4-dimethylglutaric acid. 2,4-Dimethylglutaric acid (a mixture of (±)- and *meso*-isomers) was converted into acid chloride with 1.2 equivalent of $SOCl_2$ and the product was distilled under reduced pressure to give 2,4-dimethylglutaroyl dichloride: bp. 77-85 °C (3 mmHg). The acid chloride was reacted with benzyl alcohol in the presence of excess triethylamine to give dibenzyl ester, which was optically resolved by HPLC. The optical resolution was done with a chiral HPLC column (50 x 2.0 (i.d.) cm) packed with amylose tris(3,5-dimethylphenylcarbamate)-coated macroporous silica gel[10] by using a mixture of hexane and 2-propanol (98/2 v/v, flow rate 9.9 ml/min) as an eluent. (-)-Isomer eluted at 27.2 min, *meso* isomer at 29.0 min, and (+)-isomer at 30.4 min. (-)-Isomer ($[\alpha]_D^{25}$ -31° (c 2.54, hexane)) was hydrolyzed by hydrochloric acid to give optically active acid: $[\alpha]_D^{25}$ -21° (c 0.88, CH_3OH) (lit.[11] $[\alpha]_D^{25}$ -40° (water)). Then the optically active acid was methylated with CH_2N_2, giving dimethyl ester: $[\alpha]_D^{25}$ -31° (c 0.93, CH_3OH). This optically active *(R,R)*-dimethyl ester was used for preparation of MMA-dimer in the same way as described above for the synthesis of racemic MMA-dimer.

X-ray crystal struture analysis of MMA-dimer. MMA-dimer *meso* was isolated from the mixture of oligo(MMA) derived from oligo(TrMA) prepared with Sp-FlLi at [TrMA]/[Li] = 2 by HPLC under the chromatographic conditions which will be decribed later. The single crystal of the dimer was grown from a hexane solution. The crystal data are as follows: molecular formula = $C_{23}H_{26}O_4$, molecular weight=366.46, *orthorhombic*, space group $P2_12_12_1$, a=12.296 Å, b=26.077 Å, c=6.227 Å, V=1996.7 $Å^3$, Z=4, D_c=1.219 gcm^{-1}. A total of 3604 reflections with $2\theta<125°$was collected by a Rigaku automated four-circle diffractometer (Rigaku AFC-5R) using Cu-$K\alpha$ radiation (λ=1.5418 A). The structure was solved by the direct methods (MULTAN 78),[12] and refined by the full-matrix least-squares procedure (FMLS)[13] with anisotropic thermal parameters for nonhydrogen atoms and isotropic ones for hydrogen atoms to the final R=0.032 and R_w=0.036 for 348 variables and 1836 independent reflections with Fo>3σ(Fo). HPLC analysis of the crystalline dimer showed that the crystal consisted of purely one antipode of enantiomers, consistent with the non-centro-symmetric structure.

Measurements. ^1H NMR spectra were measured on a JEOL GX-500 (500 MHz), a JEOL GSX-270 (270 MHz), and a Varian VXR-500 (500 MHz) spectrometers. Measurements were done in $CDCl_3$ at 35°C or in nitrobenzene-d_5 at 110 °C. Two dimensional spectra were taken under the same spectral conditions as described before.[14] Optical rotation was measured with a JASCO DIP-181 polarimeter. Field-desorption (FD) mass spectrum was measured by a JEOL DX-HF303 spectrometer.

The molecular weight of polymers was determined by GPC measurement of poly(MMA) derived from the original polymer on a JASCO Trirotar II^{P} chromatograph equipped with a JASCO RI-SE64 (reflective index) detector. Two commercial columns (Shodex KF-802.5, 30 x 0.72 (i.d.) cm and Shodex AC-80M, 50 x 0.72 (i.d.) cm) were connected in series and $CHCl_3$ was used as an eluent. Calibration curve was obtained with standard polystyrene.

Separation by HPLC was done by using JASCO Trirotar II and BIP-I chromatographs equipped with one or two of JASCO UVIDEC-100-III (UV), UVIDEC-100-V (UV), MULTI-320 (UV), and DIP-181C (polarimetry) detectors. An automatic eluent mixer, JASCO GR-A50 was employed for the diastereomeric separation of oligomers. Columns used and chromatographic conditions were as follows. For the GPC analysis of the oligomers, a column packed with poly(styrene-co-*p*-divinylbenzene) gel (50 x 2.2 (i.d.) cm, maximum porosity 3000) or two commercial columns connected in series (Shodex Gel-101, 50 x 0.72 (i.d.) cm) were used with $CHCl_3$ as an eluent (flow rate 3.0 ml/min for the former column and 0.5 ml/min for the latter ones). For the separation of diastereomers, columns (25 x 0.46 (i.d.) cm, 50 x 0.72 (i.d.) cm) packed with silica gel (Nomura Chem., Develosil 100-5) were used with a mixture of BuCl and CH_3CN as an eluent[9] in a programmed ratios; from 95% BuCl to 60% BuCl during 60-min period (flow rate 0.5 ml/min for the former column and 2.4 ml/min for the latter column). Optical resolution of oligo(MMA)s was done on chiral columns (25 x 0.46 (i.d.) cm) packed with cellulose derivatives using hexane-alcohol eluting system (flow rate 0.5 ml/min).[15] For the optical resolution of MMA-dimer prepared from 2,4-dimethylglutaric acid, a column packed with cellulose tris(3,5-difluorophenylcarbamate)-coated macroporous silica gel[16] was used with a mixture of hexane and 2-propanol (95/5 v/v) as an eluent. For the optical resolution of MMA-dimer obtained from oligomerization systems, a column packed with cellulose tris(3,5-dichlorophenylcarbamate)-coated macroporous silica gel[15b] was used with a mixture of hexane and 2-propanol (95/5 v/v) as an eluent. For the optical resolution of the mixture of MMA-trimers *mm* and *rm*, a column packed with cellulose tris(3,4-dichlorophenylcarbamate)-coated macroporous silica gel[15b] was used with a mixture of hexane and 2-propanol (90/10 v/v). For the optical resolution of MMA-trimers *rr* and *mr*, a column packed with cellulose tris(3,5-dichlorophenyl/dimethylphenylcarbamate)-coated macroporous silica gel[15b] was used with a mixture of hexane and 2-propanol (90/10 v/v). For the optical resolution of MMA-pentamer, -hexamer, -heptamer, and -octamer, a column packed with cellulose tris(3,5-dimethylphenylcarbamate)-coated macroporous silica gel[15b] was used with a mixture of hexane and ethanol (80/20 v/v).

A-1-3 Results and Discussion

Asymmetric polymerization of TrMA with three initiator systems

The results of asymmetric polymerization of TrMA with Sp-FlLi, DDB-FlLi, and PMP-FlLi are shown in Table A-1-1. The three initiators gave highly isotactic, optically active polymers which showed almost the same positive rotation, indicating that the polymers possess a one-handed helical conformation of the same screw sense. Triad tacticity of the polymer was determined by ^1H NMR of poly(MMA) derived from the original polymer. As an

Table A-1-1. Asymmetric polymerization of TrMA with Sp-, DDB-, and PMP-FlLi complexes in toluene at -78 °C[a]

Run	Initiator	Time (hr)	Yield[b] (%)	B/H[c]-insoluble part				
				Yield(%)	$[\alpha]_D^{25}$ [d]	DP[e]	Mw/Mn[e]	Tacticity(%)[f] *mm*
1	Sp-FlLi	24	99	82	+383°	60	1.31	>99[g]
2	DDB-FlLi	24	100	93	+344°	47	1.10	>99[g]
3	PMP-FlLi	3	100	94	+334°	39	1.12	>99[g]

[a] TrMA 1.0 g (3.05 mmol), toluene 20 ml, [TrMA]/[Li] = 20.
[b] CH_3OH-insoluble part.
[c] A mixture of benzene and hexane (1:1 v/v).
[d] c 0.5, THF.
[e] Determined by GPC of poly(MMA)s derived from poly(TrMA)s.
[f] Determined by ^{1}H NMR of poly(MMA)s derived from poly(TrMA)s.
[g] The signals due to *racemo* sequence were only found in the ω-end.

example, the spectrum of the poly(MMA) of DP = 60 derived from the poly(TrMA) obtained with Sp-FlLi (Run 1 in Table A-1-1) is shown in Figure A-1-1. In the spectrum, most peaks could be assigned to those of isotactic sequence including the methyl groups in the vicinity of the α- and ω-ends. *Racemo* sequence was obviously found only for the ω-end. The assignments of the small peaks in α-methyl region were done on the basis of the detailed studies on the ^{1}H NMR assignments of isotactic oligo- and poly(MMA) having a *t*-butyl group at the α-end[14] and the assignments of isotactic oligo(MMA)s having a 9-fluorenyl group at the α-end which will be described later. The structure and the numbering system of the monomeric units of the oligo- and poly(MMA) are illustrated in Scheme A-1-1. Slightly lower

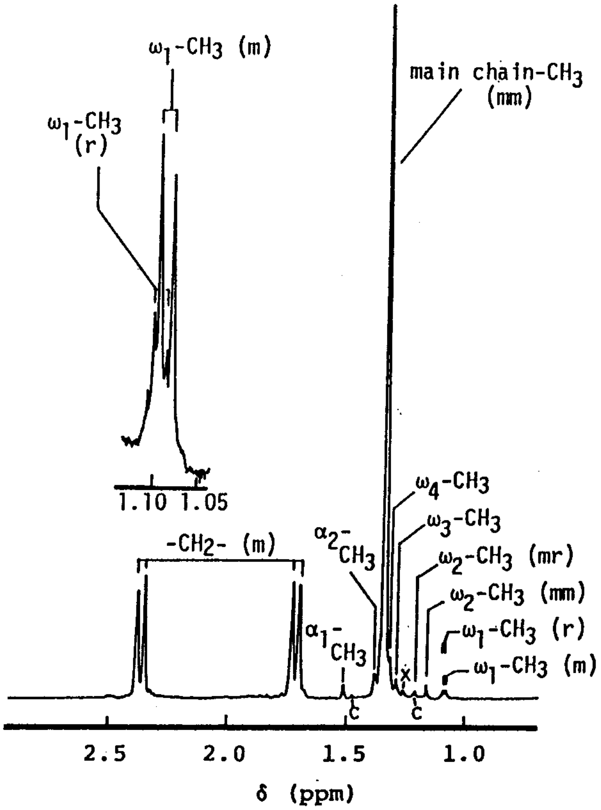
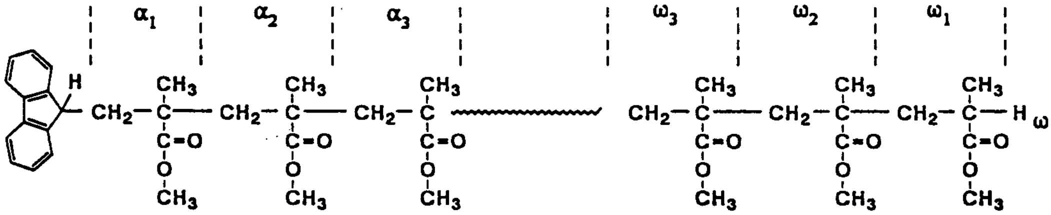


Figure A-1-1. 500 MHz ^{1}H NMR spectrum of poly(MMA) derived from benzene-hexane (1/1 v/v)-insoluble poly(TrMA) of DP = 60 (Run 1 in Table A-1-1) (nitrobenzene-d_5, 110°C). c and x denote ^{13}C satellite bands of the main chain-CH$_3$ signal and impurity, respectively.



Scheme A-1-1. Structure and numbering system of monomeric units of oligo- and poly(MMA) having a fluorenyl group at the α-end.

isotacticity of poly(TrMA) in the previous reports[1a,b] may be due to the fact that no correction was made for the end groups of the polymer chain.

GPC curves of poly(TrMA)s obtained with Sp and DDB complexes showed two peaks.[1b] However, poly(MMA) derived from these polymers showed only one GPC peak with a narrow distribution. A part of poly(TrMA) may exist in association form as in the case of poly(diphenyl-2-pyridylmethyl methacrylate).[1d]

In all the polymerization shown in Table A-1-1, the products could be separated into two fractions; a polymer of high optical rotation which was insoluble in a mixture of benzene and hexane (1/1 v/v) and an oligomer of low optical activity which was soluble in the solvent as mentioned in the previous paper.[1b] The amount of the oligomer was larger and DP of the polymer was higher in the system with Sp-FlLi than in the systems with DDB-FlLi and PMP-FlLi at the same [TrMA]/[Li] ratio. In the system with Sp-FlLi, the relative amount of less active oligomer anions may be larger and that of active oligomer anions which can propagate to the polymer may be smaller. This should result in the formation of the polymer of higher DP.

It has been reported that the polymerization of TrMA with DDB-*n*-BuLi is much faster than that with Sp-*n*-BuLi.[1c] This was based on the measurement of the change of optical activity of the polymerization system during the reaction. The optical activity of the systems increased with polymerization time and reached at the final constant value within 16 h after initiation in the system with Sp-*n*-BuLi and within 2 h in the system with DDB-*n*-BuLi.[1c] The rate of polymerization with PMP-FlLi was examined in the present study in the same way as described before.[1c] The optical rotation reached at a large positive value (α_D^{-78} +3.2°) within 10 min (Figure A-1-2). The value is comparable to the final values observed in the systems with Sp-*n*-BuLi and DDB-*n*-BuLi.[1c] The rate of polymerization with PMP-FlLi may be much higher than those with Sp-FlLi and DDB-FlLi.

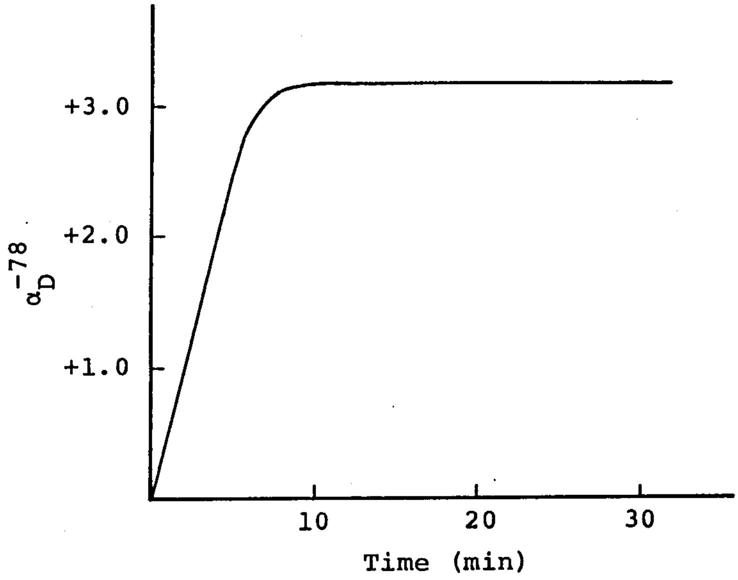


Figure A-1-2. Change of optical activity of polymerization system of TrMA with PMP-DEPDA-Li in toluene at -78°C. (TrMA 0.15 g, toluene 3 ml, [TrMA]/[Li]=20, cell length 1.0 cm)

Distribution of oligomers

In all the oligomerization, the reaction of TrMA with the initiators seems to proceed almost quantitatively to give oligomers with a 9-fluorenyl group at the α-end and a hydrogen at the ω-end because no clear sign of unreacted monomer and side products which might be produced by the attack of carbonyl group of TrMA with FlLi was found on the IR and ^{1}H NMR spectra of reaction mixtures. GPC analysis also supported this.

Figure A-1-3 shows the GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-FlLi as an initiator at [TrMA]/[Li] = 2, 3, 5, 10, and 20, and Figures A-1-4 and A-1-5 those of the oligo(MMA)s derived from oligo(TrMA)s obtained in the systems with DDB-FlLi and PMP-FlLi, respectively, at [TrMA]/[Li] = 2, 3, and 5. In these GPC curves, the ratio of the peak intensity approximately corresponds to the molar ratio of oligomers because UV detection at 254 nm is mainly due to a fluorenyl group at the α-end of each oligomer. The chromatographic patterns of the original oligo(TrMA)s were similar to those of the corresponding oligo(MMA)s. The peaks in the GPC curves were assigned by FD mass spectroscopy. The mass spectrum of oligo(MMA) derived from oligo(TrMA) prepared with Sp-FlLi and terminated by methanol at [TrMA]/[Li] = 5 showed main peaks of M/z = 366, 466, 566, 666, 766, 866, and 967 corresponding to the molecular weight of the oligomers of DP = 2~8 with the structure shown in Scheme A-1-1. The spectrum also showed another series of smaller peaks of M/z = 350, 450, 550, 650, 750, 850, and 951, though the definite structure of the oligo(MMA)s corresponding to these molecular weights is unknown at the present time. Oligo(MMA)s with a structure other than that shown in Scheme A-1-1 may be formed in the process of conversion of oligo(TrMA) into methyl esters.[17] The intensity ratio of the main peaks was similar to that of GPC curve. In the GPC curves, the peak corresponding to unimer (DP = 1) was not clearly

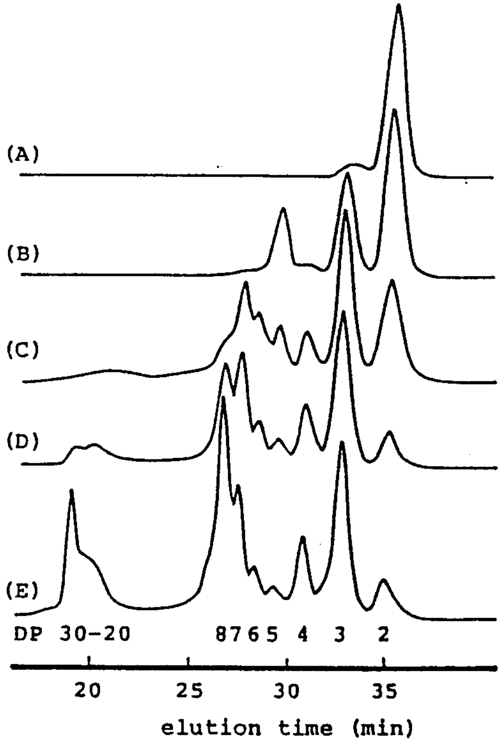


Figure A-1-3. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-FlLi at [TrMA]/[Li] = 2 (A), 3 (B), 5 (C), 10 (D), and 20 (E).

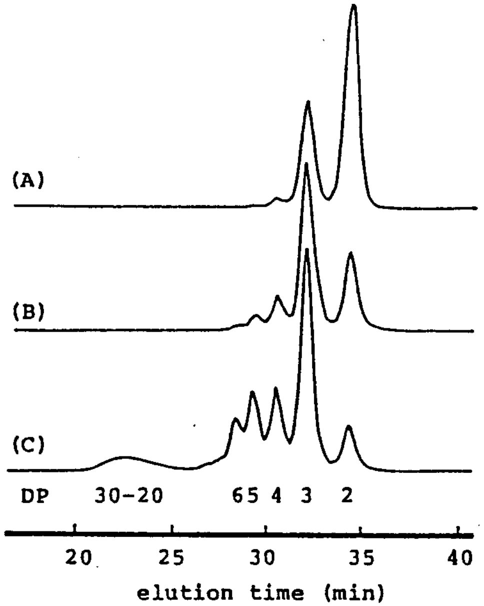


Figure A-1-4. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with DDB-FlLi at [TrMA]/[Li] = 2 (A), 3 (B), and 5 (C).

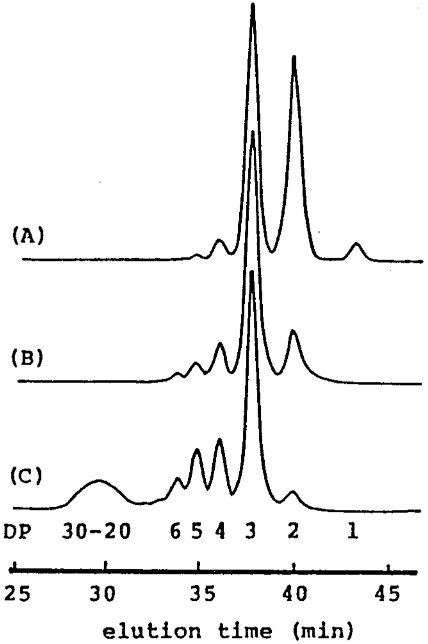
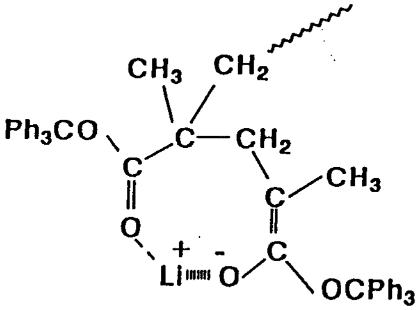


Figure A-1-5. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with PMP-FlLi at [TrMA]/[Li] = 2 (A), 3 (B), and 5 (C).

observed except for oligo(MMA) obtained with PMP-FlLi at [TrMA]/[Li] = 2 and even in that case, it was much smaller than the other peaks. The existence of unimer was not confirmed even in the equimolar reaction of TrMA and Sp-FlLi, indicating that the unimer anion is much more reactive than the initiator complex and dimer anion. The high activity of unimer anion may be due to the effect of "intramolecular solvation" proposed for anionic polymerization of methacrylates.[18] As illustrated in Scheme A-1-2, ω-end anion of the propagating species is stabilized by complex formation between Li cation and the carbonyl group of the penultimate monomeric unit. This stabilization is not possible for unimer anion. On the other hand, Wulff and coworkers reported that the significant amount of unimer was found in the system with Sp-DPHLi at [TrMA]/[Li] = 5[3a] and in the systems with Sp-DPMLi at [TrMA]/[Li] = 0.5 and 1.[3b] The activity of the unimer anion in their systems may be much lower than that in our systems. α-End group of an oligomer anion may affect its activ-



Scheme A-1-2. Intramolecular solvation of ω-end anion.

ity in the oligomerization. The oligomer distributions at [TrMA]/[Li] = 5 in all the systems were not simple. Although the oligomers of DP < 9 in the systems with Sp-FlLi and the oligomers of DP < 7 in the other two systems were observed in addition to the polymer (DP = 20~30), the oligomers of the intermediate DPs were not obviously detected. Original poly(TrMA)s (DP = 20~30) showed a high positive rotation in the GPC analysis with a polarimetric detector. Similar results were also found in the oligomerization at [TrMA]/[Li] = 10 and 20 with Sp-FlLi. Wulff and coworkers also observed a similar irregular distribution in the oligomerization with Sp-DPHLi at [TrMA]/[Li] = 5.[3a] The oligomer distribution at [TrMA]/[Li] = 3 in the system with Sp-FlLi was also apparently irregular and the relative content of tetramer was unnaturally low. These unusual oligomer distributions indicate that the reactivity of each oligomer anion depends greatly on its degree of polymerization. This is likely correlated with the specific conformation of the oligomer anions; that is, three or four monomeric units may form one turn of helix. Analogous possibility has been discussed by Wulff and coworkers.[3] Theoretical analysis of conformation of isotactic poly(TrMA) shows that 3.6 monomeric units may form one turn of helix.[19] A stable one-handed helix may start at DP $\simeq$ 9 in the system with Sp-FlLi and at DP $\simeq$ 7 in the other two systems. Once an oligomer anion grows to DP $\simeq$ 9 or 7, it may add TrMA more readily than other oligomer anions of lower DP probably because of its stable helical conformation suitable for the addition of TrMA. The much lower content of heptamer (DP = 7) and octamer (DP = 8) in the systems with DDB-FlLi and PMP-FlLi than in the system with Sp-FlLi at [TrMA]/[Li] = 5 suggests that the formation of the third turn of a helix may be easier in these systems compared with the system with Sp-FlLi. The existence of heptamer and octamer in the systems with DDB-FlLi and PMP-FlLi is not clear in the GPC curve (Figures A-1-4 and A-1-5) because the separation of the peaks is not sufficient. However, these oligomers were clearly observed in the separation by supercritical fluid chromatography of the oligo(MMA) derived from oligo(TrMA) obtained with PMP-FlLi at [TrMA]/[Li] = 10.

Separation of diastereomers

In order to get deeper information on the stereochemistry of the oligomerization, the oligomers were separated into diastereomers by HPLC on a silica gel column using a mixture of BuCl and CH_3CN as an eluent.[9] Figure A-1-6 shows the chromatograms of separation of oligo(MMA)s derived from oligo(TrMA)s obtained with Sp-FlLi, DDB-FlLi, and PMP-FlLi as initiators at [TrMA]/[Li] = 5. Dimer was fractionated into two components, which were assigned to *meso (m)* and *racemo (r)* and trimer three components; a mixture of *mm* and *rm*, *rr*, and *mr*. Tetramer consisted of many components whose assignments have not yet been completed. In contrast to these results on the trimer and tetramer, in the system with Sp-DPHLi, 90% of trimer consisted of the *mm* isomer and most of tetramer consisted of *mmm* and *mmr*.[3a] In all the systems, oligomers of DP $\geq$ 5 consisted of two main diastereomers which were assigned to the pair of isotactic oligomers having *m* and *r* ω-end configuration, indicating that the predominantly propagating oligomer anions are isotactic and its protonation

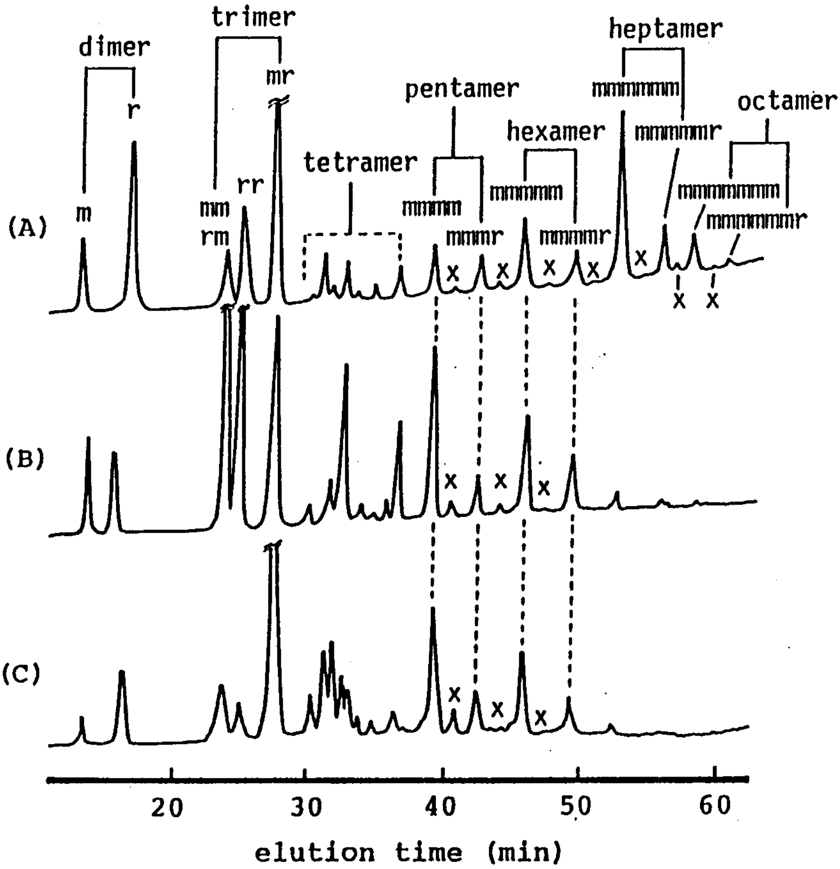


Figure A-1-6. Chromatograms of separation of diastereomers of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-FlLi (A), DDB-FlLi (B), and PMP-FlLi (C) at [TrMA]/[Li] = 5.

with CH_3OH is not highly stereospecific. The definite structure of the oligomers of small peaks marked by x in Figure A-1-6 is unknown. Molecular weights of these oligomers were of the series of 550, 650, 750, ······. These may be formed in the process of the conversion of oligo(TrMA) into oligo(MMA) as mentioned in the preceding section.[17]

The ratios of diastereomers in each oligomer at [TrMA] = 2, 3, and 5 in the three FlLi systems and those at [TrMA]/[Li] = 10 and 20 in the system with Sp-FlLi are summarized in Table A-1-2. The ratio of *m* to *r* of the ω-end of the oligomers implies the stereospecificity of protonation of the anion with CH_3OH. This is not as high as the stereospecificity of addition of TrMA favoring exclusively *m* sequence. In all the systems, protonation in *r*-fashion is favored for dimer and trimer anions, while protonation in *m*-fashion for the isotactic oligomer anions of DP $\geq$ 5 except for the hexamer anion obtained with Sp-FlLi at [TrMA]/[Li] = 10 and 20. The ratio of *m* to *r* of the ω-end of a polymer obtained with Sp-FlLi was found to be 6:1 by the ^1H NMR analysis (Figure A-1-1), though the polymer could not be separated by HPLC like oligomers. The stereospecificity of protonation of the polymer anion in the system with Sp-FlLi is similar to that of the isotactic pentamer, hexamer, heptamer, and octamer anions in this initiator system except for that of the hexamer anion at [TrMA]/[Li] = 10 and 20. This suggests that these isotactic oligomer anions may resemble the polymer anion. The unnaturally high content of the diastereomers whose ω-end has *r* configuration in hexamer in the system with Sp-FlLi at [TrMA]/[Li] = 10 and 20 will be explained later by considering

Table A-1-2. The ratios of diastereomers of oligo(MMA)s derived from oligo(TrMA) obtained with Sp-FlLi, DDB-FlLi, and PMP-FlLi at [TrMA]/[Li] = 2, 3, and 5[a]

Initiator	[TrMA] / [Li]	Dimer	Trimer	Pentamer	Hexamer	Heptamer	Octamer
		m / *r*	*mm*+*rm* / *rr* / *mr*	*mmmm* / *mmmr*[b]	*mmmmm* / *mmmmr*[b]	*mmmmmm* / *mmmmmr*[b]	*mmmmmmm* / *mmmmmmr*[b]
Sp-FlLi	2	14 / 86	14 / 35 / 51	———[c]	———[c]	———[c]	———[c]
	3	25 / 75	15 / 37 / 48	65 / 35	74 / 26	83 / 17	———[c]
	5	28 / 72	16 / 26 / 58	60 / 40	67 / 33	88 / 12	86 / 14
	10	13 / 87	7 / 14 / 79	83 / 17	22 / 78	78 / 22	91 / 9
	20	21 / 79	8 / 14 / 78	88 / 12	13 / 87	68 / 32	88 / 12
DDB-FlLi	2	23 / 77	39 / 30 / 31	———[c]	———[c]	———[c]	———[c]
	3	37 / 63	45 / 28 / 26	78 / 22	64 / 36	85 / 15	———[c]
	5	40 / 60	52 / 32 / 16	83 / 17	65 / 35	87 / 13	———[c]
PMP-FlLi	2	18 / 82	7 / 14 / 79	———[c]	———[c]	———[c]	———[c]
	3	23 / 77	9 / 14 / 78	69 / 31	67 / 33	(66 / 34)	———[c]
	5	28 / 72	13 / 6 / 81	74 / 26	71 / 29	(71 / 29)	———[c]

[a] Determined by HPLC analysis with UV detection at 254 nm.

[b] The ratio of the isotactic oligomer having *m* ω-end configuration to that having *r* ω-end configuration. The other oligomers were neglected since the amount of those was very low.

[c] Not obviously detected.

the change of the relative amount of two optical isomers of isotactic hexamer anion with progress of reaction.

Assignments of diastereomers

The assignment of diasteremers of dimer was done by X-ray crystal structure analysis. Figure A-1-7 shows the ORTEP diagram[20] of the crystalline dimer, which indicates that the diastereomer is so-called *meso* isomer (the smallest configurational sequence of an isotactic polymer chain). The configuration of the asymmetric centers (C15 and C20) is (*S*,*S*) or (*R*,*R*). The bond lengths, bond angles, and torsional angles are summarized in Table A-1-3. The conformation of the main chain (fluorenyl-C14-C15-C19-C20-H23 bond) is tg^-g^+ as the (*R*,*R*) isomer. It has been shown that the main chain of the *meso-meso* (*R*,*S*,*R*) MMA-trimer with a *t*-butyl group at the α-end has ttg^+tg^+ conformation.[14a] The conformation (g^+tg^+) of the terminal two monomeric units of the trimer is different from tg^-g^+ of the dimer. The conformations seem to depend on the preceding group. Figure A-1-8 shows the ^{1}H NMR spectra of two diastereomers of the MMA-dimer. The difference of the chemical shifts of the methylene protons of the *racemo* isomer is larger than that of the *meso* isomer. Since this result agrees with the result for the methylene protons of the ω-end of the MMA-trimer which has a *t*-butyl group at the α-end,[14a] this assignment of the stereostructure of the ω-end by the nonequivalency of the methylene protons clarified here may be applicable to higher oligo(MMA)s with a 9-fluorenyl group at the α-end.

The assignments of trimer, pentamer, hexamer, heptamer, and

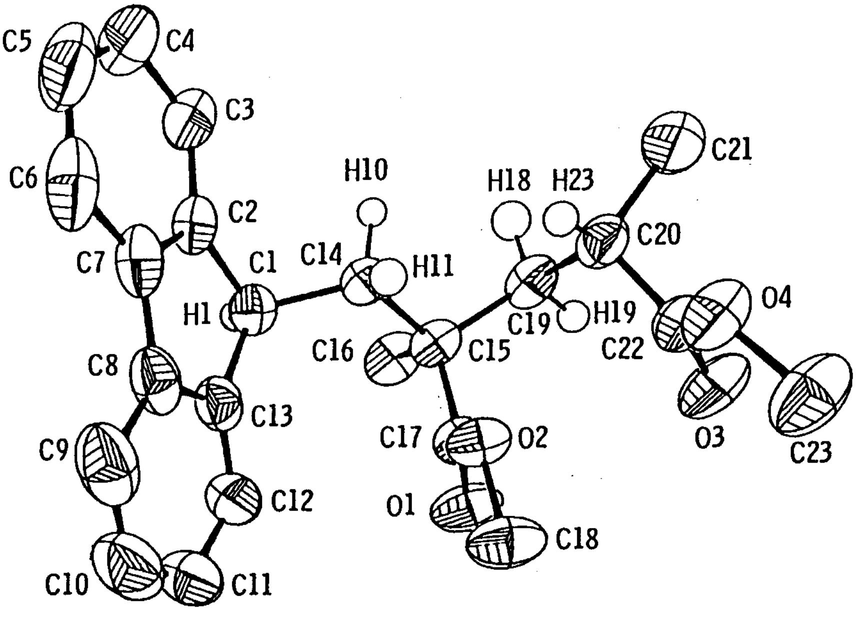


Figure A-1-7. ORTEP diagram of MMA-dimer meso.

Table A-1-3. Bond lengths, bond angles, and torsional angles in MMA units[a]

(Bond Length/Å)				(Bond Angle/deg)			
C1- C14	1.653(3)	C15-C19	1.681(3)	C1- C14-C15	120.5(1)	C15-C19-C20	120.4(2)
C14-C15	1.555(3)	C19-C20	1.557(3)	C14-C15-C19	108.9(1)	C19-C20-H23	108.9(15)
C15-C16	1.545(3)	C20-C21	1.638(5)	C16-C15-C17	107.7(2)	C21-C20-C22	105.1(2)
C15-C17	1.533(3)	C20-C22	1.511(3)	C15-C17-O2	112.0(2)	C20-C22-O4	111.7(2)
		C20-H23	1.002(26)	C17-O2- C18	116.4(2)	C22-O4- C23	116.5(2)
C17-O1	1.209(3)	C22-O3	1.206(3)	O1- C17-O2	122.6(2)	O3- C22-O4	122.5(2)
C17-O2	1.339(2)	C22-O4	1.333(3)				
O2- C18	1.451(3)	O4- C23	1.446(4)				

(Torsional Angle/deg)			
C1- C14-C15-C19	-164.5(1)	C15-C19-C20-H23	34.9(16)
C14-C15-C19-C20	-57.3(2)		
C16-C15-C17-O1	-19.9(3)	C21-C20-C22-O3	88.4(3)
O1- C17-O2 -C18	2.6(3)	O3- C22-O4- C23	-2.1(3)

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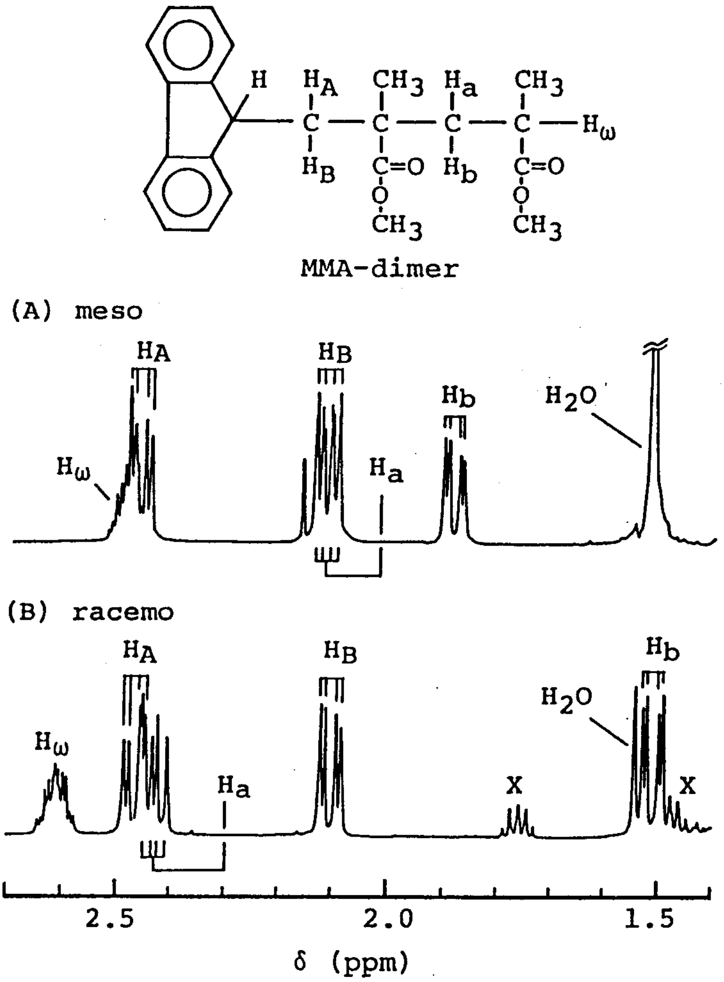
[a] Estimated standard deviations in the least significant digits are in parentheses.



Fgiure A-1-8. 500 MHz ^{1}H NMR spectra of MMA-dimers meso (A) and racemo (B) ($CDCl_3$, 35°C, TMS).

octamer were accomplished by measuring two dimensional ^{1}H NMR and FD mass spectra of the fractions of the oligomers in Figure A-1-6. The spectra of the isomers of trimer were taken in $CDCl_3$ and those of the isomers of pentamer, hexamer, heptamer, and octamer in nitrobenzene-d_5. As an example, ^{1}H NMR spectrum of MMA-heptamer *mmmmmm* is shown in Figure A-1-9. All the signals except for those of methoxy protons shown in Figure A-1-9 were reasonably assigned by using two dimensional technique. The chemical shifts and coupling constants are summarized in Tables A-1-4 and Tables A-1-5. The present assignment is based on those of pure isotactic and pure syndiotactic oligo(MMA)s (DP = 2~8) having a *t*-butyl group at the α-end and a hydrogen at the ω-

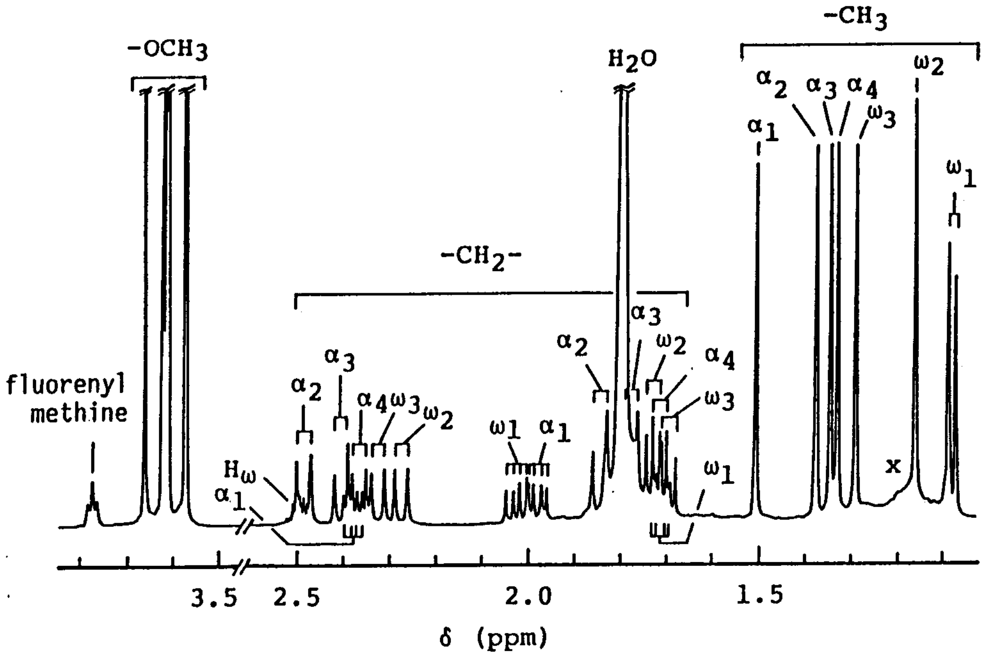


Figure A-1-9. 500 MHz ^{1}H NMR spectrum of MMA-heptamer *mmmmmm* (nitrobenzene-d_5, 110°C).

Table A-1-4. ^{1}H NMR chemical shifts (δ, ppm) and coupling constants (Hz) of methylene, α-end methine, and ω-end methine protons of MMA-dimers, -trimers, -pentamers, -hexamers, -heptamers, -octamers and a polymer having a 9-fluorenyl group at the α-end[a]

	fluorenyl[b] methine	α_1[c] $-CH_2-$	α_2[d] $-CH_2-$	α_3[d] $-CH_2-$	α_4[d] $-CH_2-$	ω_4[d] $-CH_2-$	ω_3[d] $-CH_2-$	ω_2[d] $-CH_2-$	ω_1[c] $-CH_2-$	ω-end[e] methine
dimer										
m	3.92	2.12, 2.47							1.89, 2.12	2.49
	(4.9, 5.4)	(14.9)							(14.0)	(3.9, 7.8)
r	3.92	2.10, 2.47							1.51, 2.43	2.61
	(4.9, 5.1)	(14.6)							(14.3)	(3.5, 8.9)
m[f]	3.94	2.19, 2.45							1.89, 2.12	
	(4.6, 5.4)	(14.9)							(14.2)	
r[f]	3.92	2.11, 2.45							1.50, 2.42	
	(4.9, 5.4)	(14.6)							(14.2)	
trimer										
mm[f]	3.87	2.03, 2.44	1.85, 2.37						1.73, 2.01	
	(4.4, 4.4)	(14.6)	(14.6)						(14.2)	
rm[f]	3.87	2.08, 2.40	2.20[g]						1.61, 2.06	
	(4.4, 4.9)	(14.6)	(0)						(14.2)	
rr[f]	3.86	2.08, 2.39	2.21[g]						1.37, 2.42	
	(4.9, 4.2)	(13.7)	(0)						(14.1)	
mr[f]	3.87	2.04, 2.44	1.87, 2.35						1.37, 2.39	
	(4.9, 4.2)	(14.5)	(14.2)						(14.7)	
pentamer										
mmmm	3.77	1.98, 2.38	1.83, 2.48	1.76, 2.27				1.75, 2.29	1.72, 2.03	2.49
	(5.5, 5.5)	(14.5)	(14.5)	(14.5)				(15.0)	(14.0)	(3.5, 8.0)
mmmr	3.77	1.98, 2.38	1.84, 2.48	1.77, 2.38				1.76, 2.31	1.36, 2.36	2.52
	(5.0, 4.5)	(14.0)	(14.5)	(15.0)				(14.5)	(14.5)	(3.5, 8.5)
mmmm[f]	3.76	1.97, 2.38	1.83, 2.47	1.76, 2.37				1.74, 2.28	1.71, 2.02	
	(5.0, 4.5)	(15.0)	(14.5)	(15.0)				(14.5)	(13.5)	
mmmr[f]	3.76	1.97, 2.38	1.83, 2.47	1.76, 2.38				1.76, 2.35	1.35, 2.30	
	(4.5, 3.5)	(14.0)	(14.5)	(15.0)				(13.0)	(15.0)	

(contd.)

(Table A-1-4. contd.)

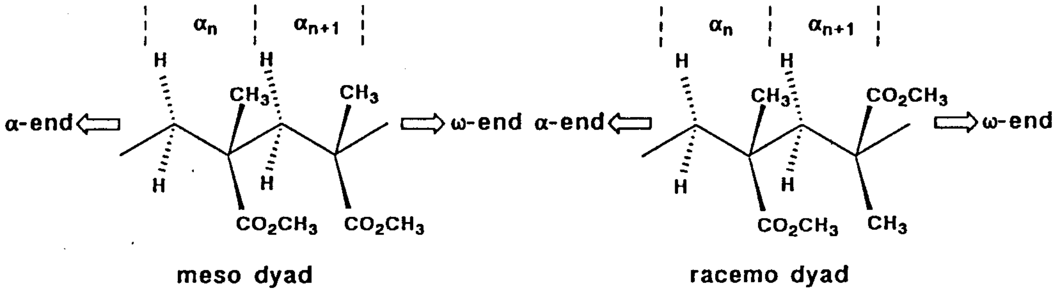
	fluorenyl[b] methine	α_1[c] $-CH_2-$	α_2[d] $-CH_2-$	α_3[d] $-CH_2-$	α_4[d] $-CH_2-$	ω_4[d] $-CH_2-$	ω_3[d] $-CH_2-$	ω_2[d] $-CH_2-$	ω_1[c] $-CH_2-$	ω-end[e] methine
hexamer										
mmmmm	3.78	1.98, 2.38	1.85, 2.49	1.77, 2.40			1.71, 2.34	1.74, 2.28	1.71, 2.03	2.50
	(5.0, 5.0)	(14.5)	(14.0)	(14.5)			(14.0)	(14.5)	(14.5)	(3.5, 8.0)
mmmmr	3.78	1.98, 2.38	1.85, 2.49	1.77, 2.40			1.72, 2.35	1.74, 2.30	1.35, 2.30	2.52
	(5.0, 5.0)	(13.5)	(14.5)	(15.0)			(15.0)	(15.0)	(14.0)	(2.5, 7.0)
mmmmm[f,h]	3.87	1.98, 2.43	1.75, 2.37	1.64, 2.24			1.59, 2.12	1.68, 2.16	1.64, 1.91	
	(4.5, 4.5)	(14.5)	(15.0)	(14.0)			(14.0)	(13.5)	(13.5)	
heptamer										
mmmmmm	3.78	1.98, 2.39	1.85, 2.49	1.78, 2.41	1.72, 2.37		1.70, 2.33	1.73, 2.28	1.71, 2.03	2.50
	(5.0, 6.0)	(14.0)	(15.0)	(14.5)	(14.0)		(13.5)	(15.5)	(14.0)	(3.0, 8.5)
mmmmmr	3.78	1.98, 2.38	1.85, 2.49	1.78, 2.41	1.72, 2.37		1.71, 2.34	1.75, 2.30	1.36, 2.36	2.52
	(5.0, 5.0)	(14.5)	(14.0)	(14.5)	(14.5)		(15.5)	(14.0)	(14.5)	(5.0, 8.5)
octamer										
mmmmmmm	3.77	1.98, 2.38	1.85, 2.49	1.78, 2.41	1.73, 2.38	1.71, 2.36	1.70, 2.33	1.73, 2.28	1.72, 2.03	2.49
	(4.5, 6.0)	(14.5)	(14.0)	(14.0)	(14.0)	(13.5)	(14.5)	(14.0)	(14.5)	(3.5, 9.0)
mmmmmmr	3.77	1.98, 2.38	1.85, 2.49	1.78, 2.41	1.73, 2.38	1.71, 2.36	1.71, 2.33	1.76, 2.29	1.36, 2.36	2.53
	(6.5, 7.0)	(13.5)	(14.5)	(15.0)	(15.0)	(14.5)	(14.5)	(13.5)	(14.0)	(5.0, 9.0)
polymer[i]						1.71, 2.36				
(DP=60)						(14.6)				

[a] The spectra of dimers and trimers were measured in $CDCl_3$ at 35°C and those of pentamers, hexamers, heptamers, octamers and the polymer in nitrobenzene-d_5 at 110°C at 500 MHz. Aromatic protons of fluorenyl group resonate in the range of 7.2-7.7 ppm both in $CDCl_3$ and in nitrobenzene-d_5 (multiplet). ^3J coupling constants between methine proton of fluorenyl group between ω_1-methylene proton, ^2J coupling constants between methylene protons, ^3J coupling constants between ω-end methine proton and ω_1-methylene protons are in parenthesis below the chemical shifts of fluorenyl methine proton, methylene protons, and ω_1-methylene proton, respectively. As for the ^3J coupling constants, the value of the left side corresponds to that between the methine proton and one of methylene protons resonating in higher field. [b] Triplet. [c] ABX double-quartet. [d] AB quartet. [e] Multiplet. [f] The oligomers having a deuterium at the ω-end prepared by termination with CD_3OD. [g] No splitting was observed. [h] Spectrum was measured in CDCl at 35°C. [i] Poly(MMA) derived from poly(TrMA) of Run 1 in Table A-1-1.

Table A-1-5. ^{1}H NMR chemical shifts (δ, ppm) and coupling constants (Hz) of α-methyl and methoxy protons of MMA-dimers, -trimers, -pentamers, -hexamers, -heptamers, -octamers and a polymer[a]

	α_1[b] CH$_3$	α_2[b] CH$_3$	α_3[b] CH$_3$	α_4[b] CH$_3$	ω_4[b] CH$_3$	ω_3[b] CH$_3$	ω_2[b] CH$_3$	ω_1[c] CH$_3$	OCH$_3$[b]
dimer									
m	1.28							1.15 (6.8)	3.58, 3.64
r	1.38							1.17 (7.0)	3.59, 3.68
m[d]	1.28							1.14	3.59, 3.65
r[d]	1.36							1.16	3.58, 3.64
trimer									
mm[d]	1.44	1.16						1.13	3.65(x3)[e] 3.64, 3.63
rm[d]	1.27	1.09						1.06	3.61
rr[d]	1.27	1.14						1.10	3.63(x2)[f], 3.62
mr[d]	1.43	1.23						1.14	3.65, 3.63, 3.58
pentamer									
mmmm	1.50	1.36	1.30				1.12	1.08 (7.5)	3.65, 3.61, 3.60, 3.57, 3.56
mmmr	1.50	1.37	1.30				1.22	1.09 (9.0)	3.66, 3.61, 3.59, 3.57, 3.56
mmmm[d]	1.50	1.36	1.30				1.16	1.07	3.65, 3.61, 3.60, 3.57, 3.56
mmmr[d]	1.50	1.36	1.30				1.21	1.08	3.65, 3.60, 3.57, 3.56, 3.55
hexamer									
mmmmm	1.51	1.37	1.34			1.30	1.16	1.08 (7.0)	3.66, 3.62, 3.61(x2)[f], 3.58, 3.57
mmmmr	1.51	1.36	1.34			1.29	1.21	1.09 (7.0)	3.66, 3.62, 3.61(x2)[f], 3.58, 3.57
mmmmm[d,g]	1.48	1.28	1.23			1.19	1.09	1.10	3.72, 3.66, 3.64, 3.62, 3.59, 3.56
heptamer									
mmmmmm	1.51	1.38	1.35	1.33		1.29	1.16	1.08 (7.0)	3.65, 3.62, 3.61(x3)[e], 3.58, 3.57
mmmmmr	1.51	1.38	1.35	1.33		1.29	1.21	1.08 (6.0)	3.66, 3.63, 3.62, 3.61, 3.59, 3.57(x2)[f]
octamer									
mmmmmmm	1.51	1.38	1.35	1.34	1.33	1.29	1.16	1.08 (6.5)	3.66(x2)[f], 3.62, 3.61, 3.61, 3.60, 3.57(x2)[f]
mmmmmmr	1.50	1.38	1.35	1.34	1.33	1.29	1.21	1.08 (6.5)	3.65, 3.62, 3.61(x2)[f], 3.58, 3.57(x2)[f]
polymer[h] (DP = 60)					1.33				3.63

[a] The conditions of measurements are the same as those in Table A-1-4. ^3J coupling constants between the methine proton and methyl proton in the ω_1-unit are shown in parentheses. [b] Singlet. [c] Doublet for the oligomers having a proton at the ω-end and singlet for the oligomers having a deuterium at the ω-end. [d] The oligomers having a deuterium at the ω-end prepared by termination with CD$_3$OD. [e] The intensity was three times as large as that of three protons of one methoxy group. [f] The intensity was twice as large as that of three protons of one methoxy group. [g] Spectrum was measured in CDCl$_3$ at 35°C. [h] Poly(MMA) derived from poly(TrMA) of Run 1 in Table A-1-1.



Scheme A-1-3. Meso and racemo dyads in the main chain of oligo- and poly(MMA).

end by two dimensional NMR and X-ray analyses.[14] The configurational relationship between two neighboring asymmetric centers in the α_n- and α_{n+1}-monomeric units (dyad) of an oligomer, *m* or *r* (Scheme A-1-3), was judged by the difference in chemical shift of nonequivalent methylene protons of α_{n+1}-monomeric unit in these studies. The assignment of *m* and *r* of each dyad in an oligomer was performed on the basis of the fact that the difference of the chemical shifts of the nonequivalent methylene protons is larger in *m* dyad than in *r* dyad except for the dyad at the ω-end. This has been confirmed by x-ray crystal analysis of a MMA-trimer having a *t*-butyl group at the α-end.[14a] The values of the difference in chemical shifts were reported to be 0.48~0.64 ppm for *m* dyad and 0.00~0.17 ppm for *r* dyad except for that at the ω-end and for isotactic oligomers, 0.20~0.27 ppm for *m* dyad and 0.42~0.48 ppm for *r* dyad at the ω-end of the chain.[14b] For the oligo(MMA)s having a 9-fluorenyl group at the α-end, the values of difference in chemical shifts of the methylene protons of the α_2~ω_2-monomeric units of the main isomers of pentamer, hexamer, heptamer, and octamer were in the range of 0.54~0.66 ppm, indicating that these isomers were isotactic. These values well agree with that of the isotactic polymer. The chemical shift difference of the ω-end methylene protons of these isomers were 0.23~0.32 ppm for *m* and 0.92~1.01 ppm for *r*, and that of the α-end methylene protons were almost constantly 0.40~0.41 ppm. The difference in the chemical shift of the methylene protons of the central (α_2-) monomeric unit of the trimer was 0.48 or 0.52 ppm for *m* and 0 ppm for *r* and that of the ω-end methylene protons was 0.29~0.45 ppm for *m* and 0.87~1.03 ppm for *r*.

Optical resolution of dimer and assignments of four isomers

The diastereomers separated above were optically resolved by HPLC on a chiral stationary phase and the absolute configuration of optical isomers was determined. In the notation of isomers, *meso* addition is represented as *RR* and *SS* in the present paper in which the left side is α-end side. Therefore, isotactic sequence is represented as ---*RRR*--- and ---*SSS*---.

Figure A-1-10 shows the chromatograms of optical resolution of MMA-dimer derived from TrMA-dimer prepared with Sp-FlLi at [TrMA]/[Li] = 2, 3, 10, and 20. The dimer was completely separated into four isomers (*SS*, *RR*, *RS*, *SR*) by using a chiral HPLC column packed with cellulose tris(3,5-dichlorophenylcarbamate)-coated silica gel.[15b] The content of the optical isomers could be determined by this separation.

The assignment of the four isomers of the dimer was done by analyzing an optically active dimer synthesized from (-)-(*R*,*R*)-

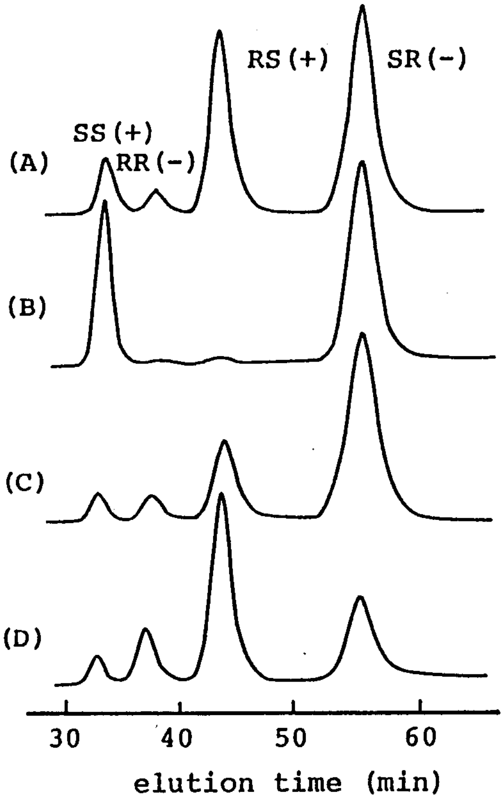
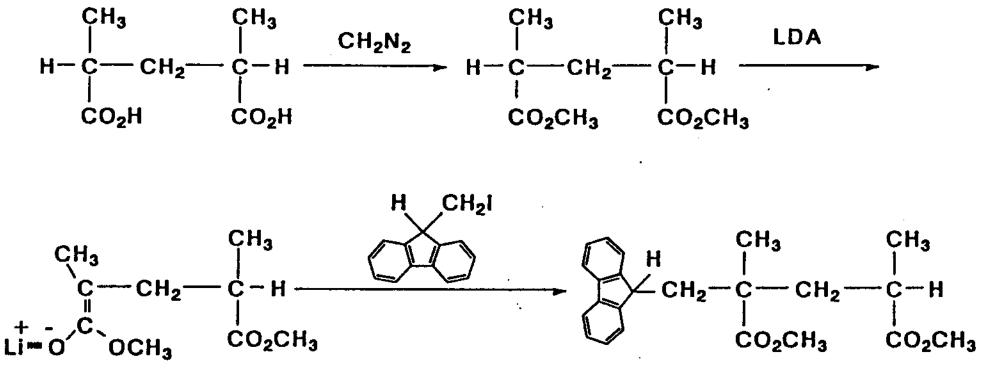


Figure A-1-10. Chromatograms of optical resolution of MMA-dimer derived from TrMA-dimer prepared with Sp-FlLi at [TrMA]/[Li]= 2 (A), 3 (B), 10 (C), and 20 (D).

2,4-dimethylglutaric acid[11] (Scheme A-1-4). This optically active acid was prepared by hydrolyzing optically active dibenzyl 2,4-dimethylglutarate (e.e. 85%) which was obtained by chromatographic separation of a mixture of (±)- and *meso*-dibenzyl ester. (-)-Acid thus obtained was methylated by CH_2N_2 followed by lithiation with an equivalent of lithium diisopropyl amide (LDA). The lithiated methyl ester was allowed to react with 9-iodomethylfluorene to introduce a fluorenylmethyl group at the 2-position of the ester. This afforded a mixture of *RR* and *SR* dimers. The possibility of lithiation of both 2- and 4-positions of the ester in this process was found to be neglectable by the following experiment. Dibenzyl ester rich in (-)-(*R*,*R*)-isomer was lithiated with an equivalent of LDA and quenched by CH_3OH. The resulting dibenzyl ester consisted mainly of (-)-(*R*,*R*)- and *meso*-isomers, and no increase of (+)-(*S*,*S*)-isomer against (-)-(*R*,*R*)-isomer was observed by the HPLC analysis. This indicates that only one of 2- and 4-positions of the benzyl ester is lithiated with an equivalent of LDA and no exchange reaction between the lithiated esters proceeds.

The optically active MMA-dimer thus obtained was separated by HPLC using a silica gel column and the structures of *m* and *r* isomers were confirmed by FD mass and ^1H NMR spectroscopic analyses. The analytical data were identical to those of the MMA-dimer obtained from the oligomerization of TrMA. The *m* and *r* isomers of the optically active dimer was optically resolved by chiral HPLC in order to learn the content of the optical isomer. The chromatograms are shown in Figure A-1-11 together with the results of analyses of the dimer prepared from a mixture of (±)-



Scheme A-1-4. Synthesis of MMA-dimer from 2,4-dimethylglutaric acid.

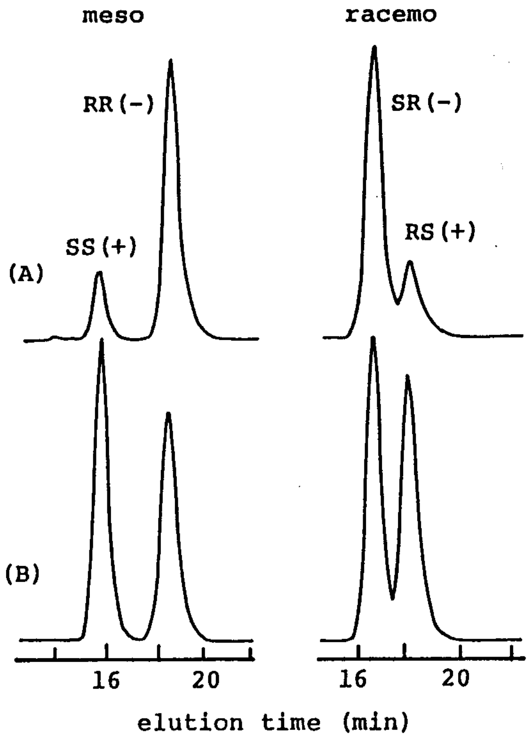
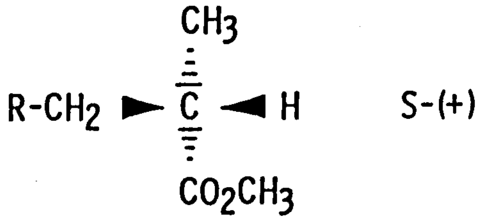


Figure A-1-11. Chromatograms of optical resolution of MMA-dimers prepared from (-)-(2R,4R)-2,4-dimethylglutaric acid (A) and (+)- and meso-dimethylglutaric acid (B) (right: meso, left: racemo).

and *meso*-2,4-dimethylglutaric acid. E.e. of both *m* and *r* isomers obtained from (*R,R*)-acid was lower than that of the original acid (65% e.e. for *m* and 58% e.e. for *r*), suggesting that some racemization occurred in the process of hydrolyzing ester group and introducing fluorenylmethyl group. However, in both the chromatograms of resolution of *m* and *r* isomers, one antipode of negative rotation predominated over the other. This indicates that the optical isomer of negative rotation is the isomer whose asymmetric center of the ω-end has *R* configuration, that is, *RR* isomer for *m* and *SR* isomer for *r*. This assignment agreed with that based on the optical rotation, referring to the model compounds (Scheme A-1-5).^{21} All the model compounds of *S* configuration show positive rotation. It was assumed that the optical rotation of an isomer of dimer depends on the configuration of the asymmetric carbon of the ω-end.



$$R\text{-}CH_2 \blacktriangleright \overset{CH_3}{\underset{CO_2CH_3}{C}} \blacktriangleleft H$$

R = alkyl, CH_2=CH-, C_6H_5
CO_2R, CH_2CO_2R

Scheme A-1-5. Model compounds for the assignment of absolute configuration of MMA-dimer and trimer. All the compounds with S-configuration exhibit positive optical rotation.

The ratios of the four isomers obtained in the three initiator systems are summarized in Table A-1-6. In the system with Sp-FlLi, contents of MMA-dimer depended greatly on [TrMA]/[Li] ratio. Relative total amount of *RR* and *RS* isomers, which are generically named *R*- isomer in this paper, greatly decreased with the increasing [TrMA]/[Li] ratio from 2 to 3. This is ascribed to the predominant propagation of $R-^-$ dimer anion with high stereoselectivity to trimer anion in the early stage of polymerization. In the present paper, $R-^-$ and $S-^-$ anions repre-

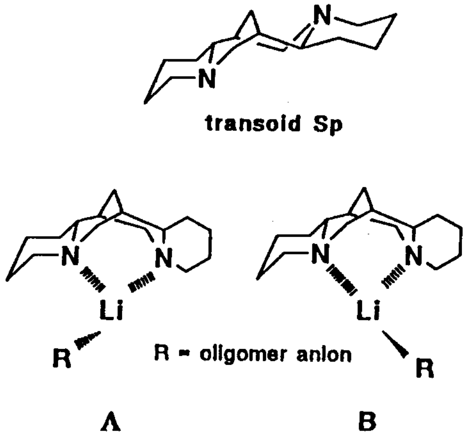
Table A-1-6. The ratios of the four optical isomers of MMA-dimer derived from TrMA-dimer prepared with Sp-FlLi, DDB-FlLi, and PMP-FlLi[a]

Initiator	[TrMA]/[Li]	Four Isomers (%) *m* *SS*(+)	*RR*(−)	*r* *RS*(+)	*SR*(−)	*S*- / *R*-[b]
Sp-FlLi	2	9	4	32	55	64 / 36
	3	25	1	3	71	96 / 4
	10	7	6	22	65	72 / 28
	20	8	13	49	30	38 / 62
DDB-FlLi	2	16	8	27	49	65 / 35
	3	27	10	19	44	71 / 29
	5	30	11	17	42	72 / 28
PMP-FlLi	2	14	4	23	59	73 / 27
	3	15	8	29	48	63 / 37
	5	19	9	22	50	69 / 31

[a] Determined by HPLC optical resolution of dimer with UV detection at 254 nm. The dimers were separated from the mixture of oligo(MMA)s by GPC.
[b] *S*- = *SS* + *SR*, *R*- = *RR* + *RS*.

sent the dimer anions which give *RR* and *RS* dimers and *SS* and *SR* dimers, respectively, by protonation with CH_3OH. Although the *R*-$^-$ dimer anion gives *RR* and *RS* dimer by protonation with CH_3OH, the configuration of the chiral center of ω-end is not important on the view point of stereochemistry of propagation, because it is determined by termination reaction with CH_3OH and has no concerning with the propagation stereochemistry.

In contrast to the change of the ratio ([*S*-]/[*R*-]) of the isomers at [TrMA]/[Li] ratio 2 and 3, as [TrMA]/[Li] ratio increased from 3 to 20, the amount of *S*- isomer (*SS* + *SR*) decreased and reached to the ratio of *R*- to *S*- 62:38 at [TrMA]/[Li] = 20 where 82 % of the product was a polymer of DP = 60 (Table A-1-1). This indicates that a significant amount of *S*-$^-$ dimer anion propagated to trimer anion till the completion of polymerization leaving the less reactive *R*-$^-$ anion. The *R*-$^-$ dimer anion may consist of at least two species of different activities. Two conformers, transoid and cisoid, are possible for Sp and when Sp forms a bidentate complex with metal cation, cisoid structure is preferred (Scheme A-1-6).[22a,b] NMR analyses of the complexes of Sp and magnesium dialkyl and butyllithium show that the alkyl group of the metal compound can exist in two different magnetic environments and the exchange between the two positions is slow.[22c,d] On the basis of this observation, two types of complex of Sp and TrMA-oligomer anion (A and B) are considered to be possible in which the anion is located in the different positions with respect to Sp backbone with skewed shape as shown in Scheme A-1-6. The shape of chiral cavity which determines stereospecificity and activity of the complex should be different



Scheme A-1-6. Transoid Sp and two types of complexes of cisoid Sp with oligomer anion.

in the complexes A and B. This is supported by the fact that a slight difference of Sp backbone showed a remarkable influence on the stereospecificity and activity of the initiator complex in the enantioselective (stereoelective) polymerization of racemic α-methylbenzyl methacrylate with the complexes of ethylmagnesium bromide with Sp and its derivatives.[23]

As for the other initiator systems, the amount of *R*- isomer in the system with DDB-FlLi and that of *S*- isomer in the system with PMP-FlLi slightly decreased as the [TrMA]/[Li] ratio increased form 2 to 3. This indicates that *R*-$^-$ dimer anion in the system with DDB-FlLi and *S*-$^-$ anion in the system with PMP-FlLi predominantly propagate to trimer anion in the early stage of polymerization, though the stereospecificity was rather low. With further increase of [TrMA]/[Li] from 3 to 5, a small decrease of *R*- isomer was again observed in the system with DDB-

FlLi, and also in the system with PMP-FlLi, a decrease of *R*-isomer was observed. The predominantly propagating dimer anion changed in the system with PMP-FlLi with the progress of polymerization, similarly to the system with Sp-FlLi. Two types of PMP complexes of dimer anion with different activities can be assumed as well as in the system with Sp-FlLi. On the other hand, two types of complexes may not be necessary for the dimer anion in the system with DDB-FlLi.

Optical resolution of trimer and assignments of eight isomers

To examine the stereochemistry of propagation from trimer anion to higher oligomer anions, trimers were analyzed in the same manner as adopted for dimer. Eight isomers exist for trimer and these were almost completely resolved by chiral HPLC. As an example, the chromatograms of resolution of MMA trimer derived from TrMA trimer prepared with Sp-FlLi at [TrMA]/[Li] = 3 is shown in Figure A-1-12. The relative amounts of the isomers obtained in the three initiator systems at [TrMA]/[Li] = 2, 3, and 5 and those in the system with Sp-FlLi at [TrMA]/[Li] = 10 and 20 are summarized in Table A-1-7.

The eight isomers were assigned on the basis of the content of isomers obtained in the system with Sp-FlLi at [TrMA]/[Li] = 2. Under this condition with Sp-FlLi, the product was mainly dimer (~93%) in addition to a small amount of trimer (Figure A-1-3 (A)), suggesting that the small amount of the trimer may be produced from the more active dimer anion. The predominantly propagating dimer anion in the early stage of polymerization was shown to be R^- from the results in Table A-1-6 as described

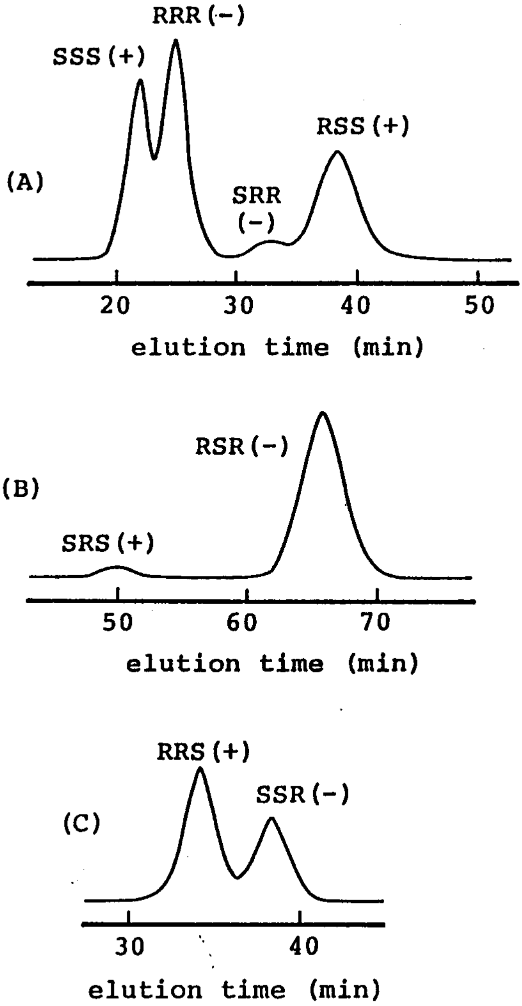


Figure A-1-12. Chromatograms of optical resolution of MMA-trimers mm and mr (A), rr (B), and mr (C) derived from TrMA-trimers prepared with Sp-FlLi at [TrMA]/[Li]=3.

Table A-1-7. The ratios of the eight optical isomers of MMA-trimer derived from TrMA-trimer prepared with Sp-FlLi, DDB-FlLi, and PMP-FlLi[a]

Initiator	$\frac{[\text{TrMA}]}{[\text{Li}]}$	Eight Isomers (%)								
		mm		*rm*		*rr*		*mr*		
		SSS(+)	*RRR*(-)	*SRR*(-)	*RSS*(+)	*SRS*(+)	*RSR*(-)	*RRS*(+)	*SSR*(-)	*SS-*/*RR-*/*SR-*/*RS-*[b]
Sp-FlLi	2	~0	11	~0	3	2	23	56	5	5 /67 / 2 /26
	3	4	6	1	4	1	36	28	20	24 /34 / 1 /41
	5	15	~0	~0	3	3	20	~0	59	74 / 0 / 3 /23
	10	6	~0	~0	1	1	13	~0	79	85 / 0 / 1 /14
	20	7	~0	~0	1	1	13	~0	78	85 / 0 / 1 /14
DDB-FlLi	2	18	6	~0	14	6	25	5	26	44 /11 / 6 /39
	3	21	8	1	16	4	24	4	22	43 /12 / 5 /40
	5	19	9	1	23	2	30	3	13	32 /11 / 3 /54
PMP-FlLi	2	5	~0	~0	~0	4	11	~0	80	85 /~0 / 4 /11
	3	7	1	~0	1	3	10	~0	78	85 / 1 / 3 /11
	5	11	1	~0	~0	2	5	3	78	89 / 4 / 2 / 5

[a] Calculated from the ratio of the diastereomers shown in Table A-1-2 and the ratio of optical isomers determined by HPLC optical resolution of each diastereomer with UV detection at 254 nm.

[b] *SS-* = *SSS* + *SSR*, *RR-* = *RRR* + *RRS*, *SR-* = *SRS* + *SRR*, *RS-* = *RSR* + *RSS*.

above. Actually, all the diastereomers of the trimer consist of predominantly one antipode of the enantiomers at [TrMA]/[Li] = 2. Therefore, the predominant optical isomers of trimer were assigned to the ones whose asymmetric carbon at the α-end has *R* configuration. This assignment agreed with that based on the optical rotation, referring to the model compounds[21] descrived above.

Similarly to dimer, the isomers of trimer are named by omitting the ω-end configuration such as *RR*- which represents *RRR* and *RRS*. In the system with Sp-FlLi, as [TrMA]/[Li] ratio increased, the amount of *SS*- (*SSR* + *SSS*) increased and that of *RR*- (*RRR* + *RRS*) decreased to zero at [TrMA]/[Li] = 5 (Table A-1-7). The amount of *RS*- (*RSR* + *RSS*) first increased with an increase of [TrMA]/[Li] ratio from 2 to 3, and then decreased with further increase of [TrMA]/[Li] ratio, though the degree of decrease was not as obvious as that of *RR*-. The change of the amount of *SR*- (*SRS* + *SRR*) was not as remarkable as that of the other isomers. These results indicate that in the system with Sp-FlLi, *RR*-$^-$ trimer anion is much more reactive than the other isomeric anions, particularly *SS*-$^-$ anion. Though *RS*-$^-$ trimer anion is also rather reactive in the latter stage of polymerization, this anion should not grow up to the higher isotactic oligomer or the polymer, because the isomers having *r* configuration at the α-end of the main chain was not obviously detected in the separation of diastereomers of pentamer to octamer (Figure A-1-6 (A)) and NMR analysis of the polymer (Figure A-1-1). *RS*-$^-$ trimer anion may grow up to tetramer anion and remain without further propagation. The trimer anions at [TrMA]/[Li] = 10 and

20 with Sp-FlLi are considered to be the less reactive anions remaining after the formation of polymer.

In the system with DDB-FlLi, the amount of *SS*- and *SR*- decreased and that of *RS*- increased with the increasing [TrMA]/[Li] ratio, though the change was not as obvious as in the system with Sp-FlLi. This indicates that *SS*-$^-$ and *SR*-$^-$ trimer anions predominantly propagate to the higher ones with less stereospecificity than that in the system with Sp-FlLi. However, since the amount of *SR*- isomer is much smaller than the others, the important species in the propagation from trimer to the higher oligomer anions should be *SS*-$^-$ anion, while in the step from dimer anion to trimer anion *R*-$^-$ dimer anion predominated over *S*-$^-$.

In the system with PMP-FlLi, the change of the amount of isomers was much smaller than the other two systems. However, here, the information on the stereospecific propagation can be drawn from the amount of isomers itself. The oligomer obtained at [TrMA]/[Li] = 3 consisted mainly of trimer (~67%) (Figure A-1-5 (b)) and *SS*- isomer comprises 85% of the trimer. This indicates that *SS*-$^-$ anion is the predominantly propagating trimer anion in this system.

Optical resolution of higher oligomers

The separation of diastereomers showed that the oligomers of DP $\geq$ 5 in all the systems consisted mainly of the isotactic ones whose ω-ends have *m* and *r* configuration (Figure A-1-6). The isotactic oligomers were optically resolved by HPLC. Figure A-1-13 shows the chromatograms of optical resolution of isotactic

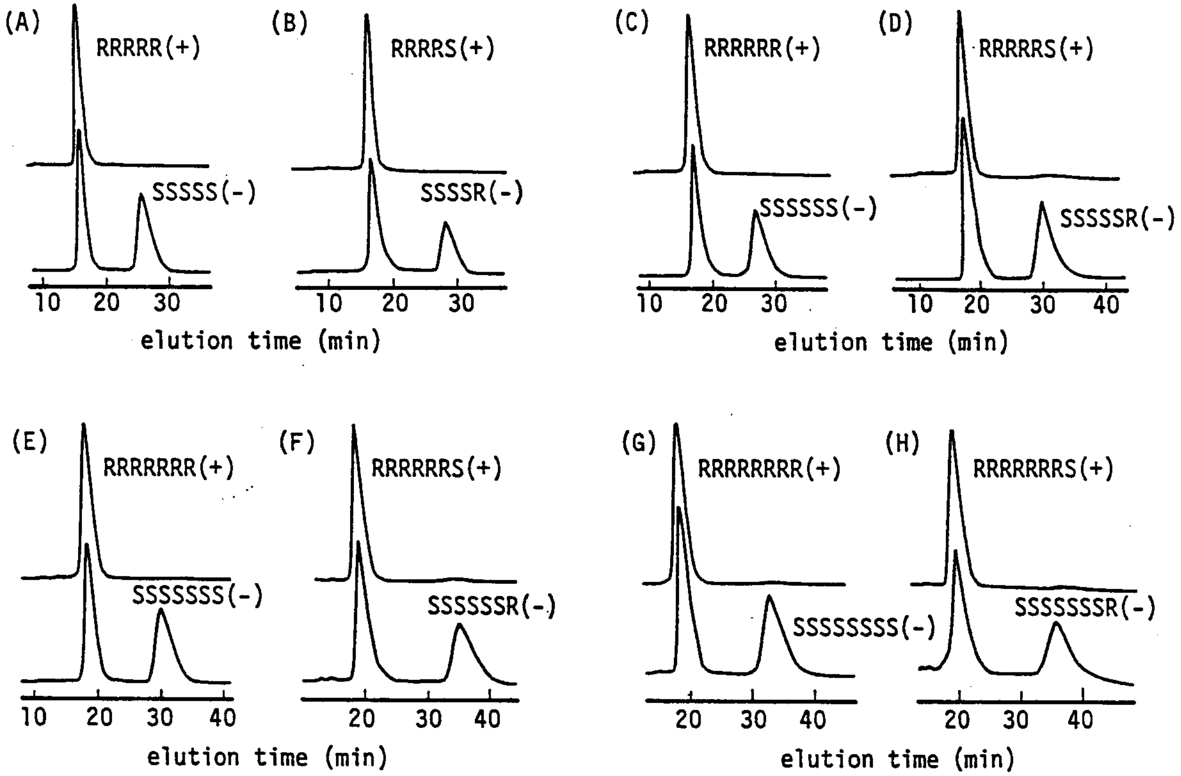


Figure A-1-13. Chromatograms of optical resolution of MMA-pentamers mmmm (A) and mmmr (B), MMA-hexamer mmmmm (C) and mmmmr (D), MMA-heptamer mmmmmm (E) and mmmmmr (F), and MMA-octamer mmmmmmm (G) and mmmmmmr (H) derived from corresponding TrMA-oligomers prepared with Sp-FlLi and corresponding racemic TrMA-oligomers prepared with FlLi in THF (top of each: optically active oligomers, bottom of each: racemic oligomers). Pentamers and hexamers were isolated from the products of oligomerization at [TrMA]/[Li]=3 and heptamers and octamers from those at [TrMA]/[Li]=5.

oligomers obtained in the system with Sp-FlLi; pentamers and hexamers obtained at [TrMA]/[Li] = 3 and heptamers and octamers obtained at [TrMA]/[Li] = 5. Racemic oligomers were obtained with FlLi in THF without a chiral ligand. As shown in the figure, all the isotactic oligomers were perfectly resolved. The ratios of the enantiomers obtained in the three systems are summarized in Table A-1-8.

The isotactic oligomers obtained in the three systems consisted mostly of one antipode of enantiomers except for the hexamer *mmmmr* in the system with Sp-FlLi at [TrMA]/[Li] = 5. The antipodes in excess in the system with Sp-FlLi are the opposite ones to those in the systems with DDB- and PMP-FlLi. This indicates that the isotactic oligomer anions of opposite absolute configuration predominantly propagate to the polymer in the system with Sp-FlLi and the other two systems. The assignments of the isomers were done as follows. In the system with Sp-FlLi at [TrMA]/[Li] = 3, pentamer and hexamer are the highest oligomers in the products, that is, those oligomers were produced from the dimer and trimer anions of higher activities. The results in Tables A-1-6 and A-1-7 showed that *R*-$^-$ dimer anion and *RR*-$^-$ trimer anion were much more reactive than the other isomeric anions in the early stage of polymerization. Therefore, these antipodes can be assigned to the oligomers whose asymmetric centers of the main chains have *R* configuration. The antipodes of heptamer and octamer were also assigned to *RRR*--- isomers in this system since they were produced from the smaller oligomer anions including hexamer and pentamer anions which consisted purely of one antipode. *Consequently, the results of optical*

Table A-1-8. The ratios of the optical isomers of isotactic oligo(MMA)s derived from oligo(TrMA)s obtained with Sp-FlLi, DDB-FlLi, and PMP-FlLi[a]

Initiator	[TrMA]/[Li]	Pentamer		Hexamer		Heptamer		Octamer	
		mmmm	*mmmr*	*mmmmm*	*mmmmr*	*mmmmmm*	*mmmmmr*	*mmmmmmm*	*mmmmmmr*
		RRRRR/SSSSS	*RRRRS/SSSSR*	*RRRRRR/SSSSSS*	*RRRRRS/SSSSSR*	*RRRRRRR/SSSSSSS*	*RRRRRRS/SSSSSSR*	*RRRRRRRR/SSSSSSSS*	*RRRRRRRS/SSSSSSSR*
Sp-FlLi	3	~100 / ~0	~100 / ~0	~100 / ~0	98 / 2	~100 / ~0	~100 / ~0	———[b]	———[b]
	5	95 / 5	85 / 15	97 / 3	54 / 46	~100 / ~0	97 / 3	~100 / ~0	~100 / ~0
DDB-FlLi	3	2 / 98	2 / 98	3 / 97	1 / 99	10 / 90	9 / 91	———[b]	———[b]
	5	3 / 97	7 / 93	1 / 99	2 / 98	1 / 99	~0 /~100	———[b]	———[b]
PMP-FlLi	3	~0 /~100	18 / 82	~0 /~100	13 / 87	———[b]	———[b]	———[b]	———[b]
	5	~0 /~100	10 / 90	~0 /~100	5 / 95	———[b]	———[b]	———[b]	———[b]

[a] Determined by HPLC optical resolution of the diastereomers with UV detection at 254 nm.

[b] Not obviously detected in the separation of diastereomers (Table A-1-2).

resolution of isotactic oligomers indicate that the isotactic oligomer anions of RRR--- configuration in the system with Sp-FlLi and those of SSS--- configuration in the systems with DDB-FlLi and PMP-FlLi predominantly propagate to the polymer of one-handed helicity, and the polymer obtained in the former system possesses RRR--- configuration and that in the latter two systems SSS--- configuration, although these polymers have the same helicity. The exceptional existence of the significant amount of *SSSSSR* hexamer in the system with Sp-FlLi at [TrMA]/[Li] = 5 may mean that the $S-^-$ dimer anion which predominantly propagated in the rather final stage of polymerization grew up to hexamer anion which remained until the completion of the polymerization.

Stereochemistry of protonation of oligomer anions

The results shown above give us the information on the stereochemistry of the protonation of oligomer anions with CH_3OH. From the results of separation of the isomers of dimer, trimer, pentamer, hexamer, heptamer, and octamer, the ratios of the isomers which differ only in the configuration of the asymmetric center at the ω-end (-*m* isomer and -*r* isomer) were calculated. The results are summarized in Table A-1-9.

In the system with Sp-FlLi, for all the isomeric anions of dimer and trimer, protonation was mainly in *r*-fashion and the ratios of -*m* isomer to -*r* isomer were not obviously dependent on the [TrMA]/[Li] ratio. As for the higher oligomers, the stereospecificity of protonation differed depending on the absolute configuration of the main chain of the isomeric anion. Protonation of *m*-fashion (*m*-protonation) was major for the isomeric

Table A-1-9. The ratios of the isomers whose ω-end possess *m* configuration to those whose ω-end possess *r* configuration[a]

Initiator	[TrMA]/[Li]	dimer		trimer				pentamer[b]		hexamer[b]		heptamer[b]		octamer[b]	
		SS/SR	*RR/RS*	*SSS/SSR*	*RRR/RRS*	*SRR/SRS*	*RSS/RSR*	*-SS/-SR*	*-RR/-RS*	*-SS/-SR*	*-RR/-RS*	*-SS/-SR*	*-RR/-RS*	*-SS/-SR*	*-RR/-RS*
Sp-FlLi	2	14/86	12/88	--/--[c]	16/84	--/--[c]	12/88								
	3	26/74	25/75	17/83	18/82	--/--[c]	10/90	--/--[c]	65/35	--/--[c]	75/25	--/--[c]	83/17		
	5			20/80	--/--[c]	--/--[c]	13/87	40/60	62/38	11/89	78/22	--/--[c]	88/12	--/--[c]	86/14
	10	13/87	21/79	7/93	--/--[c]	--/--[c]	7/93								
	20	21/79	21/79	8/92	--/--[c]	--/--[c]	7/93								
DDB-FlLi	2	25/75	23/77	41/59	55/45	--/--[c]	36/64								
	3	38/62	34/66	49/51	67/33	20/80	40/60	78/22	83/17	63/37	83/17	85/15	86/14		
	5	42/58	39/61	59/41	75/25	33/67	43/57	83/17	71/29	65/35	--/--[c]	87/13	--/--[c]		
PMP-FlLi	2	19/81	15/85	6/94	--/--[c]	--/--[c]	--/--[c]								
	3	24/76	22/78	8/92	--/--[c]	--/--[c]	9/91	73/27	--/--[c]	70/30	--/--[c]				
	5	28/72	29/71	12/88	25/75	--/--[c]	--/--[c]	76/24	--/--[c]	72/28	--/--[c]				

[a] Calculated from the data in Tables A-1-2, A-1-6, A-1-7, and A-1-8.

[b] *-SS* and *-SR* denote the isotactic oligomers whose asymmetric centers in the main chain have *S* configuration, and *-RR* and *-RS* those of *R* configuration.

[c] The ratio could not be calculated precisely because the amount of one of or both of the isomers was very low.

anions of *RRR*--- configuration and that of *r*-fashion (*r*-protonation) for the isomeric anions of *SSS*--- configuration. This reasonably explains the unnaturally high content of *mmmmr* isomer in hexamer in the system with Sp-FlLi at [TrMA]/[Li] = 10 and 20 (Table A-1-2). The hexamer at [TrMA]/[Li] = 10 and 20, which is considered to be the *remaining* oligomer, may consist mainly of *SSSSSR* isomer produced from relatively less reactive *SSSSS*-$^-$ anion.

It was confirmed that for the dimer anion in the system with Sp-FlLi at [TrMA]/[Li] = 2, the stereospecificity of protonation was not affected by the reaction time in the range of 1 min to 24 h after the reaction starts.

The ω-end configuration ---*R* and ---*S* may be determined by protonation of the enolate anion (Scheme A-1-2). This is also supported by the fact that the stereospecificity of protonation of oligo(TrMA) anions was strongly affected by the stereostructure of the protonating reagent.[24] For several α-metalated carbonyl compounds whose structure resembles to the oligomethacrylate anion, the enolate structure has been proved by NMR spectroscopic and X-ray crystallographic analyses.[25]

In the system with DDB-FlLi, for the dimer anions and *SR*-$^-$ and *RS*-$^-$ trimer anions, *r*-protonation predominated over *m*-protonation and for *RR*-$^-$ trimer anion and the isotactic anions of pentamer, hexamer, and heptamer *m*-protonation predominated. In this system, for the dimer and trimer anions, the stereospecificity of protonation changed depending on the [TrMA]/[Li] ratio. One of typical cases is that of *SS*-$^-$ trimer anion. For the *SS*-$^-$ trimer anion, *r*-protonation predominated at [TrMA]/[Li] = 2 and *m*-protonation predominated at [TrMA]/[Li] = 5. This change of stereospecificity of protonation may be ascribed either to structural factor or aggregation of oligomer anions. The existence of different complexing forms between oligomer anions and the ligand shown in Scheme A-1-5 may be less plausible in the system with DDB because this ligand is more symmetrical than Sp and PMP. Aggregation of oligomer anions may be responsible for the change of stereospecificity of protonation. Since the volume of reaction system was kept constant for all the reactions, concentration of oligomer anions decreases as [TrMA]/[Li] increases. The degree of aggregation of oligomer anions may be influenced by the concentration. It has been reported that lithium compounds with similar structures to methacrylate anions aggregate in the range of the concentration which is close to that adopted in our experiment both in hydrocarbon solvents and in polar solvents.[26] The oligomer anions with Sp may not aggregate. Since Sp is much bulkier than the other two ligands, it may prevent aggregation.

In the system with PMP-FlLi, *r*-protonation for all the isomeric anions of dimer and trimer and *m*-protonation for the higher oligomer anions predominated. The dependence of the stereospecificity on the [TrMA]/[Li] ratio was also observed in this system. The oligomer anions may aggregate.

Mechanism of the polymerization

From the results obtained above, the mechanism of asymmetric polymerization can be described as follows. The oligomer anions in the early stage of polymerization consist of the species of different activity. The highly active oligomer anion predominantly propagates to the helical polymer and the less active species remain as oligomers till the completion of polymerization. The activity of oligomer anions depends on its stereostructure and the complexing form between the anion and chiral ligand.

In all the systems, the propagation of unimer anion to dimer anion is very fast. In the early stage of polymerization with Sp-FlLi, R-$^-$ dimer anion predominantly propagates to trimer anion and in the latter stage of the polymerization, S-$^-$ dimer anion predominantly propagates to trimer anion. However, S-$^-$ dimer anion does not grow to polymer and remains as trimer, tetramer, and hexamer anions until the completion of polymerization. In the next step, RR-$^-$ trimer anion is more reactive than the other isomeric anions and is used for the formation of the higher isotactic oligomer anion with *RRR*--- configuration. Once an isotactic oligomer anion grows up to DP ~ 9, the reaction of the anion with TrMA monomer is accelerated to afford an optically active, one-handed helical polymer of *RRR*--- configuration. In the system with DDB-FlLi, R-$^-$ dimer anion is slightly more reactive than S-$^-$ dimer anion. However, in the next step and thereafter, SS-$^-$ trimer anion and *SSS*--- isotactic oligomer anions predominantly propagate to the polymer of *SSS*--- configuration. In the system with PMP-FlLi, the propagation of unimer anion to dimer anion is slower than that in the other two systems. In the step of propagation of dimer anion to trimer anion, S-$^-$ dimer anion in the early stage of polymerization and R-$^-$ dimer anion in the latter stage of polymerization predominantly propagate. In the next step and thereafter, the stereospecificity of propagation is similar to that in the system with DDB-FlLi and the polymer of *SSS*--- configuration is produced. In the systems with DDB-FlLi and PMP-FlLi, the acceleration of polymerization occurs when the oligomer anion grows to DP ~ 7. The difference of the stereochemistry of propagation with the three initiator systems must be related to the stereostructure of the complexes of oligomer anions with chiral ligands.

Though the absolute configuration of asymmetric carbons in the main chain of the polymer obtained with Sp-FlLi is opposite to that of the polymers obtained with DDB-FlLi and PMP-FlLi, all the polymers possess the same helicity. The two isotactic polymer chains of the same helicity with opposite absolute configuration are regarded as a kind of diastereomers, particularly when DP is low, because the influence of the α- and ω-end groups can not be ignored. Therefore, the stereostructure of the helices in the vicinity of the chain ends may slightly differs depending on the absolute configuration. This may be the reason why stable helix starts at different DP in the above polymerization systems. The helix with *SSS*--- configuration may be more stable than that with the opposite configuration, since the helix starts at lower DP (~ 7) and the polymerization is much faster in the systems with DDB-FlLi and PMP-FlLi than in the system with Sp-FlLi.

There exist few examples of studies on polymerization through the stereochemical investigation of each addition step of a monomer including the absolute configuration of the main chain as realized in the present study. Pino and coworkers briefly reported on such a study of polypropylene produced with an optically active zirconium catalyst.[27] The present report may be the first example of assignment of absolute configuration of the main chain of polymethacrylate, and the author could show that the polymer chains produced with the chiral initiator systems have exclusively one of *RRR*--- or *SSS*--- absolute configuration.

Summary

Asymmetric oligomerization of TrMA was carried out with the complexes of FlLi and chiral ligands in toluene at -78 °C and oligomers obtained were converted into methyl esters. The resulting oligo(MMA)s were first fractionated by gel permeation chromatography in terms of degree of polymerization and further separated into diastereomers and optical isomers by high-performance liquid chromatography. The distribution of oligomers and the ratio of isomers in each oligomer gave important information on the mechanism of the helix-sense-selective polymerization of TrMA. The reactivity of each oligomer anion depended greatly on its degree of polymerization and stereostructure. The oligomer anions whose asymmetric centers have *R* configuration in the system with Sp-FlLi and those of *S* configuration in the systems with DDB-FlLi and PMP-FlLi predominantly propagated to a one-handed helical polymer. A stable helix starts at the degree of polymerization of nine in the former system and at the degree of polymerization of seven in the latter two systems. One turn of helix seems to consist of three or four monomeric units. The main chain of the resulting polymer in the former system possessed *RRR*--- absolute configuration and that in the latter systems *SSS*---, though both the polymers are considered to be of

the same helicity, *P or M.* These results indicate that the helicity of the polymer is not governed by the configuration of main chain but by the chirality of the ligands.

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Part A: Chapter 2

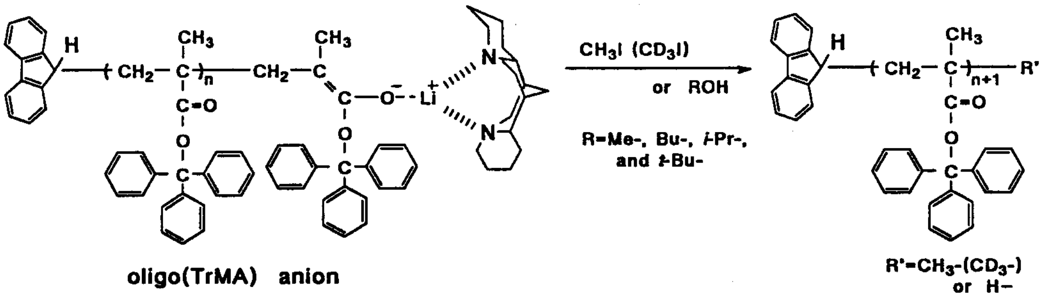
Asymmetric Oligomerization of Triphenylmethyl Methacrylate. II. The Stereochemistry of Methylation and Protonation of Oligomer Anions

A-2-1 Introduction

In Part A: Chapter 1, the author described the detailed stereochemistry of propagation in the asymmetric polymerization of triphenylmethyl methacrylate (TrMA) and also the stereochemistry of protonation reaction of oligo- and poly(TrMA) anions with methanol. In this chapter, the influence of terminating reagent on the stereochemistry of termination reaction of oligomer anions will be described. The study on termination reaction is considered to be important because the stereochemistry of termination of an oligomer anion has correlation with the nature of the anion such as its reactivity. However, in the previous studies on asymmetric polymerization of TrMA,[1] the stereochemistry of termination reaction was not examined in detail. A large numbers of studies on ω-end anion and stereochemistry of termination reaction have been reported for other polymerization systems such as those of vinylpyridines,[2] vinyl phenyl sulfoxide[3] and methyl methacrylate.[4]

The asymmetric oligomerization of TrMA with the complex of fluorenyllithium (FlLi) with (-)-sparteine (Sp) was carried out in toluene at -78°C and terminated by methylation with methyl iodide and methyl iodide-d_3 or by protonation with methanol, butanol, 2-propanol, and *t*-butanol. The resulting oligomers having a fluorenyl group at the α-end and two methyl (methyl-d_3)

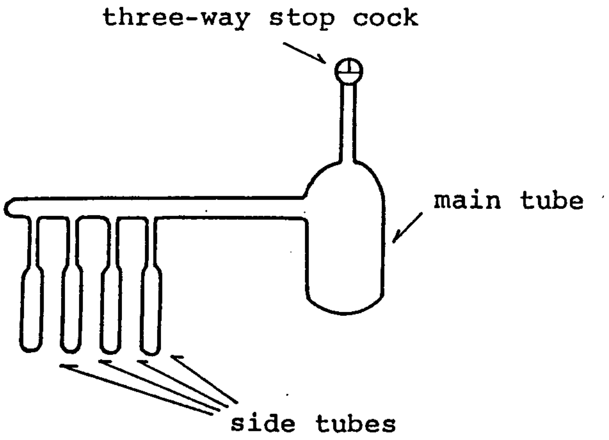
[CH_3 (CD_3)] groups or a hydrogen at the ω-end were converted into oligo(methyl methacrylate) [oligo(MMA)] and analyzed in the same manner as that described in Part A: Chapter 1.



A-2-2 Experimental Section

Materials. Methyl iodide-d_3 was purchased from Aldrich. Chem. Co.. Methyl iodide and methyl iodide-d_3 were dried over CaH_2 and distilled under high vacuum just before use. Methanol, butanol, 2-propanol, and *t*-butanol were distilled and dried over molecular sieves under dry nitrogen.

Oligomerization procedure. Oligomerization was carried out in the same manner as described in Part A: Chapter 1. In the present work, since one reaction must be terminated with plural kinds of reagents, a glass ampule attached with side tubes which is illustrated in the next page was used. The side tubes can be sealed and separated from the ampule. By using this type of reaction vessel, after the reaction completed, the reaction mixture was separated into the prescribed numbers of portions in the side tubes and then the side tubes were sealed to separate from the main ampule at -78°C. The tubes were opened under dry



nitrogen atmosphere and the terminating reagent was added to each portion in the tube at -78°C. The tube was again sealed and left 5 h at -78°C. After this procedure, the solution in the tube was allowed to warm to room temperature. The products were isolated by evaporating solvent and converted into oligo(MMA).

Measurements. ^{1}H NMR spectra were measured on a JEOL GX-500 (500 MHz) and a FX-100 (100 MHz) spectrometers. Measurements of MMA-dimer and -timer were done in $CDCl_3$ at 35°C and those of MMA-pentamer in nitrobenzene-d_5 at 110°C. Two dimensional NMR spectra of MMA-pentamer was measured under the spectral conditions described before.[5] Field-desorption (FD) mass spectra were measured on a JEOL DX-HF303 instrument.

The experimental procedures except for those described above are the same as those shown in Part A: Chapter 1.

A-2-3 Results and discussion

Stereochemistry of methylation of oligomer anions

The oligomerization of TrMA with Sp-FlLi complex was carried out at the ratio of TrMA to Sp-FlLi ([TrMA]/[Li]) 2, 3, and 5 and terminated by methyl iodide or methyl iodide-d_3. In all the reaction, IR spectra of the reaction mixtures showed no clear sign of existence of TrMA monomer indicating that the reactions were almost quantitative. The GPC curves of oligo(MMA)s derived from the obtained oligo(TrMA)s showed almost no difference from those of the oligomers terminated by methanol shown in Part A: Chapter 1. Figure A-2-1 shows the FD mass spectra of oligo(MMA)s derived from oligo(TrMA)s obtained at [TrMA]/[Li] = 3 and 5. The spectra showed peaks of M/z = 380, 480, 580, 680, 780, 880, and 980 corresponding to the oligo(MMA)s having two CH_3 groups at the ω-end, dimer, trimer, tetramer, pentamer, hexamer, heptamer, and octamer. The large peak of M/z = 274 corresponds to methyl triphenylmethyl ether produced in the process of conversion of triphenylmethyl ester into methyl ester. The peaks corresponding to the oligomers having a hydrogen at the ω-end (165+100n+1) were of much less intensity, except for tetramer obtained at [TrMA]/[Li] = 5, indicating that the methylation of oligomer anions was almost quantitative. The peaks of the series of M/z = 350, 450, 550, ···· mentioned in Part A: Chapter 1 were not observed in the spectra. A slight amount of the oligomers having a hydrogen at the ω-end may be generated by protonation of anions with proton from contaminants such as water. In Figure A-2-1 (B), only the tetramer obtained at [TrMA]/[Li] = 5 consisted of almost equal amount of those having two CH_3 groups and a hydrogen. The reactivity of tetramer anion generated at [TrMA]/[Li] = 5 with methyl iodide must be less than that of the other anions,

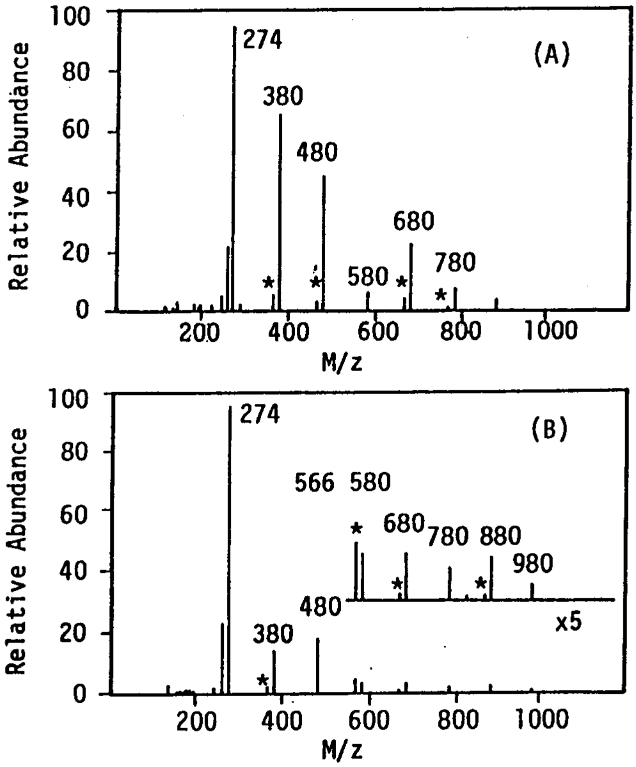


Figure A-2-1. FD mass spectra of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-FlLi at [TrMA]/[Li] =3 (A) and 5 (B) and terminated with methyl iodide. * denotes the peaks of M/z of oligo(MMA) having a hydrogen at the ω-end.

which may be brought about by its specific conformation.

Figure A-2-2 shows the chromatograms of separation of diastereomers of oligo(MMA)s derived from oligo(TrMA)s prepared at [TrMA]/[Li] = 3 and 5 and terminated with methyl iodide. Molecular weight of each fraction was determined by FD mass spectra. The assignments of tetramer are not completed. The number of asymmetric centers of the oligomers having two CH_3 groups at the ω-end is less by one than those having a hydrogen at the ω-end. The structure of oligo(MMA) having two CH_3 groups at the ω-end and numbering system of monomeric units are illustrated in Scheme A-2-1. The number of theoretically possible diastereomers is 2^{n-2} for the oligomer of DP = n (n-mer) having two CH_3 groups at the ω-end while that is 2^{n-1} for n-mer having a hydrogen at the ω-end. In the chromatograms, dimer was not fractionated because no diastereomers are possible and trimer was fractionated into two diastereomers, *meso* (*m*) and *racemo* (*r*). The oligomers of DP $\geq$ 5 prepared by termination with methanol have been found to consist mainly of two isotactic oligomers whose ω-ends have *m* and *r* configuration (Figure A-1-2 in Part A: Chapter 1). The oligomers of DP $\geq$ 5 in Figure A-2-2 (A) and (B) showed almost purely one peak for each because there is no distinction of *m* or *r* of the ω-end dyad for the isotactic oligomers. The stereostructure assignments of dimer, trimers, and pentamer terminated by methylation with methyl iodide were accomplished by ^{1}H NMR and the chemical shifts are shown in Table A-2-1. For the assignment of pentamer, two dimensional spectra were measured. The chemical shifts in NMR spectra of oligo(MMA)s having two CH_3 groups at the ω-end were rather close to those of oligo(MMA)s having a

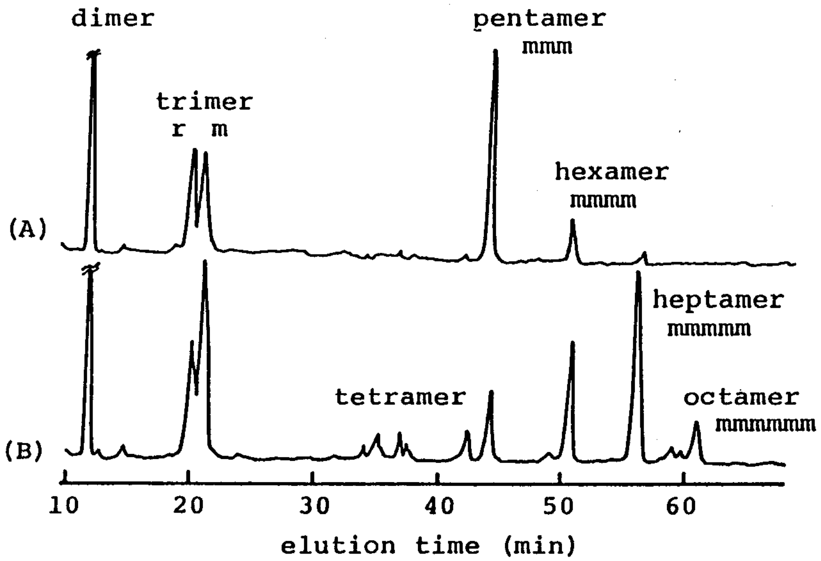
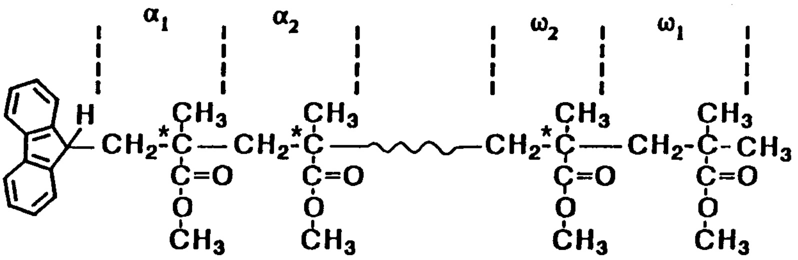


Figure A-2-2. Chromatograms of separation of diastereomers of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-FlLi at [TrMA]/[Li]=3 (A) and 5 (B) and terminated with methyl iodide.



Scheme A-2-1. Structure and numbering system of monomeric units of oligo(MMA) having two CH_3 groups at the ω-end. * denotes asymmetric centers.

Table A-2-1. ^1H NMR chemical shifts (δ, ppm) and coupling constants (Hz) of MMA-dimer, -trimer, and -pentamer having a fluorenyl group at the α-end and two CH_3 groups at the ω-end[a]

	fluorenyl	α_1		α_2		α_3		ω_2		ω_1		
	methine[b]	CH_2[c]	CH_3[d]	CH_2[e]	CH_3[d]	CH_2[e]	CH_3[d]	CH_2[e]	CH_3[d]	CH_2[d]	CH_3[d]	OCH_3[d]
dimer	3.86	2.06, 2.43	1.32							2.19, 2.21	1.21	3.65, 3.63
	(4.4, 4.4)	(14.4)								(0)	1.14	3.63
trimer												
r	3.84	2.06, 2.36	1.28	2.13, 2.25	1.17					2.07(x2)[f]	1.10	3.65, 3.64(x2)[g]
	(4.4, 4.4)	(14.4)		(14.2)						(0)	1.05	
m	3.86	2.00, 2.44	1.26	1.76, 2.33	1.16					2.09(x2)[f]	1.16	3.64(x2)[g], 3.57
	(4.9, 4.6)	(14.6)		(14.4)						(0)	1.07	
pentamer												
mmm	3.78	1.99, 2.38	1.50	1.84, 2.48	1.36	1.75, 2.38	1.34	1.65, 2.28	1.21	1.97(x2)[f]	1.11	3.66, 3.60(x2)[g]
	(4.0, 4.0)	(14.0)		(13.0)		(14.5)		(15.0)		(0)	1.07	3.58, 3.56

[a] The spectra of dimer and trimer were measured in $CDCl_3$ at 35°C (100 MHz) and that of pentamer in nitrobenzene-d_5 at 110°C (500 MHz). Aromatic protons of fluorenyl group resonated in the range of 7.2~7.7 ppm both in $CDCl_3$ and nitrobenzene-d_5 (multiplet). ^3J coupling constants between the methine proton of fluorenyl group and α_1-methylene protons and ^2J coupling constants between methylene protons are shown in parentheses below the chemical shifts of fluorenyl methine proton and those of methylene protons, respectively. The assignments of methoxy group are not completed. [b] Triplet. [c] Double-quartet. [d] Singlet or two singlets. [e] AB quartet. [f] The peak intensity was twice as large as that of one proton of a methylene group. [g] The peak intensity was twice as large as that of three protons of a methoxy group.

hydrogen at the ω-end (Tables A-1-4 and A-1-5 in Part A: Chapter 1). The obvious difference was seen only in the signals of the nonequivalent methylene protons of ω_1-monomeric unit; the methylene protons of the oligomers having two CH_3 groups at the ω-end showed no splitting. This indicates that the nonequivalency of the methylene protons of ω_1-monomeric unit is caused mainly by the chirality of the asymmetric center of ω_1-monomeric unit, though the methylene group is also neighbored by the asymmetric center of ω_2-monomeric unit.

Figure A-2-3 shows the chromatograms of optical resolution of MMA-dimers having two CH_3 groups at the ω-end obtained at [TrMA]/[Li] = 2 and 3 and Figure A-2-4 those of MMA-trimers obtained at [TrMA]/[Li] = 2, 3, and 5. These oligomers were isolated from the mixture of oligo(MMA) by GPC. The isomers of both dimer and trimer were sufficiently resolved. The assignments of the peaks were reasonably done by comparing the ratio of peak areas to the ratio of isomers of dimers and trimers obtained from the system with methanol as a terminating reagent (Tables A-1-6 and A-1-7 in Part A: Chapter 1), assuming that termination with methyl iodide does not affect the chirality of the asymmetric center except for that of the ω_1-monomeric unit as for dimer and trimer anions. The ratio of *R* isomer to *S* isomer of the dimer and the content of *RR*, *SS*, *SR* and *RS* of the trimer well agreed with those of the dimer and trimer having a hydrogen at the ω-end at all the [TrMA]/[Li] ratios which are shown in Part A: Chapter 1. This indicates that the above assumption is valid.

In order to get information on the stereochemistry of methylation of dimer anion, the ^{1}H NMR spectra of MMA-dimers having

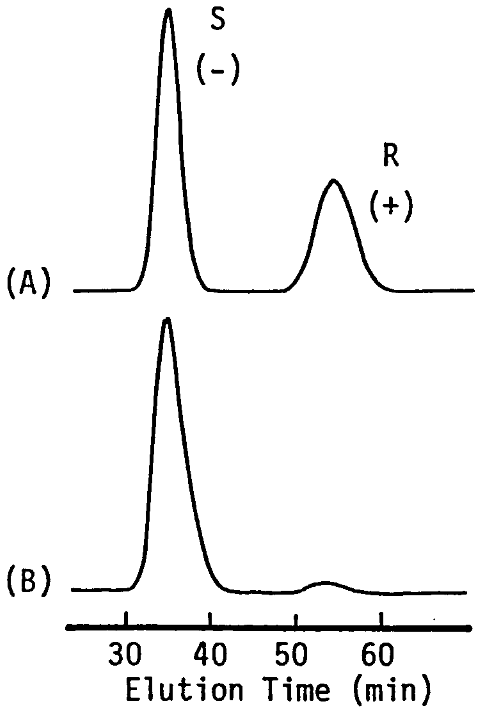


Figure A-2-3. Chromatograms of optical resolution of MMA-dimer derived from TrMA-dimer prepared with Sp-FlLi at [TrMA]/[Li]=2 (A) and 3 (B) and terminated with methyl iodide.

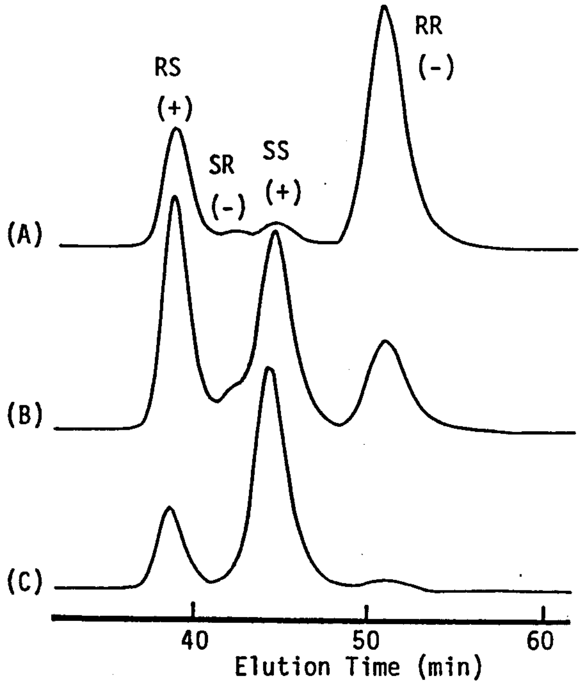


Figure A-2-4. Chromatograms of optical resolution of MMA-trimer derived from TrMA-trimer prepared with Sp-FlLi at [TrMA]/[Li]=2 (A) and 3 (B) and terminated with methyl iodide.

two CH_3 groups and one CH_3 and one CD_3 groups, one of which was introduced by methylation, prepared with methyl iodide and methyl iodide-d_3 as terminating reagents, respectively, at [TrMA]/[Li] = 2 were measured in $CDCl_3$. Figure A-2-5 shows the spectra. In the spectrum of MMA-dimer having two CH_3 groups at the ω-end (Figure A-2-5 (A)), three methyl peaks of equal intensity were observed. The peak resonating in the lower magnetic field (~1.2 ppm) was assigned to that of CH_3 protons of the α_1-monomeric unit since the chemical shift was close to those of the α_1-CH_3 groups of the MMA-dimers *m* and *r* having a hydrogen at the ω-end (Table A-1-5 in Part A: Chapter 1). The other two peaks were ascribed to CH_3 groups of the ω_1-monomeric unit, one of which should be the α-CH_3 group originated from the methacrylic unit and the other should be introduced by termination reaction. The separated peaks of ω-end CH_3 groups mean that these two CH_3 groups are spectroscopically diastereotopic by the existence of the asymmetric center of α_1-monomeric unit. On the basis of the fact that the CH_3 group of the ω_1-monomeric unit of MMA-dimer *m* having a hydrogen at the ω-end resonates in higher field than that of *r* dimer, the two peaks of the methyl group were assigned as follows; the one resonating in higher field is due to a CH_3 group located in a position of a magnetic environment similar to that of ω_1-CH_3 group of MMA-dimer *m* having a hydrogen at the ω-end ("*meso*-like" position) and the other is due to a CH_3 group in an environment similar to that of dimer *r* having a hydrogen ("*racemo*-like" position).

The stereospecificity of methylation of the oligomer anion was examined by methylation with methyl iodide-d_3 according to

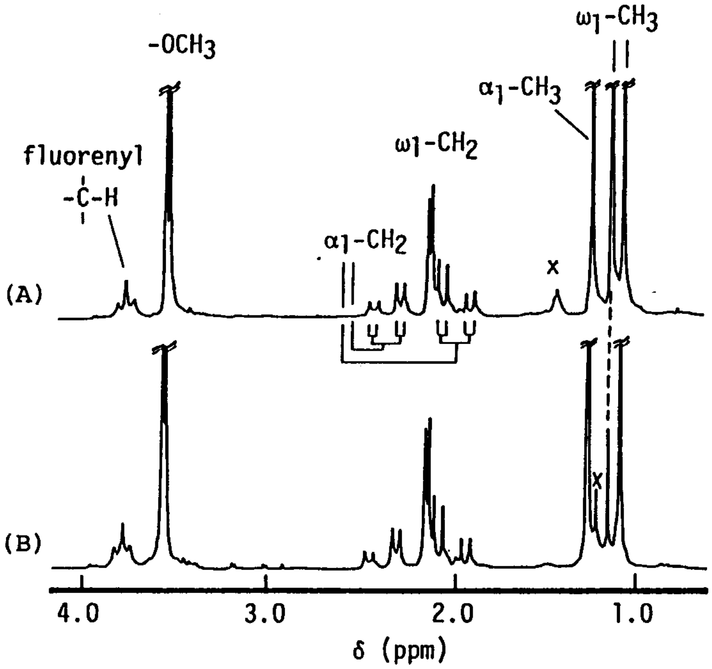


Figure A-2-5. 100 MHz ^1H NMR spectra of MMA-dimer derived from TrMA-dimer prepared with Sp-FlLi at [TrMA]/[Li]=2 and terminated with methyl iodide (A) and methyl iodide $-d_3$ (B). ($CDCl_3$, 35°C, TMS).

the above NMR assignments. In the spectrum of the dimer produced by termination with methyl iodide-d_3 (Figure A-2-5 (B)), the methyl signal due to ω_1-CH_3 group in "*racemo*-like" position was much smaller than that due to ω_1-CH_3 group in "*meso*-like" position. This indicates that methylation of dimer anion by methyl iodide-d_3 occurred selectively in the side of "*racemo*-like" position to make the ω_1-CH_3 group originated in the methacrylic unit be located in "*meso*-like" position in the same manner of making *m* dyad sequence in the ω-end by the attack of TrMA monomer to the dimer anion. This is contrast to the predominance of *r* isomer over *m* isomer in the dimer produced by termination with methanol in most cases. The intensity ratio of the "*racemo*-like" ω_1-CH_3 signal to the "*meso*-like" ω_1-CH_3 signal in Figure A-2-5 (B) implies that the stereospecificity is 2:8.

Stereochemistry of protonation of oligomer anions

In order to elucidate the influence of a protonating reagent on the stereochemistry of protonation of oligomer anions, oligomerization of TrMA was carried out at [TrMA]/[Li] = 2, 3, and 5 and terminated with methanol, butanol, 2-propanol, and *t*-butanol. The GPC curves of the oligo(MMA)s derived from oligo(TrMA)s obtained in the three systems with butanol, 2-propanol, and *t*-butanol at all [TrMA]/[Li] ratios were identical to that of the oligo(MMA) obtained from the system with methanol as a terminating reagent. The difference of terminating alcohol did not affect the oligomer distribution with respect to DP. Then, the oligomers were separated into stereoisomers by HPLC experiments. The oligomer anions are denoted as ---R^- and ---S^- in this thesis, because the ω-end configuration is determined by protonation.

The MMA-dimers derived from TrMA-dimers obtained at [TrMA]/[Li] = 2 were optically resolved by chiral HPLC in the same manner described in Part A: Chapter 1. In the present system, *R*-$^-$ and *S*-$^-$ dimer anions are regarded as diastereomers since they are the complexes of Sp. The ratio of the four isomers (*SS, RR, RS, SR*) and e.e. (%) of the asymmetric carbon of α_1-monomeric unit and that of ω_1-monomeric unit of the dimer are summarized in Table A-2-2. The ratio of the four isomers in the system with methanol is slightly different from that in Table A-1-6 in Part A: Chapter 1, though the two experiments were conducted under the same reaction conditions. The discrepancy may be caused by the slight difference of [TrMA]/[Li] ratio in the two experiments. Though the content of four isomers changed with the protonating alcohol, e.e. value of the asymmetric carbon of α_1-monomeric unit was almost constant in the termination with different alcohols. This indicates that protonation did not induced racemization of the α_1-asymmetric carbon of dimer anion. As the bulkiness of the alcohol increased, the content of *SR* isomer decreased and that of *SS* isomer increased by the same amount. On the other hand, almost no change was observed in the content of *RR* and *RS* isomers. This indicates that the bulkiness of the alcohols influences the stereochemistry of protonation of only *S*-$^-$ isomeric anion which has been found to be less reactive compared to *R*-$^-$ anion in the early stage of polymerization (Part A: Chapter 1). Protonation with a bulkier alcohol tends to produce *S* configuration at the ω-end.

Table A-2-2. The ratio of four isomers of MMA-dimer derived from TrMA-dimer prepared with Sp-FlLi at [TrMA]/[Li] = 2 and terminated by methanol, butanol, 2-propanol, and *t*-butanol[a]

Alcohol	Four isomers (%)				e.e. (%)[b]	
	meso		*racemo*			
	SS(+)	*RR*(−)	*RS*(+)	*SR*(−)	α_1-C[c]	ω_1-C[d]
Methanol	14	3	29	54	36	-15
Butanol	16	3	29	52	36	-10
2-Propanol	19	3	29	49	36	-4
t-Butanol	29	3	30	38	34	18

[a] Determined by HPLC optical resolution detected at 254 nm. The whole dimer was separated from the mixture of oligo(MMA) by GPC.

[b] Excess in *S* configuration.

[c] The asymmetric center of α_1-monomeric unit.

[d] The asymmetric center of ω_1-monomeric unit.

The MMA-trimers derived from TrMA-trimers obtained at [TrMA]/[Li] = 3 were also optically resolved and the ratios of eight isomers and e.e. of the three asymmetric centers of the trimers are summarized in Table A-2-3. Similarly to the ratio of four isomers of dimer mentioned above, the ratio of eight isomers in the system with methanol is slightly different from that in Table A-1-7 in Part A: Chapter 1. E.e. values of the asymmetric centers of the α_1- and α_2-monomeric units were almost constant, proving again that the protonation by alcohols does not affect the configuration of the asymmetric center except for that of the ω_1-monomeric unit. The obvious change in the content of isomers was observed for the pair of *SSS* and *SSR* produced from *SS*-$^-$ trimer anion and for that of *RSS* and *RSR* produced from *RS*-$^-$ trimer anion. The *SS*-$^-$ and *RS*-$^-$ anions have been found to be the less reactive anions in the reaction with TrMA monomer in propagation (Part A: Chapter 1). For these isomeric anions, protonation producing *S* configuration at the ω-end tends to occur when a bulky alcohol was used. These results indicate that the less reactive dimer and trimer anions in the propagation are more sensitive to the structure of alcohols in the protonation than the anions predominantly reacting with TrMA monomer probably because the less reactive anions are more sterically hindered.

The protonation stereochemistry of the isotactic oligomer anions of DP = 5 ~ 8 was also examined. The diastereomers of oligo(MMA)s derived from oligo(TrMA)s prepared at [TrMA]/[Li] = 5 and terminated by the four alcohols were separated by HPLC using a silica gel column. In this system, the isotactic isomers which are the predominant diastereomers of the oligomers of DP = 5 ~ 8

Table A-2-3. The ratio of eight isomers of MMA-trimer derived from TrMA-trimer prepared with Sp-FlLi at [TrMA]/[Li] = 3 and terminated by methanol, butanol, 2-propanol, and *t*-butanol[a]

	Eight Isomers (%)										
Alcohol	*mm*		*rm*		*rr*		*mr*		e.e. (%)[b]		
	SSS(+)	*RRR*(-)	*SRR*(-)	*RSS*(+)	*SRS*(+)	*RSR*(-)	*RRS*(+)	*SSR*(-)	α_1-C[c]	α_2-C[d]	ω_1-C[e]
Methanol	4	5	1	4	5	26	27	28	-24	24	-20
Butanol	6	8	1	6	6	25	23	25	-24	24	-18
2-Propanol	11	8	1	7	5	23	24	21	-24	24	-6
t-Butanol	15	2	0	11	8	22	28	14	-22	24	24

[a] Calculated from the content of diastereomers and that of enantiomer in each diastereomer which were determined by HPLC separation detected at 254 nm.

[b] Excess in *S* configuration.

[c] The asymmetric center of α_1-monomeric unit.

[d] The asymmetric center of α_2-monomeric unit.

[e] The asymmetric center of ω_1-monomeric unit.

have been found to consist of almost purely one antipode of enantiomers whose chiral centers of the main chain have *R* configuration, except for the hexamer *mmmmr*; hexamer *mmmmr* consisted of 52% of *RRRRRS* isomer and 48% of *SSSSSR* isomer in the system with methanol as a terminating reagent (Table A-1-8 in Part A: Chapter 1). The ratio of the diastereomers of dimer and trimer and that of the isotactic oligomers of DP = 5 ~ 8 whose ω-ends have *m* and *r* configuration are summarized in Table A-2-4. Also at [TrMA]/[Li] = 5, the contents of *m* dimer and *rm*+*mm* trimers increased with the increasing bulkiness of the alcohol. In contrast to this, as for the pentamer, heptamer, and octamer, the fraction of the isotactic oligomers whose ω-ends have *r* configuration increased with the increasing bulkiness of the alcohol and this tendency is more clear for octamer than for pentamer and heptamer. These results indicate that protonation of *RRR*--- isotactic pentamer, heptamer, and octamer anions tends to be in *r* fashion producing *S* configuration at the ω-end when a bulky alcohol was used. On the other hand, the ratio of *mmmmm* and *mmmmr* in the hexamer did not show clear tendency of increase or decrease with changing bulkiness of alcohols. This suggests two probabilities; one is that hexamer anion is not sensitive to the stereostructure of protonating reagent and the other is that the change of protonation mode (*m* or *r*) of *RRRRR*-$^-$ hexamer anion is opposite to that of *SSSSS*-$^-$ hexamer anion to result in no obvious change of the ratio of *mmmmm* to *mmmmr*. Assuming that the latter is more plausible, *SSSSS*-$^-$ anion must be more sensitive to the stereostructure of alcohols in protonation because the amount of *RRRRR*-$^-$ anion is much larger than that of *SSSSS*-$^-$ anion. The

Table A-2-4. The ratios of diastereomers of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-FlLi at [TrMA]/[Li] = 5 and terminated by methanol, butanol, 2-propanol, and *t*-butanol[a]

Alcohol	Dimer	Trimer	Pentamer	Hexamer	Heptamer	Octamer
	m / *r*	*mm*+*rm* / *rr*+*mr*	*mmmm* / *mmmr*	*mmmmm* / *mmmmr*	*mmmmmm* / *mmmmmr*	*mmmmmmm* / *mmmmmmr*
Methanol	22 / 78	16 / 84	58 / 42	59 / 41	75 / 25	80 / 20
Butanol	32 / 68	14 / 86	55 / 45	55 / 45	64 / 36	61 / 39
2-Propanol	42 / 58	39 / 61	50 / 50	60 / 40	53 / 47	49 / 51
t-Butanol	45 / 55	54 / 46	36 / 64	56 / 44	44 / 56	30 / 70

[a] Determined by HPLC analysis detected at 254 nm.

ratio of the amount of *RRRRR*-$^-$ anion to that of *SSSSS*-$^-$ anion in the present system is estimated to be 8:2 from the ratio of *mmmmm* hexamer to *mmmmr* hexamer produced in the termination with methanol shown in Table A-2-4 and the ratio of enantiomers in each diastereomer of hexamer at [TrMA]/[Li] = 5 shown in Table A-1-8 in Part A: Chapter 1. *SSSSS*-$^-$ anion which was found to be less reactive in propagation (Part A: Chapter 1) may be more sterically hindered similarly to the less reactive dimer and trimer anions mentioned above.

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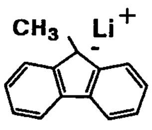
Part A: Chapter 3

Asymmetric Oligomerization of Triphenylmethyl Methacrylate. III. Influence of Initiators on the Stereochemistry of Propagation

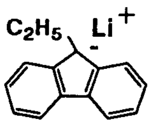
A-3-1 Introduction

The detailed mechanism of the asymmetric oligomerization of triphenylmethyl methacrylate (TrMA) initiated by the complexes of fluorenyllithium (FlLi) with chiral ligands and the stereochemistry of termination reaction of oligomer anions were described in the preceding chapters. Chiral ligands and terminating reagents greatly affected the stereochemistry of propagation and termination, respectively. In this chapter, in order to elucidate the influence of stereostructure of organolithium compounds on the stereochemistry of propagation, oligomerization of TrMA with the complexes of 9-alkyl derivatives of FlLi and (-)-sparteine (Sp) was examined. A 9-alkylfluorenyl group attached to the α-end of an oligomer anion should greatly affect its reactivity with TrMA monomer and the stereochemistry of propagation through steric effect at least in early stage of the oligomerization.

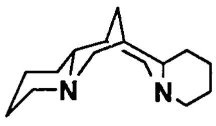
The asymmetric oligomerization of TrMA was carried out with the complexes of 9-methyl-9-fluorenyllithium (MeFlLi) and 9-ethyl-9-fluorenyllithium (EtFlLi) with Sp in toluene at -78°C and terminated with methanol. The resulting oligomers with a 9-



MeFlLi



EtFlLi



Sp

methylfluorenyl and a 9-ethylfluorenyl groups at the α-end and a hydrogen at the ω-end were converted into methyl ester [oligo(MMA)] and analyzed in the same manner as described in Part A: Chapter 1. On the basis of the results of the analyses, the influence of the substituents at 9-position of FlLi on the stereochemistry of propagation was discussed. Wulff and coworkers also reported on the asymmetric oligomerization of TrMA with Sp-complexes of 1,1-diphenylhexyllithium (DPHLi)[1] and diphenylmethyllithium (DPMLi).[2]

A-3-2 Experimental Section

Materials. 9-Ethylfluorene (Aldrich) was dried over CaH_2 and distilled under reduced pressure; b.p. 123-124°C (1 mmHg).

9-Methylfluorene was prepared by the reaction with 9-fluorenyllithium and methyl iodide. Fluorene (10.64 g, 64.1 mmol) was dissolved in 120 ml of THF under dry nitrogen atmosphere in a round-bottomed flask equipped with a three-way stopcock and cooled to -78°C. *n*-BuLi (49.1 ml, 1.37 M in hexane solution) and then freshly distilled methyl iodide (5.00 ml, 101 mmol) were added to the solution by a hypodermic syringe with gentle stirring. Then, the solvents were evaporated under high vacuum and the residue was extracted with a mixture of hexane and diethyl ether (1/1 v/v). After the solution was washed with water, the solvents were removed to give 11.4 g (99% yield) of crude product. The crude product was analyzed by ^1H NMR spectroscopy with a JNM MH-100 (100 MHz) spectrometer and by HPLC with a JASCO BIP-I chromatograph, a JASCO Multi-320 UV detector (254 nm), and a column (25 x 0.46 (i.d.) cm) packed with cellulose tris(3,5-dimethylphenylcarbamate)-coated macroporous silica gel[3] using a mixture of hexane and 2-propanol (99/1 v/v) as an eluent (flow rate 0.5 ml/min). Three compounds were found by the analyses of the crude products; 9-methylfluorene 95%, 9,9-dimethylfluorene 3%, and unreacted fluorene 2% which eluted at 12.2 min, 14.4 min, and 16.7 min, respectively, in the HPLC experiment. The product was purified by recrystallization first from methanol and then five times from hexane to give 2.10 g (18.20%) of white crystal; purity 100 % (HPLC), m.p. 46.2-46.8°C. ^{1}H NMR (100 MHz, $CDCl_3$, 60°C, TMS) δ 7.2-8.0(m, 8H, aromatic H), 3.98(q, 1H, CH), 1.48(d, 3H, CH_3). Anal. Calcd for $C_{14}H_{12}$: C, 93.29%; H, 6.71%. Found: C, 93.36%; H, 6.64%.

Measurements. ^{1}H NMR was measured on a JEOL GSX-270 (270 MHz) spectrometer. Field desorption (FD) mass spectrum was measured on a JEOL DX-HF303 instrument. Optical rotation was measured with a JASCO DIP-181 polarimeter.

The chromatographic experiments were done with the same instruments described in Part A: Chapter 1. Columns used and chromatographic conditions are described below. For separation by gel permeation chromatography (GPC) of the oligomers obtained in the system with Sp-MeFlLi, two Shodex Gel-101 columns (50 x 0.72 (i.d.) cm, maximum porosity: 3000) connected in series were used with $CHCl_3$ as an eluent (flow rate 0.5 ml/min). For the GPC separation of oligomers obtained in the system with Sp-EtFlLi, a Shodex Gel-101 column was used with $CHCl_3$ as an eluent (flow rate 0.5 ml/min). For separation of diastereomers, columns (25 x 0.46 (i.d.) cm, 50 x 0.72 (i.d.) cm) packed with silica gel were used with a mixture of butyl chloride (BuCl) and CH_3CN as an eluent in a programmed ratio; from 95% BuCl to 50% BuCl during 60-min period (flow rates 0.5 ml/min for the former column and 2.4 ml/min for the latter one). Optical resolution of oligo(MMA)s was done with chiral HPLC columns (25 x 0.46 (i.d.) cm) with hexane-alcohol eluting system (flow rate 0.5 ml/min).[3] For the optical resolution of MMA-dimers having a 9-methylfluorenyl group and a 9-ethylfluorenyl group at the α-end was done by using a column packed with cellulose tris(3,5-dichlorophenylcarbamate)-coated macroporous silica gel[3] eluted with a mixture of hexane and 2-propanol (95/5 v/v). For the optical resolution of MMA-trimers having a 9-methylfluorenyl group and a 9-ethylfluorenyl group at the α-end, a column packed with cellulose tris(3,5-dimethylphenylcarbamate)-coated macroporous silica gel[3] was used with a mixture of hexane and 2-propanol (95/5 v/v) as an eluent.

The experimental procedures except for those described above are the same as those shown in Part A: Chapter 1.

A-3-3 Results and discussion

Asymmetric polymerization with Sp-MeFlLi and Sp-EtFlLi complexes

The results of asymmetric polymerization of TrMA with Sp-MeFlLi and Sp-EtFlLi complexes in toluene at -78°C are shown in Table A-3-1 with the data of the polymerization with Sp-FlLi. In both the systems with Sp-MeFlLi and Sp-EtFlLi, the polymer was obtained almost quantitatively. The product in the system with Sp-MeFlLi was fractionated with a mixture of benzene and hexane (1/1 v/v) to remove oligomers.[4c] This fractionation could not be

Table A-3-1. Asymmetric anionic polymerization of TrMA with Sp-MeFlLi, Sp-EtFlLi, and Sp-FlLi complexes in toluene at -78°C for 24 hr[a]

Initiator	Yield[b] (%)	B/H[c]-insoluble part				
		Yield(%)	DP[d]	Mw/Mn[d]	Tacticity(%)[e] *mm*	$[\alpha]_D^{25}$
Sp-MeFlLi	100	57	112	1.67	>99	+360°[f]
Sp-EtFlLi	100	—	118[g]	1.82[g]	>99[g]	—
Sp-FlLi	99	82	60	1.31	>99	+383°

[a] TrMA 1.0 g (3.05 mmol), toluene 20 ml, [TrMA]/[Li] = 20.

[b] Methanol-insoluble part.

[c] A mixture of benzene and hexane (1/1 v/v).

[d] Determined by GPC of poly(MMA)s derived from poly(TrMA)s.

[e] Determined by ^1H NMR of poly(MMA)s derived from poly(TrMA)s.

[f] c 0.5, a mixture of THF and CH_2Br_2 (1/5 v/v).

[g] The poly(MMA) used for GPC and ^1H NMR measurements was derived from the whole of poly(TrMA).

done for the product obtained with Sp-EtFlLi as it was insoluble in solvents. The insolubility may be caused by aggregation of the polymer of high degree of polymerization (DP).[5] The benzene-hexane insoluble polymer obtained in the system with Sp-MeFlLi showed high optical activity of positive sign which was comparable to that of the poly(TrMA) obtained with Sp-FlLi. Though the specific rotation of the polymer obtained in the system with Sp-EtFlLi could not be precisely determined because of the existence of insoluble part in the mixture of THF and CH_2Br_2, the soluble part showed positive optical rotation. The both polymers were highly isotactic. These results indicate that these complexes afforded a one-handed helical polymer similarly to the other Sp complexes.[1,4] However, the degree of polymerization (DP) of the polymer obtained with Sp-MeFlLi and Sp-EtFlLi and the content of benzene-hexane soluble oligomer were much higher than those in the system with Sp-FlLi, suggesting that the substituent group at the 9-position affected the stereochemistry of propagation in the early stage of polymerization and larger amounts of the propagating species of relatively low activity were produced in these systems.

Distribution of oligomers

In all the cases of the oligomerization, IR spectra of the reaction mixture showed no clear sign of the existence of unreacted TrMA monomer, suggesting that the reaction was almost quantitative. Figure A-3-1 shows the GPC curves of oligo(MMA)s derived from oligo(TrMA)s obtained with Sp-MeFlLi at [TrMA]/[Li] = 2, 3, and 5 and Figure A-3-2 those of oligo(MMA)s derived from

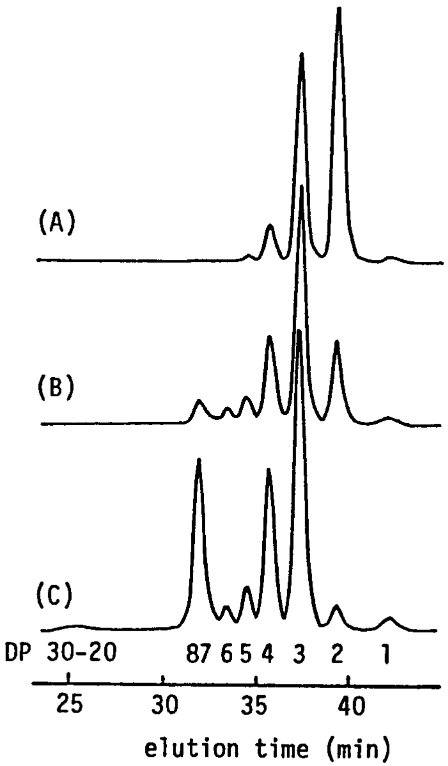
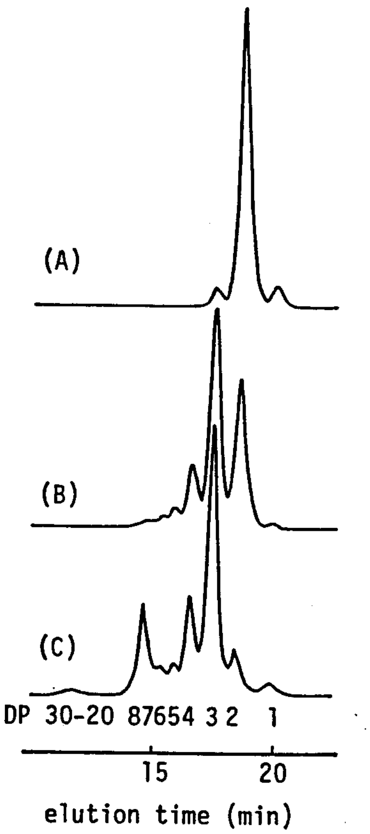


Figure A-3-1. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-MeFlLi at [TrMA]/[Li]=2 (A), 3 (B), and 5 (C).



Figrue A-3-2. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-EtFlLi at [TrMA]/[Li]=2 (A), 3 (B), and 5 (C).

oligo(TrMA)s obtained in the system with Sp-EtFlLi. The GPC curves of the original oligo(TrMA)s were of similar pattern to the corresponding oligo(MMA)s. The assignment of the peaks were done by comparing the GPC curves with the FD mass spectrum of the oligo(MMA)s. The mass spectrum of oligo(MMA) obtained with Sp-MeFlLi at [TrMA]/[Li] = 5 showed peaks of M/z = 280, 380, 480, 580, 680, 780, 881, 981, and 1081 and that of oligo(MMA) obtained with Sp-EtFlLi peaks of M/z = 294, 394, 595, 695, 795, 895, 995, and 1095 corresponding to the molecular weight of oligomers (DP = 1-9), and the intensity ratios of these peaks were similar to those of the peaks in the GPC curves. In the both spectra, no peaks of the series of M/z = 350, 450, 550, ···· which were observed as minor components in the spectra of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-FlLi (Part A: Chapter 1).

In the system with Sp-FlLi, the existence of unimer was not obvious, indicating that the unimer anion is much more reactive than dimer anion and Sp-FlLi complex. In contrast to this, the existence of unimer was clear in the systems with Sp-MeFlLi and Sp-EtFlLi at all the [TrMA]/[Li] ratios. The activity of the unimer anion having a 9-substituted fluorenyl group at the α-end should be relatively lower than that having a fluorenyl group. Although, the oligomer distributions at [TrMA]/[Li] = 3 and 5 were rather similar in the two systems with Sp-MeFlLi and Sp-EtFlLi, those at [TrMA]/[Li] = 2 showed a clear difference. In the system with Sp-MeFlLi, the amounts of trimer and higher oligomers were much higher than that in the system with Sp-EtFl-Li, suggesting that the activity of dimer anion in the system with Sp-MeFlLi may be higher than that in the system with Sp-EtFlLi. The distributions at [TrMA]/[Li] = 3 in both systems were much different from that in the system with Sp-FlLi. The relative amount of tetramer was rather higher and the existence of oligomers of DP = 6~8 was clearer in the systems with Sp-MeFlLi and Sp-EtFlLi than in the system with Sp-FlLi. Also at [TrMA]/[Li] = 5, the content of tetramer was higher than in the system with Sp-FlLi. The content of tetramer is reported to be relatively higher in the system with Sp-DPHLi[1] than that in the system with Sp-FlLi, while in the system with Sp-DPMLi[2] the content of the tetramer was lower similarly to the system with Sp-FlLi. The irregularity of distribution similar to that in the system with Sp-FlLi was again observed in these systems at [TrMA]/[Li] = 5. Although in both the systems with Sp-MeFlLi and Sp-EtFlLi at [TrMA]/[Li] = 5, the oligomers of DP < 9 were detected in addition to a small amount of polymer (DP = 20~30), the intermediate oligomers were not clearly observed. The small amount of polymers showed high positive rotation in the GPC analysis of the original oligo(TrMA) with polarimetric detection. These results indicate that the reactivity of each oligomer anion depends on its DP and a stable helix starts at DP ~ 9 as well as in the system with Sp-FlLi.

Separation of diastereomers

The diastereomers of oligo(MMA)s were separated by HPLC using a silica gel column. Figure A-3-3 shows the chromatograms of separation of diastereomers of the oligo(MMA)s derived from oligo(TrMA) obtained with Sp-MeFlLi and Sp-EtFlLi at [TrMA]/[Li]

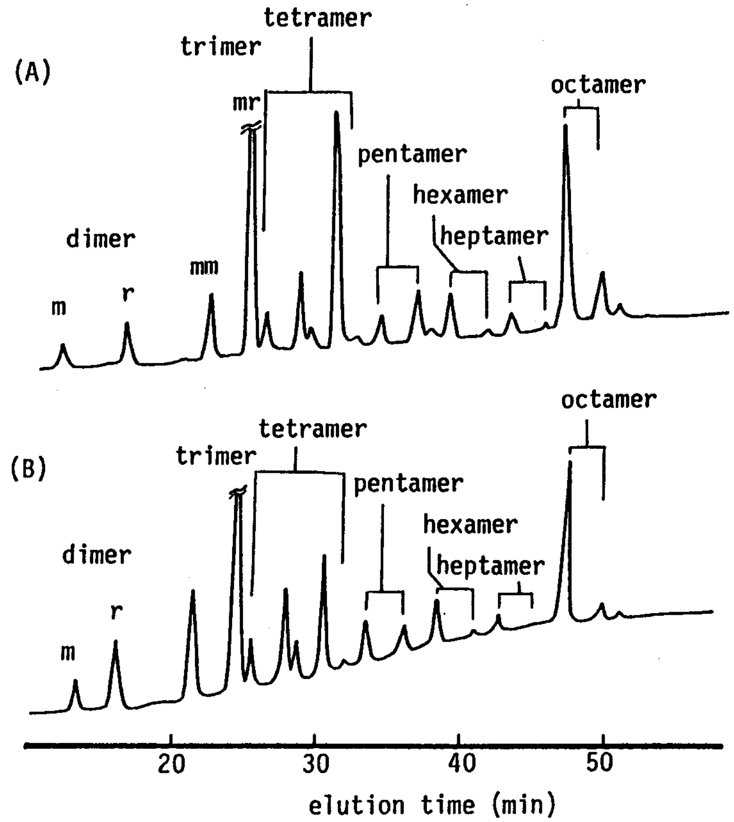
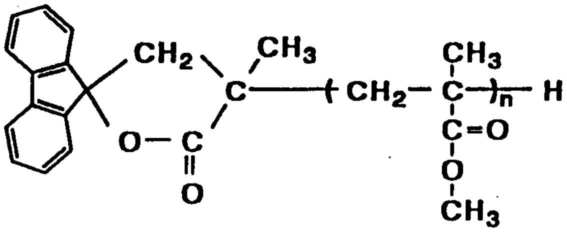


Figure A-3-3. Chromatograms of separation of diastereomers of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-MeFlLi (A) and Sp-EtFlLi (B) at [TrMA]/[Li]=5.

= 5. The molecular weight of the oligomers corresponding to each fraction was determined by FD mass spectrum. In both systems, dimer consisted of two fractions, trimer two main fractions, tetramer two main fractions and two minor fractions, and the each oligomer of DP $\geq$ 5 two main fractions. In the chromatograms, no peaks of the oligomers of unknown structure which were observed in the analysis of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp-FlLi (Part A: Chapter 1) were observed. This suggests that the unknown oligomers may have a structure as shown in Scheme A-3-1. The structure corresponds to M/z = 350, 450, 550, ····· in the FD mass. Such a structure is impossible to the oligomers produced with the present initiator systems. The stereostructure of the MMA-dimers and -trimers obtained with Sp-MeFlLi and that of the dimers obtained with Sp-EtFlLi were confirmed by ^{1}H NMR spectroscopic analysis. Although, the structure of the trimer obtained with Sp-EtFlLi was not determined by NMR spectrum, the two main fractions may be assigned to *mm* and *mr* isomers as the pattern of the separation in Figure A-3-3 (B) was almost the same as that in Figure A-3-3 (A). The assignment of



Scheme A-3-1. Structure of oligo(MMA) which corresponds to M/z = 350, 450, 550 ····· in FD mass spectrum.

the other oligomers in Figure A-3-3 can be estimated on the basis on the analogy between the chromatograms in the figure and those of oligo(MMA) in the system with Sp-FlLi (Figure A-1-2 in Part A: Chapter 1) where the oligomers of DP $\geq$ 5 consisted mainly of isotactic ones and also can be estimated on the basis of the fact that the highly isotactic polymers are produced in these systems. Similarly to these assignments, the two main components of the oligomers of DP $\geq$ 4 were assigned to the isotactic oligomers whose ω-ends have *m* and *r* configuration.

As for the trimer, *rr* and *rm* isomers were not obviously found in both the systems with Sp-MeFlLi and Sp-EtFlLi at all the [TrMA]/[Li] ratios, suggesting that the formation of *m* sequence at the α-end may be highly favored in the propagation of dimer anion to trimer anion. Though, tetramer in the system with Sp-FlLi consisted of many diastereomers which were not assigned, in the present systems the tetramer consisted of two main components which are considered to be the isotactic ones similarly to the other oligomers of DP $\geq$ 5. This suggests that the propagation stereochemistry in the step of trimer anion to tetramer anion in the present systems may different from that in the system with Sp-FlLi. Wullf and coworkers reported that in the system with Sp-DPHLi, tetramer consisted of 48~53% of *mmmm* isomer and 47~52% of *mmmr* isomer.[1] The propagation stereochemistry in the step of trimer anion to tetramer anion in the system with Sp-DPHLi may be similar to the present systems. Probably the tertiary alkyllithium compounds (MeFlLi, EtFlLi, and DPHLi) may have similar steric effect on the propagation stereochemistry of the oligomer anions of low DP.

Stereochemistry of protonation of oligomer anions

The ratios of the diastereomers in each oligomer obtained at [TrMA]/[Li] = 2, 3, and 5 are summarized in Table A-3-2. For most isomers of dimer, trimer, pentamer, and higher oligomers at all the [TrMA]/[Li] ratios in both systems, the ratio of the isomer having *m* ω-end configuration to that having *r* ω-end configuration was similar to that in the system with Sp-FlLi. The stereochemistry of protonation does not seem to be affected by the substituent group at the α-end. The exception was pentamer at [TrMA]/[Li] = 5 in the system with Sp-MeFlLi; *r*-protonation predominated for the pentamer. This is contrast to the predominance of *m*-protonation for the pentamer anion in the system with Sp-FlLi at [TrMA]/[Li] = 5 (Table A-1-2 in Part A: Chapter 1). It was revealed in Part A: Chapter 1 that in the system with Sp-FlLi, the stereospecificity of protonation of isotactic pentamer and the higher isotactic oligomer anions depended on the absolute configuration of the main chain; *m*-protonation was major for the isomeric anion of *RRR*--- configuration and *r*-protonation was major for the isomeric anion of *SSS*--- configuration (Table A-1-9 in Part A: Chapter 1). Probably the pentamer anion in the system with Sp-MeFlLi at [TrMA]/[Li] = 5 may contain a higher amount of *SSSS*-$^-$ anion than that in the system with Sp-FlLi.

As for tetramer anion in the system with Sp-MeFlLi, *r*-protonation increased with [TrMA]/[Li] ratio and became major at [TrMA]/[Li] = 3 and 5 and also as for tetramer anion in the system with Sp-EtFlLi, *r*-protonation was slightly predominant and slightly increased with [TrMA]/[Li] ratio. Although no informa-

Table A-3-2. The ratios of *m* to *r* of MMA-dimer, *mm* to *mr* of MMA-trimer, and isotactic oligo(MMA) of *m* ω-end configuration to that of *r* ω-configuration derived from oligo(TrMA)s obtained with Sp-MeFlLi and Sp-EtFlLi at [TrMA]/[Li] = 2, 3, and 5[a]

Initiator	[TrMA]/[Li]	Dimer	Trimer	Tetramer	Pentamer	Hexamer	Heptamer	Octamer
		m / *r*	*mm* / *mr*[b]	*mmm* / *mmr*	*mmmm* / *mmmr*	*mmmmm* / *mmmmr*	*mmmmmm* / *mmmmmr*	*mmmmmmm* / *mmmmmmr*
Sp-MeFlLi	2	17 / 83	18 / 82	61 / 39	——[c]	——[c]	——[c]	——[c]
	3	28 / 72	15 / 85	42 / 58	61 / 39	78 / 22	68 / 32	79 / 21
	5	31 / 69	10 / 90	20 / 80	36 / 65	86 / 14	78 / 22	86 / 14
Sp-EtFlLi	2	10 / 90	21 / 79	——[c]	——[c]	——[c]	——[c]	——[c]
	3	22 / 78	15 / 85	49 / 51	61 / 39	73 / 27	58 / 42	70 / 30
	5	38 / 62	17 / 82	46 / 54	54 / 46	74 / 26	64 / 36	87 / 13

[a] Determined by HPLC analysis detected at 254 nm.

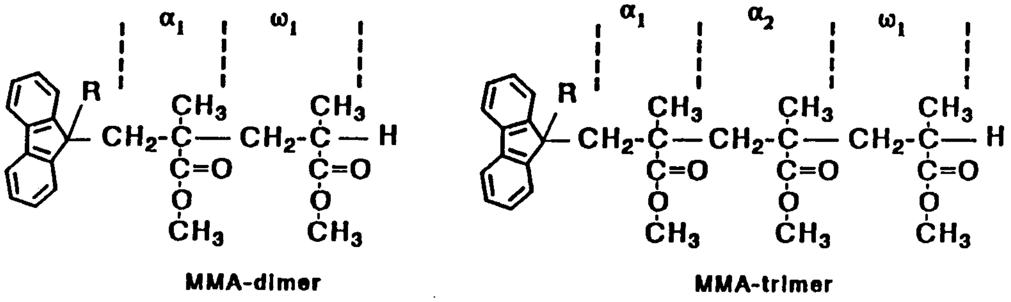
[b] Other isomers, *rr* and *rm*, were not obviously found in the HPLC separation and ^{1}H NMR analysis.

[c] Not obviously detected.

tion was obtained about the protonation stereochemistry of tetramer anion generated with Sp-FlLi in Part A: Chapter 1, the predominance of *r*-protonation of tetramer anion in the present systems may also be explained by assuming that the dependence of protonation stereochemistry on the absolute configuration of the main chain above mentioned is applicable also to the tetramer anion. The tetramer anions in the present systems may contain a significant amount of *SSS*-$^-$ anion and its amount may increase with the increase of [TrMA]/[Li] ratio.

Structure of MMA-dimer and -trimer

The ^{1}H NMR chemical shifts and coupling constants are summarized in Table A-3-3 and the numbering systems of monomeric units for MMA-dimer and -trimer are illustrated in Scheme A-3-2. The assignments of the signals were done by two dimensional spectra taken under the same conditions as those applied to the structural study of oligo(MMA)s having a *t*-butyl group at the α-end.[6]



$R = -CH_3, -C_2H_5$

Scheme A-3-2. Structure and numbering system of monomeric units of MMA-dimer and -trimer having a 9-methylfluorenyl or a 9-ethylfluorenyl group at the α-end.

Table A-3-3. ^{1}H NMR chemical shifts (δ, ppm) and coupling constants (Hz) of MMA-dimers and -trimers having a 9-methylfluorenyl group and MMA-dimers having a 9-ethylfluorenyl group at the α-end measured in $CDCl_3$ at 35°C[a]

	α_1		α_2		ω_1		fluorenyl		ω-end	
	CH_2[b]	α-CH_3[c]	CH_2[b]	α-CH_3[c]	CH_2[d]	α-CH_3[e]	CH_2[f]	CH_3[g]	-H[h]	OCH_3[c]
α-end group: 9-methylfluorenyl dimer										
m	2.34, 2.76 (14.3)	0.29			1.47, 1.73 (13.9)	0.94 (7.4)	---	1.39	2.09 (3.5, 8.4)	3.56, 3.14
r	2.34, 2.77 (14.3)	0.34			1.10, 2.06 (14.3)	0.96 (7.4)	---	1.39	2.30 (3.5, 8.9)	3.54, 3.15
α-end group: 9-ethylfluorenyl dimer										
m	2.32, 2.74 (14.3)	0.28			1.47, 1.74 (13.9)	0.94 (6.9)	1.93	0.11	2.11 (3.5, 7.9)	3.56, 3.14
r	2.32, 2.76 (14.9)	0.34			1.11, 2.07 (13.9)	0.95 (6.9)	1.93	0.10	2.31 (3.0, 8.9)	3.54, 3.15
α-end group: 9-methylfluorenyl trimer										
mm	2.32, 2.74 (14.8)	0.27	2.04, 1.55 (14.8)	0.94	1.48, 1.75 (14.3)	1.03 (6.9)	---	1.37	2.34 (2.5, 8.9)	3.60, 3.51, 3.15
mr	2.33, 2.75 (14.3)	0.27	1.58, 2.06 (14.3)	1.03	1.10, 2.13 (14.3)	1.04 (6.9)	---	1.36	2.37 (3.5, 8.4)	3.58, 3.47, 3.11

[a] Protons of fluorenyl group resonated in the range of 7.21-7.72 ppm (multiplet). ^{2}J coupling constants between methylene protons, ^{3}J coupling constants between the ω_1-methyl and ω-end methine protons, and ^{3}J coupling constants between the ω-end methine and ω_1-methylene protons are in parentheses below the chemical shifts of methylene protons, ω_1-methyl protons and ω-end methine protons, respectively. As for the ^{3}J coupling constants between the ω-end methine and ω_1-methylene protons, the value on the left side corresponds to that between the methine protons and one of the methylene protons resonating in the higher magnetic field. [b] AB quartet. [c] Singlet. [d] Double-quartet. [e] Doublet. [f] Quartet. [g] Singlet in the case of 9-methylflourenyl group and triplet in the case of 9-ethylfluorenyl group. [h] Multiplet.

The difference in chemical shifts of the methylene protons of ω_1-unit was 0.26~0.27 ppm for *m* and 0.96~1.02 ppm for *r*, that of α_2-unit of trimer 0.49 ppm for *m* and that of α_1-monomeric unit 0.42~0.44 ppm almost independently on the stereostructure. These values are close to those of the oligomers having a fluorenyl group at the α-end.

As the examples of spectra, the spectra of MMA-dimers *m* having a 9-methylfluorenyl and a 9-ethylfluorenyl groups at the α-end and MMA-trimer *mm* having a 9-methyl fluorenyl group at the α-end are shown in Figure A-3-4 with that of MMA-dimer *m* having a fluorenyl group at the α-end (Figure A-3-4 (D)). Several remarkable differences can be seen between the spectra of the oligo(MMA)s having a 9-substituted fluorenyl group and that of dimer *m* having a fluorenyl group. The α_1-CH_3 protons of the dimers and the trimer having a 9-substituted fluorenyl group resonated in the range of 0.27~0.34 ppm which was higher by about 1 ppm than that of the dimer having a fluorenyl group. Moreover, the methyl protons of the 9-ethyl group of the dimer resonated in much higher field than the usual methyl region. The α_1-CH_2 protons of the oligo(MMA)s having a 9-substituted fluorenyl group resonated constantly in lower field than those of the dimer having a fluorenyl group. The signal of one of the methoxy groups, whose assignments to the monomeric units could not be done by two dimensional NMR spectroscopy, shifted to higher field by about 0.5 ppm with the replacement of a hydrogen at the 9-position of fluorenyl group by an alkyl group. These observations suggest that MMA-dimer and -trimer having a 9-substituted fluorenyl group may possess a specific conformation different

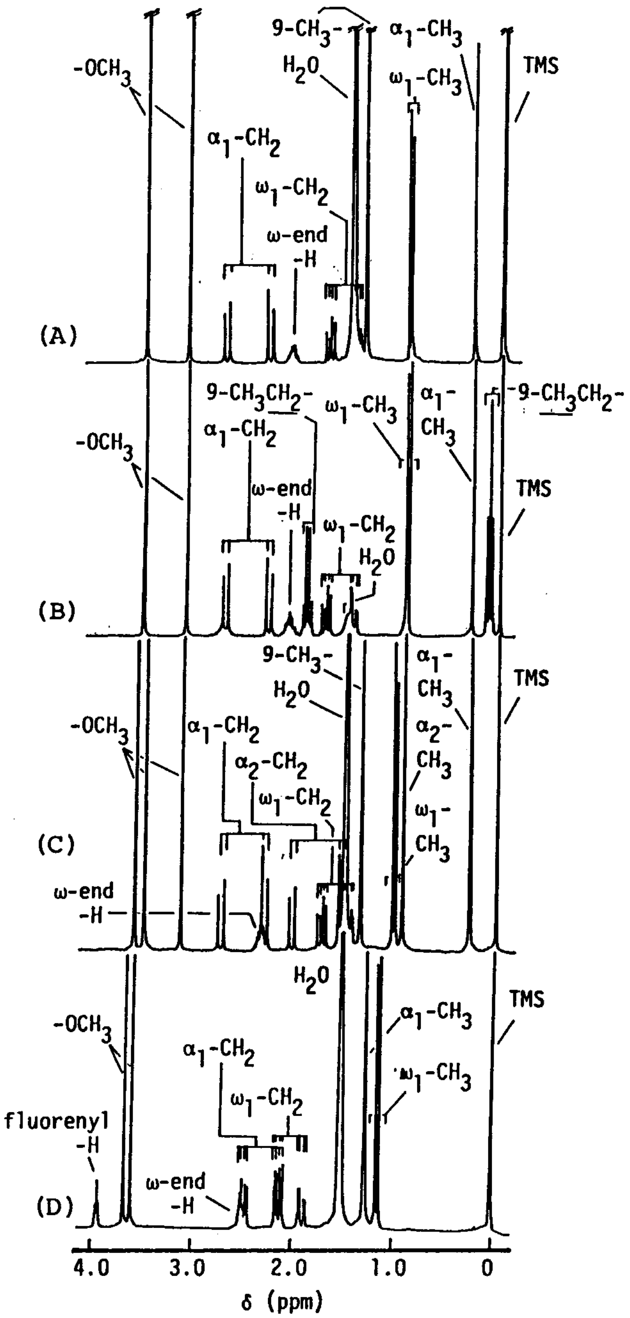


Figure A-3-4. 270 MHz ^{1}H NMR spectra of MMA-dimer m having a 9-methylfluorenyl group at the α-end (A), MMA-dimer m having a 9-ethylfluorenyl group (B), MMA-trimer mm having a 9-methylfluorenyl group (C), and MMA-dimer m having a fluorenyl group (D). ($CDCl_3$, 35°C, TMS) from that of MMA-dimer having a fluorenyl group by the steric effect of the 9-substituent group. This may force the α_1-CH_3 and -CH_2 groups and methyl moiety of the 9-ethyl group, and one of the methoxy groups to be located in the positions of strong anisotropic effect by the aromatic ring of the fluorenyl group. Similarly to the oligo(MMA), TrMA-dimer and -trimer anions may possess a specific conformation by the steric effect of 9-substituent group and this may be the reason why the propagation stereochemistry of dimer anion to trimer anion and that of trimer anion to tetramer anion are different from those in the system with Sp-FlLi.

Optical resolution of MMA-dimer and trimer

The optical isomers of MMA-dimers and trimers were separated by chiral HPLC and the contents of the isomers were determined in order to get detailed information on the propagation stereochemistry. Figure A-3-5 shows the chromatograms of optical resolution of MMA-dimers *m* and *r* and MMA-trimers *mm* and *mr* derived from TrMA-dimers and -trimers obtained in the system with Sp-MeFlLi at [TrMA]/[Li] = 2 and Figure A-3-6 those of the dimers and trimers obtained in the system with Sp-EtFlLi at [TrMA]/[Li] = 2. These dimers and tetramers were isolated by the diastereomeric separation described above. All the isomers were sufficiently resolved.

The assignment of the isomers was done on the basis of the relationship between the sign of optical rotation and the absolute configuration of the model compounds[7] illustrated in Scheme A-1-5 in Part A: Chapter 1. The assignment based on the model

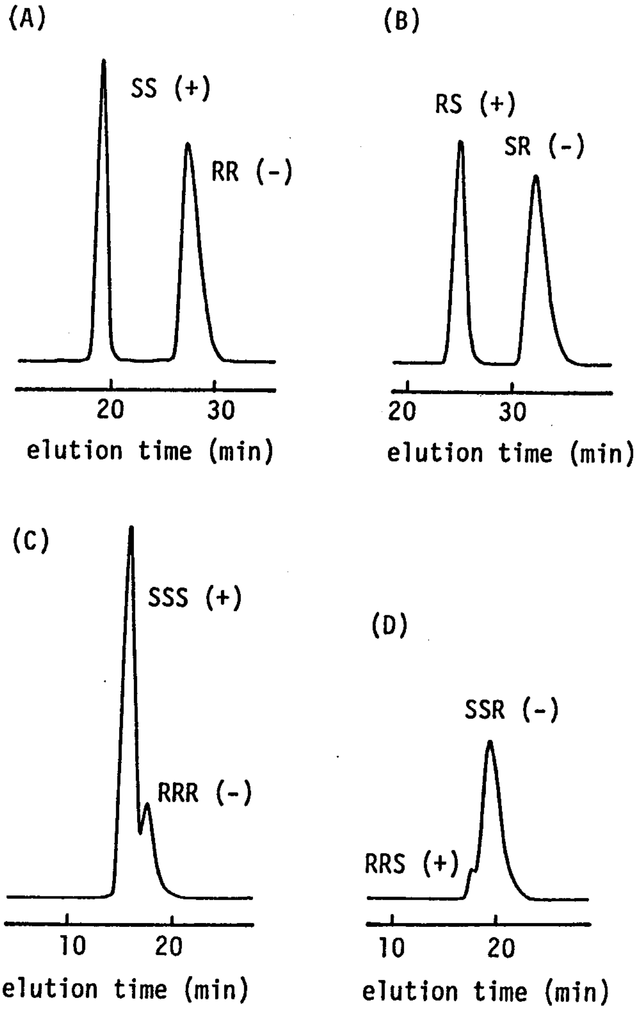


Figure A-3-5. Chromatograms of optical resolution of MMA-dimers m (A) and r (B) and MMA-trimers mm (C) and mr (D) derived from corresponding oligo(TrMA) preapred with Sp-MeFlLi at [TrMA]/[Li]=2.

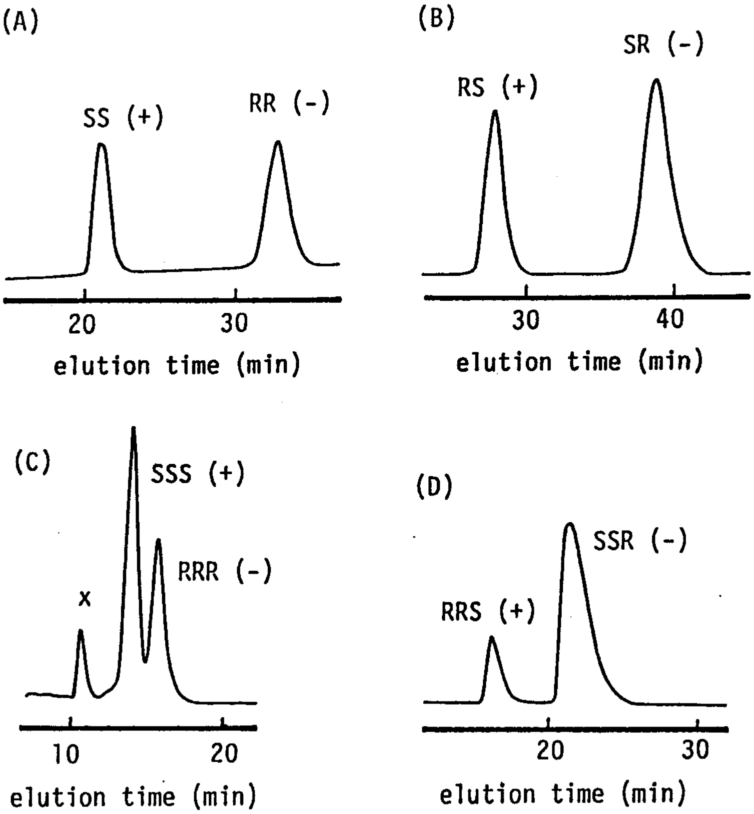


Figure A-3-6. Chromatograms of optical resolution of MMA-dimers m (A) and r (B) and MMA-trimers mm (C) and mr (D) derived from corresponding oligo(TrMA) prepared with Sp-EtFlLi at [TrMA]/[Li]=2.

compound assuming that the optical rotation of MMA-dimer and -trimer depends only on the ω-end absolute configuration was consistent with the actual assignment on the basis of experiment in the case of the oligo(MMA) having a fluorenyl group as shown in Part A: Chapter 1.

The ratio of the four isomers of the dimer and the four isomers of the trimer obtained at [TrMA]/[Li] = 2, 3, and 5 are summarized in Table A-3-4. In the both systems, the ratio of the total amount of *S*- isomer (*SS*+*SR*) decreased with the increasing [TrMA]/[Li] ratio. This result indicates that $S\text{-}^{-}$ dimer anion which produces *SS* and *SR* dimers by protonation is more active to TrMA than $R\text{-}^{-}$ anion which produces *RR* and *RS* dimers. The two kinds of complexes of oligomer anion and Sp mentioned in Part A: Chapter 1 do not seem to be necessary to explain the present results. The stereospecificity in this step of the present systems was opposite to that in the system with Sp-FlLi. This must be brought about by the conformational difference between the dimer anion having a 9-substituted fluorenyl group and that having a 9-fluorenyl group mentioned above. Trimers obtained in the both systems were rich in the *SS*- (*SSS*+*SSR*) at all the ratio. With the increasing [TrMA]/[Li] ratio, the total amount of *RR*-(*RRS*+*RRR*) decreased to give almost optically pure *SS*- trimer at [TrMA]/[Li] = 5. This indicates that the $RR\text{-}^{-}$ trimer anion which produces *RRR* and *RRS* trimers is more active than $SS\text{-}^{-}$ anion which produces *SSS* and *SSR* trimer in the propagation to tetramer anion similarly to the system with Sp-FlLi. Though $SS\text{-}^{-}$ trimer anion may also propagate to tetramer anion, this is considered to remain as tetramer and pentamer anions. This explanation is

Table A-3-4. The ratios of four isomers of MMA-dimer and four isomers of MMA-trimer derived from TrMA-dimer and -trimer obtained with Sp-MeFlLi and Sp-EtFlLi at [TrMA]/[Li] = 2, 3, and 5[a]

Initiator	[TrMA]/[Li]	Isomers of dimer (%)					Isomers of trimer (%)				
		m		*r*			*mm*		*mr*		
		SS(+)	*RR*(-)	*RS*(+)	*SR*(-)	*S*-[b]/ *R*-[b]	*SSS*(+)	*RRR*(-)	*RRS*(+)	*SSR*(-)	*SS*-[c]/*RR*-[c]
Sp-MeFlLi	2	5	10	38	47	52 / 48	12	6	9	73	85 / 15
	3	11	18	43	28	38 / 62	12	3	5	80	92 / 8
	5	13	18	45	24	37 / 63	10	1	1	88	98 / 2
Sp-EtFlLi	2	4	6	33	57	61 / 39	12	9	14	65	77 / 23
	3	9	13	35	43	52 / 48	12	3	6	79	91 / 9
	5	14	24	32	30	44 / 56	16	1	3	80	96 / 4

[a] Determined by HPLC optical resolution of each diastereomer detected at 254 nm and the ratio of the diastereomers shown in Table A-3-2.

[b] *S*- denotes generically *SS* and *SR* and *R*- *RR* and *RS*.

[c] *SS*- denotes generically *SSS* and *SSR* and *RR*- *RRR* and *RRS*.

consistent with the previous assumption that tetramer and pentamer may contain a significant amount of *SSS*-- isomers. The stereospecificity in the steps to higher oligomers in the present systems may be similar to that of the system with Sp-FlLi yielding *RRR*--- configuration because the same chiral ligand was used and the stereochemistry of protonation of higher oligomer anions was similar to that in the system with Sp-FlLi.

The higher molecular weight of the polymer produced in the systems with MeFlLi and EtFlLi should be caused by the predominant propagation of *S*-$^{-}$ dimer anion. This anion produces a significant amount of *SS*-$^{-}$ trimer, *SSS*-$^{-}$ tetramer, and *SSSS*-$^{-}$ pentamer anions which are not considered to propagate to a polymer. Consequently, the amounts of the species for the optically active polymer are less than that in the system with Sp-FlLi, and this results in higher molecular weight of the polymer.

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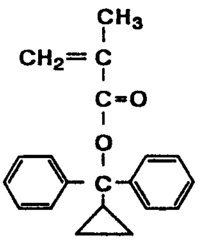
Part B: Chapter 1

Asymmetric Polymerization of 1,1-Diphenylalkyl Methacrylates

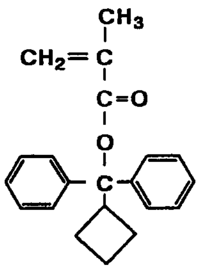
B-1-1 Introduction

As described in Part A, triphenylmethyl methacrylate (TrMA) affords a highly isotactic, optically active polymer of one-handed helical conformation by asymmetric polymerization with a chiral anionic initiator. Similarly to TrMA, diphenyl-2-pyridylmethyl methacrylate (D2PyMA) gives an optically active, helical polymer by asymmetric polymerization.[1] The helical structure of the polymers is considered to be maintained by mutual steric repulsion between the bulky ester groups. The helix of poly(D2PyMA) is less stable than that of poly(TrMA) and undergoes helix-helix transition in solution, in which the one-handed helix changes to a mixture of right- and left-handed helices.[2] On the other hand, 1,1-diphenylethyl methacrylate which is less bulky than TrMA and D2PyMA gives an atactic polymer under similar polymerization conditions as those applied to TrMA and D2PyMA.[3] Therefore, the stereostructure of ester group greatly affects the formation and stability of the helix.

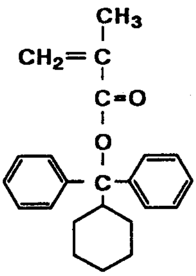
In the present study, cyclopropyldiphenylmethyl, cyclobutyldiphenylmethyl, cylclohexyldiphenylmethyl, and 1,1-diphenyloctadecyl methacrylates (CPDPMA, CBDPMA, CHDPMA, and DPODMA) were synthesized and polymerized with chiral anionic initiators to get information on the stereostructure of ester group suitable to obtain a helical polymethacrylate. Asymmetric anionic polymerization was carried out with the complexes of *N,N'*-diphenylethylenediamine monolithium amide (DPEDA-Li) and chiral ligands, (−)-sparteine (Sp), (+)-(2*S*,3*S*)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB), and (+)-(*S*)-2-(1-pyrrolidinylmethyl)pyrrolidine (PMP) in toluene at low temperature. The anionic polymerization was also initiated by butyllithium (*n*-BuLi) and phenylmagnesium bromide (PhMgBr). Radical polymerization was done with diisopropylperoxy dicarbonate ((*i*-PrOCOO)$_2$).



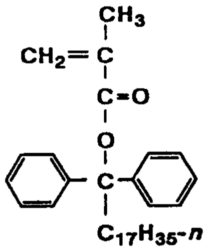
CPDPMA



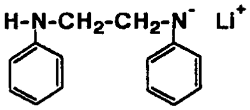
CBDPMA



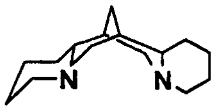
CHDPMA



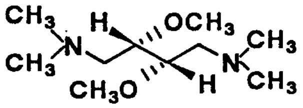
DPODMA



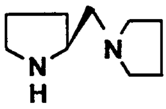
DPEDA-Li



Sp



DDB



PMP

B-1-2 Experimental

Syntheses of monomers. CPDPMA Cyclopropyldiphenylmethanol (Aldrich) (5.5 g, 0.025 mol) was converted into sodium alkoxide with sodium hydride (60% oil suspension, 1.20 g, 0.030 mol) at 50°C in dry tetrahydrofuran (THF) (50 ml) under dry nitrogen atmosphere. Then methacryloyl chloride (3 ml, 0.028 mol) dissolved in dry THF (10 ml) was added dropwise to the solution at 0°C. After stirring for 3 h, the solvent was evaporated, and diethyl ether and water were added to the residue. The ethereal layer was washed with saturated aqueous sodium bicarbonate and water, and then dried over $MgSO_4$. After ether was evaporated, the residue was recrystallized twice from a mixture of hexane and diethyl ether (1/1 v/v) and once from hexane. Yield 1.85 g, (26.1%); m.p. 69.7~70.1°C. ^1H NMR (270 MHz, $CDCl_3$, 35°C, TMS), 0.12 and 0.59 (m, 4H, CH_2 of cyclopropyl), 1.99 (s, 3H, α-CH_3), 2.63 (m, 1H, methine of cyclopropyl), 5.57 and 6.21 (m, 2H, CH_2=C), 7.19~7.35 ppm (m, 10H, aromatic-H); IR (nujol), 1725 (C=O), 1635 cm^{-1} (C=C). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16%; H, 6.89%. Found: C, 82.27%; H, 6.98%.

CBDPMA PhMgBr was synthesized from magnesium turnings and phenyl bromide in diethyl ether. Methyl cyclobutanecarboxylate (34.1 g, 0.299 mol) dissolved in diethyl ether was added dropwise to PhMgBr (0.79 mol) in diethyl ether (100 ml) with vigorous stirring under nitrogen atmosphere. The reaction mixture was stirred for 1 h with refluxing after completion of addition, and decomposed with saturated aqueous ammonium chloride (150 ml). The ethereal solution was decanted and the residue was washed with diethyl ether. The combined ether solution was washed with saturated aqueous ammonium chloride and dried over $MgSO_4$. After the removal of the solvent, a white yellow solid was obtained (69.2 g, 97%). This was recrystallized first from hexane and then from ethanol to give cyclobutyldiphenylmethanol. Yield 17.2 g (24%); m.p. 54.3~55.0°C.

The alcohol (14.4 g, 0.060 mol) was converted into lithium alkoxide with *n*-BuLi (0.060 mol) in hexane at -78°C in dry THF (100 ml) under dry nitrogen atmosphere. Then methacryloyl chloride (8.0 ml, 0.081 mol) was added to the solution with a syringe. After 30 min of stirring at -78°C, the reaction mixture was warmed to room temperature and left under stirring for 1 h. After the solvent was evaporated, diethyl ether and water were added to the mixture, and the separated organic layer was collected. The ethereal layer was washed first with saturated aqueous sodium bicarbonate and then with saturated aqueous sodium carbonate, and dried over $MgSO_4$. Ether was evaporated to give yellow crystal 15.6 g (84.1 %). This was recrystallized twice from ether and once from hexane. Yield 4.38 g (24%); m.p. 66.4~67.0°C. ^1H NMR (200 MHz, $CDCl_3$, 25°C, TMS), 1.35~1.95 (m, 6H, CH_2 of cyclobutyl), 1.99 (s, 3H, α-CH_3), 4.16 (m, 1H, methine of cyclobutyl), 5.58 and 6.19 (m, 2H, CH_2=C), 7.2~7.4 ppm (m, 10H, aromatic-H); IR (KBr), 1721 (C=O), 1638 cm^{-1} (C=C). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32%; H, 7.24%. Found: C, 82.31%; H, 7.18%.

CHDPMA Methyl cyclohexanecarboxylate (22.0 g, 0.16 mol) dissolved in diethyl ether was added dropwise to PhMgBr (0.46 mol) in diethyl ether (100 ml) with vigorous stirring under nitrogen atmosphere. The reaction mixture was stirred for 2 h with refluxing after completion of addition, and decomposed with saturated aqueous ammonium chloride. The ethereal solution was decanted and the residue was washed with diethyl ether. The combined ether solution was dried over $MgSO_4$. After the removal of the solvent, a white solid was obtained. This was recrystallized twice from petroleum ether to give cyclohexyldiphenylmethanol. Yield 21.9 g (53%); m.p. 68.1~68.9°C.

The alcohol (28.1 g, 0.11 mol) was converted into lithium alkoxide with *n*-BuLi (0.11 mol) in cyclohexane at -78°C in dry THF (200 ml) under dry nitrogen atmosphere. Then the solution was warmed to 0°C and methacryloyl chloride (20.2ml, 0.22 mol) dissolved in dry THF (60 ml) was added dropwise to the solution. After 4 h of stirring at 0°C, the reaction mixture was heated at 30°C and stirred for 1 h. After the solvent was evaporated, diethyl ether and water were added to the mixture, and the separated organic layer was collected. The ethereal layer was washed with saturated aqueous sodium bicarbonate and water, and dried over $MgSO_4$. After ether was evaporated, the residue was recrystallized six times from a mixture of hexane and ether (10/3 v/v), once from ethanol, and once from hexane. Yield 2.6 g (7%); m.p. 73.6~74.6°C. ^1H NMR (270 MHz, $CDCl_3$, 35°C, TMS), 0.64~1.87 (m, 10H, CH_2 of cyclohexyl), 1.92 (s, 3H, α-CH_3), 3.36 (m, 1H, methine of cyclohexyl), 5.50 and 6.11 (m, 2H, CH_2=C), 7.26~7.33 ppm (m, 10H, aromatic-H); IR (nujol), 1725 (C=O), 1635 cm^{-1} (C=C). Anal. Calcd for $C_{23}H_{26}O_2$: C, 82.60%; H, 7.84%. Found: C, 82.40%; H, 7.86%.

<u>DPODMA</u> Ethyl stearate (100 g, 0.32 mol) dissolved in diethyl ether (50 ml) was added dropwise to PhMgBr (1.27 mol) in diethyl ether (150 ml) with vigorous stirring under nitrogen atmosphere. The reaction mixture was stirred for 1 h with refluxing after completion of addition, and decomposed with saturated aqueous ammonium chloride. The ethereal solution was filtrated and the residue was washed by diethyl ether. The combined ether solution was dried over $MgSO_4$. After ether was evaporated, the residue was recrystallized from hexane to give 1,1-diphenyloctadecanol. Yield 75.1 g (55.6%); m.p. 57.5~58.1°C.

The alcohol (74.0 g, 0.18 mol) was converted into sodium alkoxide with sodium hydride (60% oil suspension, 9.12 g, 0.23 mol) in dry THF by stirring for 18 h with refluxing. Then methacryloyl chloride (22.3 ml, 0.228 ml) was added dropwise to the solution at 0°C. After the solution was stirred for 6 h at 0°C, the solvent was evaporated, and ether and water were added to the residue. The ethereal layer was washed with saturated aqueous sodium bicarbonate and water, and then dried over $MgSO_4$. After ether was evaporated, the residue was dissolved in ethanol (100 ml) and a small amount of insoluble part was filtrated by Selite 545 (Nakalai Tesque). Recrystallization twice from ethanol and once from hexane gave the pure monomer. Yield 25.2 g (28%); m.p. 39.0~39.6°C. ^1H NMR (270 MHz, $CDCl_3$, 35°C, TMS), 0.87 (t, 3H, CH_3 of octadecyl group), 1.25 (s, 30H, CH_2 of octadecyl group), 2.01 (s, 3H, α-CH_3), 2.78 (t, 2H, CH_2 at 2-position of octadecyl group), 5.59 and 6.22 (m, 2H, CH_2=C), 7.16~7.37 ppm (m, 10H, aromatic-H); IR (nujol), 1725 (C=O), 1635 cm^{-1} (C=C). Anal. Calcd for $C_{34}H_{50}O_2$: C, 83.27%; H, 10.20%. Found: C, 83.19%; H, 10.33%.

Other materials were purified in the manner described in Part A: Chapter 1.

Polymerization procedure. DPEDA-Li was synthesized from *N,N'*-diphenylethylenediamine with 1.0 equiv amount of *n*-BuLi in toluene. A chiral ligand (1.2 equiv) was added to DPEDA-Li in toluene. DPEDA-Li was scarcely soluble in toluene but became soluble in the presence of 1.2 equiv amount of a chiral ligand.

Asymmetric anionic polymerization was carried out in a 1.0-cm optical cell under dry nitrogen to monitor the change of optical activity of the polymerization systems or in a usual glass ampule. The polymerization was terminated by the addition of a small amount of methanol and the polymer was precipitated in methanol to be collected by centrifugation. The obtained polymer was converted into methyl ester [poly(MMA)][4] for the determination of degree of polymerization (DP) and molecular weight distribution by gel permeation chromatography (GPC).

Measurements. ^{1}H NMR spectra were taken on a JEOL GX-270 (270 MHz) and a Varian Gemini-200 (200 MHz) spectrometers. Circular dichroism (CD) spectra were taken on a JASCO J-500 spectrometer equipped with a computerized data processor. Optical resolution of the polymer was done on a JASCO Trirotar II chromatograph equipped with a JASCO UVIDEC-100-V (UV) and a JASCO DIP-181C (polarimetry) detectors using a column (25 x 0.46 (i.d.) cm) packed with optically active poly(TrMA) chemically bonded to macroporous silica gel.[1,5] $CHCl_3$ was used as an eluent.

B-1-3 Results and Discussion

Polymerization of CPDPMA

The results of polymerization of CPDPMA are shown in Table B-1-1. The polymers obtained with PMP-DPEDA-Li and DDB-DPEDA-Li did not show significant optical activity and were not isotactic (Run 1,2 in Table B-1-1). Cyclopropyldiphenylmethyl group seems to be too small as an ester group to form a helical polymethacrylate. CPDPMA afforded a highly isotactic polymer by anionic

Table B-1-1. Polymerization of CPDPMA in toluene for 24 h[a]

Run	Initiator	Temp. (°C)	Yield (%)	DP[b]	Mw/Mn[b]	Tacticity(%)			$[\alpha]_{365}^{25}$ [c]
						mm	*mr*	*rr*	
1	PMP-DPEDA-Li	-78	99	34	1.10	28	31	41	-1°
2	DDB-DPEDA-Li	-78	97	36	3.71	44	32	24	-4°
3	PhMgBr	-78	83	30	3.53	91	8	1	
4	PhMgBr	0	95	65	1.40	94	5	1	
5	$(i\text{-PrOCOO})_2$	40	89	94	1.93	22	51	27	

[a] CPDPMA 0.15 g, toluene 3 ml, [CPDPMA]/[Li] = 20 (Run 1,2); CPDPMA 0.4 g, toluene 20 ml, [CPDPMA]/[Mg] = 20 (Run 3,4); CPDPMA 0.75 g, toluene 2.5 ml, [CPDPMA]/[initiator] = 50 (Run 5).

[b] Determined by GPC of poly(MMA)s derived from poly(CHDPMA)s.

[c] Measured in $CHCl_3$.

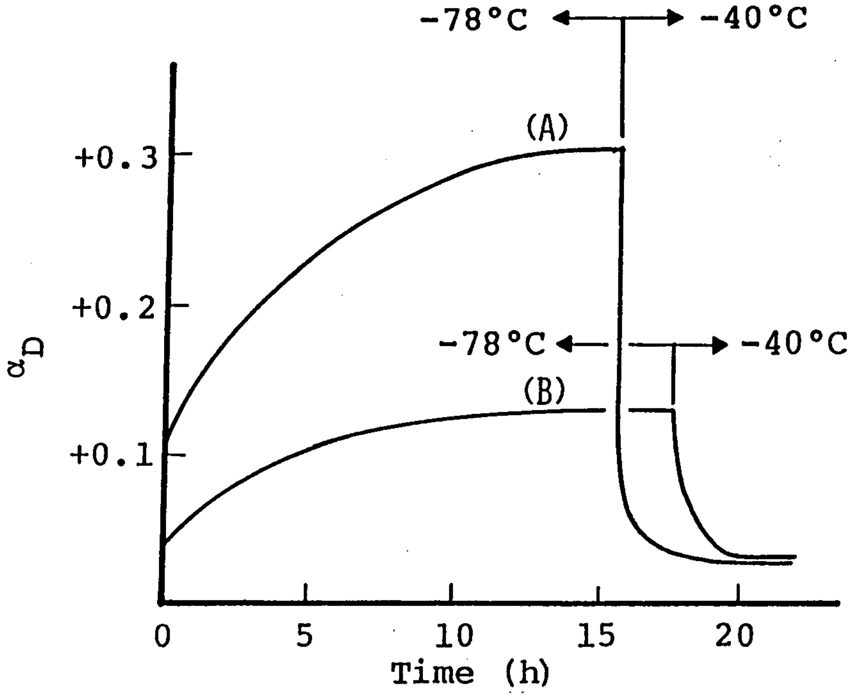


Figure B-1-1. Change of optical activity of polymerization systems of CPDPMA with DDB-DPEDA-Li (A) and with PMP-DPEDA-Li (B) in toluene at -78°C and -40°C. (CPDPMA 0.15 g, toluene 3 ml, [CPDPMA]/[Li]=20, cell length 1.0 cm) polymerization with PhMgBr and an atactic polymer by radical polymerization with (i-PrOCOO)$_2$ (Run 3-5 in Table B-1-1). The isotactic polymer was not be optically resolved into (+)- and (-)-polymers by chiral HPLC at a temperature range of -30°C~+15°C as poly(D2PyMA) was resolved,[2,5] suggesting that the polymer may not take a helical conformation.

Figure B-1-1 shows the change of optical activity of the polymerization systems of CPDPMA with DDB-DPEDA-Li and PMP-DPEDA-Li. Though the isolated polymers in the systems with DDB-DPEDA-Li and PMP-DPEDA-Li were almost optically inactive, the polymerization systems at -78°C showed positive optical activity increasing with the reaction time which reached constant values corresponding to specific rotations $[\alpha]_D^{-78}$ +64° in DDB-system and +26° in PMP-system. These optical activities decreased quickly to very small values when the temperature of the systems was raised to -40°C. These results suggest that an optically active helical conformation may be partly formed in isotactic sequence of the polymer at -78°C and it may change to an optically inactive random-coil conformation at higher temperature. This possibility is supported by the fact that the final optical activity of the polymerization system at -78°C was higher in the system with DDB-DPEDA-Li which gave the polymer of higher isotacticity.

Polymerization of CBDPMA

Figure B-1-2 shows the change of optical activity of polymerization systems with DDB-DPEDA-Li and PMP-DPEDA-Li. The both polymerization systems showed increasing optical activity at

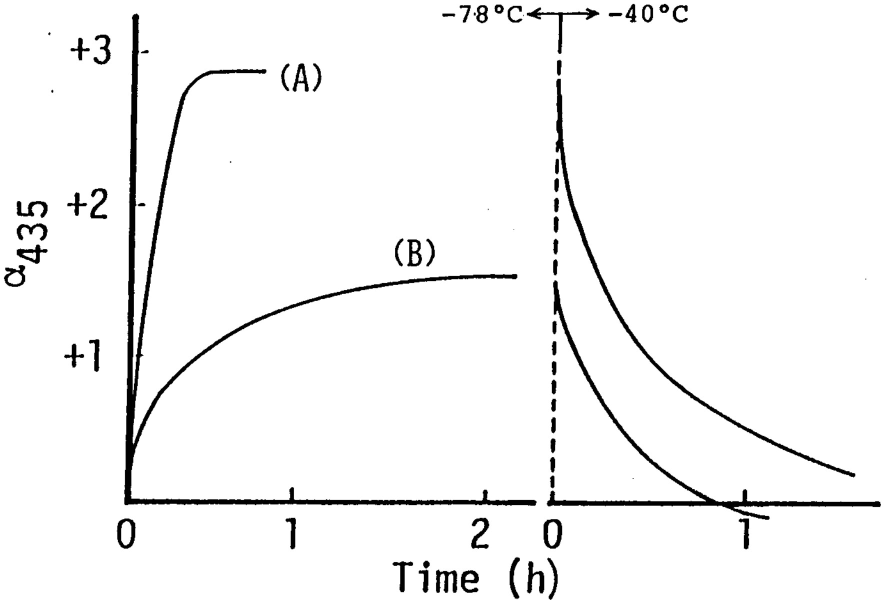


Figure B-1-2. Change of optical activity of polymerization systems of CBDPMA with DDB-DPEDA-Li (A) and with PMP-DPEDA-Li (B) in toluene at -78°C and -40°C. (CBDPMA 0.15 g, toluene 3 ml, [CBDPMA]/[Li]=20, cell length 1.0 cm)

Table B-1-2. Polymerization of CBDPMA in toluene[a]

Run	Initiator	Temp. (°C)	Time (h)	Yield (%)	DP[b]	Mw/Mn[b]	Tacticity(%)			$[\alpha]_{365}^{25}$ [c]
							mm	*mr*	*rr*	
1	PMP-DPEDA-Li	-78	3	100	29	1.65	66	19	15	-1°
2	Sp-DPEDA-Li	-78	27	97	59	1.99	76	19	5	n.d.[d]
3	DDB-DPEDA-Li	-78	1	98	50	1.43	87	8	5	n.d.[d]
4	(i-PrOCOO)$_2$	40	24	84	103	2.81	48	36	16	

[a] CBDPMA 1 g, toluene 20 ml, [CBDPMA]/[Li] = 20 (Run 1-3); CBDPMA 0.5 g, toluene 2.5 ml, [CBDPMA]/[initiator] = 50 (Run 4).

[b] Determined by GPC of poly(MMA)s derived from poly(CBDPMA)s.

[c] Measured in $CHCl_3$-2,2,2-trifluoroethanol (TFE) (9/1 v/v).

[d] Insoluble in $CHCl_3$-TFE.

-78°C with polymerization time which reached constant large positive values corresponding to specific rotations $[\alpha]_{435}^{-78}$ +673° in DDB-system and +358° in PMP-system. However, these optical activities decreased to the values around zero when the temperature of the systems was raised to -40°C. These results suggest that optically active helical polymers may be formed at -78°C and the conformation may change into an optically inactive one at higher temperature.

The results of polymerization of CBDPMA are summarized in Table B-1-2. All the polymers obtained with chiral initiators were isotactic and the polymer obtained by radical polymerization was also rich in isotacticity. This suggests that the optical activity of the polymerization systems at -78°C above mentioned may be due to a one-handed helical structure of polymers. However, the polymer obtained with PMP-DPEDA-Li did not show significant optical activity at 25°C.

In order to get information on the conformation of the optically inactive, isotactic polymer, ^{1}H NMR spectrum of the polymer obtained with PMP-DPEDA-Li was taken at 25°C (Figure B-1-3). In the spectrum, the signal which may be due to α-methyl protons was observed in a chemical shift range of 0.5~1.3 ppm. In the case of oligo(D2PyMA), protons of the α-methyl group based on helical structure resonate in the range of 0~0.5 ppm and those based on random-coil conformation in the range of 0.5~1.0 ppm.[6] On the basis of this fact, the optically inactive, isotactic polymer may have a random-coil conformation. Cyclobutyldiphenylmethyl group may be bulky enough as an ester group to form a helical polymethacrylate at -78°C and too small to

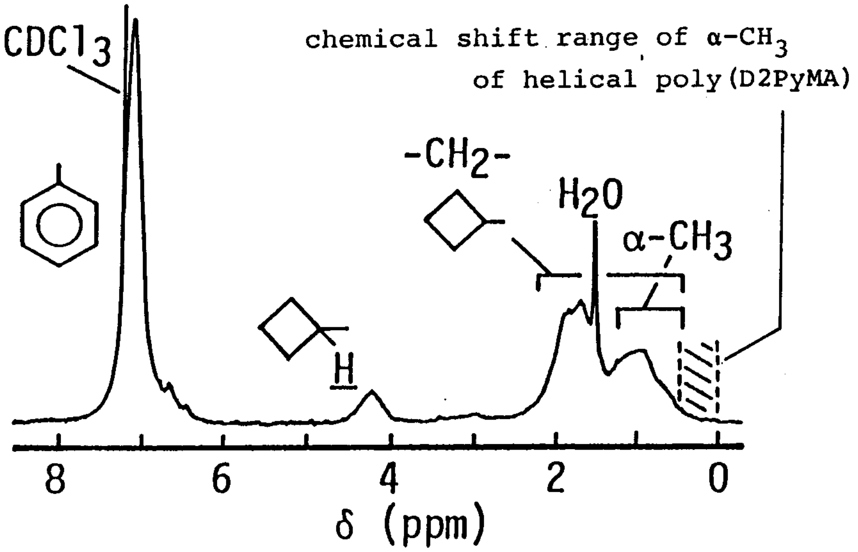


Figure B-1-3. 200 MHz ^{1}H NMR spectrum of poly(CBDPMA) of DP=29 (Run 1 in Table B-1-2). ($CDCl_3$, 25°C) maintain the conformation at higher temperature.

Polymerization of CHDPMA

The results of polymerization of CHDPMA are summarized in Table B-1-3. All the polymers obtained with the chiral anionic initiators were highly isotactic and the polymers obtained with PMP and DDB complexes showed high dextrorotatory specific rotation. GPC analysis of these (+)-poly(CHDPMA)s with UV and polarimetric detectors did not show the existence of (-)-polymer. These results suggest that the polymers may possess a helical conformation of single screw sense. Radical polymerization of CHDPMA also gave a polymer rich in isotacticity (Run 5 in Table B-1-3). Cyclohexyldiphenylmethyl group appears to be suitable as an ester group for the formation of a helical polymethacrylate. The molecular weight distribution of the polymers obtained with Sp-DPEDA-Li was much broader than that of the polymers obtained with PMP-DPEDA-Li and DDB-DPEDA-Li and the former polymers contained the polymer of higher DP. This may be the reason for insolubility of the polymers.

The rate of polymerization of CHDPMA with PMP-DPEDA-Li and that with Sp-DPEDA-Li were estimated by monitoring the change of optical activity of polymerization systems during the reaction (Figure B-1-4). Both the systems showed the positive optical rotation which increased with polymerization time. The optical rotation of the system with PMP reached a constant high positive value (α_{435}^{-78} +3.0°) which corresponds to a specific rotation $[\alpha]_{435}^{-78}$ +622° within about 6 h. This result indicates that the polymerization of CHDPMA is much slower than those of D2PyMA

Table B-1-3. Polymerization of CHDPMA in toluene[a]

Run	Initiator	Temp. (°C)	Time (h)	Yield (%)	DP[b]	Mw/Mn[b]	Tacticity(%)			$[\alpha]_{365}^{25}$ [c]
							mm	*mr*	*rr*	
1	PMP-DPEDA-Li	-78	48	99	34	1.10	98	2	0	+758°
2	Sp-DPEDA-Li	-40	48	97	36	3.71	91	6	3	n.d.[d]
3	Sp-DPEDA-Li	-78	168	83	30	3.53	87	7	6	n.d.[d]
4	DDB-DPEDA-Li	-78	48	95	65	1.40	98	1	1	+589°
5	$(i\text{-PrOCOO})_2$	40	24	89	103	2.30	45	36	19	

[a] CHDPMA 0.5 g, toluene 10 ml, [CHDPMA]/[Li] = 20 (Run 1-4); CHDPMA 0.75 g, toluene 2.5 ml, [CHDPMA]/[initiator] = 50 (Run 5).

[b] Determined by GPC of poly(MMA)s derived from poly(CHDPMA)s.

[c] Measured in $CHCl_3$.

[d] Insoluble in $CHCl_3$.

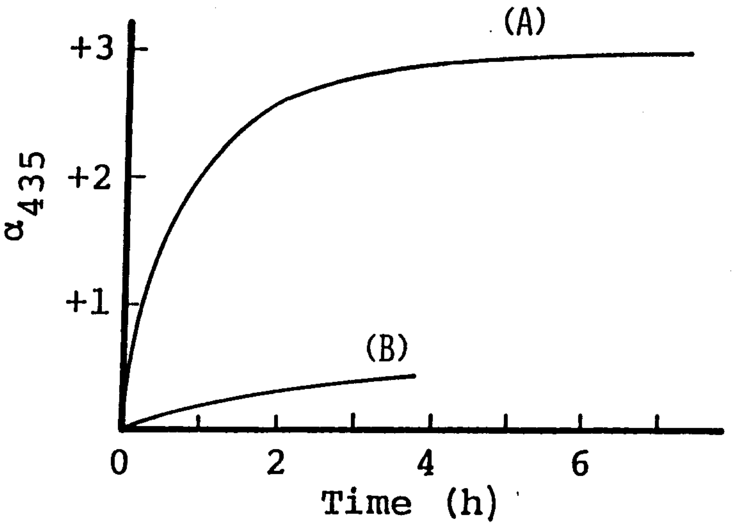


Figure B-1-4. Change of optical activity of polymerization systems of CHDPMA with PMP-DPEDA-Li at -78°C (A) and with DDB-DPEDA-Li at -40°C (B) in toluene. (CHDPMA 0.15 g, toluene 3 ml, [CHDPMA]/[Li]=20, cell length 1.0 cm) and TrMA. The optical activity of the polymerization systems of D2PyMA[1] and TrMA (Figure A-1-2 in Part A: Chapter 1) under the same conditions reached large constant values within 10 min. CHDPMA may be bulkier than D2PyMA and TrMA. The polymerization of CHDPMA with Sp-DPEDA-Li at -78°C was very slow, and the optical activity of the system with Sp-DPEDA-Li at -40°C could not be completely followed because the system gelled in the course of polymerization.

The poly(CHDPMA) of DP = 34 prepared with PMP-DPEDA-Li (Run 1 in Table B-1-3) showed a remarkable change of optical activity in $CHCl_3$ at 60°C (Figure B-1-5). The optical rotation of the polymer changed rather quickly from a high positive value ($[\alpha]_{365}^{60}$ ~+770°) to a negative one ($[\alpha]_{365}^{60}$ ~-480°). GPC analysis of the levorotatory polymer with UV and polarimetric detectors showed that the polymer consisted of only (-)-polymer. Such a change of optical rotation has been found for optically active poly(D2PyMA) and the change is ascribed to helix-helix transition of the polymer chain.[2] The CD and ^1H NMR spectra of poly(CHDPMA) were measured under similar conditions to that shown in Figure B-1-5. Figure B-1-6 shows the CD spectra of the poly(CHDPMA). Clear CD band which may be due to carbonyl and phenyl groups was observed in the range of 220~260 nm. Immediately after being dissolved in $CHCl_3$, poly(CHDPMA) showed a large positive absorption which rather quickly changed to a negative trough with a similar spectral shape. In the ^1H NMR spectrum of the same polymer in $CDCl_3$, almost no change was observed (Figure B-1-7) and the signal of α-methyl group in the range of 0~0.5 ppm supports the helical conformation of the polymer. These

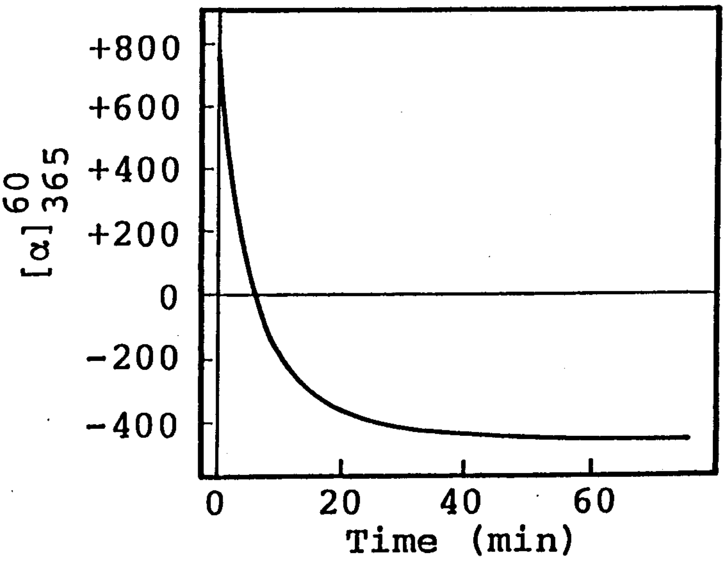


Figure B-1-5. Change of specific rotation of poly(CHDPMA) of DP=34 (Run 1 in Table B-1-3) in $CHCl_3$ at 60°C.

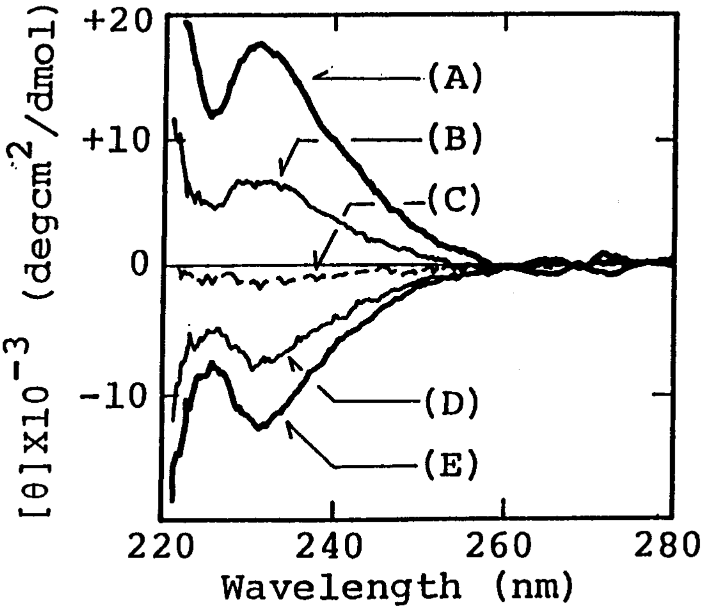


Figure B-1-6. Change of CD spectra of poly(CHDPMA) of DP=34 (Run 1 in Table B-1-3) in $CHCl_3$ at 60°C: 0 min (A), 5 min (B), 10 min (C), 20 min (D), and 60 min (E) after dissolution in $CHCl_3$.

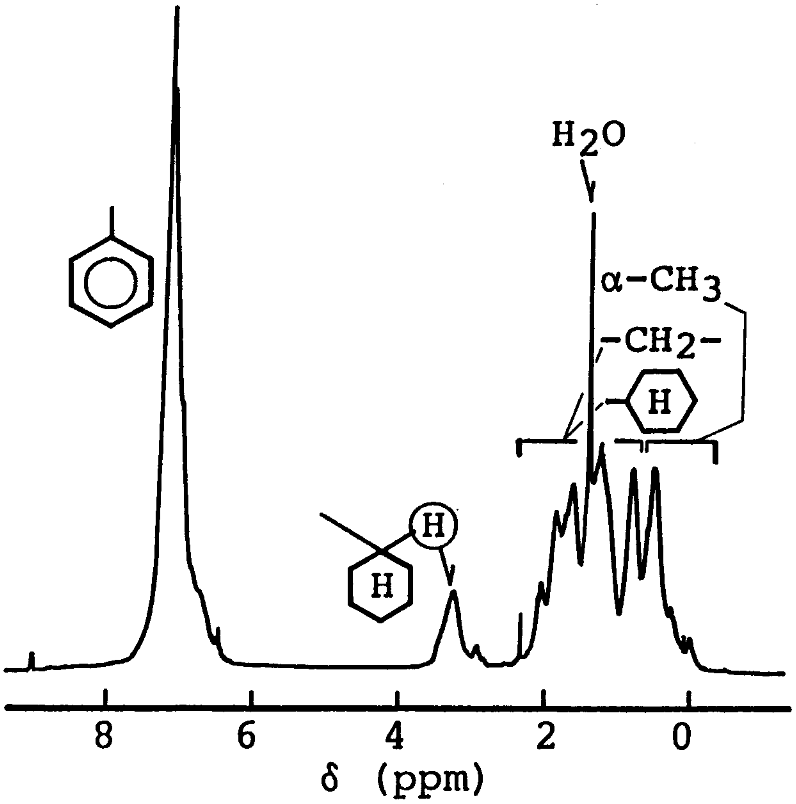


Figure B-1-7. 270 MHz ^1H NMR spectrum of poly(CHDPMA) of DP=34 (Run 1 in Table B-1-3). ($CDCl_3$, 60°C) findings suggest that the change of optical rotation may be attributable to the helix-helix transition of the polymer. Similarly to the optically active poly(D2PyMA), the helix of poly(CHDPMA) seems to be less stable than that of the optically active poly(TrMA). The change of optical rotation from a positive value to a negative value means that the content of the right- and left-handed helices changed from an excess of one of the two to an excess of the other. Poly(CHDPMA)s of right- and left-handed helical conformations are regarded as enantiomers if ends groups are neglected, and therefore their NMR spectra should be same and CD spectra should be in mirror images. However, poly(CHDPMA)s obtained here are rather low molecular weight and their ends groups may not be neglected. In that case, right- and left-handed helices are a kind of diastereomers with different stabilities. The helix-helix transition observed for poly(CHDPMA) in the present study can be interpreted as a transition from less stable helix which was predominantly formed in the polymerization process at -78°C to a more stable one at 60°C.

To confirm the helix-helix transition of the polymers, optical resolution of the polymer by HPLC after the transition was tried on a chiral column packed with optically active poly(TrMA)[1,5] using $CHCl_3$ as an eluent at -30~+15°C. However, no effective resolution was observed. A possible reason to explain this is that the chiral discrimination between the stationary phase of the column and the poly(CHDPMA) was not enough to achieve effective resolution.

Polymerization of DPODMA

The polymerization systems of DPODMA with Sp-, DDB-, and PMP-DPEDA-Li complexes did not show any significant optical activity during the polymerization reaction. The results of anionic polymerization of DPODMA are summarized in Table B-1-4. The polymers obtained with PMP-DPEDA-Li in toluene were almost optically inactive and were not isotactic. However, the polymer obtained with *n*-BuLi in THF at -78°C was isotactic. Under such a polymerization condition, MMA is known to afford a syndiotactic polymer,[7] DPEMA an atactic one,[3] and TrMA an isotactic one[8]. The result of polymerization of DPODMA with *n*-BuLi at -78°C resembles to that of TrMA. This suggests that a helical polymer may be obtained if a branched structure at 2-position of the alkyl group of DPODMA is introduced.

The radical polymerization of DPODMA was carried out with $(i\text{-PrOCOO})_2$ at 40°C in three solvents; toluene, ethanol, and methanol. The results are shown in Table B-1-5. Isotacticity of the polymers obtained in the alcohols was higher by about 5 % than that obtained in toluene. Moreover, the molecular weight of the polymer was larger in the alcohols. The heptadecyl moiety may take more compact conformation in alcohols than in toluene and larger steric effect in alcohols may result in production of more *mm* sequences. The effect of aggregation of aliphatic moiety of the ester group in polar solvents may be responsible for the higher DP of the polymer obtained in alcohols.

Conclusion

Cyclohexyldiphenylmethyl group is bulky enough and cyclopropyldiphenylmethyl and 1,1-diphenyloctadecyl groups are too small

Table B-1-4. Anionic polymerization of DPODMA for 24 h[a]

Run	Initiator	Solvent	Temp. (°C)	Yield (%)	DP[b]	Mw/Mn[b]	Tacticity(%)			$[\alpha]_{365}^{25}$[c]
							mm	*mr*	*rr*	
1	PMP-DPEDA-Li	Toluene	-78	56	19	1.38	34	44	22	-4°
2	PMP-DPEDA-Li	Toluene	-40	98	26	1.34	36	49	15	-6°
3	PMP-DPEDA-Li	Toluene	0	88	24	1.44	38	47	15	-3°
4	PMP-DPEDA-Li	Toluene	30	33	9	4.79	--	--	--	0°
5	*n*-BuLi	THF	-78	89	71	1.68	71	22	7	
6	*n*-BuLi	THF	0	83	28	1.66	40	43	17	
7	PhMgBr	Toluene	0	32	33	1.56	96	4	0	

[a] DPODMA 0.5 g, solvent 10 ml, [DPODMA]/[initiator] = 20.

[b] Determined by GPC of poly(MMA)s derived from poly(DPODMA)s.

[c] Specific rotation of polymerization mixture after termination.

Table B-1-5. Radical polymerization of DPODMA with $(i\text{-PrOCOO})_2$ at 40°C for 24 h[a]

Run	Solvent	Yield (%)	DP[b]	Mw/Mn[b]	Tacticity(%)		
					mm	*mr*	*rr*
1	Toluene	77	107	5.29	25	52	23
2	Ethanol	92	352	3.63	30	46	24
3	Methanol	50	499	5.59	31	46	23

[a] DPODMA 0.5 g, solvent 5 ml (Run 1, 2), 25 ml (Run 3), [DPODMA]/[initiator] = 50.

[b] Determined by GPC of poly(MMA)s derived from poly(DPODMA)s.

or too flexible to form optically active, helical polymethacrylates. Cyclobutyldiphenylmethyl group seems to be of critical bulkiness in the view point of formation of a helical polymethacrylate. Optically active poly(CHDPMA) undergoes a helix-helix transition. Less stable helix which was formed in excess in the process of polymerization changed into a more stable helix of an other screw sense. This is slightly different from stereomutation of poly(D2PyMA) in which one-handed helix nearly racemizes.[2]

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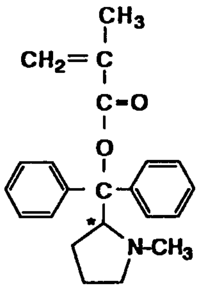
Part B: Chapter 2

Synthesis and Reversible Helix-Helix Transition of Optically Active Poly[(*S*)-diphenyl(1-methylpyrrolidin-2-yl)methyl methacrylate]

B-2-1 Introduction

Some helical, optically active polymethacrylates bearing achiral ester groups such as poly(diphenyl-2-pyridylmethyl methacrylate) [poly(D2PyMA)] and poly(cyclohexyldiphenylmethyl methacrylate) undergo helix-helix transition as described in the preceding chapter. It has been also found that poly((+)-phenyl-2-pyridyl-*m*-tolylmethyl methacrylate) [poly((+)-PPymTMA)] undergoes a conformational change which induces inversion of the helicity of the polymer chain;[1] that is, (-)-poly((+)-PPymTMA) which is prepared by asymmetric (helix-sense-selective) polymerization of (+)-PPymTMA at -78 °C undergoes irreversible stereomutation to (+)-poly((+)-PPymTMA) due to the chiral side group of the polymer in solution at 60 °C. In this chapter, the author describes the synthesis and conformational change of a new optically active polymer, poly[(*S*)-(-)-diphenyl(1-methylpyrrolidin-2-yl)methyl methacrylate] [poly(DMPMA)]. The optical rotation of the polymer was reversibly



DMPMA

varied by changing the acidity of the solution in a mixture of methanol and acids. This polymer may be the first example of a vinyl polymer which undergoes nearly perfect slow reversible transition from one helix to the other. Such a transition has been observed for poly-L-proline,[2] its derivatives,[3] and polynucleotides.[4]

B-2-2 Experimental

Synthesis of DMPMA. Methyl ester of (*S*)-(-)-*N*-benzoyloxycarbonylproline was prepared by the method of literature.[5] $[\alpha]_D^{20}$ -50.1° (c 1.0, CH_3OH) [lit. $[\alpha]_D^{20}$ -59.1° (c 1.0, CH_3OH)].

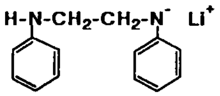
(*S*)-(+)-Diphenyl(1-methylpyrrolidin-2-yl)methanol was synthesized from the methyl ester.[6] $[\alpha]_D^{22}$ +56.3° (c 1.0, $CHCl_3$) [lit. $[\alpha]_D^{22}$ +57.0° (c 1.0, $CHCl_3$)].

The optically active alcohol (16.2 g, 0.065 mol) was converted into the sodium alkoxide at 0°C in dry tetrahydrofuran (THF) (160 ml) under dry nitrogen with sodium hydride (60% oil suspension, 4.94 g, 0.34 mol) washed with dry diethyl ether just before use. After heated at 50°C with stirring for 2 days, methacryloyl chloride was added dropwise to the solution at 0°C. The solution was allowed to stand with stirring at 0°C for 1 h. Diethyl ether and water were added to the reaction mixture, and the separated organic layer was collected. The ethereal layer was washed by saturated aqueous sodium bicarbonate and water, and then dried over $MgSO_4$. After ether was evaporated, the oily residue was purified by silica gel column chromatography with a mixture of hexane and diethyl ether as an eluent. The eluate was evaporated to give white crystal. Yield 11.75 g (58%).

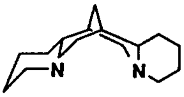
The crude product was recrystallized from hexane. $[\alpha]_D^{25}$ -40.9°, $[\alpha]_{365}^{25}$ -82.2° (c 1.0, benzene). Yield 6.9 g (34%); m.p. 83.0~84.8°C. ^{1}H NMR (270 MHz, $CDCl_3$, 35°C, TMS) 0.24 and 1.25 (m, 2H, 4-CH_2 of pyrrolidinyl ring), 1.74 and 2.02 (m, 2H, 3-CH_2 of pyrrolidinyl ring), 1.93 (s, 3H, α-CH_3), 2.25 and 2.67 (m, 5-CH_2 of pyrrolidinyl ring), 2.36 (s, 3H, N-CH_3), 4.25 (q, 1H, 1-CH of pyrrolidinyl ring), 5.53 and 6.13 (m, 2H, CH_2=C), 7.23~7.46 ppm (m, 10 H, aromatic-H); IR (nujol), 1705 (C=O), 1630 (C=C), 1165~1150 cm^{-1} (C-O). Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.81%; H, 7.46%; N, 4.18%. Found: C, 78.90%; H, 7.45%; N, 4.16%.

Other materials were purified in the manner described in Part A: Chapter 1.

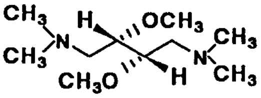
Polymerization procedure. Asymmetric anionic polymerization of DMPMA was carried out with the complexes of *N,N'*-diphenylethylenediamine monolithium amide (DPEDA-Li) with (-)-sparteine (Sp), (+)-(2*S*,3*S*)- and (-)-(2*R*,3*R*)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB), (+)-(*S*)-2-(1-pyrrolidinylmethyl)-pyrrolidine (PMP), and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in toluene at -78°C and -40°C in a glass ampule or in a 1.0-cm optical cell to monitor the optical activity of the polymerization system. Initiator solutions were prepared in the manner shown in Part B: Chapter 1. The polymerization was terminated with a small amount of methanol and the polymer was precipitated in methanol to be collected by centrifugation. The obtained polymer was converted into poly(methyl methacrylate)



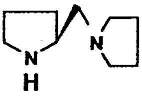
DPEDA-Li



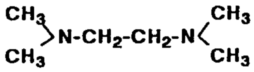
Sp



(+)-DDB



PMP



$(CH_3)_2N\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2$

TMEDA

[poly(MMA)] in the way described in Part A: Chapter 1 to determine tacticity, degree of polymerization (DP), and the molecular weight distribution of the original polymer.

Solvolysis of DMPMA in methanol. The solvolysis rate of DMPMA was measured in an NMR sample tube by means of ^{1}H NMR spectroscopy in a mixture of $CDCl_3$ and CD_3OD (1/1 v/v) at 35°C. DMPMA (53.3 mg, 0.159 mmol) was dissolved in the deuterated solvent (0.4 ml, Conc. 0.40 mol/l). Solvolysis rate was estimated from the intensity ratio of olefinic proton signals of DMPMA to those of methacrylic acid produced by solvolysis.

Measurement. ^{1}H NMR spectra were taken on a JEOL GX-500 (500 MHz), a JEOL GSX-270 (270 MHz), and a JEOL FX-100 (100 MHz) spectrometers. Circular dichroism (CD) spectra were taken on a JASCO J-500 spectrometer equipped with a computerized data processor. Optical rotation was measured by a JASCO DIP-181 polarimeter. Gel permeation chromatographic (GPC) analysis of poly(MMA) was done in the same manner as described in Part A: Chapter 1.

B-2-3 Results and Discussion

Polymerization of DMPMA

The polymerization of DMPMA with the DPEDA-Li complexes of (+)-DDB and TMEDA at the ratio of monomer to initiator ([DMPMA]/[Li]) 20 was carried out at -78°C in a 1-cm optical cell in order to monitor the change of optical activity during the polymerization (Figure B-2-1). In both cases, the optical activity at 435 nm very slowly increased to negative direction. It took about 2 weeks to get the constant values of optical rotation. The final optical rotation values were -1.55° ($[\alpha]_{435}^{-78}$ -326°) in the system with (+)-DDB-DPEDA-Li and -2.28° ($[\alpha]_{435}^{-78}$ -588°) in the system with TMEDA-DPEDA-Li.

Table B-2-1 shows the results of polymerization at -78°C. The isolated polymers were insoluble in common organic solvents but soluble in methanol containing a small amount of acids. The isolated polymers showed similar positive rotation ($[\alpha]_{365}^{25}$ ca. +800°) in methanol containing 20vol% of CH_3SO_3H (CH_3OH-20%CH_3SO_3H). Considering the negative rotation during the polymerization, some conformational change must occur during the isolation or dissolution in the solvent. All the polymers obtained were highly isotactic. The large positive rotations of the polymers, which are opposite to that of the monomer in sign, and the high isotacticity suggest that the polymer may possess a one-handed helical conformation. The positive optical rotations of the polymers with similar degree indicate that the helicity of the polymer was controlled by the chirality of ester group of the polymer.

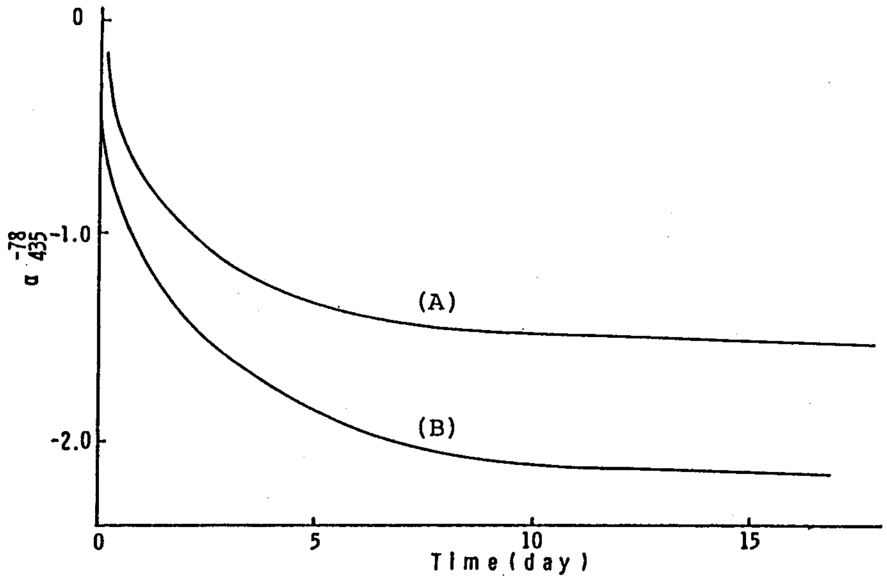


Figure B-2-1. Change of optical activity of polymerization systems of DMPMA with (+)-DDB-DPEDA-Li (A) and with TMEDA-DPEDA-Li (B) in toluene at -78°C. (DMPMA 0.15 g, toluene 3 ml, [DMPMA]/[Li]=20, cell length 1.0 cm)

Table B-2-1. Polymerization of DMPMA with DPEDA-Li complexes in toluene at -78°C

Run	Ligand	Yield(%)	DP^b	Mw/Mn^b	Tacticity(%)			$[\alpha]_{365}^{25}$ [c]
					mm	*mr*	*rr*	
1	(+)-DDB	100	21	1.47	95	4	1	+786°
2	(-)-DDB	98	20	1.36				+846°
3	PMP	100	22	1.36	95	4	1	+798°
4	TMEDA	99	23	1.17				+809°
5	TMEDA	88	37	1.32	99	1	0	+939°

[a] DMPMA 0.5 g, toluene 10 ml, time 15 days, [DMPMA]/[Li] = 20 (Run 1-3); DMPMA 1.0 g, toluene 20 ml, time 23 days, [DMPMA]/[Li] = 20 (Run 4); DMPMA 1.0 g, toluene 20 ml, time 23 days, [DMPMA]/[Li] = 40 (Run 5).

[b] Determined by GPC of poly(MMA)s derived from poly(DMPMA)s.

[c] Measured in CH_3OH-20%CH_3SO_3H 2 h after being dissolved.

Since the polymerization at -78°C was very slow, the preparation of the polymers of higher DP was difficult under the conditions described above. To obtain a polymer of high molecular weight, polymerization was carried out with TMEDA-DPEDA-Li in toluene at -40°C and at higher concentration of monomer (DMPMA 0.3 g in toluene 3.0 ml). The change of optical activity of the polymerization systems at [DMPMA]/[Li] = 20 and 40 is shown in Figure B-2-2 (A). Both systems showed negative rotation increasing with polymerization time to large negative values; -5.14° ($[\alpha]_{435}^{-40}$ -663°) in the system at [DMPMA]/[Li] = 20 and -4.30° ($[\alpha]_{435}^{-40}$ -554°) in the system at [DMPMA]/[Li] = 40. Both the systems gave the polymer almost quantitatively. At -40°C, the polymerization was much faster than at -78°C. Figure B-2-2 (B) shows the change of optical activity of the polymerization system at [DMPMA]/[Li] = 20 after termination. The optical activity changed to positive direction at room temperature, though the solution gelled in the course of measurement. This suggests that the terminated polymer underwent some conformational change at room temperature and became insoluble in toluene. The solubility of the polymer in toluene appears to be dependent on the conformation.

The results of polymerization with TMEDA-DPEDA-Li at -40°C are summarized in Table B-2-2. In all the cases, the obtained polymers showed high optical activity and were highly isotactic though the molecular weight distribution was rather broad.

Change of optical activity of the polymers in CH_3OH-20%CH_3SO_3H solution

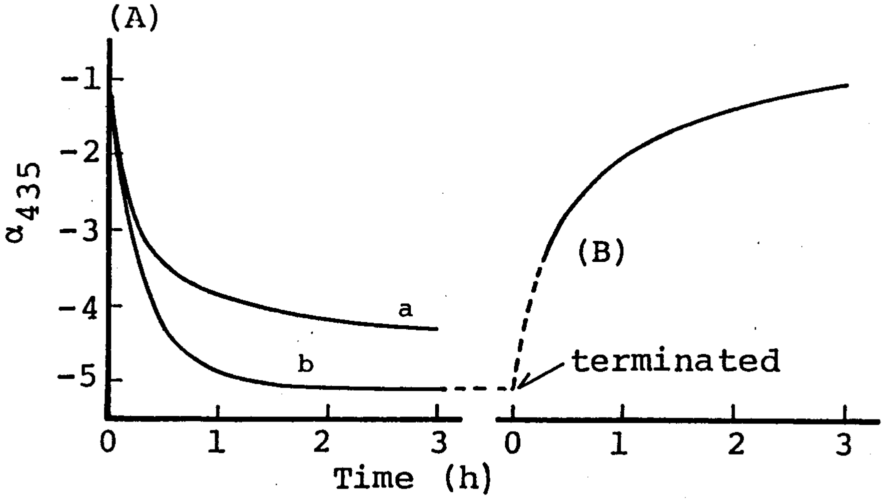


Figure B-2-2. Change of optical activity of polymerization systems of DMPMA with TMEDA-DPEDA-Li in toluene at -40°C (A) and at room temperature after termination (B); a: [DMPMA]/[Li]=40 and b: [DMPMA]/[Li]=20.

Table B-2-2. Polymerization of DMPMA with TMEDA-DPEDA-Li in toluene at -40°C for 3 days[a]

Run	[DMPMA]/[Li]	Yield (%)	DP[b]	Mw/Mn[b]	Tacticity(%) *mm*	Tacticity(%) *mr*	Tacticity(%) *rr*	$[\alpha]^{25}_{365}$[c]
1	40	100	65	1.45	99	1	0	+1110°
2	60	96	105	1.59	~100	0	0	+1260°
3	80	99	130	1.36	~100	0	0	+1310°
4	100	98	160	1.93	~100	0	0	+1360°
5	200	51	300	1.95	99	1	0	n.d.[d]

[a] DMPMA 1.5 g, toluene 15 ml (Run 1, 2); DMPMA 0.8 g, toluene 8 ml (Run 3-5).

[b] Determined by GPC of poly(MMA)s derived from poly(DMPMA)s.

[c] Measured 15 h (Run 1, 2) or 50 min (Run 3-5) after being dissolved in CH_3OH-20%CH_3SO_3H

[d] Insoluble in CH_3OH-20%CH_3SO_3OH.

Figure B-2-3 shows the change of optical activity of the polymers obtained with TMEDA-DPEDA-Li in CH_3OH-20%CH_3SO_3H solution. The polymers showed positive optical rotation slowly increasing with time in a solvent containing a large amount of acid. The optical activity of the polymers of DP = 37, 65, and 105 reached constant values within about 100 min, while the polymers of DP = 130 and 160 precipitated in the course of the change. These changes should be caused by the conformational change of the polymers.

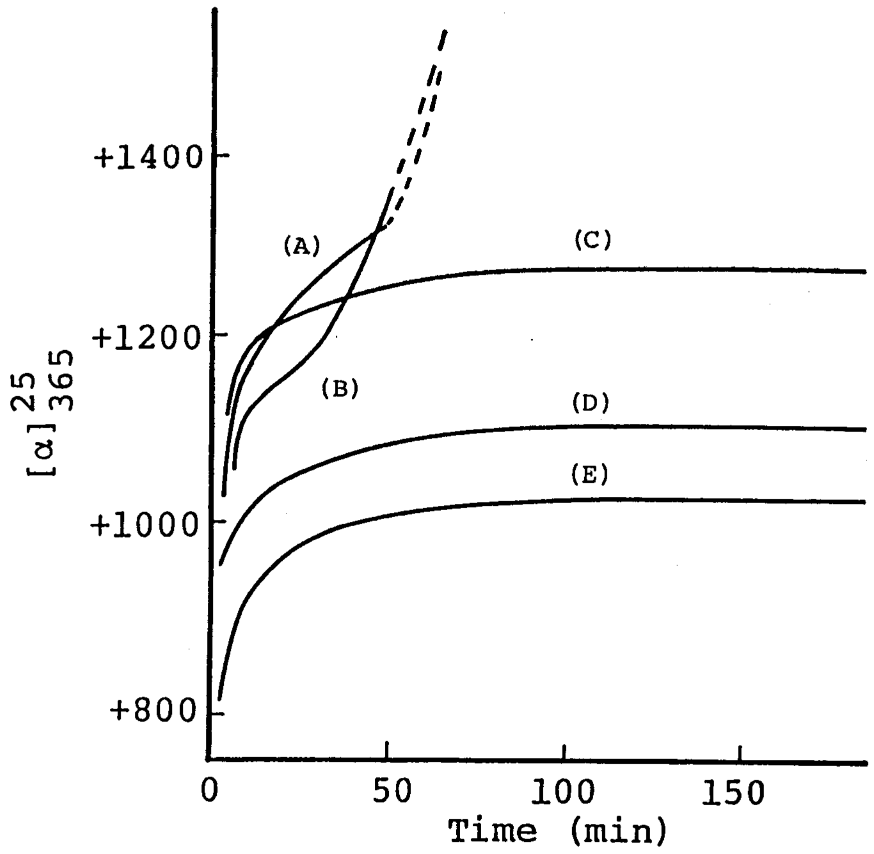


Figure B-2-3. Change of specific rotation of poly(DMPMA)s of DP=130 (A), 160 (B), 105 (C), 65 (D), and 37 (E) in CH_3OH-20%CH_3SO_3H at 25°C.

Change of optical activity of the polymers depending on acidity of the solution

The optical activity of the polymers also changed in the solution containing a small amount of acid. Figure B-2-4 shows the change of optical rotation of the polymer of DP = 37 obtained with TMEDA-DPEDA-Li (Run 5 in Table B-2-1). The CH_3OH-0.01%CH_3SO_3H solution first showed a positive rotation ($[\alpha]_{365}^{25}$ +780°) which slowly moved with time to a negative value ($[\alpha]_{365}^{25}$ -410°) (curve A). A further addition (13%) of the acid induced the returning optical activity arriving at a positive value ($[\alpha]_{365}^{25}$ +779°) (curve B). Addition of LiCl (9wt%) was also effective for the returning of the optical rotation arriving at a positive value ($[\alpha]_{365}^{25}$ +119°). The CH_3OH-1.5%CF_3CO_2H solution of the polymer also showed a similar change from a positive value ($[\alpha]_{365}^{25}$ +420°) to a negative value ($[\alpha]_{365}^{25}$ -890°) (curve C), which also returned to a positive value ($[\alpha]_{365}^{25}$ +770°) by the addition of CH_3SO_3H (curves D and E). The polymer of higher weight molecular weight (DP = 105) also showed similar change of optical rotation though the change was slower than that of the polymer of DP = 37.

These changes may be attributed to the change of helicity of the main chain. In order to confirm this possibility, CD spectra were taken under the same condition of the change of optical rotation. Figure B-2-5 shows the CD spectra of the polymer of DP = 37 in CH_3OH-0.01%CH_3SO_3H solution and those taken in the presence of 13%CH_3SO_3H after completion of the former change. Clear CD bands were observed in the range of 200~240 nm. A strong peak at 208 nm and a shoulder at 220 nm may

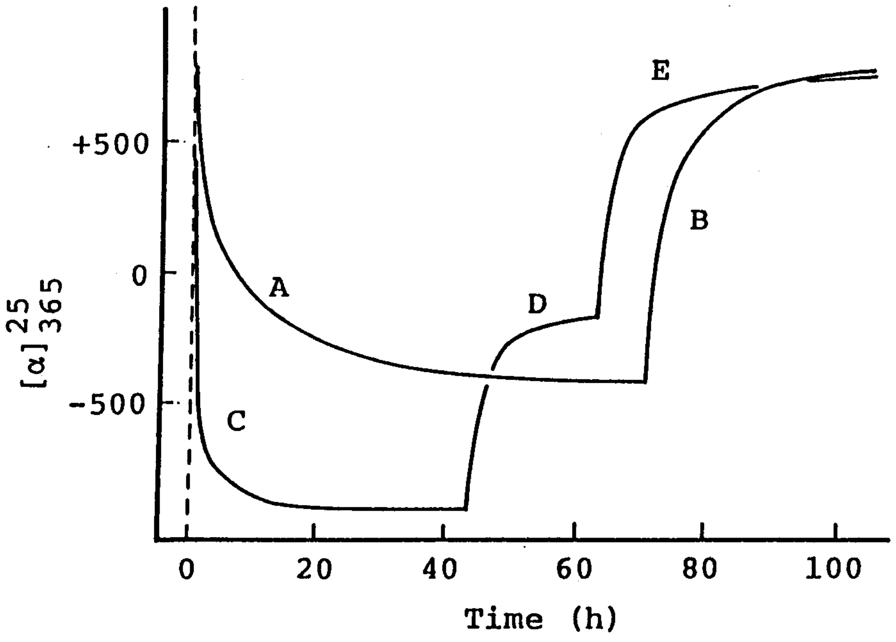


Figure B-2-4. Change of specific rotation of poly(DMPMA) of DP=37 (Run 5 in Table B-2-1) in the mixtures of CH_3OH and acids at 25°C; in CH_3OH-0.01%CH_3SO_3H (curve A), in CH_3OH-13.0%CH_3SO_3H (curve B), in CH_3OH-1.5%CF_3CO_2H (curve C), in CH_3OH-0.9%CF_3CO_2H-0.5%CH_3SO_3H (curve D), and in CH_3OH-0.5%CF_3CO_2H-9.5%CH_3SO_3H (curve E).

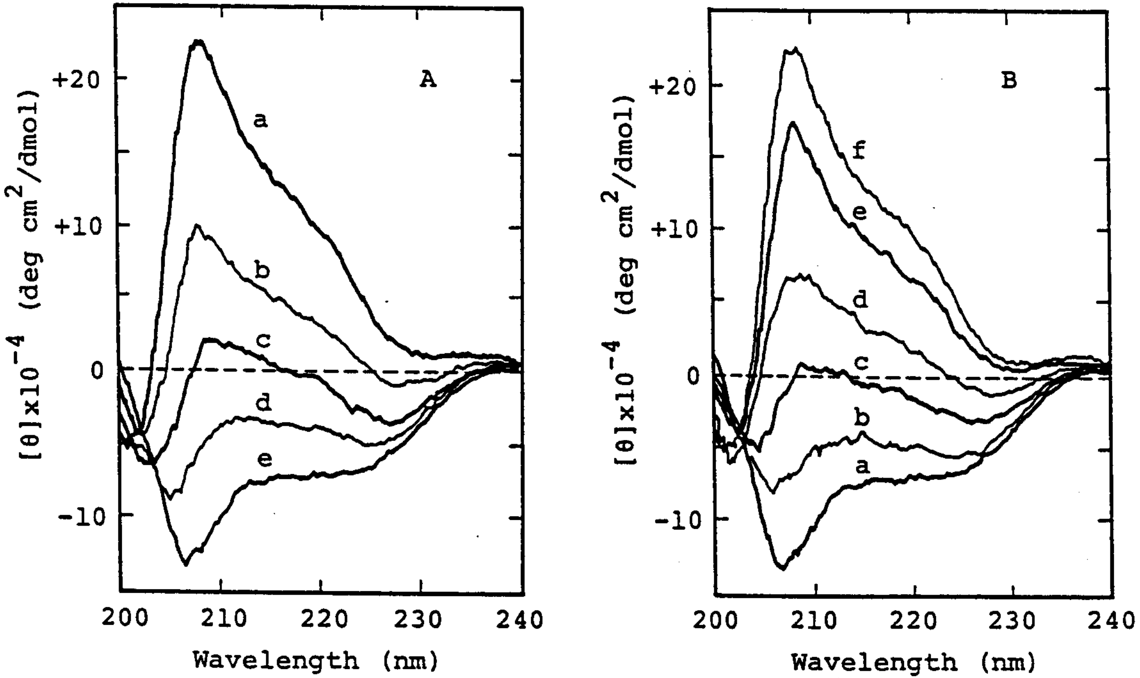


Figure B-2-5. Change of CD spectra of poly(DMPMA) of DP=37 (Run 5 in Table B-2-1) at 25°C. A: in CH_3OH-0.01%CH_3SO_3H; (a) immediately after dissolution ($[\alpha]^{25}_{365}$ +780°), (b) 2 h 5 min (+240°), (c) 4 h 4 min (+81°), (d) 22 h 18 min (-163°), and (e) 70 h (-410°). B: in CH_3OH-13%CH_3SO_3H after completion of the change in A; (a) the last spectrum in A, (b) 5 min after the addition of CH_3SO_3H (13%) (-278°), (c) 52 min (-26°), (d) 2 h 30 min (+252°), (e) 16 h 20 min (+570°), and (f) 30 h (+779°).

be assigned to the absorptions due to phenyl and carbonyl groups, respectively. The intensity of the CD band seems to be almost proportional to the optical activity. The maximum $[\theta]$ values are comparable to those of the purely one-handed helical poly(TrMA) and poly(D2PyMA).[7] The polymer solution in CH_3OH-0.1%CH_3SO_3H first showed the positive CD band with a large intensity which changed gradually to the negative trough (Figure B-2-5 (A)). A reversed change of the spectral pattern was observed when the content of CH_3SO_3H was increased to 13% (Figure B-2-5 (B)). These results indicate that a reversible stereomutation from one helix to the other was achieved by changing the acidity of the solvent.

The helix-helix transition of the polymer in CD_3OD-8.3%CF_3CO_2D solution was monitored by means of ^1H NMR spectroscopy under the conditions similar to those for curve C in Figure B-2-4. The results are shown in Figure B-2-6. The broadening of the peaks in the spectra must be due to the rigidity of the helical polymer, and no peaks of a low molecular weight compound which may be produced by the solvolysis of the ester group were observed during the measurement. Several characteristic increases and decreases of peaks were observed. Especially, the spectral pattern in methyl region (0~1 ppm) and phenyl region (7~9 ppm) greatly changed. These changes of the spectral pattern must reflect the transition of helicity accompanying with the conformational change of ester group. The two helical structures of opposite screw sense are not enantiomeric but diastereomeric. Therefore, they show different spectral patterns. In the case of poly(D2PyMA), no clear spectral change of ^1H NMR was observed

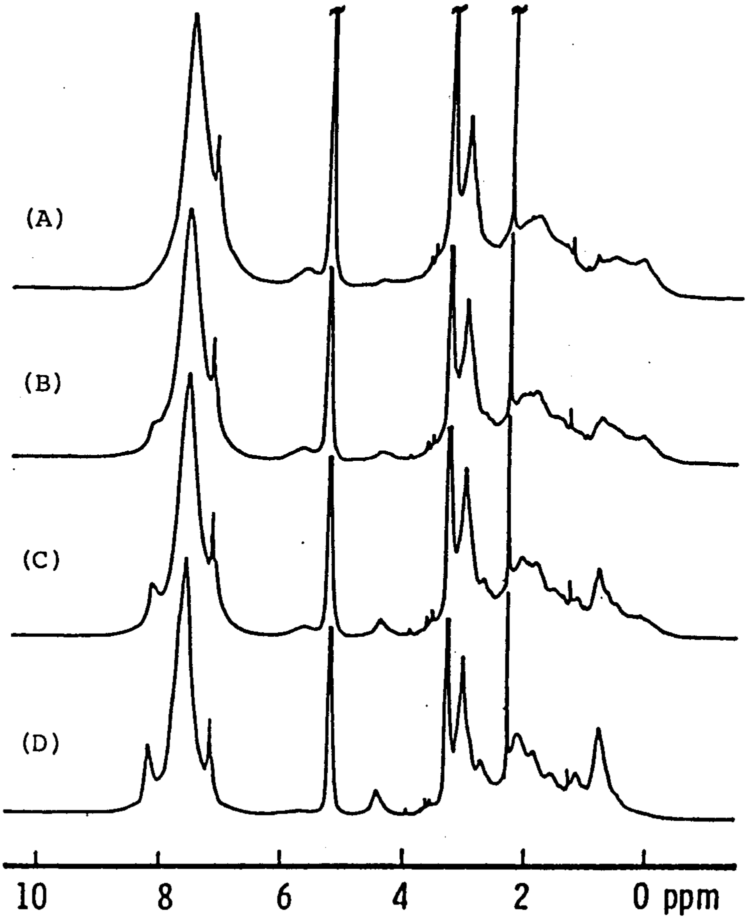


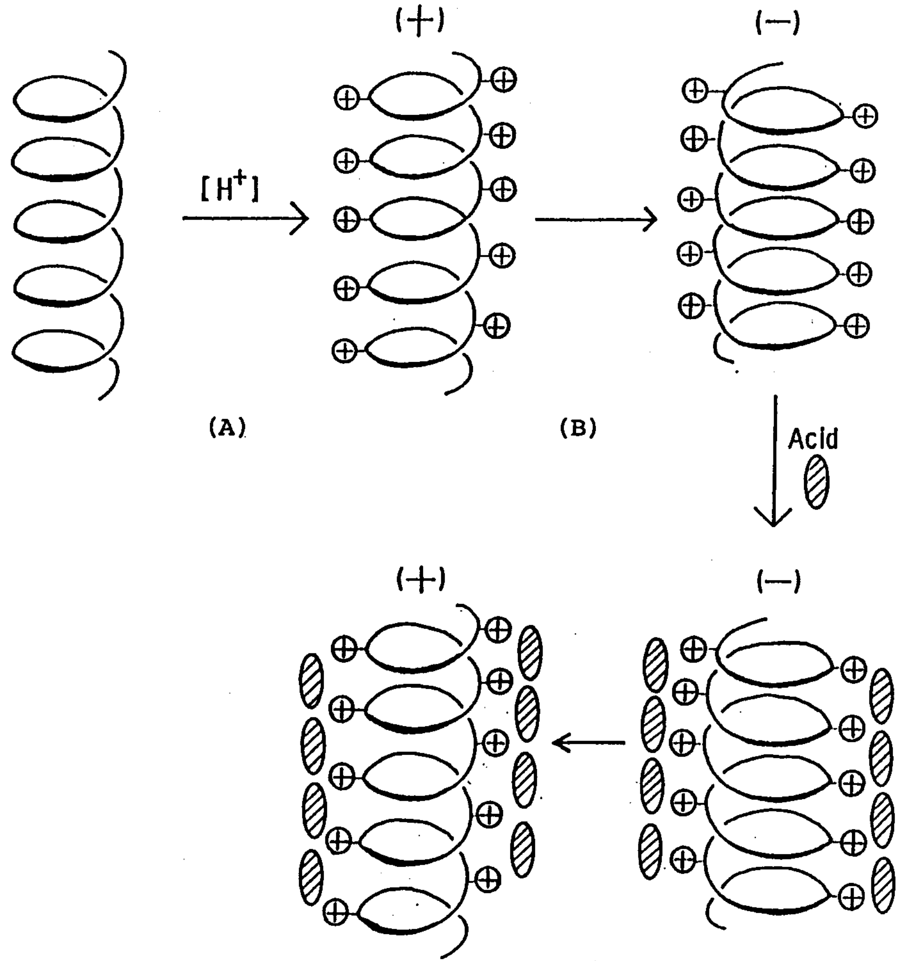
Figure B-2-6. Change of ^{1}H NMR spectra of poly(DMPMA) of DP=37 (Run 5 in Table B-2-1) in CD_3OD-8.3%CF_3CO_2D at 25°C: 7 min (A), 33 min (B), 65 min (C), and 200 min (D) after dissolution.

during the helix-helix transition,[8] because two helical structures are almost enantiomeric.

The activation energy (Ea) of the transition of the polymers of DP = 37, 65, and 105 was estimated to be 24, 24, and 21 kcal/mol, respectively, from the initial change (decrease) of optical activity in CH_3OH-0.2%CH_3SO_3H solution at 25, 40, and 60°C.

Mechanism of helix-helix transition

The mechanism of the transition is speculated as follows (Scheme B-2-1). The protonation of amino group makes the polymer soluble in polar solvents. The polymer takes a conformation corresponding to a positive rotation immediately after being dissolved (A). This conformation is thermodynamically more stable at room temperature for the polymer which is not protonated. This reasonably explains the change of optical rotation of the polymerization system after termination in Figure B-2-2, assuming that the conformation formed in the process of polymerization at low temperature is opposite to the conformation of isolated polymer. The mutual electrostatic repulsion between the protonated side groups makes the conformation corresponding to positive rotation unstable and forces the polymer to take a conformation corresponding to negative rotation which is more stable for the protonated polymer (B). The mutual repulsion between the protonated ester groups is reduced by coordination with polar substances such as acid and metal halide, and the conformation of the polymer changes into that corresponding to the positive rotation (C).



Scheme B-2-1. A possible mechanism of reversible helix-helix transition of poly(DMPMA) dependent on acidity of solution.

Solvolysis rate of DMPMA

Solvolysis of aromatic tertiary ester group of methacrylate readily occurs especially in alcohols. The solvolysis rate was measured in a mixture of $CDCl_3$ and CD_3OD (1/1 v/v) at 35°C by means of ^1H NMR spectroscopy. The values of rate constant (k) and half-life period were 0.0017 h^{-1} and 420 h, respectively. DMPMA showed much higher resistance against solvolysis compared with TrMA (k = 2.86 h^{-1}). The protonation of the amino group appears to protect the ester bond from being attacked by proton.

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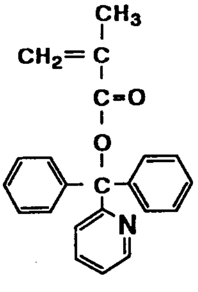
Part B: Chapter 3

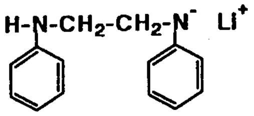
Reversible Stereomutation of Oligomer of Diphenyl-2-pyridylmethyl Methacrylate

B-3-1 Introduction

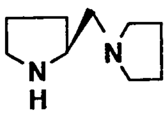
Diphenyl-2-pyridylmethyl methacrylate (D2PyMA) gives a purely one-handed helical polymer in the polymerization with the complex of *N,N'*-diphenylethylenediamine monolithium amide (DPEDA-Li) and (+)-(*S*)-2-(1-pyrrolidinylmethyl)pyrrolidine (PMP),[1] and the polymers of degree of polymerization (DP) about 30 undergoes a helix-helix transition.[2] In this transition, the one-handed helix becomes a mixture of right- and left-handed helices which can be separated by high-performance liquid chromatography (HPLC) using optically active poly(triphenylmethyl methacrylate) [poly(TrMA)] as a chiral stationary phase.[2,3] In this chapter, conformational analysis of oligo(D2PyMA) of DP = 4~12 by means of ^{1}H NMR spectroscopy is described. A reversible stereomutation, probably a helix-coil transition was found to take place in the oligomers of DP = 6~12. Although this type of conformational change has been extensively studied for poly(α-



D2PyMA



DPEDA-Li



PMP

amino acid)s,[4] little is known for the optically active vinyl polymers.

B-3-2 Experimental

Preparation of samples. The sample of poly(D2PyMA) of DP = 27 (Mw/Mn=1.04, $[\alpha]^{25}_{365}$ +1325° in a mixture of $CHCl_3$ and 2,2,2-trifluoroethanol (9/1 v/v)) was prepared previously,[1] and oligo(D2PyMA) was synthesized at [monomer]/[initiator] = 3 with PMP-DPEDA-Li complex in the same way as used for polymerization. Conversion of oligo(D2PyMA) into methyl ester (oligo(MMA)) was also done according to the manner described in Part A: Chapter 1. Fractionation of the oligo(D2PyMA) was performed by gel permeation chromatography (GPC) on a column (50 x 2.0 (i.d.) cm, maximum porosity 3000) packed with poly(styrene-*co*-divinylbenzene) gel using $CHCl_3$ as an eluent (flow rate 3.0 ml/min) on a JASCO BIP-I HPLC pump equipped with a UVIDEC-100-V (UV) detector.

Measurements. GPC analysis of oligo(MMA) was done on two Shodex Gel-101 columns (50 x 0.72 cm (i.d.) cm) connected in series with $CHCl_3$ as an eluent. Molecular weight of oligo(MMA) was calibrated with oligostyrene (TSK-A300) standard in the GPC analysis. ^1H NMR spectra were taken in $CDCl_3$ with a JEOL GX-500 (500 MHz) and a Varian VXR-500 (500 MHz) spectrometers. Field desorption (FD) mass spectra were measured on a JEOL DX-HF303 instrument. Optical rotation was measured with a JASCO DIP-181 polarimeter.

B-3-3 Results and Discussion

The IR and ^1H NMR spectra of the oligomerization products did not clearly show the signals due to unreacted monomer and side products. GPC curve the oligomerization products and FD mass spectrum of oligo(MMA) derived therefrom are shown in Figures B-3-1 and B-3-2, respectively. The product was a mixture of oligo(D2PyMA)s of DP = 1~12. The DP of each oligomer was confirmed by the FD mass spectrum of the oligo(MMA) derived from the mixture. In the spectrum, the peaks of M/z = 312, 412, 512, 612, 712, 812, 912, 1012, 1113, 1212, 1312, and 1412 which correspond to the molecular weight of the oligo(MMA) of the DPs from 1 to 12, respectively, were observed (Figure B-3-2). In the mass spectrum, another series of smaller peaks of M/z = 326, 426, 526, ···· was also observed. This series of oligomers appears to contain one additional methylene group to the original oligo(MMA). Since in the case of oligo(MMA) derived from oligo(TrMA) having a fluorenyl group at the α-end, such a series of oligomers was not detected (Part A: Chapter 1), this methylene group may be introduced on *N,N'*-diphenylethylenediamine group of the present oligo(MMA) in the process of conversion of oligo(D2PyMA) into oligo(MMA). The oligo(D2PyMA)s used for the NMR analyses were obtained by GPC fractionation. The oligomers (oligomer A) eluted in the range of 21.0 min to 23.0 min and those (oligomer B) eluted in the range of 24.5 min to 25.0 min were collected for NMR analyses. Specific rotation ($[\alpha]^{25}_{365}$) of oligomers A and B in $CHCl_3$ were +12.0° and +4.0°, respectively. These values were much smaller than that of the polymer. This indicates that these oligomers can not maintain stable one-handed helical structure like poly(D2PyMA). DP and distributions of oligomers A and B were determined by FD mass spectra

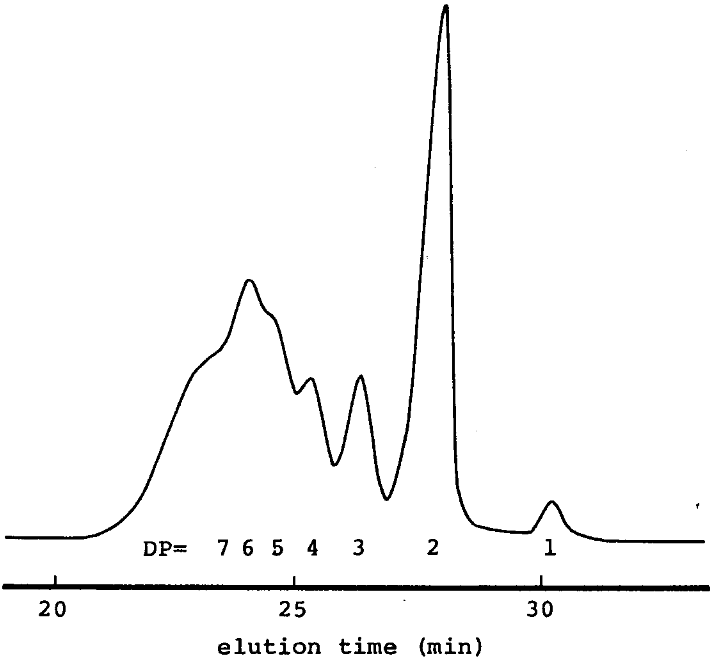


Figure B-3-1. GPC curve of oligo(D2PyMA) prepared with PMP-DPEDA-Li at [D2PyMA]/[Li]=3 in toluene at -78°C.

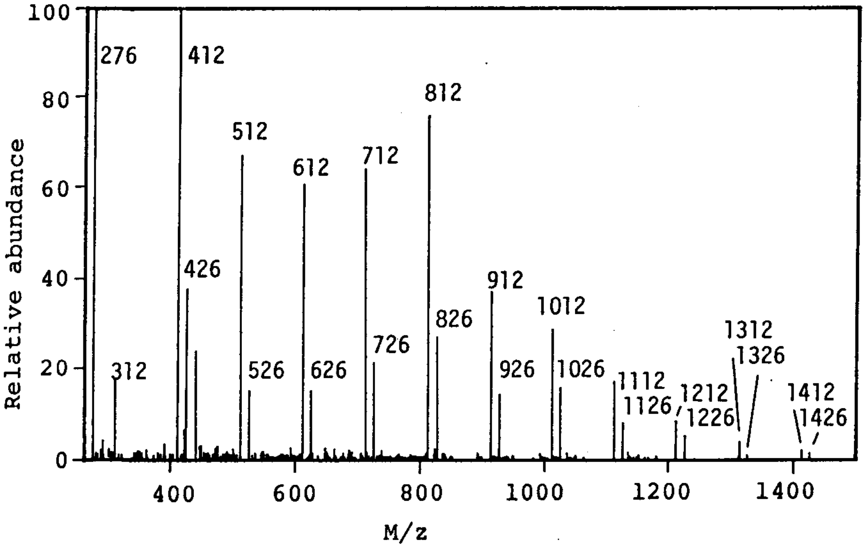
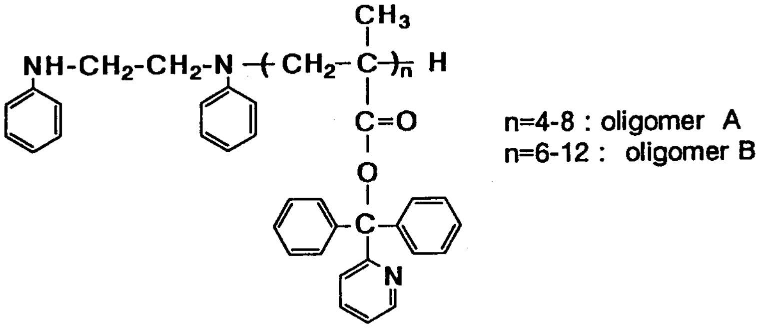


Figure B-3-2. FD mass spectrum of oligo(MMA) derived from oligo(D2PyMA) prepared with PMP-DPEDA-Li at [D2PyMA]/[Li]=3 in toluene at -78°C. The peak of M/z=276 corresponds to the molecular weight of methyl diphenyl-2-pyridylmethyl ether produced in the process of conversion of ester group.



oligo(D2PyMA)

of oligo(MMA)s derived from the original oligomers. FD mass spectra showed that oligomer A was a mixture of the oligomers of DP = 6~12 in which the oligomers of DP = 7~10 were the predominant component (~80%) and fraction B a mixture of the oligomers of DP = 4~8 in which the oligomer of DP = 5 was the predominant component (~50%). The average DP ($\overline{DP}$) and molecular-weight-distribution ($\overline{Mw}/\overline{Mn}$) determined by GPC were $\overline{DP}$ = 10.7 and $\overline{Mw}/\overline{Mn}$ = 1.03 for oligomer A and $\overline{DP}$ = 5.5 and $\overline{Mw}/\overline{Mn}$ = 1.01 for oligomer B. Most of these oligomers must have isotactic structure because a highly isotactic polymer was almost quantitatively obtained in the polymerization with the same initiator system.[1]

Figure B-3-3 shows the ^{1}H NMR spectra of poly(D2PyMA) of DP = 27 at 35°C, oligomer A at 30°C, and oligomer B at 35°C taken in $CDCl_3$. In the spectrum of the optically active polymer of DP=27, α-CH_3 signals appeared in the range of 0~0.5 ppm. The ^{1}H NMR spectrum of optically active poly(TrMA) also exhibited α-CH_3 signal at similar chemical shifts.[5] Most polymethacrylates such as PMMA and poly(benzyl methacrylate) show α-CH_3 signal at 0.7~1.2 ppm in $CDCl_3$.[6] The upfield shifts of α-CH_3 of the

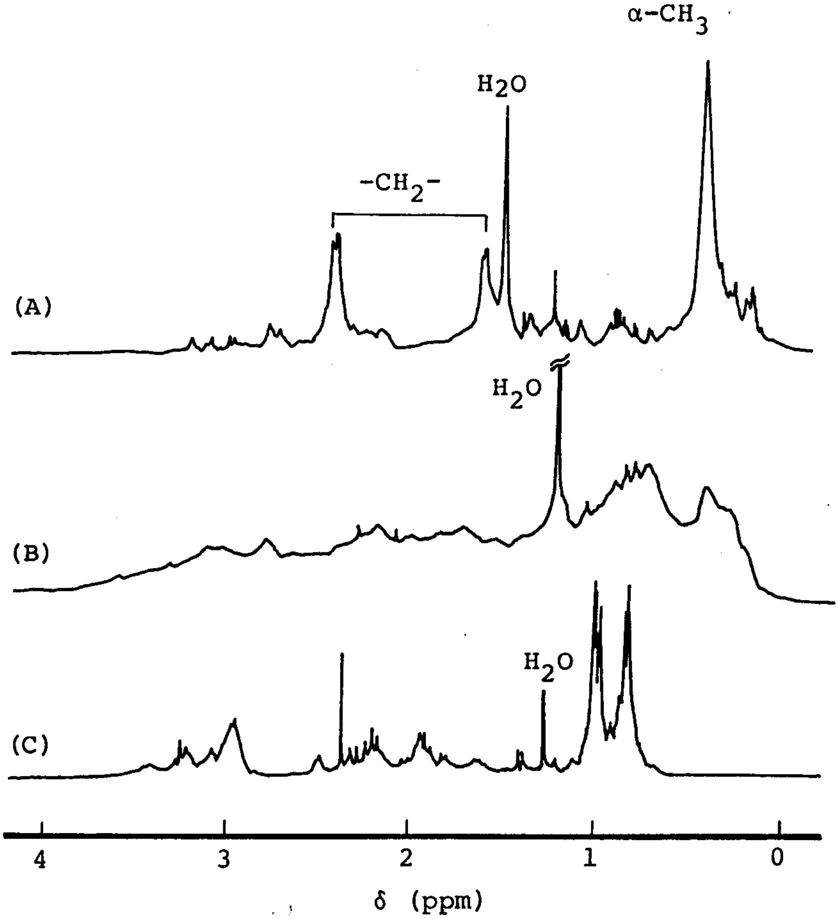


Figure B-3-3. 500 MHz ^1H NMR spectra of poly(D2PyMA) of DP=27 at 35°C (A), oligomer A at 30°C (B), and oligomer B at 35°C. ($CDCl_3$)

poly(triarylmethyl methacrylate)s may be ascribed to the helical conformation and shielding effect of the triaryl groups. On the other hand, in the spectrum of oligomer B, all α-CH_3 signals appeared in the range of 0.5~1 ppm. As described in Part A: Chapter 1, in the polymerization of TrMA with the complexes of fluorenyllithium and chiral ligands, a stable helical structure starts at DP 7~9. These results suggest that the α-CH_3 protons in a helical conformation resonate in the range of 0~0.5 ppm and those in a different conformation, probably random-coil conformation, in the range of 0.5~1 ppm. In the spectrum of the oligomer A, the α-CH_3 signals were observed in the both ranges, indicating that this sample contained the oligomers of both helical and coil conformations. Oligomer A likely contains the oligomer with the critical chain length suitable to form a helical conformation. The DP agrees with the critical DP = 7~9 at which a stable helix starts in the asymmetric polymerization of TrMA (Part A: Chapter 1).

In order to examine the stability of helical conformation of oligomer A, the ^{1}H NMR spectra were taken at 30~60°C (Figure B-3-4). The intensity of the α-CH_3 signal in the range of 0~0.5 ppm decreased with the increase of temperature, and at 60°C, α-CH_3 signal was clearly observed only in the range of 0.5~1 ppm. The spectral change was reversible in this range of temperature. In the case of poly(D2PyMA)s of DP = 27 and 35, almost no change was observed in the ^{1}H NMR spectra in the course of the helix-helix transition.[2] These results indicate that oligomer A undergoes a reversible stereomutation, probably helix-coil transition. Though, in the case of poly(D2PyMA) of

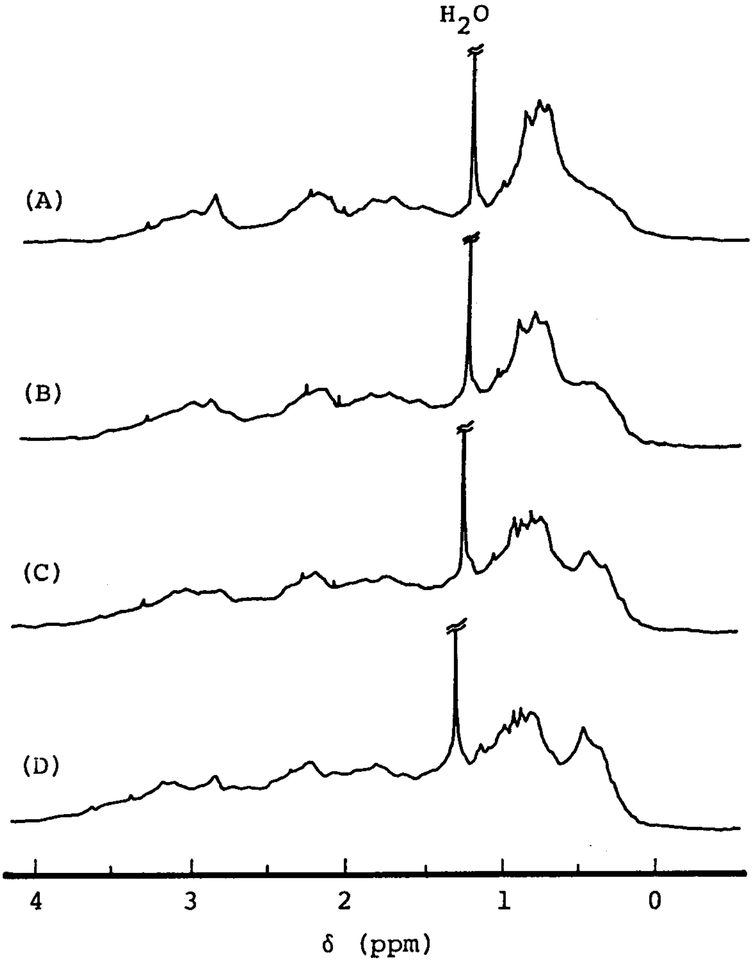


Figure B-3-4. 500 MHz ^1H NMR spectra of oligomer A taken at 60°C (A), 50°C (B), 40°C (C), and 30°C (D). ($CDCl_3$)

DP = 27, two helices are separable by chromatography, oligomer A was not effectively separated under the same chromatographic conditions at the temperature range of -30~+15°C. The stereomutation is considered to be slow enough to be detected by NMR, but may be too fast to separate each conformer, right- and left-handed helices and coil, by chromatography.

This kind of slow reversible helix-coil transition probably has not yet been reported for vinyl oligomers and polymers.

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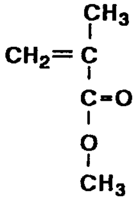
Part B: Chapter 4

Optical Activity of Isotactic Oligomers of Methyl Methacrylate

B-4-1 Introduction

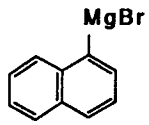
Recently, Cram and Sogah[1] reported that optically active, isotactic oligo- and polymethacrylates with high optical rotation ($[\alpha]_{578}$ 70-350°) are obtainable by asymmetric polymerization of methyl methacrylate (MMA) and several other methacrylates with potassium *t*-butoxide-chiral crown ether or butyllithium-chiral diamine complexes in toluene at -78°C. The optical activity has been ascribed to the helical structure of the oligomers and polymers. The activity decreased slowly in solution at room temperature, which has been attributed to uncoiling (mutarotation) of the helix. However, as described in Part B: Chapter 1, optically active polymers can not be obtained in the polymerization of bulky cyclopropyldiphenylmethyl and 1,1-diphenyloctadecyl methacrylates with chiral initiator. Therefore, the author believes that a methyl group is not bulky enough to form and maintain a helical structure of polymethacrylate.

In the present study, oligomerization of MMA with 1-naphthylmagnesium bromide (1-NpMgBr) was carried out in toluene at



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_3$

MMA



1-NpMgBr

$-78^\circ C$ and the obtained isotactic oligomers were optically resolved immediately after terminating the reaction in order to get information on the conformational stability and optical activity of the optically pure antipodes of isotactic oligo(MMA).

B-4-2 Experimental

Materials. MMA, toluene, and the other materials were purified by the usual method.

1-NpMgBr was prepared from 1-naphthyl bromide and magnesium turnings in dry diethyl ether. After the reaction completed, the reaction solution changed into a dark green colored solid which is considered to be the complex of 1-NpMgBr and diethyl ether. A small amount of dry toluene was added to dissolve the solid ([naphthyl] = 0.46 M, [Mg] = 0.43 M).

Polymerization and oligomerization procedure. Polymerization and oligomerization were carried out in toluene at $-78^\circ C$ or $0^\circ C$. A solution of 1-NpMgBr in a mixture of diethyl ether and toluene was added to a toluene solution of MMA cooled to $-78^\circ C$ or $0^\circ C$. The reaction was terminated by the addition of a small amount of methanol. In the case of polymerization at [MMA]/[1-NpMgBr] = 20, the polymer was precipitated in hexane and collected by filtration. The polymer was washed with water and freeze-dried from a benzene solution. In the case of oligomerization at $-78^\circ C$ at [MMA]/[1-NpMgBr] = 5, a half of the reaction solution was washed with water after termination reaction, and then the solvent was evaporated. The obtained oligomer was fractionated into hexane-soluble and -insoluble parts. The other half of the reaction solution was kept at -78°C for the optical resolution of pentamer and octamer.

Measurements. ^1H NMR spectra of polymer were taken in $CDCl_3$ at 60°C with a JEOL FX-100 (100 MHz) spectrometer and those of pentamer and octamer were taken in nitrobenzene-d_5 at 110°C with a JEOL GX-500 (500 MHz) spectrometer. Field desroption (FD) mass spectra were taken with a JEOL DX-HF303 spectrometer. GPC analyses of polymer and oligomer were done in the same manner as described in Part A: Chapter 1. The separation of diastereomers of oligomer was performed on a silica gel column by using a mixture of butyl chloride and CH_3CN as an eluent[2] under the same conditions as those described in Part A: Chapter 3.

HPLC optical resolution of pentamer and octamer was done by using a column (25 x 0.46 (i.d.) cm) packed with cellulose tris(3,5-dimethylphenylcarbamate)-coated macroporous silica gel[3] with a mixture of hexane and ethanol (80/20 v/v) as an eluent (flow rate 0.5 ml/min). A JASCO Trirotar II chromatograph equipped with a JASCO UVIDEC 100-V (UV) and a JASCO DIP-181C polarimetric detectors was used for the HPLC experiments.

A-4-3 Results and Discussion

Polymerization and oligomerization of MMA with 1-NpMgBr

The results of polymerization of MMA at [MMA]/[1-NpMgBr] = 20 are summarized in Table B-4-1. Both at -78°C and 0°C, highly isotactic polymer was obtained almost quantitatively, although the molecular weight distribution was rather broad. This result suggests that the isotactic oligomers must be obtained in the

Table B-4-1. Polymerization of MMA with 1-NpMgBr in toluene[a]

Run	Temp (°C)	Time (h)	Yield (%)	Mn	Mw/Mn	Tacticity (%)		
						mm	*mr*	*rr*
1	0	1	98	2560	1.77	87	8	5
2	−78	24	100	3840	1.65	97	3	0

[a]MMA 1 g (10 mmol), toluene 10 ml, [MMA]/[1-NpMgBr] = 20.

reaction at smaller [MMA]/[1-NpMgBr] ratio.

Figures B-4-1 and B-4-2 show the GPC curve and FD mass spectrum, respectively, of the hexane-soluble oligo(MMA)s prepared at [MMA]/[1-NpMgBr] = 5 at −78°C. The mass numbers were observed at M/z 328, 428, 529, ... which correspond to the dimer, trimer, tetramer, ... of MMA (Mw=100) having a 1-naphthyl group (Mw=127). The peaks in the GPC curve were directly assigned as shown in Figure B-4-1 on the basis of similarity in molecular weight distribution shown in the GPC curve and FD mass spectrum. This is also supported by previous results on oligo(MMA) having a fluorenyl group at the α-end (Part A: Chapter 1).

Figure B-4-3 shows the chromatogram of separation of diastereomers of the whole part of oligo(MMA) prepared at −78°C at [MMA]/[1-NpMgBr] = 5. The molecular weight of each peak was determined by FD mass spectroscopy. The oligomers of DP$\geq$4 consist of two main components of diastereomers. The pentamer and

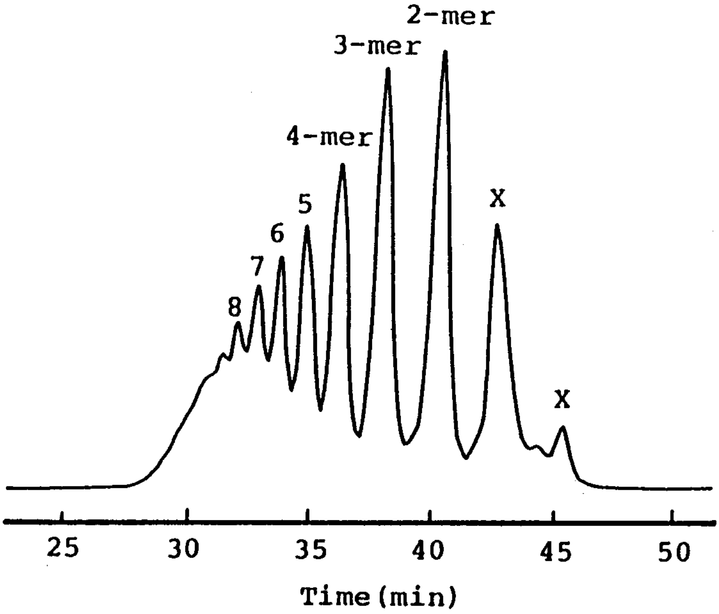


Figure B-4-1. GPC curve of hexane-soluble oligo(MMA) prepared with 1-NpMgBr at [1-NpMgBr]/[MMA]=1/5 in toluene at -78°C. x denotes unknown products.

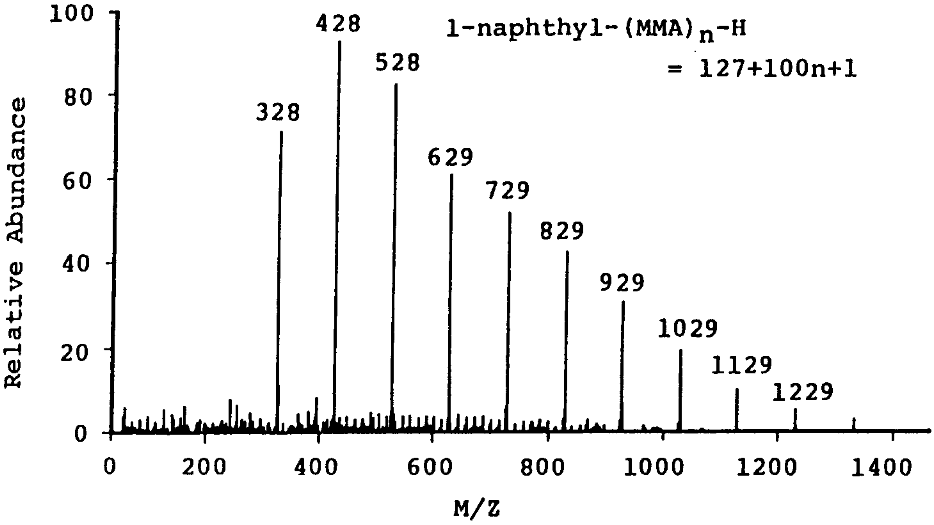


Figure B-4-2. FD mass spectrum of hexane-soluble oligo(MMA) prepared with 1-NpMgBr.

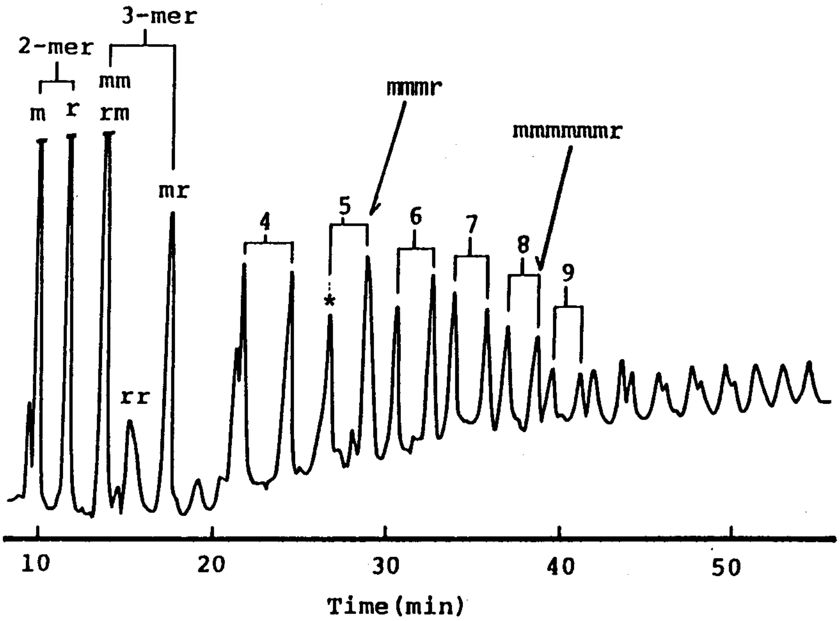


Figure B-4-3. Chromatogram of separation of diastereomers of oligo(MMA) prepared with 1-NpMgBr.

the octamer marked by arrows in Figure B-4-3 were assigned to *mmmr* isomer and *mmmmmmr* isomer, respectively, by ^{1}H NMR analysis. The spectrum of pentamer *mmmr* is shown in Figure B-4-4. The chemical shifts and coupling constants are summarized in Tables B-4-2 and B-4-3. The numbering system of monomeric units is the same as that for the oligo(MMA)s having a fluorenyl group at the α-end in Part A: Chapter 1. The *m/r* assignments of each unit were accomplished in the same manner as that adopted to the oligo(MMA) having a fluorenyl group at the α-end. The difference in chemical shifts of the in chain methylene protons were in the range of 0.54~0.73 ppm and that of the ω-end

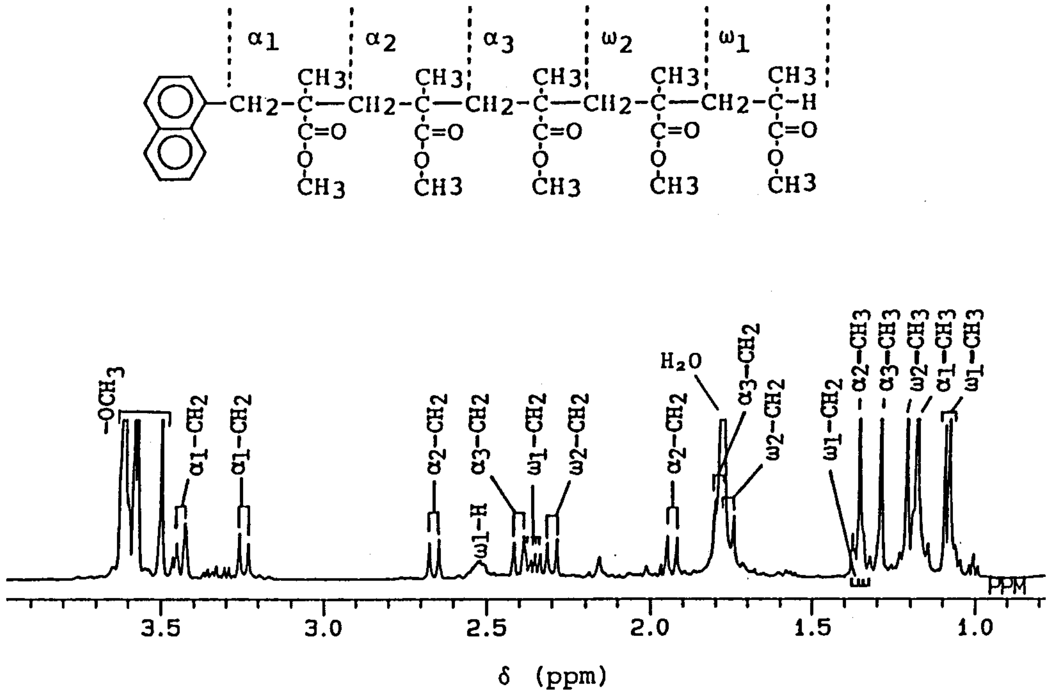


Figure B-4-4. 500 MHz ^{1}H NMR spectrum of MMA-pentamer mmmr having a 1-naphthyl group at the α-end. (Nitrobenzene-d_5, 110°C)

Table B-4-2. ^{1}H NMR Chemical shifts (δ, ppm) and coupling constants (Hz) of methylene protons of MMA-pentamer *mmmr* and -octamer *mmmmmmr* having a 1-naphthyl group at the α-end[a]

	α_1[b]	α_2[b]	α_3[b]	α_4[b]	ω_4[b]	ω_3[b]	ω_2[b]	ω_1[c]
pentamer *mmmr*	3.24, 3.44 (14.0)	1.93, 2.66 (14.5)	1.79, 2.40 (14.5)				1.76, 2.30 (14.0)	1.36, 2.36 (14.5)
octamer *mmmmmmr*	3.25, 3.44 (14.5)	1.95, 2.67 (14.5)	1.81, 2.44 (14.5)	1.73, 2.37 (15.0)	1.71, 2.35 (14.5)	1.71, 2.34 (14.5)	1.75, 2.30 (15.0)	1.36, 2.36 (14.0)

[a]Measured in nitrobenzene-d_5 at 110°C (500 MHz). ^2J coupling constants between the methylene protons are shown in parentheses below the chemical shifts values.
[b]AB quartet. [c]Double-quartet.

Table B-4-3. ^{1}H NMR chemical shifts (δ, ppm) and coupling constants (Hz) of α-methyl, methine, and methoxy protons of MMA-pentamer *mmmr* and -octamer *mmmmmmr* having a 1-naphthyl group at the α-end[a]

	α-methyl								ω-end methine[d]	methoxy[b]
	α_1[b]	α_2[b]	α_3[b]	α_4[b]	ω_4[b]	ω_3[b]	ω_2[b]	ω_1[c]		
pentamer *mmmr*	1.18	1.35	1.29				1.21	1.09 (7.0)	2.52 (4.0, 8.0)	3.61[e], 3.58, 3.57, 3.50
octamer *mmmmmmr*	1.19	1.37	~1.34[f]	~1.34[f]	~1.34[f]	1.29	1.21	1.09 (7.5)	2.52 (3.0, 9.0)	3.61[g], 3.59, 3.57, 3.50

[a]Measured in nitrobenzene-d_5 at 110°C (500 MHz). ^3J coupling constants between the ω_1-methyl protons and ω-end methine proton are shown in the parentheses below the chemical shifts of the ω_1-methyl protons. ^3J coupling constants between the ω_1-methylene protons and the ω-end methine proton are shown in the parentheses below the chemical shifts of the ω-end methine protons. The value on the left side is that between methine and the methylene proton resonating in higher field.
[b]Singlet. [c]Doublet. [d]Multiplet. [e]Having an intensity of two methoxy groups. [f]Not sufficiently resolved. [g]Having an intensity of five methoxy groups.

methylene protons was 1.0 ppm both for the pentamer and the octamer. This indicates that both the pentamer and octamer are isotactic ones having *r* ω-end configuration.[4] On the basis of the assignment of pentamer and octamer, the two components of the oligomers of DP $\geq$ 4 were assigned to the pairs of the isotactic oligomers whose tacticities of ω-end are *r* and *m*. The almost equal intensities of the two main peaks indicate that protonation of isotactic oligomer anions with methanol is not stereospecific in the present system, though monomer addition occurs mainly in *m* fashion.

Optical resolution of isotactic pentamer and octamer

The *mmmm* pentamer (marked by * in Figure B-4-3) and the *mmmmmmr* octamer were separated from the product obtained by oligomerization at -78°C immediately after terminating the reaction and were optically resolved by HPLC equipped with UV (254 nm) and polarimetric (Hg 365 nm) detectors. Optical resolution was accomplished within 1.5 hr after reaction stopped. The results are shown in Figure B-4-5. The enantiomers of both pentamer and octamer showed very small rotation though they were sufficiently resolved. Specific rotations ($[\alpha]_{365}$) were estimated to be about 26° (pentamer) and about 23° (octamer) from the chromatograms in Figure B-4-5. Concentration of the sample was calculated from the weight of the oligomer injected (pentamer 2.1 mg, octamer 2.0 mg) and the volume of the flow cell of the polarimetric detector (length 5 cm, diameter 0.20 cm). The small specific rotations of pentamer and octamer indicate that the isotactic oligo(MMA)s isolated in our experiment

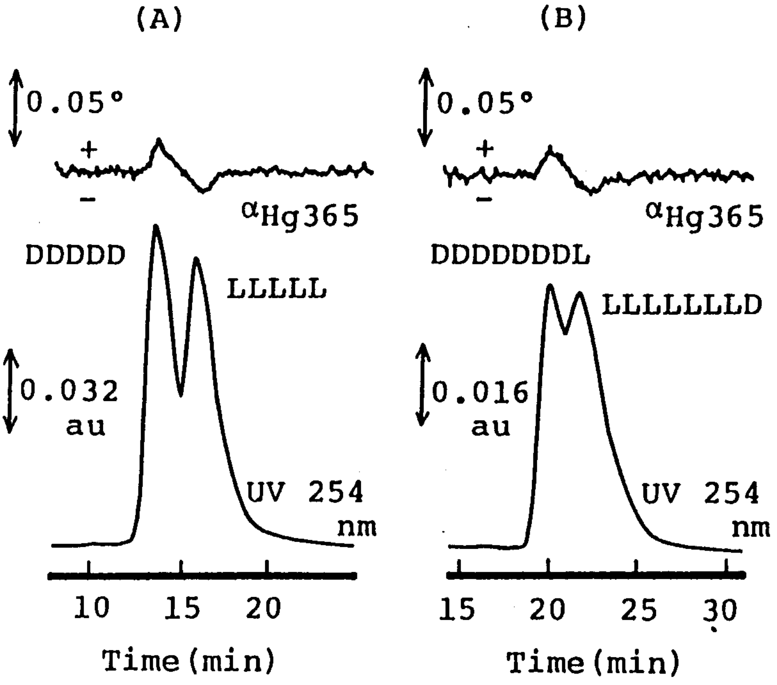


Figure B-4-5. Chromatograms of MMA-pentamer mmmm (A) and octamer mmmmmmr (B) prepared with 1-NpMgBr (sample 2.1 mg (A), 2.0 mg (B)).

did not possess such a stable helical conformation as reported by Cram and Sogah,[1] and that methyl ester is too small to maintain such a helical structure in solution.

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List of Publications

Papers

1. "Mechanism of Asymmetric Polymerization of Triphenylmethyl Methacrylate. Separation and Optical Resolution of Oligomers"
   Yoshio Okamoto, Eiji Yashima, Tamaki Nakano, and Koichi Hatada
   Chem. Lett., 1987, 759-762.

2. "Optical Activity of Isotactic Oligomers of Methyl Methacrylate"
   Yoshio Okamoto, Tamaki Nakano, and Koichi Hatada
   Polym. J., 21, 199-201 (1989).

3. "Crystal Structure of Methyl Methacrylate Dimer. Revised *meso/racemo* Assignment for the Dimer"
   Tamaki Nakano, Koichi Ute, Yoshio Okamoto, Yoshiki Matsuura, and Koichi Hatada
   Polym. J., 21, 935-939 (1989).

4. "Synthesis and Reversible Stereomutation of Optically Active Poly[(*S*)-diphenyl-(1-methylpyrrolidin-2-yl)methyl methacrylate]"
   Yoshio Okamoto, Tamaki Nakano, Etsuko Ono, and Koichi Hatada
   Chem. Lett., 1991, 525-528.

5. "Asymmetric Polymerization of Cyclopropyldiphenylmethyl and Cyclohexyldiphenylmethyl Methacrylates and Stereomutation of the Polymers"
   Yoshio Okamoto, Tamaki Nakano, Tetsuya Fukuoka, and Koichi Hatada
   Polym. Bull., in press.

6. "Asymmetric Polymerization of Triphenylmethyl Methacrylate Leading to One-handed Helical Polymer: Mechanism of Polymerization"
Tamaki Nakano, Yoshio Okamoto, and Koichi Hatada
J. Am. Chem. Soc., to be submitted.

7. "Stereochemistry of Methylation and Protonation of Oligo- and Poly(triphenylmethyl methacrylate) Anions Initiated with the Complex of Fluorenyllithium and (-)-Sparteine"
Tamaki Nakano, Yoshio Okamoto, and Koichi Hatada
in preparation.

8. "Asymmetric Anionic Oligomerization of Triphenylmethyl Methacrylate with the Complexes of 9-Fluorenyllithium Derivatives and (-)-Sparteine. Influence of Initiators on the Propagation Stereochemistry"
Tamaki Nakano, Yoshio Okamoto, and Koichi Hatada
in preparation.

9. "Reversible Conformational Change of Oligo(diphenyl-2-pyridylmethyl methacrylate) in Solution"
Yoshio Okamoto, Tamaki Nakano, and Koichi Hatada
in preparation.

Reviews

1. "Asymmetric Polymerization of Methacrylates and Optical Resolution on the Polymers"
Yoshio Okamoto, Tamaki Nakano, Haruhiko Mohri, Eiji Yashima, and Koichi Hatada

In *Frontiers of Macromolecular Science*, T. Saegusa, T. Higashimura, and A. Abe, Eds., Blackwell Scientific Publications, 1989, pp 37-42.

2. "Synthesis and Utilization of Helical, Optically Active Polymers"
Yoshio Okamoto and Tamaki Nakano
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Other Related Papers

1. "Haloaldehyde Polymers 34. ^{1}H and ^{13}C NMR Spectra of Chloral Oligomers Prepared by Lithium *tert*-Butoxide Initiation and the Assignment of the *meso/racemo* Addition Products of the Dimers"
Koichi Hatada, Koichi Ute, Tamaki Nakano, Frantisek Vass, and Otto Vogl
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2. "Haloaldehyde Polymers 35. ^{1}H, ^{19}F, and ^{13}C NMR Spectra and Stereochemistry of Bornyl Esters of Fluorochlorobromoacetic Acid"
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5. "Asymmetric Polymerization of *N*-Phenylmaleimide"

   Yoshio Okamoto, Tamaki Nakano, Hiroyuki Kobayashi, and Kochi Hatada

   Polym. Bull., **25**, 5-8 (1991).

6. "Helix-sense-selective Polymerization of Diphenyl-2-pyridylmethyl Methacrylate with Chiral Anionic Initiators"

   Yoshio Okamoto, Haruhiko Mohri, Tamaki Nakano, and Koichi Hatada

   Chirality, in press.

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