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ANIONIC COPOLYMERIZATIONS INVOLVING 1,1-DIPHENYLETHYLENE OR TRANS-STILBENE AS PRINCIPAL COMPONENTS

by

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CONTENTS

Introduction

In the field of polymer chemistry the study of copolymerization is one of the best ways not only to synthesize new polymers but also to learn the reactivities of monomers. So far many free-radical copolymerizations have been studied in detail, but not so many works on anionic copolymerization have been done. One of the characteristics in the anionic polymerizations of vinyl compounds is a possibility of "living polymerization," which involves neither termination nor transfer reaction. Anionic copolymerization may therefore form a new copolymer which has not been prepared by free-radical copolymerization. For instance, the living polymerization can yield a copolymer in which each polymer molecule has the same monomer composition, while radical polymerization usually forms a copolymer containing a variety of polymer molecules having different compositions. In such an anionic living system, the analysis of the copolymerization is rather easy because there is neither termination nor transfer reaction.

There are four propagating steps in the copolymerization reaction:

$$\sim\!\sim\!\sim M_1^- + M_1 \xrightarrow{k_{11}} \sim\!\sim\!\sim M_1^-$$

$$\sim\!\sim\!\sim M_1^- + M_2 \xrightarrow{k_{12}} \sim\!\sim\!\sim M_2^-$$

$$\sim\!\sim\!\sim M_2^- + M_1 \xrightarrow{k_{21}} \sim\!\sim\!\sim M_1^-$$

$$\sim\!\sim\!\sim M_2^- + M_2 \xrightarrow{k_{22}} \sim\!\sim\!\sim M_2^-$$

where M_1 and M_2 denote monomers and k is a rate constant. In these steps, if the M_2 monomer can not be homopolymerized; i.e., $k_{22}=0$, and if $\sim\sim M_1^-$ anion can add more easily to the M_2 monomer than to the M_1 monomer; i.e., $k_{12}>>k_{11}$, an alternating copolymer, $\sim\sim M_1M_2M_1M_2^-$, will be formed.

In the present work, the author investigated on the anionic copolymerizations of 1,1-diphenylethylene or trans-stilbene (M_2), which can not be homopolymerized, with butadiene, isoprene, 2,3-dimethylbutadiene, styrene, *o*- and *p*-methoxystyrene (M_1). Benzene, toluene, and tetrahydrofuran (THF) were mainly used as solvents, and n-butyllithium (n-BuLi), Na-naphthalene, Na- and K-dispersions were used as initiators. Many of these copolymerizations could gave alternating copolymers. With minor exceptions, the M_1 monomers used here were completely incorporated into the copolymers after a prolonged time. Therefore, the monomer reactivity ratio, r_1, could be readily calculated by using integrated Mayo-Lewis copolymer composition equation. From the r_1 values obtained, the reactivities of the monomers were discussed.

In the following, the outline of this work will be briefly stated. In Chapter 1, the anionic copolymerization of styrene and 1,1-diphenylethylene carried out under various reaction conditions was described. The r_1 values were less than 0.7 in all the copolymerizations. An alternating copolymer was formed in THF when $[M_2]_0>[M_1]_0$. Chapter 2 consisted of the copolymerization of 2,3-dimethylbutadiene and 1,1-diphenylethylene by n-BuLi in benzene. The r_1 value was 0.23. Chapter 3 and 4 treated the anionic copolymerizations of 1,1-diphenylethylene with isoprene and butadiene respectively. In these copolymerizations the r_1 values were affected greatly by the reaction conditions; i.e., in THF alternating copolymers were obtained, while in hydrocarbon with n-BuLi 1,1-diphenylethylene was little incorporated into the copolymers. In Chapter 5, stereospecific polymerization of *o*-methoxystyrene by anionic initiators was studied. This Chapter closely related to the next One. The relationship between polymerization conditions and stereoregularity of polymer was investigated in detail. Although an atactic polymer was formed in THF regardless of the reaction conditions, in toluene a crystalline isotactic polymer was obtained by n-BuLi at low temperature. The anionic copolymerization of *o*-methoxystyrene and 1,1-diphenylethylene by n-BuLi was stated in Chapter 6, where the connection with the proceeding Chapter was discussed. The obtained results were very similar to those found in Chapter 3 and 4; e.g., *o*-methoxystyrene had higher reactivity in hydrocarbon than in THF. The anionic copolymerization of *p*-methoxystyrene and 1,1-diphenylethylene was also investigated in this Chapter. The *p*-isomer had similar reactivity in both THF and hydrocarbon, and the alternating copolymer prepared in THF was crystalline. All the copolymerizations employing 1,1-diphenylethylene gave alternating copolymers in THF and were completed without termination and transfer reactions except the copolymerizations with *o*- and *p*-methoxystyrene.

On the other hand, termination and chain-transfer reactions were observed in the copolymerizations using trans-stilbene in THF. Chapter 7 treated the copolymerization of styrene and trans-stilbene in THF and benzene by n-BuLi. The chain-transfer to trans-stilbene was observed and the color of the reaction mixture changed in time. Styrene was more reactive than trans-stilbene in both the solvents. The reaction of trans-stilbene with n-BuLi in THF was investigated in Chapter 8 in order to clarify the mechanisms of the chanin-transfer and the change of color of the reaction mixture found in the above Chapter. The transfer was caused by the abstraction of a proton from α-position of trans-stilbene and the change of the color was owing to the production of a 1,2,3-triphenylpropene anion. In Chapter 9, copolymerizations of trans-stilbene with butadiene, isoprene, and 2,3-dimethylbutadiene by n-BuLi in THF and benzene were described. In THF, all copolymerizations gave alternating copolymers. Isoprene and 2,3-dimethylbutadiene were not consumed completely because of the termination reaction, although butadiene was perfectly consumed. In benzene, trans-stilbene was not copolymerized with butadiene and isoprene but copolymerized with 2,3-dimethylbutadiene. The change of the color observed in THF was not detected in benzene.

I wish to express my sincerest thanks to Professors Shunsuke Murahashi and Heimei Yuki for his constant guidance and encouragement throughout the work. I am grateful to Dr. Koichi Kosai and Assistant Professor Koichi Hatada for their helpful advices during the course of study. I also with to thanks to Messrs. Katsuya Tsubota, Katsutoshi Sadamoto, Yoshiteru Kuwae, and especially to the late Mr. Masahiko Kato for their active collabo-

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Chapter 1

Anionic Copolymerization of Styrene and 1,1-Diphenylethylene

Synopsis

The anionic copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2) was investigated. 1,1-Diphenylethylene, which can not homopolymerize by itself, was copolymerized with styrene by means of an anionic initiator. The copolymerization reaction seemed to proceed without termination or chain transfer, and gave a high molecular alternating copolymer under appropriate reaction conditions. The monomer reactivity ratio, r_1, was obtained from the copolymer composition at the complete consumption of M_1, assuming the rate constant $k_{22} = 0$. The monomer reactivity ratio was affected by the solvent (n-hexane, benzene, toluene, or THF), but not by the catalyst (n-BuLi, Na-dispersion, Na-naphthalene, or K-dispersion) or the reaction temperature. It was 0.4 in toluene at 30°C.

Introduction

Alternating copolymerization in the radical mechanism has been known with various combinations of monomers, such as styrene and maleic anhydride.1) On the other hand, the alternating copolymer had not been obtained by an ionic mechanism until Natta and his co-workers2) found that the alternating copolymer of ethylene and cis-butene-2 could be produced by a Ziegler-type catalyst. Recently they also obtained an alternating copolymer from ethylene and cyclopentene3) or butadiene4) with the same type of catalyst.

It has previously been found that, if a suitable combination of monomers was chosen, an alternating copolymer can also be obtained by an anionic mechanism. One of the monomers in the pair was 1,1-diphenylethylene or trans-stilbene; the comonomers used were styrene, butadiene, isoprene, and 2,3-dimethylbutadiene. The copolymerization had already been reported briefly.5) Natta et al.6) also reported the alternating copolymerization of 2-vinylpyridine and α-stilbazole by an anionic mechanism.

In the present paper a detailed study of the copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2) will be described.

Experimental

Monomer. 1,1-Diphenylethylene (DPE) was prepared from phenylmagnesium bromide and ethyl acetate.7) Bp 105-110°C/3-4 mmHg, n_D^{20} 1.6085. Styrene (St) was purified in the usual manner.

Solvent. Benzene, toluene, and n-hexane were purified in the usual manner and were dried over metallic sodium. Tetrahydrofuran (THF) was purified, dried over sodium, and distilled from calcium hydride before use.

Catalyst. According to the method of Ziegler8) n-butyllithium (BuLi) was prepared in n-heptane, and the concentration (14.9%)

was determined by double titration.[9] Sodium dispersion (Na-disp) in n-octane and potassium dispersion (K-disp) in n-decane were used; the concentrations were 30 and 3% respectively. Sodium naphthalene (Na-Naph) was prepared in tetrahydrofuran; the concentration was 0.3 mmol/ml.

Procedure. Copolymerization was carried out in a glass ampoule under nitrogen. Solvent, monomers, and catalyst were placed in the ampoule by using syringes. The ampoule was then allowed to stand in a bath. The reaction was terminated by adding a trace of methanol, and then the contents of the ampoule were poured into a large amount of methanol. The precipitated polymer was separated by filtration, dried, and weighed.

Measurement. The infrared spectrum of the polymer was measured on a Nihon Bunko DS 402G Spectrometer. The conventional KBr method was used for sample preparation. The NMR spectrum of the polymer was obtained in carbon tetrachloride at room temperature with a Varian A60 Spectrometer at 60 Mc/sec. The viscosity was measured in a 1.0 g/dl toluene solution at 30.0°C.

Fractionation. The fractionation of the polymer was carried out with a Soxhlet extractor by using diethyl ether or methyl ethyl ketone as the solvent.

Results

The copolymerization by BuLi in toluene was carried out, varying the initial molar ratio of styrene to 1,1-diphenylethylene at 30°C for a prolonged time. The composition of the copolymer was calculated from the ratio of the number of phenyl protons to non-phenyl protons in the NMR spectrum. On the other hand, the composition was also calculated from the polymer yield, assuming that the carbanion of 1,1-diphenylethylene can not add 1,1-diphenylethylene; the reaction proceeded sufficiently for the styrene to be completely incorporated into the copolymer. The results are summarized in Table 1.

The polymer yield (weight per cent against the total of monomers charged) decreased with a decrease in the styrene in the initial monomer mixture. The values of the copolymer composition obtained by the two different methods, NMR spectrum and polymer yield, were consistent with each other within the range of experimental error. The composition of the copolymer approached unity when the initial molar ratio of styrene to 1,1-diphenylethylene was less than unity. The reduced viscosity of the copolymer obtained was around 0.1, but the softening point rose with the increase in the 1,1-diphenylethylene in the copolymer.

The copolymerization was carried out with BuLi in toluene at 0, 30, and 50°C, equimolar amounts of monomers being used. The results are shown in Table 2. The polymer compositions, St/DPE, were about 1.5; this value seemed to be independent of the reaction temperature. In the copolymerization at 0°C, however, a difference was found between the values calculated by means of the two methods. This must be caused by the styrene remaining unchanged at this temperature, where the reaction rate was rather slow.

The effects of solvent and catalyst in the copolymerization were investigated at 30°C with an equimolar feed composition of monomers. n-Hexane, benzene, and toluene were used as solvents, and BuLi, Na-dispersion, K-dispersion, and Na-naphthalene, as catalysts. Table 3 shows the results. Depending on the solvent and catalyst used, the reaction mixture formed a homogeneous or heterogeneous system. The heterogeneity of system decreased with an increase in the polarity of the reaction mixture. The homogeneous system generally gave the copolymer in a good yield, but the heterogeneous one resulted in a low yield. In THF, the reaction proceeded in a homogeneous system independently of the catalyst used, and the values of copolymer composition calculated by the two methods showed a good coincidence. When the reaction proceeded in a heterogeneous system, some discrepancy was observed between the values of copolymer composition calculated from the polymer yield and from the NMR spectrum. In this case the reaction did not proceed completely, both the monomers remaining unchanged.

The monomer reactivity ratio, r_1, in the copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2) was calculated from the copolymer composition by using Eq. (9), which will be described in the next section. The values of r_1 obtained are listed in Tables 1, 2, and 3. As a mean value 0.4 was obtained for r_1 in the copolymerization carried out with BuLi in toluene. This value seemed to be independent of the initial molar ratio of monomers (Table 1) and of the reaction temperature from 0 to 50°C (Table 2).

It was found that the monomer reactivity ratio, r_1, was affected by the nature of the solvent; i.e., the value was smaller in a polar solvent, and the relative reactivity of styrene appeared to increase in a non-polar solvent (Table 3). Little effect on r_1 was observed with the catalyst.

The copolymerization with BuLi was carried out in THF at 0°C. In this reaction the amount of catalyst was minimized in order to obtain a large molecular weight of the polymer. The results are shown in Table 4. In the copolymerization when the initial molar ratio of styrene to 1,1-diphenylethylene was large enough, the copolymer was obtained quantitatively after 48 hours. However, when the ratio was less than unity, the reaction proceeded slowly, unchanged styrene existing even after 6 days. The polymer viscosity increased with an increase in the initial ratio of the total quantity of monomers to that of BuLi. Probably the copolymerization proceeded in a living system and no chain transfer occurred, although it was impossible to compare the molecular weights of copolymers possessing different compositions. The softening point of the copolymer rose with the increase in the amount of 1,1-diphenylethylene in the copolymer.

In order to obtain more information about the homogeneity of the copolymer with regard to its composition and molecular weight, some of the copolymers were fractionated by extraction. The results (Table 5) showed that the copolymer rich in styrene is soluble in methyl ethyl ketone, even at a high molecular weight, but was insoluble in both diethyl ether and acetone, while the alternating copolymer with a high molecular weight is not soluble in methyl ethyl ketone. It was found that the lower-molecular-weight polymers had contained some soluble fractions in diethyl ether or methyl ethyl ketone. However, only small changes in the copolymer composition and viscosity were observed in the insoluble fractions. In these cases the original polymers were obtained by a heterogeneous catalyst or at higher catlyst concentrations; thus they contained lower molecular-weight fractions, for the initiation reaction did not take place at once. In general, the copolymers produced in these copolymerization have been shown to be essentially homogeneous.

Discussion

Evans and his co-workers have reported that in benzene n-butyllithium adds rather faster to 1,1-diphenylethylene than to styrene,10) and that the former olefin can dimerize but not polymerize to a higher polymer,11) probably because of the steric hindrance due to the second phenyl group in the 1,1-diphenylethylene. From their experimental results, even the dimerization of 1,1-diphenylethylene seems not to be so fast, because 1,1-diphenylhexane, the addition product of n-butyllithium and 1 mole of 1,1-diphenylethylene, remained in the reaction mixture after the reaction. The higher reactivity of 1,1-diphenylethylene to the carbanion than that of styrene may be interpreted by the resonance stabilization of the 1,1-diphenylethylene anion being larger than that of the styryl anion. These results suggest that, in the copolymerization of 1,1-diphenylethylene and styrene, the styryl anion may add faster to 1,1-diphenylethylene than to styrene, and that the 1,1-diphenylethylene anion adds more easily to styrene than to 1,1-diphenylethylene. Thus, the reaction may lead to the production of an alternating copolymer of these two monomers. Strictly speaking, in the following copolymerization reactions:

$$\sim\sim M_1^- \quad + \quad M_1 \xrightarrow{k_{11}} \sim\sim M_1M_1^- \tag{1}$$

$$\sim\sim M_1^- \quad + \quad M_2 \xrightarrow{k_{12}} \sim\sim M_1M_2^- \tag{2}$$

$$\sim\sim M_2^- \quad + \quad M_1 \xrightarrow{k_{21}} \sim\sim M_2M_1^- \tag{3}$$

$$\sim\sim M_2^- \quad + \quad M_2 \xrightarrow{k_{22}} \sim\sim M_2M_2^- \tag{4}$$

if the rate constant, k_{22}, is small enough, and if k_{12} is sufficiently larger than k_{11}, the crossover propagation must occur predominantly and result in an alternating copolymer at $(M_2)_0/(M_1)_0>1$, where (M_2) and (M_1) are the concentrations of M_2 and M_1 respectively.

As shown in Table 1, this situation held in the copolymerization of 1,1-diphenylethylene and styrene. The coincidence of the copolymer composition obtained by NMR spectroscopy and that calculated from the polymer yield at a complete consumption of the monomer M_1 suggests the validity of the assumption that $k_{22}=0$, which indicates that not even a dimeric unit of the monomer M_2 exists in the copolymer.

In the copolymerization of M_1 and M_2, if the M_2 anion does not add M_2, that is, if $k_{22}=0$, the copolymer composition equation reduces to:

$$\frac{d(M_1)}{d(M_2)} = r_1 \frac{(M_1)}{(M_2)} + 1 \qquad (5)$$

On the other hand, the next equation is deduced easily:

$$\frac{d(M_1)/(M_2)}{d(M_2)} = - \frac{(M_1)}{(M_2)^2} + \frac{1}{(M_2)} \frac{d(M_1)}{d(M_2)} \qquad (6)$$

Substituting (5) into (6), we have:

$$\frac{d(M_1)/(M_2)}{d(M_2)} = \frac{1}{(M_2)} \left(r_1 \frac{(M_1)}{(M_2)} - \frac{(M_1)}{(M_2)} + 1 \right) \qquad (7)$$

The integration of Eq. (7) gives:

$$\ln \frac{(M_2)}{(M_2)_0} - \frac{1}{r_1 - 1} \ln \frac{[(M_1)/(M_2)]\ (r_1 - 1) + 1}{[(M_1)_0/(M_2)_0]\ (r_1 - 1) + 1} = 0 \qquad (8)$$

where $r_1 \neq 1$ and where $(M_1)_0$ and $(M_2)_0$, and (M_1) and (M_2), represent the initial and final monomer concentrations respectively. When unchanged M_1 does not exist in the copolymerization system, i.e., when $(M_1) = 0$, we have:

$$\ln \frac{(M_2)}{(M_2)_0} + \frac{1}{r_1 - 1} \ln \left[\frac{(M_1)_0}{(M_2)_0} (r_1 - 1) + 1 \right] = 0 \qquad (9)$$

Equation (9) gives r_1 when $(M_1)_0$, $(M_2)_0$, and (M_2) are known.

As Table 1 shows, r_1 was found to be 0.30-0.45 (mean value = 0.4) in toluene at 30°C at a variety of $(M_2)_0/(M_1)_0$ ratios. The reaction temperature and the species of counter ion seemed not to affect the reactivity ratio, while an influence of the solvent used for the reaction was apparent; i.e., the r_1 value increased with a decrease in the polarity of the solvent. The cause of this change in the reactivity ratio is not certain at the present time, but it seems to concern the degree of dissociation of the ion-pair to the free ions in the solution.

Szwarc et al.12) have reported the anionic copolymerization of styrene and 1,1-diphenylethylene by Na in THF at 25°C. From their kinetic study they obtained the rate constants, k_{12}, for the ion-pair (250 l/mol sec) and the free ion (400,000 l/mol sec), and the apparent rate constant, k_{21} (0.5-0.7 l/mol sec). They concluded that the step (3) in the above equations is reversible (the equilibrium constant $K_{21} = 5\times10^{-2}$ l/mol) and rate determining, while the reaction (2) is very fast and prevents the reaction (1). The monomer reactivity ratio, r_1, in THF at 25°C with the Na^+ counter ion can be calculated as 0.21 from Szwarc's data ($k_{11} = 210$ l/mol sec and $k_{12} = 1{,}000$ l/mol sec),12,13) which represent the apparent rate constants at the same concentration of the living end (0.04 mol/l) as that employed in the present work. The value shows a good agreement with the 0.2 obtained in the present copolymerization in THF with Na.

The reduced copolymer composition equation, (5), suggests that if the initial molar ratio of monomers $(M_1)_0/(M_2)_0$ is

$1/(1 - r_1)$, where $r_1<1$, i.e., $k_{11}<k_{12}$, the copolymerization proceeds azeotropically. At $(M_1)_0/(M_2)_0>1/(1 - r_1)$, both the monomers can be consumed completely by the copolymerization, and so the copolymer composition must be the same with the monomers fed. However, in this case the monomers react alternatingly in the initial stage, with M_1 remaining predominantly and with this incorporated in the copolymer more and more in the later stage. As we can expect, from the chemical structures of styrene and 1,1-diphenylethylene, that neither termination nor chain transfer occurs in this copolymerization, the polymer molecule obtained must have a constitution obeying this change in reaction. At $(M_1)_0/(M_2)_0<1/(1 - r_1)$, an essentially alternating copolymerization proceeds, but the deviation takes place at the initial stage and a more strict alternating condtion is reached at the final stage, the monomer M_2 remaining unchanged.

From the results of fractionation, it may be concluded that the high-molecular-weight polymer produced in the copolymerization with a careful procedure included no low molecular fraction, and that probably there was also no fraction with a composition deviating greatly from that to be anticipated from the amounts of charged monomers.

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Table 1. Anionic copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2)—— Effect of monomer composition

Total monomer 2×10^{-2} mol, solvent: toluene 10 ml, temp. 30°C, time 48 hr

St/DPE (mol/mol) in monomer	BuLi 10^{-4} mol	Yield[a)] %	St/DPE in copolymer from Yield	St/DPE in copolymer from NMR	η_{sp}/C	S.P.[b)] °C	r_1[c)]
	5.5	100.0		—	0.09	110	—
2.40	5.5	100.0	2.40	2.45	0.08	145	—
1.57	5.8	98.2	1.62	1.68	0.08	170	0.45
1.04	5.5	86.7	1.32	1.33	0.08	172	0.44
0.92	17.0	84.4	1.21	1.31	—	117	0.35
0.67	4.4	71.4	1.13	0.96	0.11	175	0.30
0.69	8.2	70.5	1.19	0.93	0.07	140	0.41
0.33	5.8	45.1	0.97	—	—	165	—
0.17	5.8	24.6	0.95	1.00	—	158	—

a) Wt% against total monomer. b) Softening point.

c) Calculated from the copolymer composition obtained from polymer yield.

Table 2. Anionic copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2) ——— Effect of temperature

Total monomer 2×10^{-2} mol, solvent: toluene 10 ml, time 48 hr

Temp.	St/DPE (mol/mol) in monomer	BuLi 10^{-4} mol	Yield %	St/DPE in copolymer from Yield	St/DPE in copolymer from NMR	η_{sp}/C	S.P.[a)] °C	r_1[b)]
0	1.00	5.6	68.3	2.02[c)]	1.32	0.12	171	0.47[d)]
30	1.04	5.5	86.7	1.32	1.33	0.08	172	0.44
50	1.10	5.3	87.3	1.40	1.25	0.09	169	0.55

a) Softening point.

b) Calculated from the copolymer composition obtained from polymer yield.

c) Reaction did not proceed completely.

d) Calculated from the copolymer composition obtained from NMR.

Table 3. Anionic copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2)

——— Effects of solvent and catalyst

Total monomer 2 × 10^{-2} mol, temp. 30°C, solvent 10 ml

St/DPE (mol/mol) in monomer	Solvent	Catalyst(10^{-4} mol)		Time hr	Yield %	St/DPE in copolymer		η_{sp}/C	r_1[b]
						from Yield	from NMR		
1.02	THF	BuLi	4.0	48	95.1	1.11	1.04	0.11	0.13
1.10	THF	Na-Naph	1.2×10	48	97.6	1.14	1.19	0.11	0.14
0.99	THF	Na-disp	3.1×10	48	88.5	1.21	—	0.18	0.29
1.00	THF	K-disp	7.2	48	90.5	1.18	—	0.31	0.23
1.04	Toluene	BuLi	5.5	48	86.7	1.32	1.33	0.08	0.44
0.96	Toluene	Na-disp	6.2×10	96	73.7[a]	1.62	1.83	0.08	—
0.93	Toluene	K-disp	1.1×10	96	83.4[a]	1.25	1.06	0.15	—
0.93	Benzene	BuLi	8.0	72	77.8	1.40	1.35	0.16	0.71
0.97	Benzene	Na-disp	2.2×10^2	96	62.5[a]	2.32	0.98	0.21	—
0.97	Benzene	K-disp	9.5	96	74.4[a]	1.68	1.14	0.35	—
1.03	Hexane	BuLi	4.0	72	80.8[a]	1.38	1.40	—	0.63
0.98	Hexane	Na-disp	1.9×10^2	72	30.1[a]	—	1.30	0.39	—

a) a) Reaction proceeded in heterogeneous system.

b) Calculated from the copolymer composition obtained from polymer yield.

Table 4. Anionic copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2)

Solvent THF, catalyst BuLi, temp. 0°C

Monomers (10^{-2} mol)	St/DPE (mol/mol) in monomer	BuLi (10^{-4} mol)	Monomers / BuLi	Time hr	Yield %	Copolymer		
						St/DPE	η_{sp}/C[a]	S.P.
4.42		0.72	610	0.5	100		0.85	160
42.54	13.5	2.57	1650	24	100	13.5	2.21	180
11.14	3.71	1.14	980	24	98	3.7	0.77	180
19.20	2.74	1.14	1690	48	99	2.7	1.76	180
12.32[b]	0.72	1.14	1080	144	56	1.0[c]	1.08	245

a) Benzene solution, c = 1.0 g/dl, at 30.0°C.

b) Styrene was added every six hours dividing into four portions.

c) Obtained from NMR.

Table 5. Fractionation of copolymer

Polymerization		Original polymer		Insoluble polymer[a]			
Solvent	Catalyst	St/DPE	η_{sp}/C	Solvent[b]	%	St/DPE	η_{sp}/C
Toluene	BuLi	1.33	0.08	Et_2O	74	1.33	—
Benzene	K-disp	1.14	0.35	MEK	69	1.00	0.38
THF	K-disp	0.95	0.31	MEK	71	1.04	0.38
THF	BuLi	0.96	—	Et_2O	88	1.04	—
THF	BuLi	3.70	0.77	MEK	0	—	—
				Et_2O	100	3.70	0.77
				Acetone	100	3.70	0.77
THF	BuLi	1.00	1.08	MEK	100	1.00	1.08
				Et_2O	100	1.00	1.08

a) After extraction for 10 hr.

b) Et_2O: diethyl ether, MEK: methyl ethyl ketone.

Chapter 2

Anionic Copolymerization of 2,3-Dimethylbutadiene and 1,1-Diphenylethylene with n-Butyllithium in Benzene

Anionic copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) by n-butyllithium (n-BuLi) in tetrahydrofuran (THF) has been studied by means of NMR spectroscopy,1) in which the rates of consumptions of the two monomers were followed. The copolymerization proceeded alternately, when the initial molar ratio of the monomers, $[M_1]_0/[M_2]_0$, was less than unity. In the present study, the copolymerization of the same monomer pair is investigated in benzene at 40°C with n-BuLi as an initiator.

Experimental

Meterials. 2,3-Dimethylbutadiene was synthesized by the dehydration of pinacol.2) The monomer purified by fractional distillation was redistilled in vacuo from lithium aluminum hydride. Bp 69°C/760 mmHg, n_D^{20} 1.4360.

1,1-Diphenylethylene prepared from diphenylmethyl carbinol3) was first treated with a small amount of Na-K alloy and distilled. Bp 115°C/3 mmHg, n_D^{20} 1.6085. Then n-BuLi was added to the monomer until the red color of its anion appeared. The monomer was redistilled from the colored mixture in vacuo.

Benzene purified by the usual method was redistilled in the presence of a small amount of n-BuLi under high vacuum before use.

n-BuLi was prepared in n-heptane according to the method of Ziegler.$^{4)}$

Polymerization. Copolymerization was carried out in a glass ampoule which had been previously heated with a gas burner in vacuo. Benzene and 2,3-dimethylbutadiene were transferred to the ampoule on a vacuum line, and then 1,1-diphenylethylene and n-BuLi were added with hypodermic syringes under dry nitrogen. The copolymerization was terminated by adding methanol. The polymer precipitated in methanol was filtrated, washed with methanol, and dried.

Viscosity. The viscosity of the copolymer was measured in toluene solution at 30.0°C.

Results and Discussion

The copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) by n-BuLi was followed in benzene at 40°C, the initial molar ratio of M_1 to M_2 being 0.683. The results are shown in Fig. 1. The copolymerization proceeded slowly to reach a constant polymer yield in about 50 hr. In this period 2,3-dimethylbutadiene was completely consumed and only unchanged 1,1-diphenylethylene remained in the system. The softening point of the copolymer was about 135°C.

In Fig. 2 the plot of log$[\eta]$ vs. log yield of polymer is shown. The linear relationship suggests that the copolymerization proceeded without termination and chain transfer, probably to give a living polymer.

The copolymerization was carried out for a prolonged time and the material balance was checked in order to confirm the complete consumption of the M_1 monomer. The results are listed in Table 1. It was found that the total amount of the monomers charged, $M_1 + M_2$ (g), was substantially equal to the sum of the polymer obtained and the unchanged M_2 monomer recovered from the mother liquor of the polymer precipitation. This fact means that 2,3-dimethylbutadiene was completely incorporated into the copolymer. Then, the molar ratio of the monomers in the copolymer, $[m_1]/[m_2]$, can be calculated from the polymer yield. The $[m_1]/[m_2]$ ratio decreased with a decrease in the ratio of the charged monomers, $[M_1]_0/[M_2]_0$.

The monomer reactivity ratio, r_1, is obtained by means of the integrated copolymer composition equation, assuming that the M_2 monomer does not homopolymerize and the M_1 monomer has been completely consumed.5) The r_1 values are shown in Table 1. As the mean value, 0.23 was obtained. This indicated that 1,1-diphenylethylene is more reactive to 2,3-dimethylbutadienyl anion than 2,3-dimethylbutadiene. In the copolymerization in THF, the r_1 value was almost zero and an alternating copolymer was obtained, when the $[M_1]_0/[M_2]_0$ ratio was less than unity.

In the copolymerizations of styrene and butadiene,6) styrene and isoprene,7) and 1,1-diphenylethylene (M_2) and isoprene (M_1)8) by lithium catalysts, greater relative reactivities of conjugated dienes than the comonomers have been found in a nanpolar solvent, contrary to the less reactivities in a polar solvent. In the last pair of monomers, the r_1 values were 0.13 in THF and 37 in benzene. The relative reactivities of the two monomers against isoprene anion reversed in these two solvents. In the comolymerization of 2,3-dimethylbutadiene and 1,1-diphenylethylene, the latter was always more reactive in both THF and benzene.

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Table I

Anionic copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) in benzene by n-BuLi

Benzene: 15.0 ml, n-BuLi: ca. 1 mol% against total monomers, temp.: 40°C, time: 96-140 hr.

M_1 g	M_2 g	$[M_1]_0/[M_2]_0$ mol/mol	Polymer g	Yield mol%	Unchanged M_2, g	$[m_1]/[m_2]$[a] mol/mol	r_1
0.405	0.873	1.017	1.150	92.7	0.127	1.19	0.25
0.335	0.776	0.960	0.978	91.8	0.210	1.14	0.21
0.405	0.960	0.925	1.081	90.0	0.284	1.18	0.27
0.405	0.976	0.910	1.099	89.3	0.189	1.14	0.22
0.405	1.057	0.84	1.190	85.8	0.265	1.14	0.23
0.269	0.848	0.694	0.810	76.1	0.178	1.09	0.18
						Average	0.23

[a] Molar ratio of monomers in the copolymer.

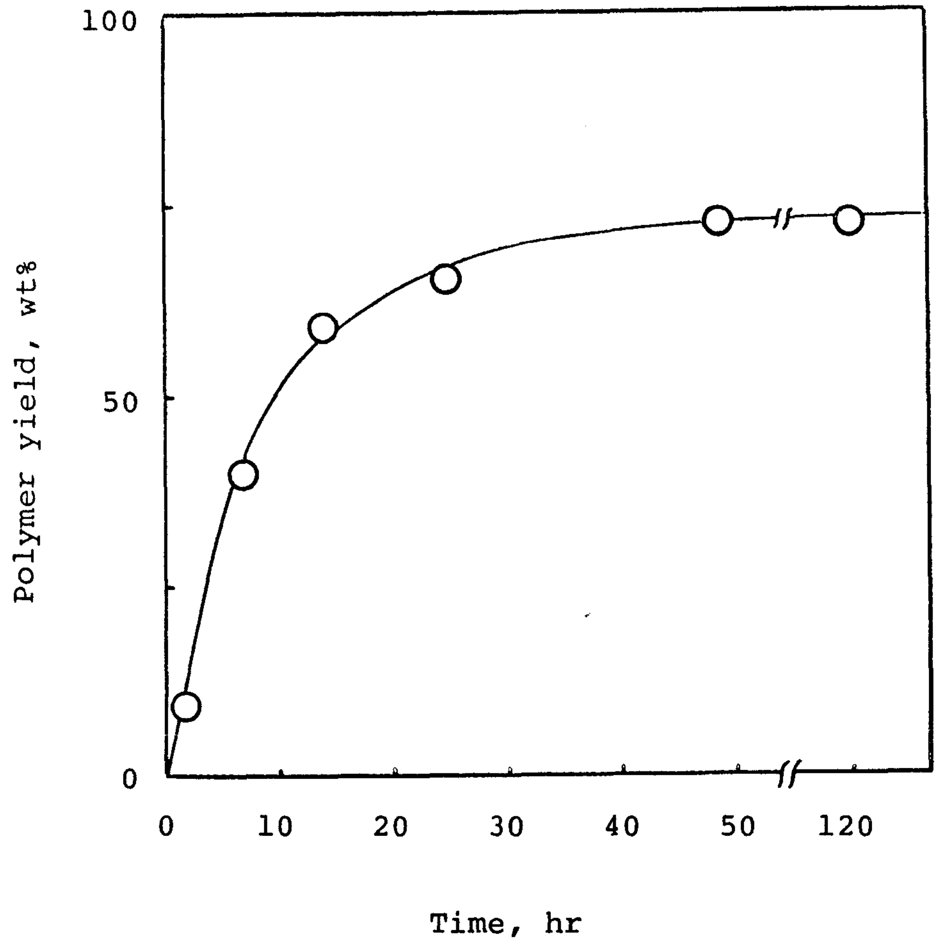

Fig. 1. Anionic copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) in benzene by n-BuLi—— Time vs. polymer yield.

Total monomer : 9.89 mmol, $[M_1]_0/[M_2]_0$: 0.683, benzene: 15.0 ml, n-BuLi: 0.090 mmol, temp.: 40°C.

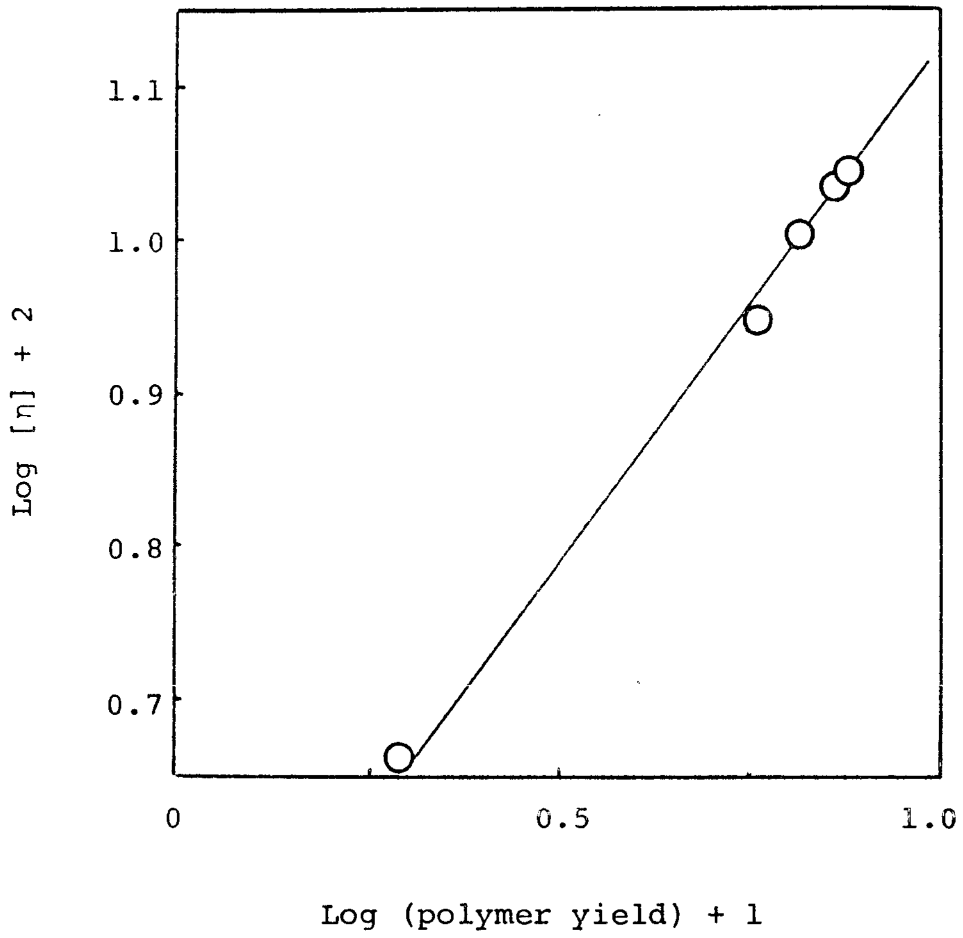

Fig. 2. Anionic copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) in benzene by n-BuLi—— Relationship between polymer yield and viscosity of polymer.

Chapter 3

Anionic Copolymerization of Isoprene and 1,1-Diphenylethylene

Synopsis

Anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) was carried out in tetrahydrofuran (THF), dioxane, and n-heptane by using n-butyllithium (n-BuLi), Na-naphthalene, Na- and K-dispersions as initiators. An alternating copolymer was obtained in the copolymerization in THF, which proceeded without a chain transfer and a termination. Monomer reactivity ratios, r_1, obtained by assuming the rate constant $k_{22} = 0$, were 0.12 (Li^+), 0.11 (Na^+), and 0.11 (K^+) in THF at 0°C. The r_1 value in benzene at 40°C, however, was affected by the counter ion as follows: 37 (Li^+), 0.38 (Na^+), and 0.05 (K^+). With Li^+ counter ion the values were 0.50 in dioxane at 30°C and 29 in n-heptane at 40°C. The order of rate constants in the copolymerization in THF with n-BuLi at 0°C was $k_{12}>k_{11}>k_{21}$, the last of which was 2.64×10^{-3} l/mol sec.

Introduction

Among the anionic copolymerizations of the monomer pairs which copolymerize alternatingly,[1)] the results of the detailed studies were previously reported on the copolymerizations of

1,1-diphenylethylene and styrene,[2)] of 1,1-diphenylethylene and 2,3-dimethylbutadiene,[3)] and of trans-stilbene and styrene.[4)]

In the present study, the copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) will be investigated under various reaction conditions. The results will be correlated with those of the copolymerization reported previously.

Experimental

Materials. Isoprene. The purified monomer (Phillips polymerization grade) was redistilled in vacuo from lithium aluminum hydride before use.

1,1-Diphenylethylene. This was first stirred with Na-K alloy under dry nitrogen, and then n-butyllithium (n-BuLi) in heptane was added to the mixture until a red color due to 1,1-diphenylhexyllithium appeared. The colored solution was carefully distilled in vacuo to obtain the pure monomer.

Tetrahydrofuran (THF) and Dioxane. Each of these solvents was refluxed over metallic sodium and then over lithium aluminum hydride, from where it was distilled onto Na-K alloy and naphthalene. From the green solution the solvent was transferred to a reaction vessel on a vaccum system before use.

Benzene and n-Heptane. Each of these solvents purified in the usual manner was distilled under high vacuum in the presence of n-BuLi.

n-BuLi. n-BuLi was prepared in n-heptane and the concentration was determined by double titration.[5)]

Na-Naphthalene (Na-Naph.). The concentration of the solution was determined by the titration of a sample solution after hydrolysis by water.[6)]

n-Butyl Alcohol. A small amount of metallic sodium was added to the alcohol (spectro grade). The alcohol containing sodium butoxide was then distilled under high vacuum to prepare a standard n-butyl alcohol solution in n-heptane. The solution was used for the colorimetric titration of a carbanion solution.

Polymerization. The polymerization was carried out in a glass ampoule under dry argon. To the ampoule, isoprene and a solvent were distilled by means of a vacuum line, and then 1,1-diphenylethylene and an initiator were added with hypodermic syringes. The polymerization was terminated after the manner of titration with the n-butyl alcohol solution in n-heptane to estimate the concentration of living ends.

Electronic Spectrum. The electronic spectrum of a reaction mixture was measured with a Hitachi 124 Spectrophotometer. The sample solution was prepared in a high vacuum system.

NMR Spectrum. The spectrum of the polymer was taken in a carbon tetrachloride solution with a JNM-4H-100 Spectrometer (Japan Electron Optics Laboratory Co. Ltd.) at 60°C.

Molecular Weight. The molecular weight of the polymer was measured on a Mechrolab Vapor Pressure Osmometer, Model 301A, using benzene as a solvent.

Viscosity. The solution viscosity of the polymer in toluene was measured at 30.0°C.

Results

The copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) in THF at 0°C was carried out with n-BuLi as an initiator, the initial molar ratio of monomers, $[M_1]_0/[M_2]_0$, being 0.650. The results are shown in Fig. 1. The reaction proceeded so slowly that it took 80 hr to be completed, when unchanged 1,1-diphenylethylene remained in the system, but isoprene was completely consumed. Since 1,1-diphenylethylene can not be homopolymerized, the yield of the copolymer is maximum when the two monomers copolymerize alternatingly, if $[M_1]_0/[M_2]_0<1$. In Fig. 1, the yield against the theoretical amount of the alternating copolymer is also shown. It reaches 100%, indicating the formation of the alternating copolymer in the system. It was observed that the concentration of the living ends titrated by n-butyl alcohol was constant regardless of the reaction time and was nearly equal to the concentration of the initiator used.

The relationship between the polymer yield (curve B in Fig. 1) and the polymer molecular weight is shown in Fig. 2. A linear relationship was found between the two and the line almost agreed with the theoretical line for the living polymer produced by alternating copolymerization. There was also a linearity between log yield and log $[\eta]$.

The material balance after the prolonged copolymerization reaction was examined. A part of the results is listed in Table 1. As isoprene was completely incorpolated into the copolymer, the copolymer composition, $[m_1]/[m_2]$, was calculated from the polymer yield and the initial monomer concentrations.[14) The $[m_1]/[m_2]$ ratio in the copolymer obtained in THF slightly exceeded unity with increasing the $[M_1]_0/[M_2]_0$ ratio from 0.6 to 0.9. The alternating copolymer was powder. On the other hand, the copolymer obtained in benzene was viscous and contained a great deal of isoprene, even at $[M_1]_0/[M_2]_0 = 0.6$.

The copolymer composition was also examined by other methods as is shown in Table 2. The elementary analyses of the copolymers are well consistent with the calculations based on the copolymer compositions derived from the polymer yields. The copolymer compositions obtained from the ratios of aromatic to aliphatic protons in their NMR spectra are also in accord with the above compositions within analytical errors.

The monomer reactivity ratio, r_1, was obtained from the polymer yield using the integrated Mayo-Lewis copolymer composition equation, assuming $k_{22} = 0$.2) Thr r_1 values thus obtained are listed in Tables 3-5. In the copolymerizations in THF at 0°C using n-BuLi, Na-naphthalene, and K-dispersion as initiators, the r_1 values were almost constant (0.11-0.12). In benzene at 40°C, however, the values were 37, 0.38, and 0.05 with n-BuLi, Na-dispersion, and K-dispersion respectively. With n-BuLi in dioxane at 30°C and in n-heptane at 40°C, the values were 0.50 and 29 respectively. Thr r_1 value at 25°C in THF seemed to be smaller that that at 0°C. The copolymerization carried out in benzene without an initiator gave no polymer even after 216 hr at 40°C (Table 5), suggesting that no polymerization occurred by free radical mechanism under the reaction conditions employed.

The NMR spectrum of the alternating copolymer obtained with n-BuLi in THF is shown in Fig. 3. The homopolymerization of isoprene by n-BuLi in the same solvent yielded a polymer with 17% 1,2-, 61% 3,4- and 22% trans-1,4-structures. The analysis was done with NMR spectrum according to the method of Chen.7) The alternating copolymer showed no peak in its NMR spectrum at the same position as that of the polyisoprene. On the other hand, in the IR spectrum of the copolymer, an absorption due to the vinyl group was found at 910 cm^{-1}, but very weak suggesting that there was little 1,2-structure in the copolymer. Therefore, assuming that the isoprene was incorporated in the copolymer through 3,4- and 1,4-additions, the ratio of 3,4- to 1,4-addition was 17:83, on the basis of the NMR spectrum.

At $[M_1]_0/[M_2]_0 = 0.650$, the copolymerization by n-BuLi carried out in THF at 0°C was followed spectrophotometrically. As soon as n-BuLi was added, the reaction mixture showed an absorption maximum at 496 mμ due to the diphenylethylene anion; its optical density had been constant during 150 hr at least. The molar extinction coefficient*1) was 1.7×10^4, which agrees closely with 1.8×10^4 of 1,1-diphenylhexyllithium anion.8) These results apparently indicate that the most of the living ends present in the system were 1,1-diphenylethylene anion.

Discussion

The copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) initiated by n-BuLi in THF under a condition of $[M_1]_0/[M_2]_0<1$ proceeded without termination and chain transfer to give an alternating copolymer. Among the rate constants of the propagation reactions, k_{22} must be zero and k_{12} must be greater than k_{11} in such a copolymerization reaction.

$$\sim\!\sim\!\sim M_1^- \quad + \quad M_1 \quad \xrightarrow{k_{11}} \quad \sim\!\sim\!\sim M_1^- \tag{1}$$

$$\sim\!\sim\!\sim M_1^- \quad + \quad M_2 \quad \xrightarrow{k_{12}} \quad \sim\!\sim\!\sim M_2^- \tag{2}$$

$$\sim\!\sim\!\sim M_2^- \quad + \quad M_1 \quad \xrightarrow{k_{21}} \quad \sim\!\sim\!\sim M_1^- \tag{3}$$

$$\sim\!\sim\!\sim M_2^- \quad + \quad M_2 \quad \xrightarrow{k_{22}} \quad \sim\!\sim\!\sim M_2^- \tag{4}$$

The sum of the concentrations of the living ends, $[M_1^-] + [M_2^-]$, should be equal to that of the initiator, $[C]_0$.

$$[M_1^-] \quad + \quad [M_2^-] = [C]_0 \tag{5}$$

In eq. (5), $[M_1^-]$ is negligible because the anion existing in the system was mostly M_2^-, which must be far more stable than the M_1 anion owing to the conjugation with its two benzene rings. So we can assume $k_{12}>>k_{21}$ and get eq. (6).[3)]

$$-\frac{d[M_1]}{dt} = k_{21}[C]_0[M_1] \tag{6}$$

The equation shows that process (3) is the rate determining step in the copolymerization.

Recently, Ureta et al.[9)] have reported the anionic copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2), in which they found that process (3) was a reversible reaction as follows:

$$\sim\!\sim\!\sim M_2^- \quad + \quad M_1 \quad \underset{k_{-21}}{\overset{k_{21}}{\rightleftarrows}} \quad \sim\!\sim\!\sim M_2M_1^- \qquad (7)$$

If so in the present copolymerization, eq. (6) must be rewritten as eq. (8):

$$-\frac{d[M_1]}{dt} = k_{21}[M_2^-][M_1] \times \frac{k_{12}[M_2]}{k_{-21} + k_{12}[M_2]} \qquad (8)$$

The analysis of the results in Fig. 1 gave a linear relationship between log $[M_1]$ and t as is shown in Fig. 4, indicating that the rate of the consumption of isoprene is first order with respect to its own concentration as represented by eq. (6). Consequently, there must be $k_{12}[M_2] >> k_{-21}$ in eq. (8) and the reversible reaction (7) may be neglected. From Fig. 4, we can get $k_{21} = 2.64 \times 10^{-3}$ l/mol sec in THF at 0°C. Taking into account of the difference of the reaction temperature, the above value seems to be greater than $k_{21} = 1.3 - 1.8 \times 10^{-3}$ l/mol sec found in the copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) by means of n-BuLi at 22°C. The values indicate that isoprene is sterically and electronically more reactive than 2,3-dimethylbutadiene because the latter has one more methyl group.

The monomer reactivity ratios, r_1, obtained in the copolymerizations of 1,1-diphenylethylene (M_2) with three comonomers (M_1) by n-BuLi are summarized in Table 6. 1,1-Diphenylethylene was always more reactive to the M_1 anion than the corresponding M_1 monomer in THF. In benzene, 1,1-diphenylethylene was more reactive, when the comonomer was styrene or 2,3-dimethylbutadiene, while less reactive, when isoprene was the comonomer. In the copolymerization of isoprene and 1,1-diphenylethylene with n-BuLi, the monomer reactivity ratio was strongly influenced by the solvent (Table 5). The r_1 value in hydrocarbon solvent was larger than unity, while in dioxane and THF, the value approached zero with the increasing polarity of the solvent. No effect of the initiator on the r_1 value was observed in the copolymerization in THF, but in benzene the value varied in the order of $Li^+ >> Na^+ > k^+$. When the counter ion was either Na^+ or K^+, a small influence of the solvent was observed on the r_1 value. These tendencies suggest that the r_1 value may decrease with an increase in the ionic character of the carbon-metal bond. Similar results have been reported in the anionic copolymerization of butadiene and styrene,10) and of isoprene and styrene.11) The high reactivity of the dienes observed in these copolymerizations was explained by preferential absorption of the dienes at the active center.*2) Such an absorption may be excluded for 2,3-dimethylbutadiene because of its steric hindrance.

It is well known that $NaB(Ph)_4$ depresses the dissociation of an ion pair to free ions in the anionic polymerization of styrene.12) The presence of $NaB(Ph)_4$ in the present copolymerization with Na^+ counter ion in THF had no infuence on the r_1 value as is shown in Table 3. The fact demonstrates that, if the copolymerization may involve two kinds of propagating species, a free ion and an ion pair, the r_1 values for these two species will be very similar.

The alternating copolymer consisted of isoprene unit having 83% of 1,4-structure, in comparison with 22% in the polyisoprene polymerized under the same conditions. In the copolymerization isoprene adds to the bulky 1,1-diphenylethylene anion at the sterically less hindered 4-position, and then the resultant isoprenyl anion adds to 1,1-diphenylethylene at the less hindered 1-position than the 3-position. A similar result was observed in the alternating copolymer of 2,3-dimethylbutadiene and 1,1-diphenylethylene,3) in which the microstructure of 2,3-dimethylbutadiene was only 1,4-addition. A small portion of the 3,4-addition appeared in the copolymer of isoprene and 1,1-diphenylethylene may be attributed to the less steric hindrance than that of 2,3-dimethylbutadiene.

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*1) Calculated for the initiator concentration assuming the living polymer system.

*2) Worsfold denied the above explanation from the result of the kinetic study on the copolymerization of styrene and isoprene. D. J. Worsfold, J. Polymer Sci. A-1, 5, 2783 (1967).

Table 1

Anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2).

——Material balance

M_1: 0.442 g, initiator: n-BuLi 0.11 mmol, temp.: 0°C in THF, 40°C in benzene.

Solvent 15.0 ml	Time hr	M_2 g	$[M_1]_0/[M_2]_0$ mol/mol	Polymer g	Unchanged[a] M_2, g	$[m_1]/[m_2]$[b] mol/mol
THF	96	1.293	0.904	1.544	0.187	1.06
THF	96	1.522	0.770	1.589	0.370	1.02
THF	96	1.797	0.607	1.625	0.630	1.00
Benzene	120	0.506	2.32	0.494	0.440	24.8
Benzene	120	1.162	1.01	0.562	1.042	9.87
Benzene	120	1.733	0.653	0.600	1.554	7.47

[a] Contained ca. 7 mg of Li-compounds.

[b] Molar ratio of monomers in copolymer.

Table 2

Anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2).

—— Copolymer composition

Initiator: n-BuLi

Solvent	Yield	$[m_1]/[m_2]$[a]	Elementary analysis Calcd[b]		Found		NMR
15.0 ml	wt%		C%	H%	C%	H%	$[m_1]/[m_2]$[c]
THF	11.1	1.00	91.76	8.24	91.95	8.20	—
THF	23.4	1.00	91.86	8.14	91.86	8.07	—
THF	72.6	1.00	91.88	8.12	92.00	8.11	0.96
Dioxane	78.7	1.23	91.56	8.44	91.23	8.23	1.27
Dioxane	97.4	2.34	90.88	9.12	90.98	8.98	2.40
Benzene	27.9	7.47	89.16	10.50	89.16	10.41	7.10
Benzene	43.6	13.9	88.98	11.02	88.93	10.89	—

[a] Copolymer composition calculated from polymer yield.

[b] Based on the copolymer composition. Correction was done for end group of low molecular weight polymer.

[c] Copolymer composition obtained from NMR spectrum.

Table 3

Anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2).

——— Monomer reactivity ratio, r_1 (THF)

$[M_1]_0$: 6.53-6.62 mmol, solvent: 15.0 ml, temp.: 0°C

Initiator 0.11 mmol	$[M_1]_0/[M_2]_0$	Time hr	Yield mol%	$[m_1]/[m_2]^{a)}$	η_{sp}/C dl/g	r_1
Na-Naph.	1.07	96	96.9	1.15	0.190	0.16
Na-Naph.	1.00	96	94.7	1.11	0.211	0.15
Na-Naph.	0.962	96	94.3	1.09	0.200	0.11
Na-Naph.	0.852	96	90.8	1.03	0.204	0.05
Na-Naph.$^{b)}$	0.997	96	95.2	1.10	0.213	0.13
					Average	0.12
K-disp.	1.00	96	94.0	1.14	—	0.17
K-disp.	0.906	123	86.5	1.11	—	0.15
K-disp.	0.830	144	85.4	1.03	—	0.05
K-disp.	0.781	144	81.3	1.03	—	0.06
					Average	0.11

[a] Molar ratio of monomers in copolymer.

[b] Contained 0.50 mmol of $NaB(Ph)_4$

Table 4

Anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2).

——— Monomer reactivity ratio, r_1 (benzene, n-BuLi)

$[M_1]_0$: 6.51-6.57 mmol, solvent: 15.0 ml, initiator: 0.12 mmol, temp.: 40°C.

$[M_1]_0/[M_2]_0$	Time hr	Yield mol%	$[m_1]/[m_2]^{a)}$	η_{sp}/C dl/g	r_1
2.32	120	72.8	24.8	0.122	47.4
1.53	120	64.8	13.9	0.120	34.7
1.01	120	55.3	9.87	0.122	33.5
1.00	72	54.7	10.7	0.115	37.5
0.654	120	45.8	7.47	0.123	31.7
				Average	36.8
1.00$^{b)}$	216	0	—	—	—

[a] Molar ratio of monomers in copolymer.

[b] Without initiator.

Table 5

Anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2)

—— Monomer reactivity ratio, r_1

Solvent	Initiator	Temp. °C	Number of experiment	r_1
THF	n-BuLi	0	5	0.11
THF	n-BuLi	25	2	0.04
THF	Na-Naph.	0	4	0.12
THF	K-disp.	0	4	0.11
Dioxane	n-BuLi	30	6	0.50
Benzene	n-BuLi	40	5	37
Benzene	Na-disp.	40	5	0.38
Benzene	K-disp.	40	4	0.05
n-Heptane	n-BuLi	40	4	29

Table 6

Monomer reactivity ratio, r_1, in anionic copolymerization of 1,1-diphenylethylene and other monomers by n-BuLi

M_2 monomer / M_1 monomer	1,1-Diphenylethylene	
	in THF	in Benzene
Isoprene	0.11	37
2,3-Dimethylbutadiene	0	0.23
Styrene	0.13	0.71

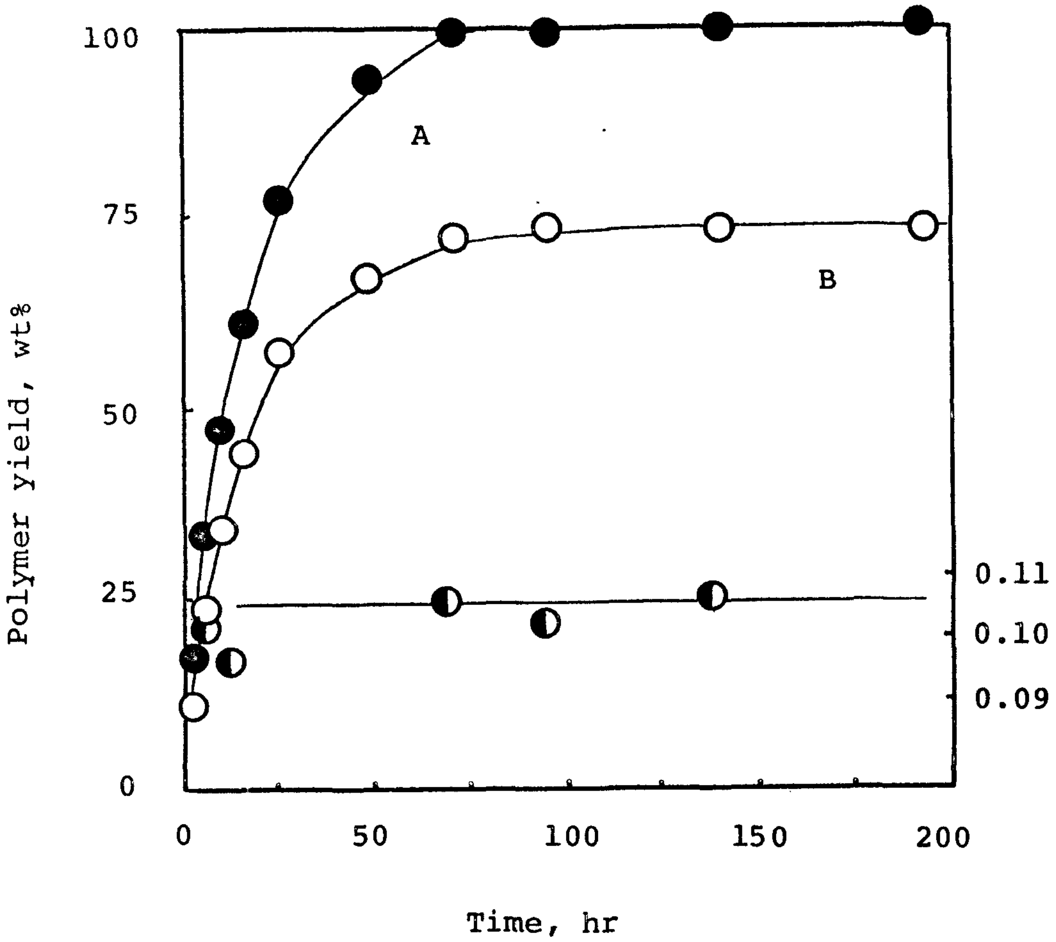

Fig. 1. Anionic copolymerization of isoprene and 1,1-diphenylethylene.—— Time vs. polymer yield (THF).

A: Polymer yield against total monomers.

B: Polymer yield as alternating copolymerization.

◑: n-Butyl alcohol required for terminating copolymerization.

$[M_1]_0$: 6.48 mmol, $[M_2]_0$: 9.97 mmol, [n-BuLi]: 0.107 mmol, THF: 15 ml, temp.: 0°C.

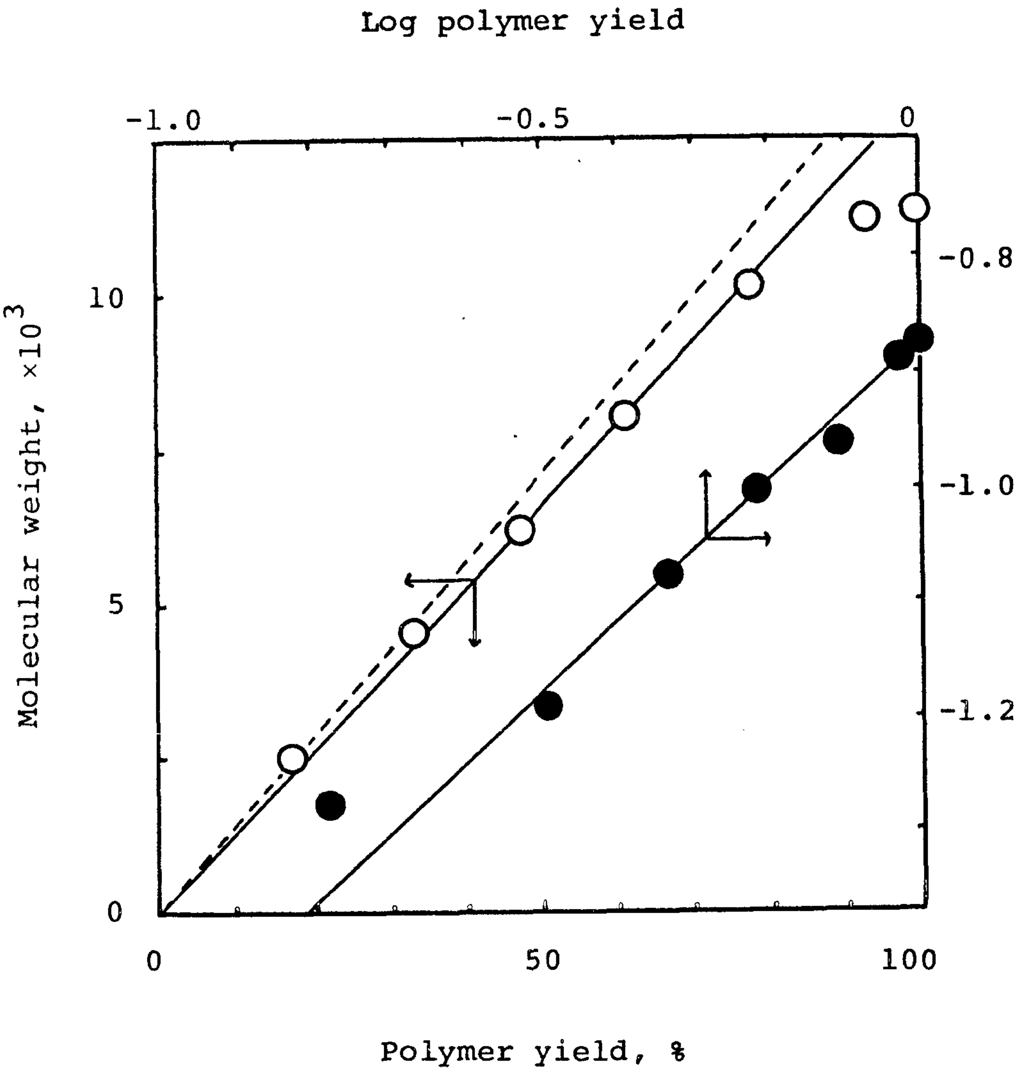

Fig. 2. Anionic copolymerization of isoprene and 1,1-diphenylethylene.—— Relationship between polymer yield and molecular weight.

Dotted line: Molecular weight calculated as living polymer.

$[M_1]_0$: 6.48 mmol, $[M_2]_0$: 9.97 mmol, [n-BuLi]: 0.107 mmol, THF: 15.0 ml, temp.: 0°C.

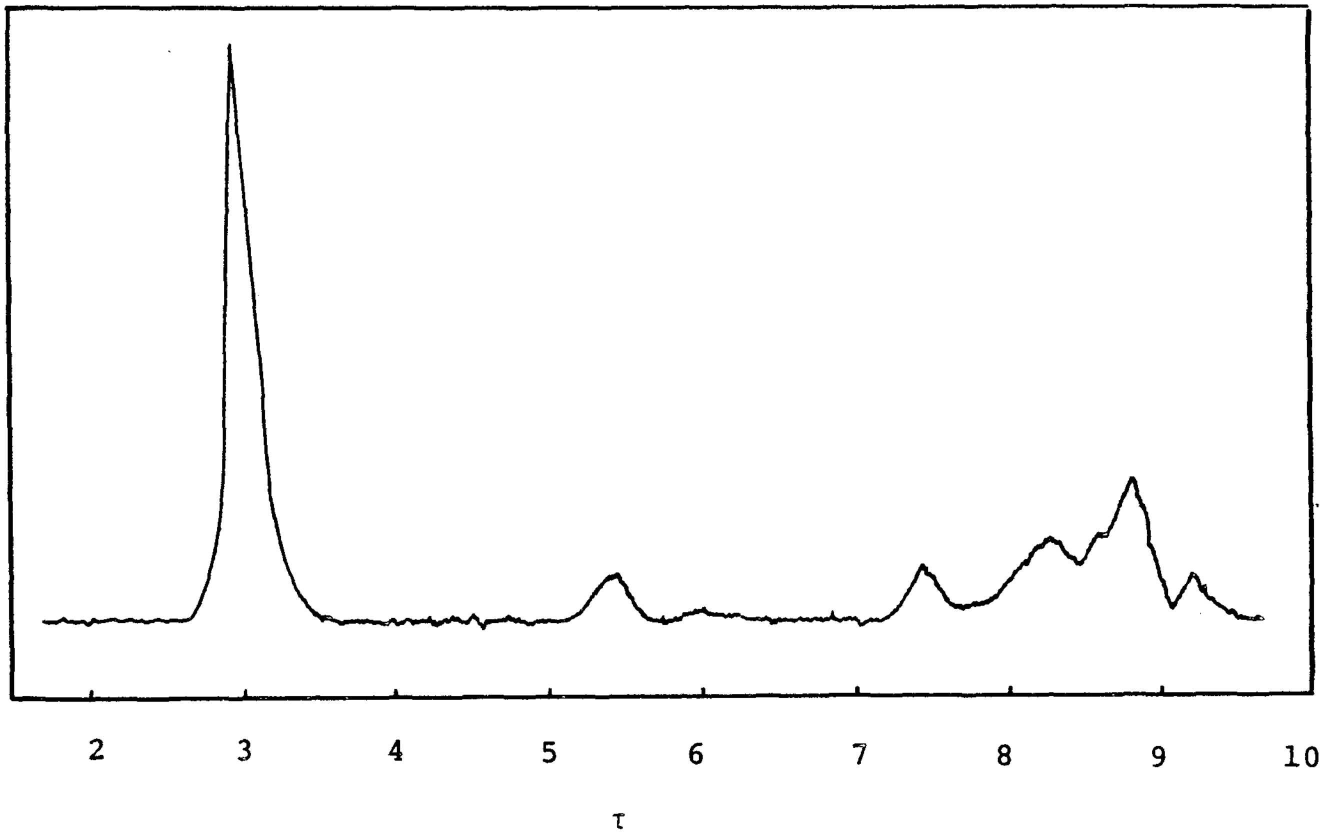

Fig. 3. NMR spectrum of the alternating copolymer of isoprene and 1,1-diphenylethylene in carbon tetrachloride at 60°C.

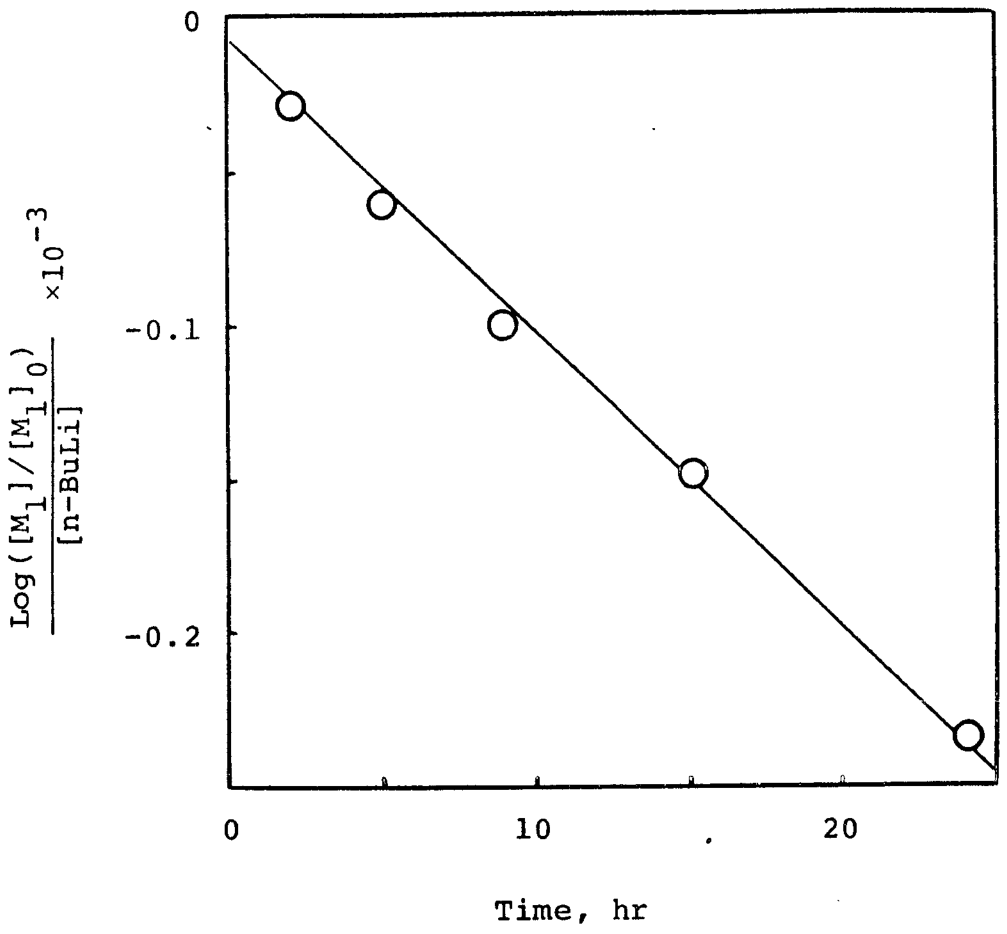

Fig. 4. Anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) —— First order plot.

$[M_1]_0$: 6.48 mmol, $[M_2]_0$: 9.97 mmol, [n-BuLi]: 0.107 mmol, THF: 15.0 ml, temp.: 0°C.

Chapter 4

Anionic Copolymerization of Butadiene and 1,1-Diphenylethylene

Synopsis

Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene was investigated in tetrahydrofuran (THF) and benzene by means of n-butyllithium (n-BuLi), Na-naphthalene, Na- and K-dispersions as initiators. An alternating copolymer was formed in THF, where the reaction proceeded without termination and chain transfer. Monomer reactivity ratios, r_1, were 0.13 (Li^+), 0.09 (Na^+), and 0.09 (K^+) in THF at 0°C. The r_1 values in benzene at 40°C were 54 (Li^+), 0.71 (Na^+), and 0.10 (K^+). The order of rate constants in THF was $k_{12}>k_{11}>k_{21}$, the last of which was found to be 0.27 l/mol sec in the copolymerization with n-BuLi at 0°C.

Introduction

In the proceeding chapter, the author reported the anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2), in which the following results were obtained:

1) The copolymerization in THF proceeded in a liivng system to give an alternating copolymer.

2) Monomer reactivity ratios, r_1, were 0.12 (Li^+), 0.11 (Na^+), and 0.11 (K^+) in THF at 0°C, and 37 (Li^+), 0,38 (Na^+), and 0.05 (K^+) in benzene at 40°C.

3) The order of rate constants in the copolymerization in THF at 0°C was $k_{12}>k_{11}>k_{21}$; k_{21} was 2.64×10^{-3} l/mol sec.

In the present work, the anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2) was investigated. The results obtained were very similar to those reported in the proceeding chapter.

Experimental

Materials. Butadiene. The monomer (Phillips, polymerization grade) dried over Molecular Sieves was mixed with solvent-free n-BuLi just before use, and then redistilled into a glass ampoule in vacuo.

The preparations and purifications of the other materials, such as THF, benzene, and n-BuLi, were shown in the proceeding paper.$^{4)}$

Polymerization. The purified butadiene was first transferred to a weighed quantity of a solvent on the vacuum line, and the solution was weighted to get the amount of the monomer transferred. The solution was then distilled under high vacuum to the solvent without any loss. The solution thus obtained was transferred to a glass ampoule with a hypodermic syringe under dry argon. To the ampoule, 1,1-diphenylethylene and an initiator were added with hypodermic syringes. After the reaction was carried out for a definite time, the polymerization was terminated by adding a small portion of methanol. The polymer precipitated in methanol was filtrated, dried, and weighed. The mother liquor of the polymer precipitation was evaporated at reduced pressure, and unchanged 1,1-diphenylethylene was recovered as the residue.

Electronic Spectrum. The electronic spectrum of a reaction mixture was taken with a Hitachi 124 Spectrophotometer; a sample solution was prepared under the same condition as that described for the polymerization method.

NMR Spectrum. The spectrum of the polymer was measured on a JNM-4H-100 Spectrometer (Japan Electron Optics Laboratory Co. Ltd.) in a carbon tetrachloride solution using tetramethylsilane as an internal standard at 60°C.

Molecular Weight. The molecular weight of the polymer was measured with a Mechrolab Vapor Pressure Osmometer, Model 301A; benzene was used as a solvent.

Viscosity. The solution viscosity of the polymer was taken in toluene at 30.0°C.

Results

The results obtained in this work were very similar to those found in the copolymerization of isoprene and 1,1-diphenylethylene. Namely, the present copolymerization in THF also proceeded in a living system to give an alternating copolymer and the r_1 values were very similar to those derived in the copolymerizations carried out under the same reaction conditions.

The rate of the copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2) was investigated in THF at 0°C with n-BuLi. Fig. 1 shows the results. The reaction was completed in 60 min, in which butadiene was almost consumed. Since 1,1-diphenylethylene can not be homopolymerized, the maximum polymer yield is obtained in the case that the copolymerization proceeds alternatingly. The yield for the alternating copolymerization is also shown in Fig. 1. This yield reaches nearly 100%, indicating the formation of the alternating copolymer.

A linear relationship was obtained between the polymer yield (curve B in Fig. 1) and the molecular weight of the polymer, as is shown in Fig. 2. The molecular weight measured almost agreed with that calculated for the living polymer system which proceeds alternatingly. There was also a good linearity between log Yield and log $[\eta]$.

The monomer composition of the copolymer, $[m_1]/[m_2]$, was calculated from the polymer yield as butadiene was completely incorporated into the copolymer. A part of the results is shown in Table 1. The copolymer obtained in THF was powder having a softening point of ca. 130°C, while the copolymer obtained in benzene was viscous liquid.

The copolymer composition was checked by elementary analysis and NMR spectroscophy. The results are listed in Table 2. Both the methods supported the composition calculated in the above manner.

Monomer reactivity ratio, r_1, was calculated by means of the integrated Mayo-Lewis copolymer composition equation.$^{1)}$ The r_1 values are shown in Tables 3-5. In THF at 0°C, the values were almost constant regardless of the initiators used. The r_1 value was not affected by the presence of $NaB(Ph)_4$ in the copolymerization initiated Na-naphthalene in THF. In benzene at 40°C, however, the values were 0.10, 0.71 and 54 with n-BuLi, Na- and K-dispersions respectively. The copolymerization carried out in benzene without an initiator gave no polymer even after 187 hr at 40°C (Table 4), meaning that no polymer is obtained by free radical mechanism under the reaction conditions employed here.

The microstructures of butadiene in the homopolymer and the alternating copolymer were investigated by NMR spectrum. Fig. 3 is the spectrum of the alternating copolymer obtained with n-BuLi in THF. The microstructure of the polybutadiene by n-BuLi in THF was 82% 1,2- and 18% 1,4-structures. On the other hand, the microstructure of the alternaitng copolymer was 30% 1,2- and 70% 1,4-structures.

The copolymerization in THF at 0°C was followed spectrophotometrically. As soon as n-BuLi was added to the monomer solution at $[M_1]_0/[M_2]_0 = 0.53$, an absorption maximum due to the diphenylethylene anion appeared at 496 mμ. Its optical density had been constant during 5 hr. The molar extinction coefficient was 1.7×10^4, which agrees the value found in the copolymerization of isoprene and 1,1-diphenylethylene.4) These results suggest that the most of the living ends in the system were 1,1-diphenylethylene anion.

Discussion

The copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2) in THF proceeded without termination and chain transfer to give an alternating copolymer. In such a case, eq. (1) can be induced as has been shown in the copolymerization of isoprene and 1,1-diphenylethylene.4)

$$-\frac{d[M_1]}{dt} = k_{21}[M_2^-][M_1] \times \frac{k_{12}[M_2]}{k_{-21} + k_{12}[M_2]} \qquad (1)$$

where k_{-21} is the rate constant of the reverse reaction in the reaction of 1,1-diphenylethylene anion with butadiene. Fig. 4 indicates that a linear relationship between log $[M_1]$ and t was derived by analyzing the results in Fig. 1. This means that the rate of the consumption of butadiene is first order with respect to its own concentration as had been found in the proceeding work. Therefore, the reverse reaction can be neglected. From Fig. 4, we can get k_{21} = 0.27 l/mol sec in THF at 0°C. The rate constants were 2.64×10^{-3} l/mol sec in the copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) at 0°C,4) and $1.3\text{-}1.8\times10^{-3}$ l/mol sec in the copolymerization of 2,3-dimethylbutadiene and 1,1-diphenylethylene at 22°C.2) These results fairly suggest that in THF butadiene is most reactive and the reactivity of the dienes to the 1,1-diphenylethylene anion decreases with an increase in the methyl group.

The monomer reactivity ratios, r_1, obtained in the copolymerization of 1,1-diphenylethylene (M_2) and other monomers (M_1) by means of n-BuLi are summarized in Table 6. In THF, 1,1-diphenylethylene is more reactive to the M_1 anion than the corresponding M_1 monomer. In benzene, however, isoprene and butadiene are more reactive than 1,1-diphenylethylene.

With Li^+ as a counter ion, the r_1 value was strongly influenced by the solvent (Table 5); with Na^+ and K^+ less influence of the solvent was observed. While little effect of the initiator on the r_1 value was found in the coplymerization in THF, in benzene the value increased in the order of $Li^+ >> Na^+ > K^+$. These results are very similar to those reported in the copolymerization of isoprene and 1,1-diphenylethylene,[4)] suggesting that the r_1 value may increase with the decreaseing polarity of the carbon-metal bond.

Although it has been shown that $NaB(Ph)_4$ depresses the dissociation of an ion to free ions,[7)] in the present copolymerization no effect of $NaB(Ph)_4$ on the r_1 value was observed. Then, if this copolymerization may proceed by both free ion and ion pair, the r_1 value for these two species will be very similar as reported in the proceeding paper.[4)]

The microstructures of butadiene, isoprene, and 2,3-dimethylbutadiene in the homopolymers and in the alternating copolymers with 1,1-diphenylethylene are summarized in Table 7. (P.154) All polymers were polymerized in THF by means of n-BuLi. The dienes in the alternating copolymers had more 1,4-structure than those in their homopolymers, and the order of percentage of the 1,4-structure content was 2,3-dimethylbutadiene>isoprene>butadiene. In the alternating copolymer of 2,3-dimethylbutadiene and 1,1-diphenylethylene, no 1,2-structure was present because of its big steric hindrance. However, in the case of butadiene-diphenylethylene alternating copolymer, the 1,2-structure existed because of its less steric hindrance. These results suggest that the microstructure of the dienes in the alternating copolymer must be controlled strongly by steric effect.

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Table 1. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2)—— Material balance

M_1: 0,302 g, initiator: n-BuLi 0.11 mmol, temp.: 0°C in THF, 40°C in benzene

Solvent 15.0 ml	Time hr	M_2 g	$[M_1]_0/[M_2]_0$ mol/mol	Polymer g	Unchanged[a] M_2, g	$[m_1]/[m_2]$[b] mol/mol
THF	24	0.949	1.07	1.182	0.064	1.15
THF	48	1.009	1.00	1.226	0.096	1.09
THF	48	1.328	0.758	1.254	0.382	1.06
Benzene	96	0.596	1.68	0.344	0.534	23.2
Benzene	120	0.924	1.08	0.372	0.826	14.2
Benzene	96	1.348	0.744	0.394	1.242	10.8

a) Contained ca. 7 mg of lithium compounds.

b) Molar ratio of the monomers in the copolymer.

Table 2. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2)—— Copolymer composition

Solvent 15 ml	Initiator	$[m_1]/[m_2]$[a]	Elementary analysis Calcd.[b]		Found		NMR $[m_1]/[m_2]$[c]
			C%	H%	C%	H%	
THF	n-BuLi	1.00	92.26	7.74	92.00	7.70	0.97
Benzene	K-disp.	1.08	92.20	7.80	92.03	7.69	1.05
Benzene	Na-disp	1.50	91.98	8.02	91.75	7.85	1.40
Benzene	n-BuLi	10.8	89.80	10.20	89.60	9.82	9.50

a) Copolymer composition calculated from polymer yield.

b) Based on the copolymer composition.

c) Copolymer composition obtained from NMR spectrum.

Table 3. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2)—— Monomer reactivity ratio, r_1 (THF, n-BuLi)

$[M_1]_0$: 5.60 mmol, THF 15 ml, [n-BuLi]: 0.11 mmol, temp.: 0°C

$[M_1]_0/[M_2]_0$	Time hr	Yield mol%	$[m_1]/[m_2]^{a)}$	r_1
1.065	24	96.4	1.15	0.17
1.000	48	94.1	1.09	0.17
0.833	24	88.7	1.05	0.10
0.758	48	83.9	1.06	0.12
0.731	24	82.3	1.05	0.11
0.508	18	66.1	1.04	0.10
			Average	0.13

a) Molar ratio of monomers in the copolymer.

Table 4. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2)—— Monomer reactivity ratio, r_1 (Benzene, Na-disp.)

$[M_1]_0$: 5.57 mmol, benzene: 15 ml, Na-disp.: ca. 0.5×10^{-3} atom, temp.: 40°C.

$[M_1]_0/[M_2]_0$	Time hr	Yield mol%	$[m_1]/[m_2]^{a)}$	η_{sp}/C dl/g	r_1
1.046	187	85.2	1.50	0.50	0.79
0.961	187	83.3	1.42	0.52	0.70
0.929	187	83.2	1.38	0.74	0.71
0.814	187	78.2	1.35	0.42	0.75
0.724	187	75.7	1.25	0.68	0.61
				Average	0.71
$0.976^{b)}$	187	0	-	-	-

a) Molar ratio of monomers in the copolymer.

b) Without initiator.

Table 5. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2)—— Monomer reactivity ratio, r_1

Solvent	Initiator	Temp. °C	Run of experiment	r_1
THF	n-BuLi	0	6	0.13
THF	Na-naph.	0	6	0.09
THF	K-disp.	0	5	0.09
Benzene	n-BuLi	40	5	54
Benzene	Na-disp.	40	5	0.71
Benzene	K-disp.	40	5	0.10

Table 6. Monomer reactivity ratio, r_1, in the copolymerizations of 1,1-diphenylethylene (M_2) and dienes (M_1) by n-BuLi

M_1	THF[a)]	Benzene[b)]	Ref.
Butadiene	0.13	54	This work
Isoprene	0.11	37	4
2,3-Dimethylbutadiene	0[c)]	0.23	2,3

a) At 0°C. b) At 40°C. c) At 22°C.

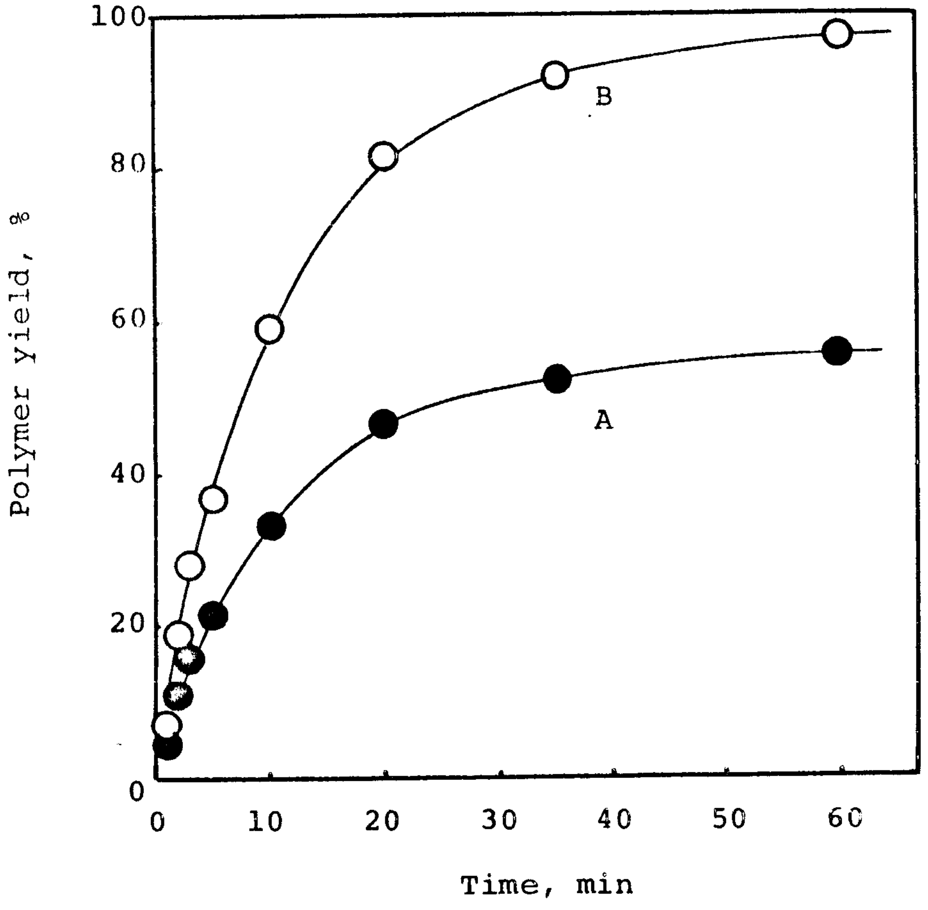

Fig. 1. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2) —— Time vs. polymer yield.

A: Polymer yield against total monomers.

B: Polymer yield as alternating copolymerization.

$[M_1]_0$ = 5.74 mmol, $[M_2]_0$ = 11.39 mmol, [n-BuLi] = 0.11 mmol, THF = 15.0 ml, temp. = 0°C.

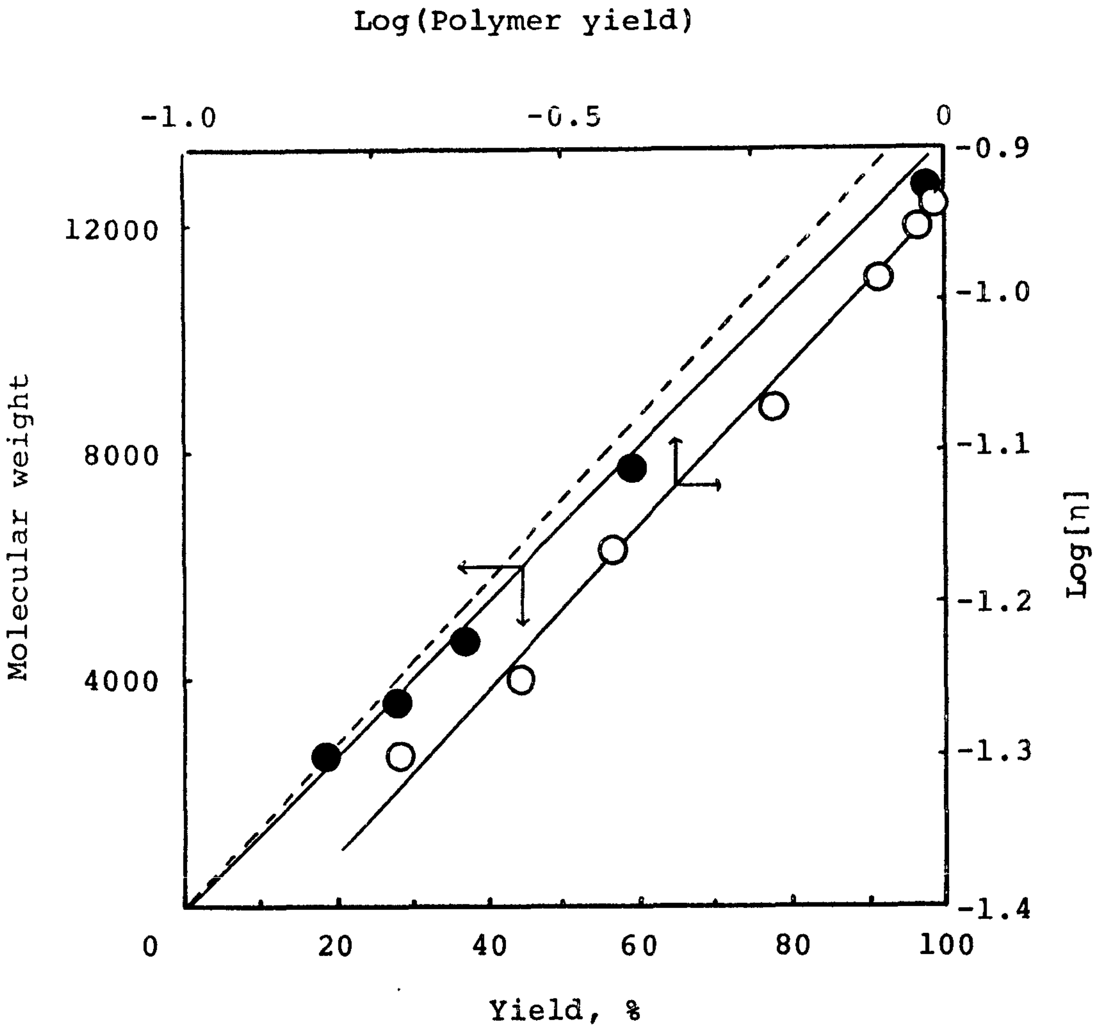

Fig. 2. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2) —— Relationship between polymer yield and molecular weight.

Dotted line: Molecular weight calculated as living Polymerization.

Reaction conditions are shown in Fig. 1.

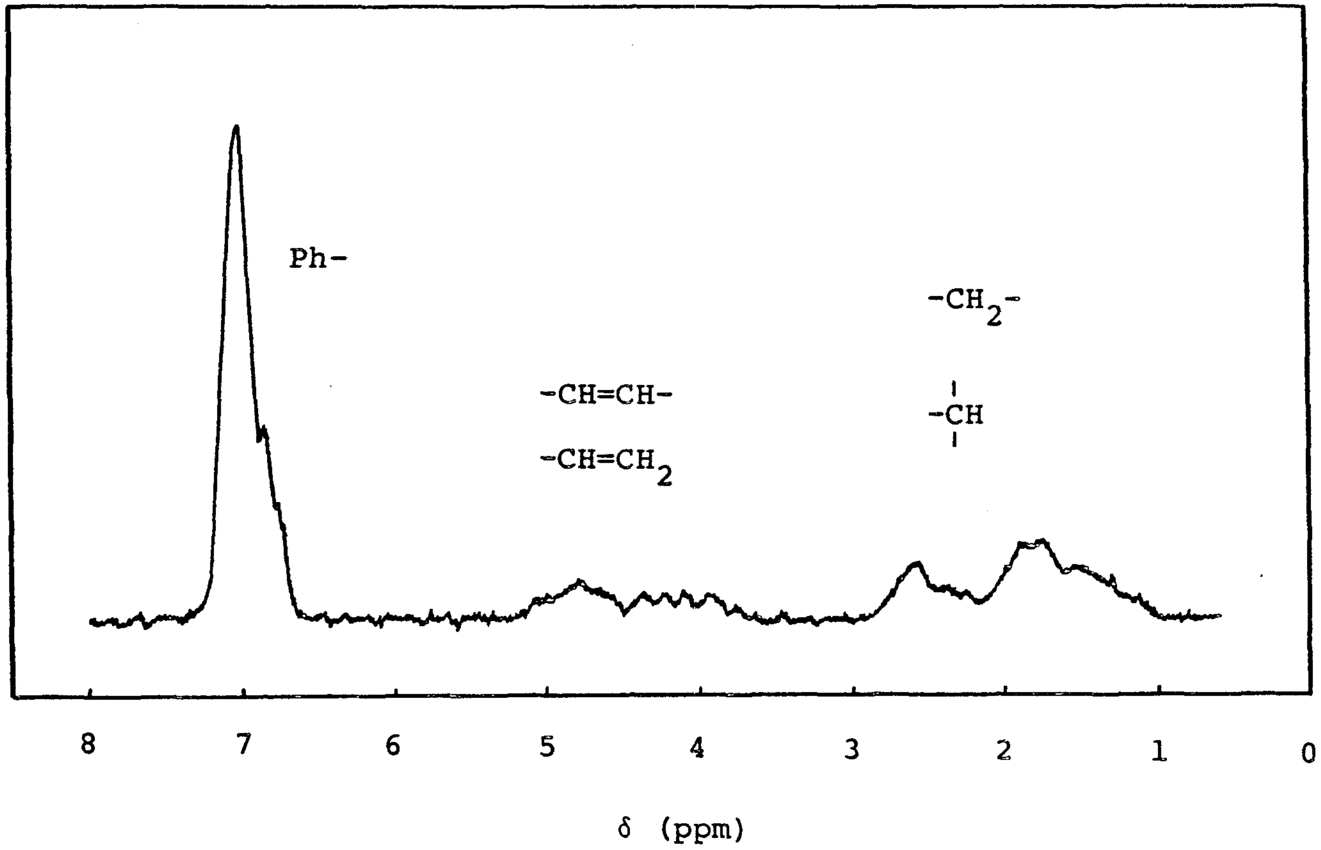

Fig. 3. NMR spectrum of the alternating copolymer of butadiene and 1,1-diphenylethylene. (in CCl_4 at 60°C).

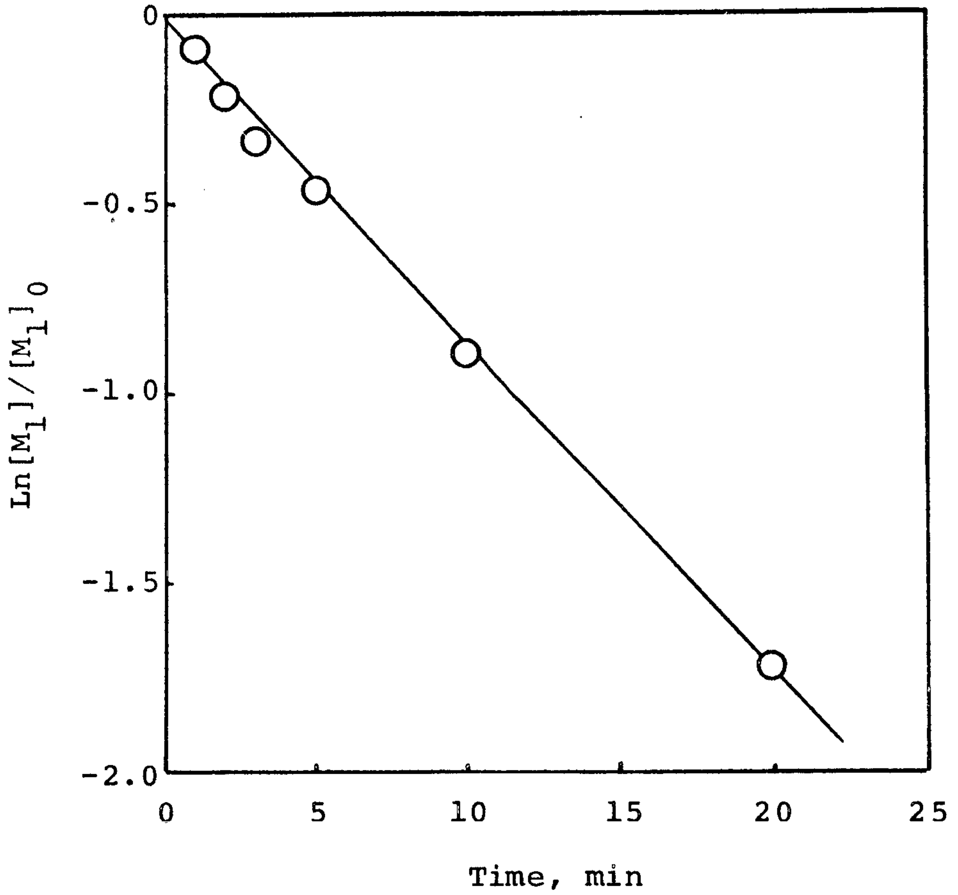

Fig. 4. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2) —— First order plot.

$[M_1]_0$ = 5.74 mmol, $[M_2]_0$ = 11.39 mmol, [n-BuLi] = 0.11 mmol, THF = 15.0 ml, temp. = 0°C.

Chapter 5

Stereospecific Polymerization of *o*-Methoxystyrene by Anionic Initiators

Synopsis

o-Methoxystyrene was polymerized with n-butyllithium (n-BuLi) Na-naphthalene, and K-dispersion as initiators, in tetrahydrofurar (THF) and toluene. The stereoregularity of the polymer was investigated by means of the NMR spectroscopy. The methoxy resonance of the spectrum split into ten components due to the tactic pentads. It was found by X-ray examination that the polymer obtained by n-BuLi in toluene at -45°C was crystalline and highly isotactic. In THF, the stereospecificity of the polymerization was independent of the initiator, and the isotacticity of the polymer increased with raising the reaction temperature. In toluene, the stereospecificity depended on the initiator; i.e., n-BuLi gave the polymer with higher isotacticity than that given by phenyl sodium. The fraction of isotactic triad of the polymer obtained by n-BuLi in toluene at -78°C was more than 90%, but 50% at 50°C. The presence of ca. 1% THF in toluene led to a steep decrease in the isotacticity even at -78°C. The tacticity of the polymer given by Na-naphthalene was not affected by the existence of $NaB(Ph)_4$ in THF. The polymerization in THF could be explained by the "Bovey's single σ" process, while a penultimate effect was

observed in the polymerization by n-BuLi in toluene.

INTRODUCTION

Natta et al.[1] have studied the stereospecific polymerization of *o*-methoxystyrene (*o*-MeOSt) with $EtAlCl_2$. Recently, Higashimura et al.[2] have investigated the cationic polymerization of *o*-MeOSt and examined the stereoregularity of the polymer using NMR spectroscopy.

On the other hand, the stereospecific polymerization of this monomer has not been studied with an anionic initiator. It is well known that a compound containing ether oxygen can easily coordinate with alkali metal cations such as Li^+ and Na^+. Therefore, it is expected that in the anionic polymerization of *o*-MeOSt the ether oxygen in the monomer or in the chain end of the growing polymer anion may interact with the counter ion to affect sterically the addition of the monomer. In the present work, the anionic polymerization of *o*-MeOSt is studied, and the relationships between the polymerization conditions and the stereoregularity of the polymer (P-*o*-MeOSt) are discussed on the basis of the NMR spectroscopy.

EXPERIMENTAL

Materials

o-MeOSt was synthesized by dehydration of methyl-(2-methoxyphenyl)-carbinol over $KHSO_4$ at 220-230°C, which was prepared by Grignard reaction of acetaldehyde and *o*-bromoanisole. The obtained monomer was fractionally distilled, and then redistilled from lithium aluminum hydride. Bp 80-81°C/10 mmHg, n_D^{20} 1.5605. No impurity was detected by gas chromatography and NMR spectroscopy.

Tetrahydrofuran (THF) which had been previously refluxed over metallic sodium and then over lithium aluminum hydride, was distilled onto Na-K alloy and naphthalene. From the green solutio the solvent was transferred to a reaction vessel on a vacuum line just before use.

Toluene was purified by the usual method and was stored over sodium. Before use the solvent was transferred to a flask containing a small amount of n-butyllithium (n-BuLi) in toluene, from where it was distilled under high vacuum.

n-BuLi was synthesized from n-butyl chloride and metallic lithium in n-heptane, according to the method of Ziegler.[3] The concentration was determined by double titration.[4]

Na-naphthalene (Na-Naph.) was prepared in THF; the concentration was determined by the titration of a hydrolyzed sample with standard hydrochloric acid.

Phenyl sodium (Ph-Na) was obtained according to the method of Gilman from chlorobenzene and sodium dispersion in n-heptane.[5]

Potassium dispersion (K-disp.) was prepared in a n-heptane medium.

Polymerization

To a glass ampule which had been evacuated and heated with a gas burner, a solvent was first transferred on the vacuum line.

Then, the monomer and an initiator were added to the ampule in a thermostat with hypodermic syringes under the atmosphere of dry argon. After the polymerization was terminated by adding a small portion of methanol, the reaction mixture was poured into a large amount of methanol. The precipitated polymer was filtrated, washed with methanol, and dried.

Measurement

The NMR spectrum of the polymer was obtained at 60°C with a JNM-4H-100 spectrometer at 100 MHz by using chloroform or carbon tetrachloride as a solvent. The concentration of a sample was ca. 20% (w/v), and tetramethylsilane was used as an internal standard. The spectrum was analyzed with a du Pont 310 Curve Resolver for the determination of pentad sequences. The Lorentzian was assumed in the shape of resonance, and half width of each peak was given tentatively. The relative intensity of the peak was determined with the Integration Meter equipped on the Curve Resolver.

The X-ray diffraction measurement was made with a Rigakudenki 4001 X-ray diffractometer.

The solution viscosity of the polymer was determined in toluene or in chloroform at 30.0±0.03°C.

RESULTS

The polymerizations of *o*-MeOSt were carried out with n-BuLi, Na-naphthalene, and K-dispersion as initiators in THF at 0 and -78°C. The results are shown in Table I. All of the polymerizations smoothly proceeded to give the polymers quantitatively, the softening points of which were 120-130°C.

Table II shows the results of the polymerization of o-MeOSt in toluene. The rate of the polymerization by n-BuLi at low temperature was much slower than that in THF. The solution viscosity of the polymer obtained at low temperature was high, even if the yield of the polymer was low. No polymer was obtained with Na- as well as with K-dispersions in toluene, but the polymerization was initiated with Ph-Na to form the polymer in a good yield.

When the solution of the reaction mixture either in THF or in toluene was kept to stand above 0°C for one or two days, the color of the solution gradually disappeared, although the polymerization had already finished. It is considered that the carbanion reacted with the methoxy group to give a phenolate anion,[6] but its amount was so small that no effect was observed on the polymer produced.

The polymer obtained by n-BuLi in toluene at low temperature showed a high crystallinity under a polarizing microscope. It was insoluble in n-hexane and diethyl ether, partially soluble in toluene, and soluble in chloroform and THF. Its melting point was 290-295°C. The X-ray diffraction (Fig. 1) showed the fiber period of this polymer to be 8.0 Å. The value is well consistent with the fiber period (8.10 Å) of isotactic poly(o-methylstyrene)[7] similar to P-*o*-MeOSt in the chemical structure, suggesting the crystalline P-*o*-MeOSt to be isotactic.

The NMR spectrum of P-*o*-MeOSt prepared with n-BuLi in THF at -78°C is shown in Figure 2. Since the intensity ratio of the peaks at 3.5, 6.7, 7.5, and 8.6τ is 4:3:1:2, they can be attributed to the protons of phenyl, methoxy, methine, and methylene groups with increasing magnetic field.

Figure 3 shows the spectra of the methoxy groups in the polymers obtained under various reaction conditions. The polymers obtained in THF at the same temperature gave very similar spectra regardless of the initiators used. The polymerization temperature, however, affected the NMR spectrum of the polymer (A and B in Fig. 3). The crystalline polymer obtained by n-BuLi in toluene at -45°C showed a very narrow peak at 6.78τ (C in Fig. 3), but the spectrum was broaden by elevating the polymerization temperature (D in Fig. 3). The spectrum of the polymer prepared at -78°C with n-BuLi in toluene containing ca. 1% THF (E in Fig. 3) is similar to those of the polymers prepared with Ph-Na in toluene at 0°C and with $EtAlCl_2$ in toluene at -78°C.

The complicated splits in the spectra of the methoxy protons must be due to the differences of stereochemical structures of the protons because splits by spin-spin coupling can not be considered. Furthermore, the differences seem not to be of conformational because the spectra measured in *o*-dichlorobenzene at 150°C were very similar to those shown in Figure 3.

We can expect that the methoxy resonance is resolved into ten pesks, corresponding to ten configurationally different pentad sequences.[8] Then, the assignments were attempted to the fine peaks of the methoxy resonance in the NMR spectrum assuming that the split is due to the pentad signals and that the crystalline polymer is isotactic. The detailed observations of the spectra indicate that the peaks are divided into three groups; i.e., they are at $6.60 \sim 6.75\tau$, $6.75 \sim 6.88\tau$, and $6.88 \sim 6.95\tau$. Consequently, the peaks at $6.75 \sim 6.88\tau$ were assigned to the isotacti triad (I), which was split into three components 6.78, 6.82, and 6.86τ by pentad sequences. Then, it is anticipated that if the peaks at the lower fields are the components of the heterotactic triad (H), those at the higher fields belong to the syndiotactic one (S), or vice versa. Some polymers showed the spectra composed of the isotactic peaks and those in the lower fields but only small peaks in the higher fields, e.g., spectrum D in Figure 3. If the peaks in the lower fields belong to the syndiotactic triad, the polymer having such a spectrum is composed mainly of isotactic and syndiotactic sequences with only a small portion of heterotactic triad, as if it is a stereo-block polymer composed of isotactic and syndiotactic blocks. The formation of such a polymer is unlikely in a homogeneous polymerization system employed in this work. Accordingly, the peaks at 6.60, 6.65, 6.67, and 6.71τ are assigned to the four components of the heterotactic triad and the peaks at 6.90, 6.93, and 6.95τ to the components of the syndiotactic one.

The fractions of I, H, and S were determined by the relative intensities of the corresponding absorptions; i.e., the absorption areas. When the absorptions were overlapped, some of the spectra which were typical were analyzed with a curve resolver into the ten pentad peaks and the others were resolved into the triads referring the analogous spectra already analyzed with the resolver.

The effect of polymerization temperature on the tacticity of P-*o*-MeOSt was investigated in THF with n-BuLi as an initiator analyzing the tacticity based on the assignments described above. The results are shown in Figure 4. Although the fraction of H was about 50% independently of the temperature, the fraction of I increased and that of S decreased with a rise in the temperature.

The results of the polymerization in toluene with n-BuLi are shown in Figure 5. With raising the temperature, the fraction of I decreased to 50%, and H and S, especially the former, increased steeply.

The tacticity of P-*o*-MeOSt which was polymerized in a toluene-THF mixture with n-BuLi at -78°C is shown in Figure 6. The presence of ca. 1% of THF in toluene led to a drastic decrease in the fraction of I and to increases in those of H and S.

The influence of $NaB(Ph)_4$ on the tacticity was studied in the polymerization initiated by Na-naphthalene in THF at 0 and -78°C. The results are listed in Table III. No influence on the tacticity of P-*o*-MeOSt was observed.

In Table IV are shown the fractions of the triad sequences in the polymer obtained with various initiators. The tacticity of the polymer obtained in THF was not affected by the initiators used. In toluene, however, n-BuLi gave a more isotactic polymer than Ph-Na. For comparison the tacticities of the polymers which were prepared by the cationic and radical polymerizations are also shown in the table.

The methoxy resonance in the NMR spectra of the polymers prepared in THF were submitted to a curve resolver and analyzed as ten components in the pentad sequences. The one of the results is shown in Figure 7, and the assignment of each component and its relative intensity measured are shown in Table V. If the polymerization in THF can be expressed by a Bernoulli-trial process or "Bovey's single σ" process[9] with regard to the configurational sequence, the relative intensities of ten components of the pentads can be calculated from the fractions of triad sequences. Table V shows that the observed values are in accord with the calculated ones. The positions of the components seemed to be slightly shifted by the polymerization conditions.

The NMR spectrum of poly(*p*-methoxystyrene) prepared under the same conditions of the polymerization of *o*-MeOSt could not give an information about the tacticity of the polymer, because its methoxy resonance was not split satisfactorily.

DISCUSSION

Since in THF the alkali metal counter ion is solvated[10] and the coordination by THF may be stronger than those by ether groups of P-*o*-MeOSt and *o*-MeOSt, the steric course of the monomer addition might be determined only by the chain end, as has been found in many radical polymerizations. As expected from this mechanism the tacticity of the polymer was independent of the initiator. Bovey's single σ plots for P-*o*-MeOSt prepared in THF are shown in Figure 8, where σ is defined as the probability that an adding monomer generates the same configuration as that of the end of a growing chain. The observed values are well consistent with the theoretical curves. This together with the results shown in Table V may support that the assignments of the peaks in the NMR spectra are correct, although the assignments were rather tentative.

Two propagating species, a free ion and an ion pair have been found in the anionic polymerizations of styrene and α-methylstyrene in THF.[11] The propagations by these two species may yield configurationally different polymers. The existence of sodium tetraphenylboran which depresses the dissociation of an ion pair into free ions, did not affect the tacticity of P-*o*-MeOSt obtained in the polymerization in THF with Na-naphthalene. The fact may be that the above two species give configurationally same polymers, or that the predominant propagating species is an ion pair.

The Bovey's single σ plots for P-*o*-MeOSt prepared with n-BuLi in toluene is shown in Figure 9. Experimental results deviate from the theoretical curves. In this polymerization the ether groups of the monomer units at the chain end and/or of the adding monomer may interact with the lithium counter ion. The interaction should be a cause for the isotactic polymerization at low temperatures. However, the energy of the interaction may be so small that the stereospecificity of the polymerization decreases steeply with a small rise of the reaction temperature.

Figure 10 shows that Chujo's $\Delta\varepsilon = -kT \times \ln(4IS/H^2)$[12] is almost zero in the polymerization in THF regardless of the temperature. However, $\Delta\varepsilon$ in the polymerization in toluene with n-BuLi decreased with a decrease in the polymerization temperature, suggesting the penultimate effect exists and increases with lowering the temperature.

In a mixture of toluene and THF, THF coordinates preferentially with lithium counter ion, resulting in the prevention of the isotactic propagation of the polymer chain. The effect of THF is similar to that on the polymerization of isoprene with n-BuLi in a hydrocarbon solvent, where the 1,4-cis-structure steeply decreased by the addition of a small amount of THF in toluene.[13] The interaction of Na^+ with the methoxy groups may be weaker than that of Li^+ and the former gave a less isotactic polymer than that given by the latter.

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Table I

Anionic Polymerization of *o*-Methoxystyrene in THF.

Solvent; 15 ml.

Monomer mmol	Initiator (mmol)	Temp. °C	Time hr	Yield %	η_{sp}/C^b dl/g
4.42	n-BuLi (0.073)	-78	2.5	98	0.16
4.52	n-BuLi (0.073)	0	2.5	97	—
4.28	Na-Naph. (0.063)	-78	1.0	95	0.13
4.72	Na-disp. (0.086)	0	2.5	97	0.78
4.28	Na-Naph. (0.063)[a]	0	1.0	96	—
4.28	K-disp. (0.125)	-78	1.0	95	0.15
3.81	K-disp. (0.114)	0	2.5	98	—

[a] $NaBPh_4$ (0.29 mmol) was added.

[b] Toluene solution, C = 0.50 g/dl.

Table II

Anionic Polymerization of *o*-Methoxystyrene in Toluene.

Solvent: 15 ml

Monomer mmol	Initiator (mmol)	Temp. °C	Time hr	Yield %	η_{sp}/C^b dl/g
4.72	n-BuLi (0.073)	-78	144	trace	—
4.60	n-BuLi (0.056)	-78	600	4.2	3.1
4.59[a]	n-BuLi (0.113)	-78	144	96	—
11.4	n-BuLi (0.056)	-45	168	80	7.0
4.25	n-BuLi (0.073)	0	24	100	0.24
4.25	Na-disp. (0.107)	30	96	0	—
4.34	K-disp. (0.114)	30	96	0	—
3.27	Ph-Na (0.050)	0	72	71	—

[a] Solvent contained 1.3 vol% of THF.

[b] Chloroform solution C = 0.50 g/dl.

Table III

Tacticity of Poly(*o*-Methoxystyrene) Initiated by Na-Naphthalene in the Presence of NaB(Ph)$_4$ in THF.

Solvent: 15 ml, monomer: 4.3-4.7 mmol, initiator: 0.063 mmol.

NaB(Ph)$_4$ mmol	Temp. °C	Time hr	Yield %	Tacticity, % H	I	S
0	-78	1.0	95	50	22	28
0.29	-78	24.0	90	51	21	28
0	0	1.0	95	46	39	15
0.29	0	1.0	96	46	40	16

Table IV

Tacticity of Poly(*o*-methoxystyrene) Obtained with Various Initiators.

Solvent	Initiator	Temp. °C	Yield %	Tacticity, % H	I	S
THF	n-BuLi	0	95	47	39	14
THF	Na-Naph.	0	95	46	39	15
THF	K-disp.	0	98	44	41	15
Toluene	n-BuLi	0	100	25	67	8
Toluene	Ph-Na	0	71	39	43	18
Toluene	$EtAlCl_2$	-78	31	33	43	23
Toluene	$BF_3 \cdot OEt_2$	0	45	47	38	15
Bulk	None	60	26	43	38	10

Table V

Curve resolution of methoxy peaks NMR spectrum of P-*o*-MeOSt[a]

	Pentads	HHS	HHH	IHS	IHH	III	IIH	HIH	HSH	SSH	SSS
	τ	6.60	6.65	6.67	6.71	6.78	6.82	6.86	6.90	6.93	6.95
A	Calcd.	16.8	13.0	13.0	8.2	2.6	8.2	5.3	5.3	16.8	10.9
	Found	17.8	13.4	14.3	7.4	2.5	7.9	4.3	4.0	17.0	11.6
B	Calcd.	15.2	12.0	12.0	9.8	4.0	9.8	6.2	6.2	15.2	9.6
	Found	18.5	11.5	10.7	8.2	3.9	8.7	8.6	7.6	13.5	8.7
C	Calcd.	6.6	11.3	11.3	18.3	15.2	18.3	5.5	5.5	6.6	2.0
	Found	5.3	9.4	8.6	18.1	15.3	17.1	7.5	7.7	6.4	3.9

[a] Obtained by n-BuLi in THF at -105°(A), -78°(B) and 0°C(C).

The assignments were done as the each calculated intensity agrees mostly with found one except the peak at 6.78τ.

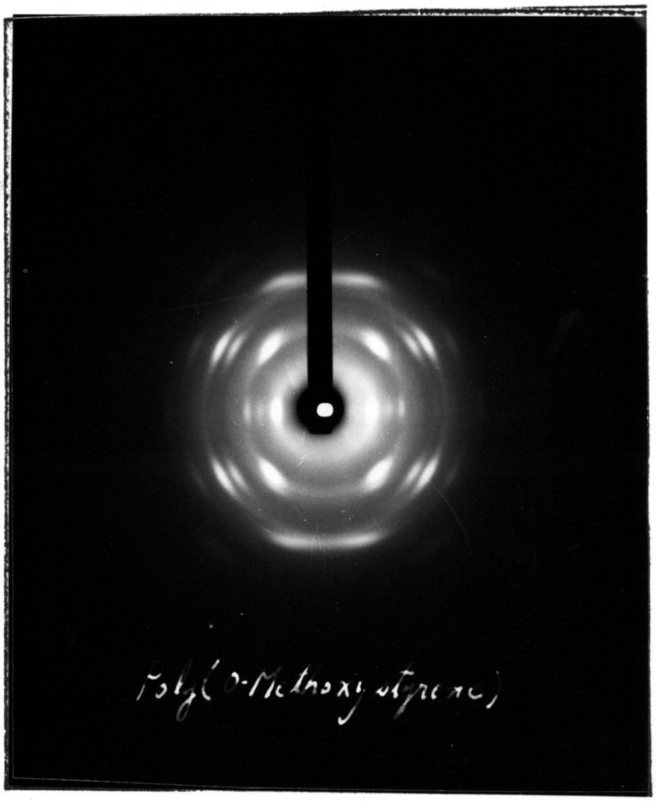


Fig. 1. X-ray diagram of orientated film of crystalline P-*o*-MeOSt.

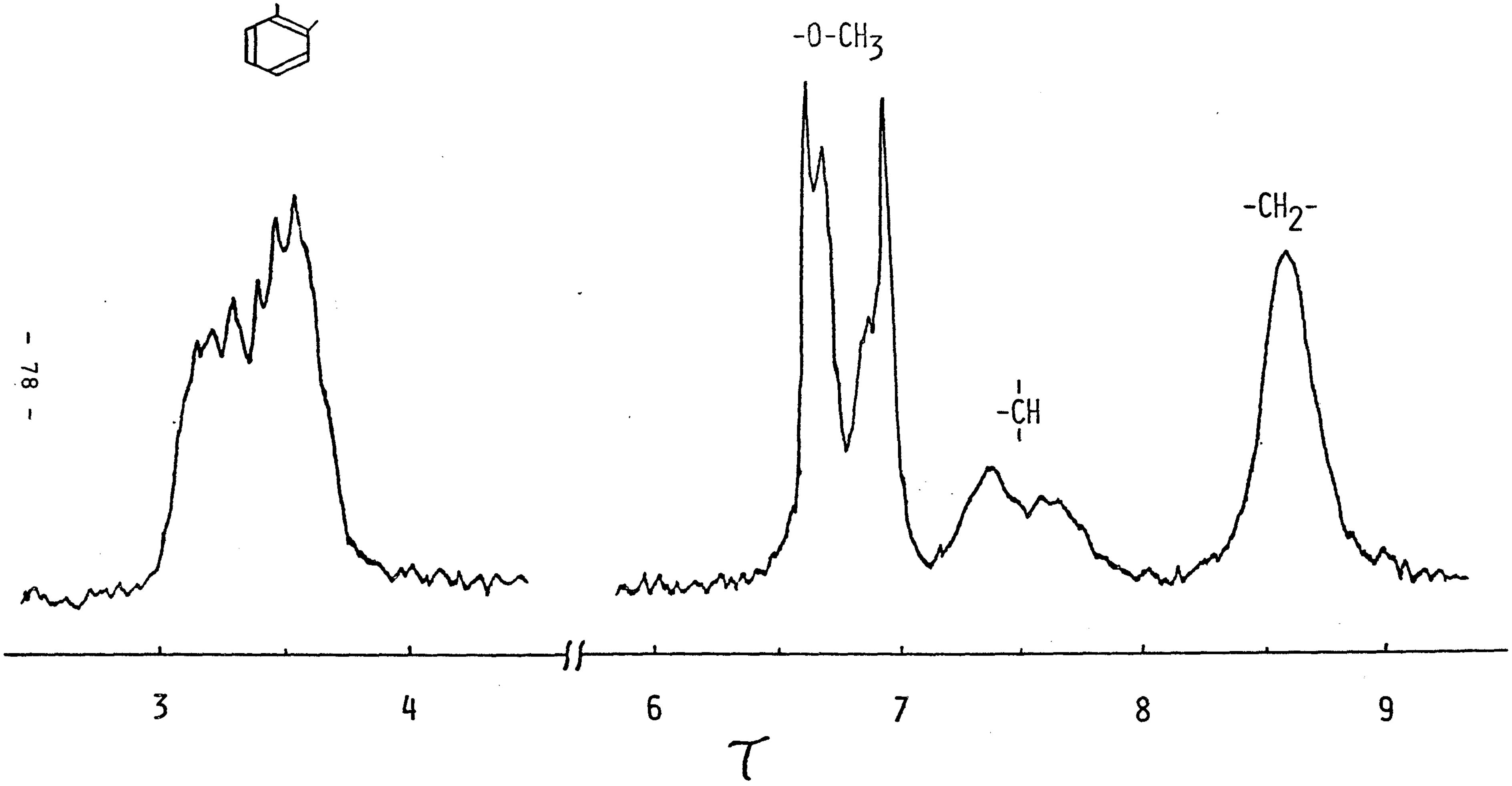


Fig. 2. NMR spectrum of P-*o*-MeOSt in CCl_4 at 60°C.

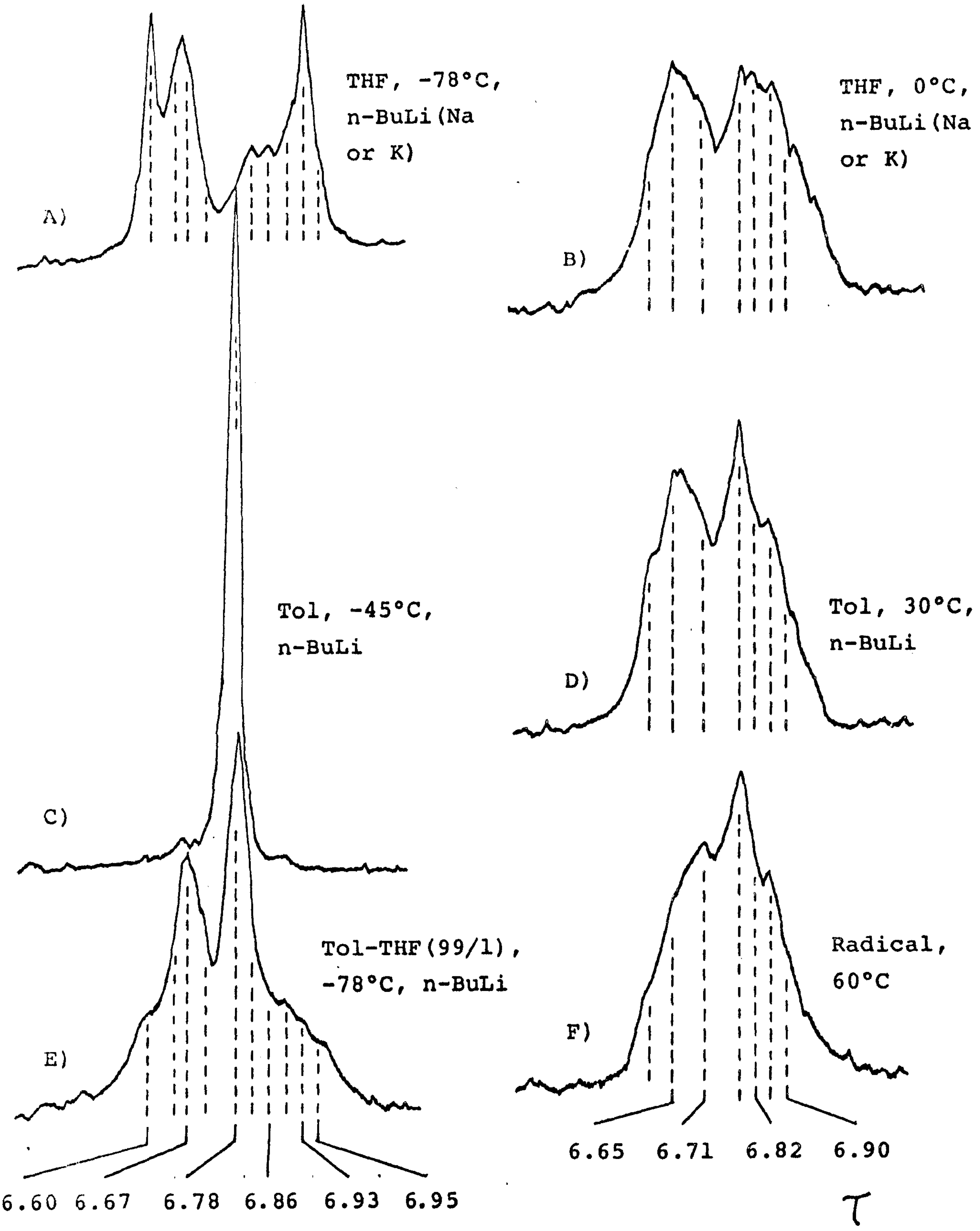


Fig. 3. NMR spectrum of P-*o*-MeOSt in $CHCl_3$ at 60°C.

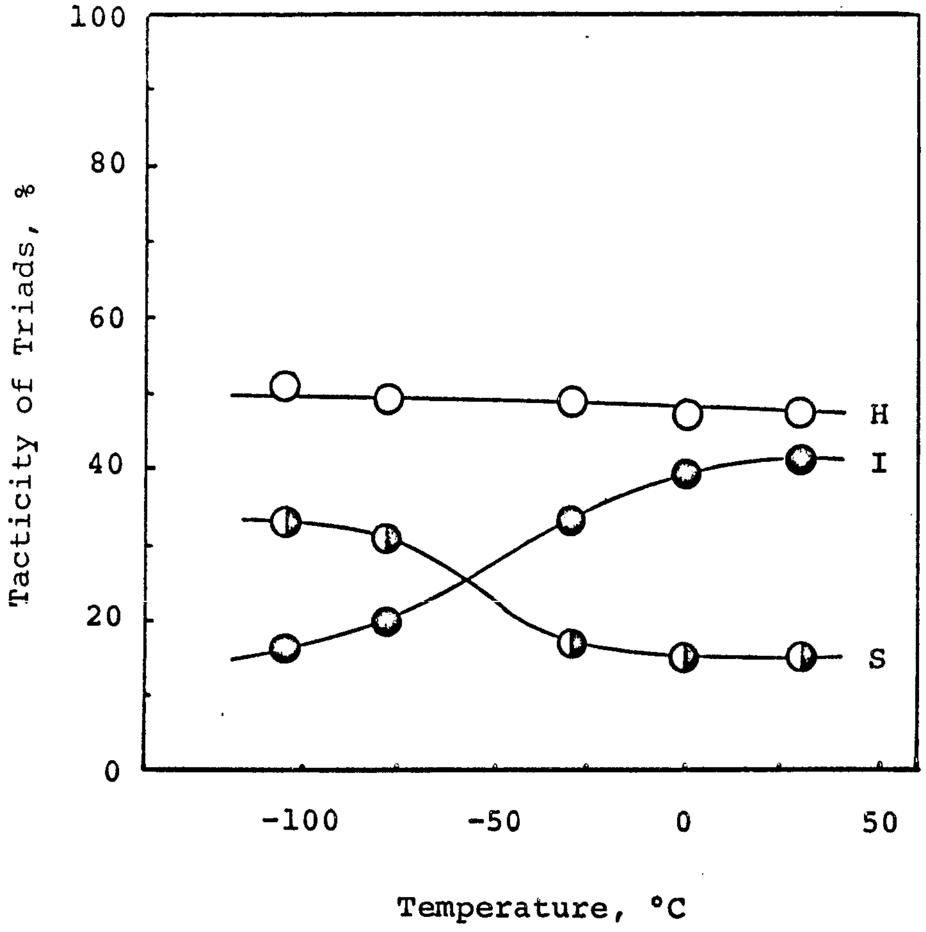


Fig. 4. Dependency of tacticity on the polymerization temperature (in THF).

Solvent 15 ml; monomer ca. 0.6 g; n-BuLi ca. 1 mol% against monomer.

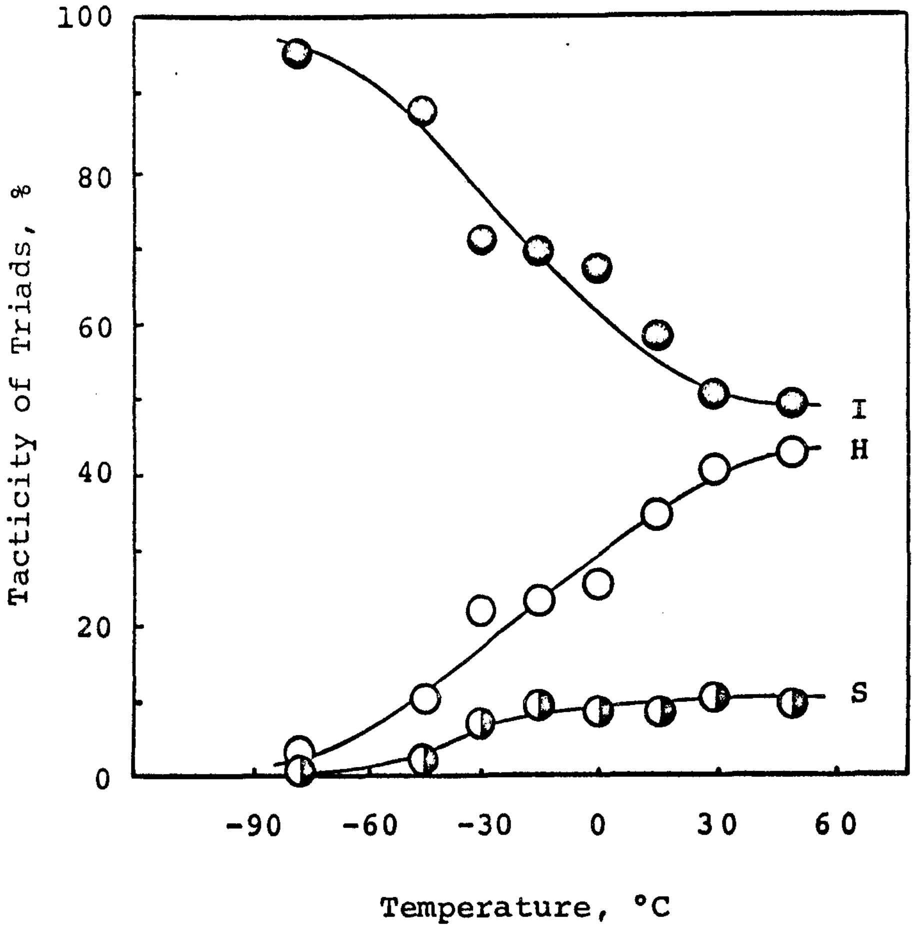


Fig. 5. Dependency of tacticity on the polymerization temperature (in toluene).

Solvent 15 ml; monomer ca. 0.6 g; n-BuLi ca. 1 mol% against monomer.

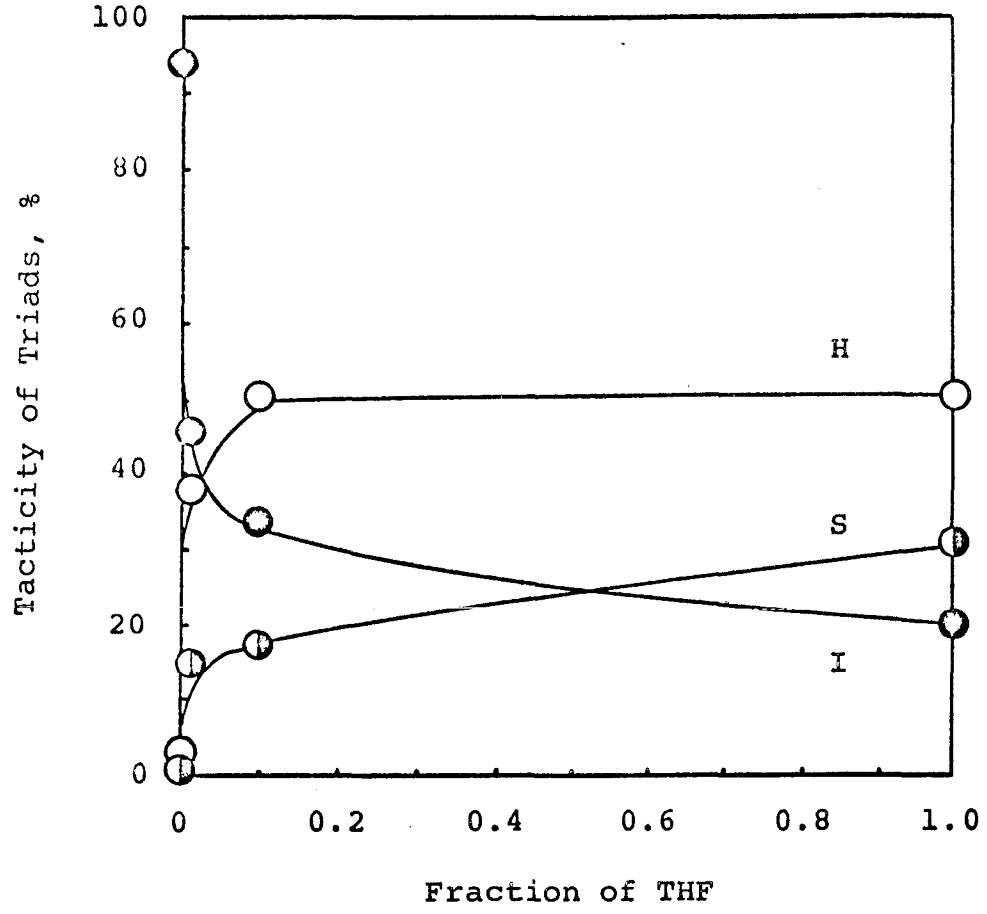


Fig. 6. Relationship between the tacticity of P-*o*-MeOSt and solvent composition of toluene-THF mixture.

(Toluene + THF) 15 ml, monomer ca. 0.6 g; n-BuLi ca 1 mol% against monomer.

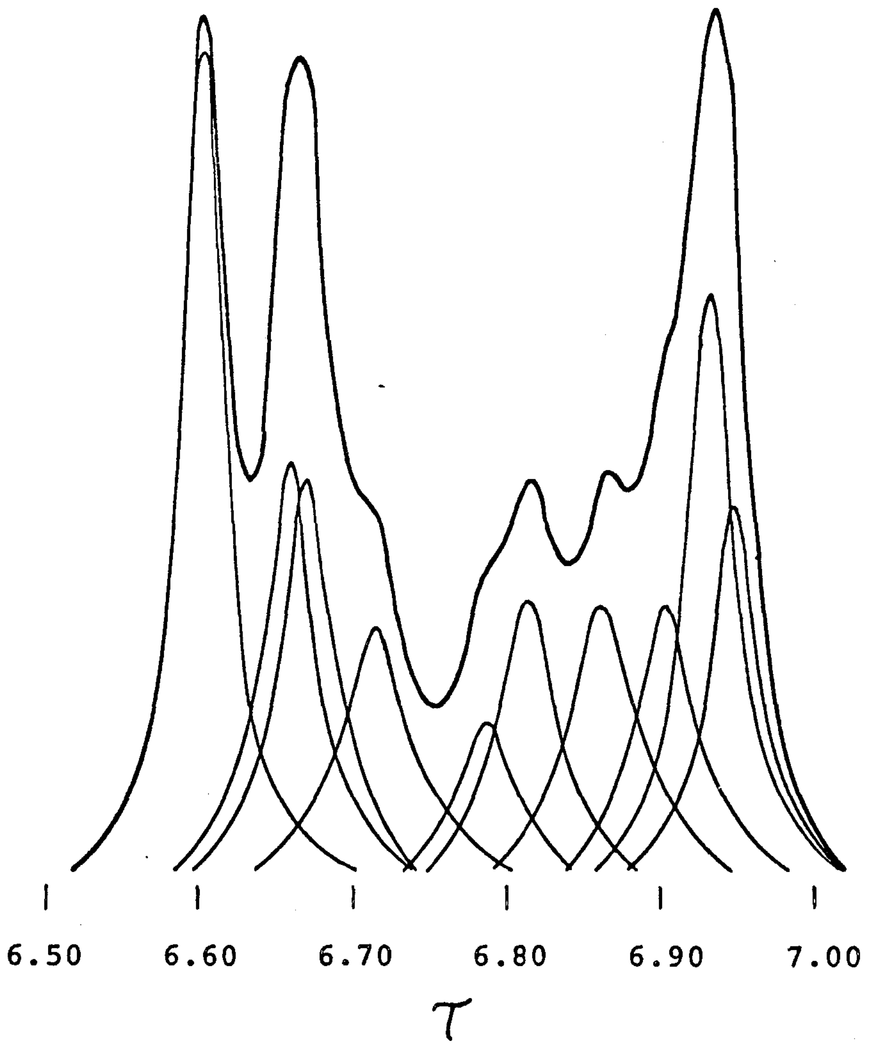


Fig. 7. Curve resolution of methoxy resonance in the NMR spectrum of P-*o*-MeOSt initiated by n-BuLi in THF at -78°C.

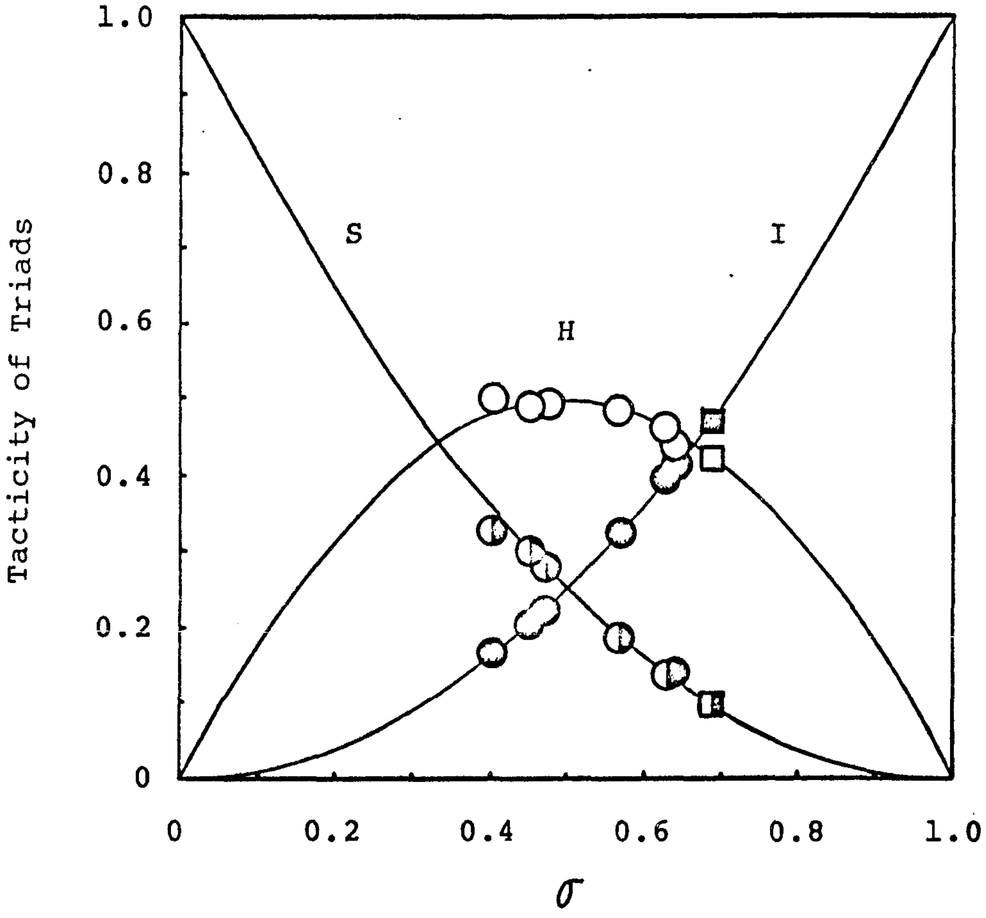


Fig. 8. Bovey's plot for P-*o*-MeOSt obtained by n-BuLi in THF.

(□) radical polymerization.

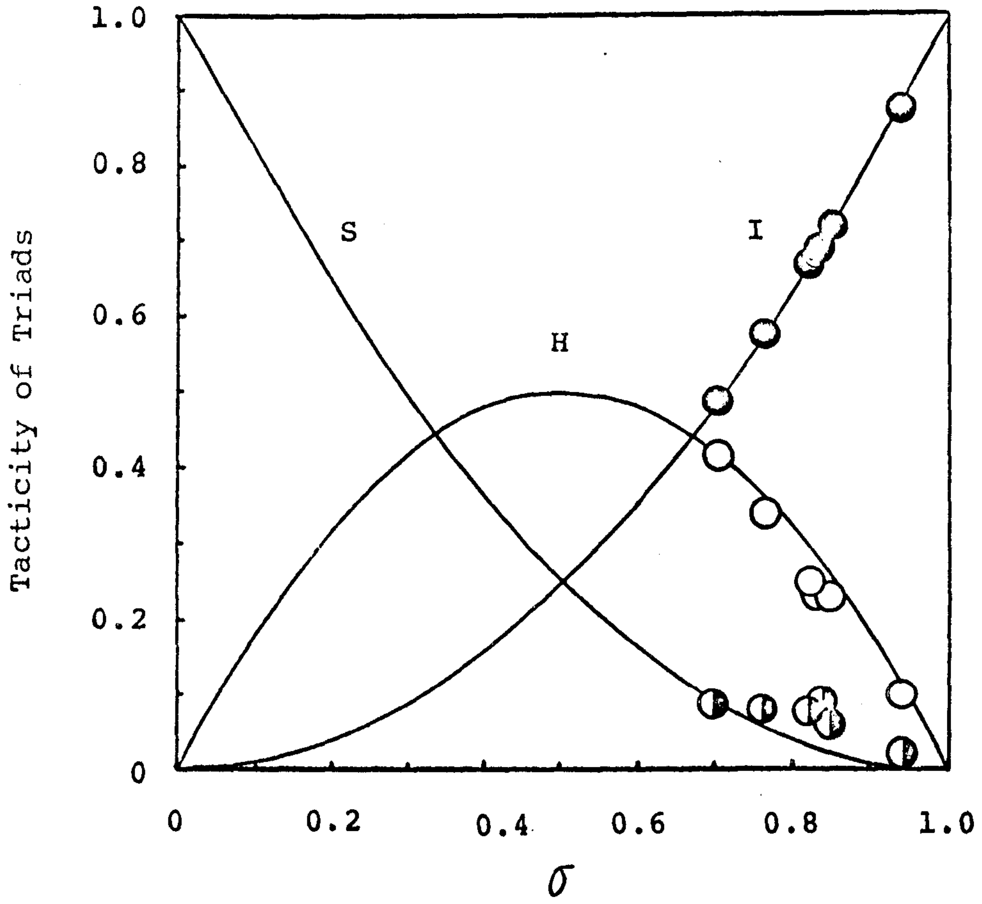


Fig. 9. Bovey's plot for P-*o*-MeOSt obtained by n-BuLi in toluene.

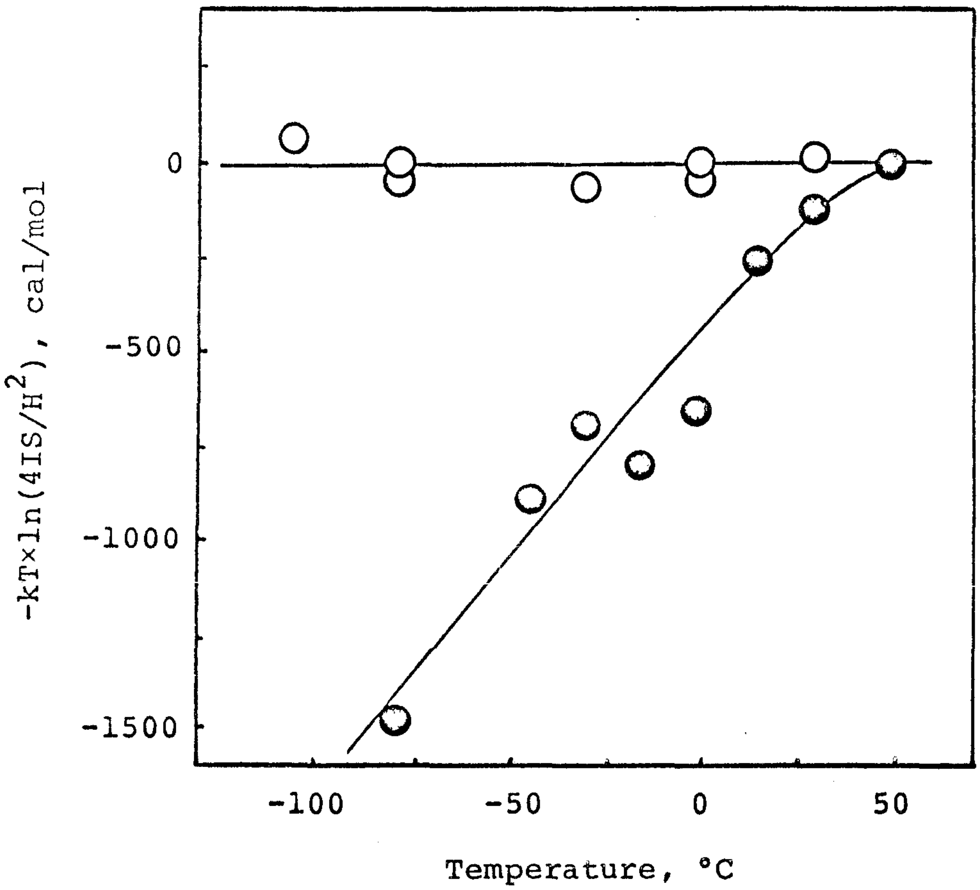


Fig.10. Relationship between $\Delta\varepsilon = -kT \times \ln(4IS/H^2)$ and plymerization temperature for P-*o*-MeOSt obtained by anionic initiators.

(O) in THF by n-BuLi or by Na-Naph.; (●) in toluene by n-BuLi.

Chapter 6

Anionic Copolymerizations of 1,1-Diphenylethylene with *o*- and *p*-Methoxystyrene

Synopsis

The copolymerizations of 1,1-diphenylethylene (DPE) with *o*- and *p*-methoxystyrene (*o*- and *p*-MeOSt) were investigated by n-butyllithium (n-BuLi) and other anionic initiators. In THF, alternating copolymers of DPE with *o*- and *p*-MeOSt were obtained. In aromatic hydrocarbons, the copolymerization of DPE and *o*-MeOSt with n-BuLi gave a polymer containing higher *o*-MeOSt content, while an almost alternating copolymer was obtained in the copolymerization of DPE and *p*-MeOSt. The NMR spectrum of the alternating copolymer of DPE and *o*-MeOSt showed the splitting due to the tactic difference concerning the methoxy group, while the spectrum of the alternating copolymer of DPE and *p*-MeOSt obtained in THF showed a narrow peak due to the methoxy group. The latter copolymer was crystalline by X-ray examination.

INTRODUCTION

In the previous works, the anionic copolymerizations of various monomer pairs have been carried out in order to get in information on the reactivities of the monomers and to form new polymers.[1-5] Some of the copolymerization gave alternating copolymers. On the other hand, *o*-methoxystyrene (*o*-MeOSt) formed a crystalline isotactic polymer in a nonpolar solvent by means of n-butyllithium (n-BuLi), but an atactic polymer in tetrahydrofuran (THF).[6] It was supposed that the driving force to form the isotactic poly(*o*-methoxystyrene) (P-*o*-MeOSt) was the interactions of the ether oxygens of the monomer and/or the polymer with lithium counter ion, and the interactions would be deminished in a solvent of higher solvating power such as THF.

Probably, the interaction stated above will exist in the copolymerization of *o*-MeOSt and 1,1-diphenylethylene (DPE), and greatly affect the reactivity of this monomer. In the present paper, besides the copolymerization of these two monomers, the copolymerization of *p*-methoxystyrene (*p*-MeOSt) and DPE is also reported in order to learn the properties of the copolymers and the reactivities of the isomers.

EXPERIMENTAL

Materials

o-MeOSt. This was synthesized by dehydration of methyl-(2-methoxyphenyl)-carbinol over acid potassium sulfate at 220-230°C,[6] and then the crude product was fractionally distilled. The monomer was dried over lithium aluminum hydride under the atomosphere of dry nitrogen, and then it was redistilled. Bp 80-81/ 10 mmHg, n_D^{20} = 1.5605. No impurity was detected by gas chromatography and NMR spectroscopy.

p-MeOSt. *p*-MeOSt was obtained by distillation of methyl-(4-methoxyphenyl)-carbinol in the presence of a small amount of hydrochloric acid. The monomer purified by distillation was dried over lithium aluminum hydride and redistilled. Bp 85°C/13 mmHg, $n_D^{20} = 1.5615$. No impurity was detected by gas chromatography and NMR spectroscopy.

DPE. This was prepared by dehydration of methyl-diphenylcarbinol with sulfuric acid.[7] The monomer was first stirred with Na-K alloy, and then to this n-BuLi in n-heptane was added until a red color appeared. The colored solution was fractionally distilled under dry nitrogen. Bp 97-98/1.5 mmHg, $n_D^{20} = 1.6085$.

THF. The solvent refluxed over lithium aluminum hydride was distilled onto benzophenone and Na-K alloy. The solvent was then distilled in vacuo from the solution before use.

Benzene and Toluene. Each solvent purified in the usual manner was mixed with n-BuLi prepared in the same solvent, and was distilled under high vacuum before use.

n-BuLi. The initiator was prepared in n-heptane according to the method of Ziegler.[8]

Polymerization

Polymerization was carried out in a glass ampoule under dry argon. Solvent was first transferred to the ampoule on a vacuum line, and then monomers and initiator were added by using syringes. The initiator solution was added dropwise until the red color of the DPE anion was stable; usually ca. 0.012 mmol of the initiator was required. Then an additional 0.060 mmol of initiator was added. The polymerization was terminated by a small amount of methanol, and the mixture was poured into methanol. The precipitated polymer was filtrated, washed with methanol, dried, and weighed. On the other hand, the mother liquor of the polymer precipitation was evaporated under reduced pressure. The composition of the recovered monomer mixture obtained from the residue was estimated from the refractive index.

Measurement

MNR Spectrum. The spectrum was taken on a JNM-4H-100 (Japan Electron Optics Laboratory Co. Ltd.) in carbon tetrachloride or in chloroform at 60°C by using tetramethylsilane as an internal standard.

X-ray Diffraction. The X-ray diffraction was measured with a Rigakudenki 4001 X-ray Diffractometer.

Viscosity. The solution viscosity of the polymer was measured in chloroform at 25.0°C; the concentration was 1.0 g/dl.

Reaction of The Copolymer with Hydriodic Acid

In order to assign the position of the methoxy group in the NMR spectrum of the alternating *o*-MeOSt-DPE copolymer, the conversion of the methoxy group to a hydroxy group was tried through the reaction of the copolymer with hydriodic acid. The copolymer (0.30 g) and 56% hydriodic acid (6 ml) was heated in glacial acetic acid (6 ml) at 120-130°C. The reaction proceeded heterogeneously with respect to the polymer. After 6 hr, the reaction mixture was poured into a large amount of methanol. The precipitated polymer was filtrated, washed with methanol, and dried. The polymer was then reprecipitated twice from benzene-methanol and colorless polymer was recovered.

Anal. Calcd. for alternating *o*-MeOSt-DPE copolymer: C, 87.86; H, 7.05. Calcd. for alternating *o*-hydroxystyrene-DPE copolymer: C, 87.96; H, 6,71. Found: 87.33; H, 6.92.

RESULTS

The results of the copolymerization of *o*-MeOSt (M_1) and DPE (M_2) in THF by anionic initiators are shown in Table I. Copolymer composition was determined by elementary analysis and from the relative intensity of aromatic to aliphatic proton signals in the NMR spectrum. In all cases the compositions were nearly unity, meaning that the copolymers were alternating. Although the color of the polymerization system had been stable for a prolonged time, *o*-MeOSt remained unchanged in the system.

The results of the copolymerizations in aromatic hydrocarbons are shown in Table II. In these copolymerizations *o*-MeOSt was almost completely incorporated into the copolymer, as is shown in Table III. Then, the copolymer composition could also be obtained from the polymer yield; the values are in accord with those derived from other two methods; elementary analysis and NMR spectroscopy. The copolymers had higher *o*-MeOSt content. In toluene, the copolymer composition, $[m_1]/[m_2]$, at -30°C was greater than that at 0°C, suggesting the higher reactivity of *o*-MeOSt at low temperature. However, the addition of a small amount of THF steeply increased the incorporation of DPE. Since the M_1 monomer was completely consumed, the monomer reactivity ratio, r_1, is calculated by means of the integrated Mayo-Lewis copolymerization equation;[1] the values are shown in Table II.

The copolymerizations of *p*-MeOSt (M_1) and DPE (M_2) were carried out in THF and aromatic hydrocarbons with n-BuLi. The results are listed in Table IV. The yield of copolymer was low, and in both THF and toluene, especially in the former, the polymer precipitation was clearly observed during the polymerization. The copolymer composition was nearly unity in THF and aromatic hydrocarbons. The alternating copolymer obtained in THF was crystalline under a polarizing microscope. The X-ray diffraction pattern is shown in Fig. 1. The pattern had reflections at 2Θ = 7°10' (d = 12.3 Å), 8°10' (d =10.8 Å), and 15°20' (d = 5.8 Å). The melting point of the crystalline copolymer was 180-185°C and it was soluble in chloroform and partially soluble in carbon tetrachloride.

The NMR spectrum of the alternating copolymer of *o*-MeOSt and DPE is shown in Fig. 2. Based on the area intensity of the spectrum, the peaks at 2.27, 2.35, and 3.39 ppm may be assigned to the methoxy group. The NMR spectrum of the polymer which had been treated with hydriodic acid showed that only the peaks at 2.27, 2.35, and 3.39 ppm were diminished by ca. 20% compared with other peaks. The polymer treated with hydriodic acid had an absorption due to a hydroxy group at 3300 cm^{-1} in the IR spectrum. These results indicate that the assingment of the methoxy group is correct. In the NMR spectrum of P-*o*-MeOSt under the same conditions as the copolymerization, the methoxy resonance was found at 3.03-3.40 ppm.[6] No peak was, however, observed at 3.05-3.25 ppm in Fig. 2, indicating that the alternating copolymer had no contineous unit which existed in the P-*o*-MeOSt; i.e., *o*-MeOSt unitin the copolymer was not continous.

The NMR spectrum of the alternating crystalline copolymer of *p*-MeOSt and DPE is shown in Fig. 3. A narrow peak of the methoxy group was observed at 3.61 ppm and the peaks of the phenyl groups were observed separately at 6.9, 6.3, and 5.8 ppm. The methoxy resonance of poly-*p*-MeOSt appeared at 3.75 ppm as a narrow peak.

DISCUSSION

The following results fairly support that the copolymers of DPE with *o*- and *p*-MeOSt prepared in THF were alternating.

1) The copolymer composition was 1:1.

2) DPE can not be homopolymerized.

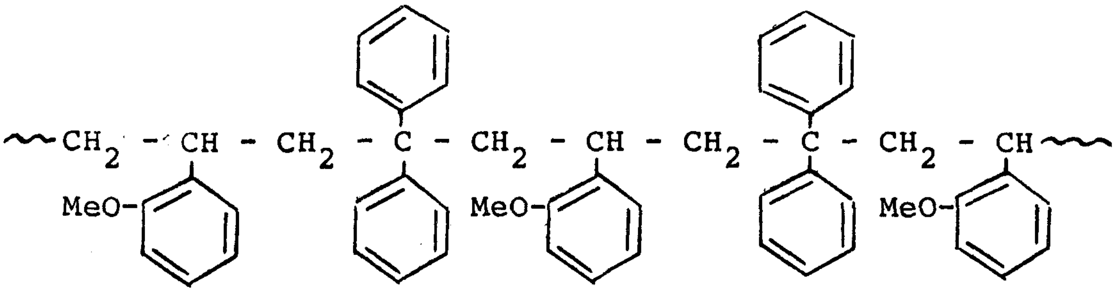
3) No peak due to the contineous *o*-MeOSt unit was observed in the NMR spectrum.

In the copolymerizations of DPE (M_2) with styrene (M_1) and the dienes (M_1) as have been shown in the previous papers, the M_1 monomers were completely consumed in a prolonged time.
In the present work, however, both *o*- and *p*-MeOSt were not completely incorporated into the copolymers in THF even after a prolonged time. A probable reason for this may be equilibrium polymerization.

The monomer reactivity ratio, r_1, obtained in the copolymerizations of DPE with other comonomers by means of n-BuLi are collected in Table V. It is very interesting that *o*-MeOSt in analogy with butadiene and isoprene is much more reactive in hydrocarbon than in THF, although *p*-MeOSt and styrene are less reactive even in hydrocarbon. This may be because, in hydrocarbon, *o*-MeOSt can coordinate to lithium counter ion in the manner as a polymer end easily attacks the vinyl group of the monomer. Probably, such an arrangement would be difficult for *p*-MeOSt. These results may be correlated with that *o*-MeOSt gave an isotactic polymer in toluene by n-BuLi,[6] while *p*-MeOSt gave an atactic polymer.[10] The coordination is strong at low temperature, which would result in higher relative reactivity of *o*-MeOSt (Table II). The addition of THF to the system prevents the coordination of *o*-MeOSt because THF is a stronger base. Therefore, the relative reactivity of the *o*-MeOSt in THF should be low as is shown in Table II. For 2,3-dimethylbutadiene such an absorption seems to be less important because of its steric hidrance. Similar phenomena have been found in the copolymerizations of styrene with butadiene[11] and isoprene,[12] in which the higher reactivity of the dienes in hydrocarbon with lithium initiator were explained by suggesting the preferential absorptions of the dienes to the counter ion. Overberger et al.[13] have suggested a nonhomogeneous distribution of the monomers by complexing lithium gengenion with aromatic π-electron systems in the copolymerization of styrene with other styrene derivatives.

Recently, Worsfold[14] denied the preferential absorption of isoprene to lithium counter ion on the basis of kinetic study of the copolymerization of styrene and the diene. He found that the rates of the addition of styrene to isoprenyllithium are nearly constant whether isoprene exists in the system or not. Then, he concluded that there is no preferential absorption of isoprene. However, we can assume other explanation; namely, in the copolymerizations of styrene or DPE with the dienes in hydrocarbon with lithium counter ion, while the dienes will be incorporated into the polymer after the coordination of the lithium counter ion, styrene willbe directly incorporated without such a coordination. If this is true, the rate of the addition of styrene to isoprenyllithium will be similar to that in the absence of isoprene. O'Driscoll et al.[15] have also proposed that the positive counter ion of a chain end can form a π-complex with a monomer, which can then rearrange to incorporate the complexed monomer unit into the chain, and another monomer unit can simply add to the monomer-complexed ion pair.

The NMR spectrum of the alternating copolymer of *o*-MeOSt and DPE shows three peaks due to the methoxy group (Fig. 2). Since there is no such a steric isomer in the three units, DPE-*o*-MeOSt-DPE as well known for poly(methylmethacrylate) as isotactic, syndiotactic, and heterotactic triads, more monomer units, at least five units, must be considered for this methoxy splitting.



In the above units, when the DPE units are neglected, the configuration of the methoxy groups is just the same as that of isotactic triad in poly(methylmethacrylate). Then, three different configurations in the above five monomer units are possible, which will have corresponding resonance peaks in the NMR spectrum as is shown in Fig. 2. In the NMR spectrum of the P-*o*-MeOSt the methoxy resonance was split into ten peaks by the pentad sequence.[6] These results show that the resonances of the *o*-methoxy groups in both the homopolymer and copolymer are very sensitive to the configurational difference in the polymers.

On the other hand, the NMR spectrum of the alternating copolymer of *p*-MeOSt and DPE showed a narrow peaks at 3.61 ppm (Fig. 2). Two probable reason for this can be suggested; one is that the methoxy resonance is quite independent of the configration of the copolymer, and the other is that the copolymer has only one configuration such as isotactic triad. The former reason is supported by the fact that poly(*p*-MeOSt) did not show the splitting of the methoxy resonance, and the latter is supported by that the copolymer obtained was crystalline.

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Table I

Anionic copolymerization of *o*-MeOSt (M_1) and DPE (M_2) in THF

$[M_1]_0$ = 3.67 mmol, THF = 15 ml, temp. = 0°C

Initiator	$[M_1]_0/[M_2]_0$	Time	Yield	$[m_1]/[m_2]$		η_{sp}/C
0.06 mmol	mol/mol	day	wt%	E.A.[a]	NMR[b]	dl/g
n-BuLi	0.953	16	77.3	1.0	-	-
n-BuLi	0.909	9	73.4	0.9	1.1	0.10
n-BuLi	0.826	16	77.6	1.0	-	-
n-BuLi	0.350	13	48.5	1.0	1.0	-
Na-naph.	0.909	16	71.4	1.0	-	0.15
K-disp.	0.909	16	52.3	1.1	1.1	0.15

[a] Monomer composition in the copolymer obtained by elementary analysis. Calcd. for P-*o*-MeOSt: C, 80.56; H, 7.52. Calcd. for alternating copolymer: C, 87.86; H, 7.05.

[b] Copolymer composition derived by NMR spectroscopy.

Table II

Anionic copolymerization of *o*-MeOSt (M_1) and DPE (M_2) in aromatic hydrocarbon by n-BuL

$[M_1]$ = 3.68-3.89 mmol, [n-BuLi] = 0.06 mmol

Solvent	$[M_1]_0/[M_2]_0$	Temp.	Time	Yield	$[m_1]/[m_2]$			r_1	η_{sp}/C
15 ml	mol/mol	°C	day	wt%	Yield[a]	E.A.	NMR		dl/g
Toluene	0.862	-30	13	45.7	7.9	7.5	8.0	29	0.14
Toluene	0.714	-30	14	42.0	6.5	6.5	-	27	-
Toluene	0.893	0	14	49.3	5.8	6.3	7.2	22	0.09
Toluene	0.641	0	16	41.3	4.8	4.8	-	18	-
Toluene[b]	0.357	0	5	22.2	-	1.3	1.6	-	-
Benzene	0.925	40	8	48.9	6.7	6.2	7.8	20	0.09
Benzene	0.820	40	8	46.0	6.3	6.7	-	20	-

[a] Monomer compositon in the copolymer obtained from the yield.

[b] This contained 3% of THF.

Table III

Anionic copopolymerization of *o*-MeOSt (M_1) and DPE (M_2) in aromatic hydrocarbon by n-BuLi

[n-BuLi] = 0.06 mmol

Solvent 15 ml	M_1 g	M_2 g	Temp. °C	Time day	Polymer g	Recovered[a] monomer, g	n_D^{20}[b]
Toluene	0.494	0.739	-30	14	0.609	0.616	1.6080
Toluene	0.522	0.813	0	13	0.611	0.725	1.6070
Benzene	0.494	0.718	40	8	0.593	0.584	1.6078

[a] Contained ca. 5 mg of lithium compounds.

[b] Refractive index of the recovered monomer.

Table IV

Anionic copolymerization of *p*-MeOSt (M_1) and DPE (M_2) by n-BuLi

$[M_1]_0$ = 3.97 mmol, [n-BuLi] = 0.06 mmol

Solvent 15 ml	$[M_1]_0/[M_2]_0$ mol/mol	Temp. °C	Time day	Yield wt%	$[m_1]/[m_2]$[a] E.A.	 NMR	η_{sp}/C dl/g
THF	0.971	0	16	35.6	1.0	1.0	-
THF	0.885	0	17	33.1	1.0	-	-
THF	0.827	0	17	31.5	1.0	0.95	0.14
Toluene	0.901	0	14	11.9	1.2	-	0.06
Toluene	0.747	0	16	11.1	1.2	1.17	-
Benzene	0.918	40	8	9.6	1.2	1.06	-
Benzene	0.769	40	8	7.4	1.2	-	-

[a] Copolymer composition derived from elementary analysis and NMR spectroscophy.

Table V

Monomer reactivity ratio, r_1, in the copolymerization of DPE (M_2) with other comonomers (M_1) by n-BuLi

M_1	THF[a]	Benzene[b]	Ref.
Styrene	0.13	0.44[c]	1
o-MeOSt	0	20	This work
p-MeOSt	0	<0.3	This work
Butadiene	0.13	54	16
Isoprene	0.11	37	3
2,3-Dimethyl-butadiene	0[d]	0.23	2,4

[a] At 0°C. [b] At 40°C. [c] In toluene at 30°C. [d] At 22°C.

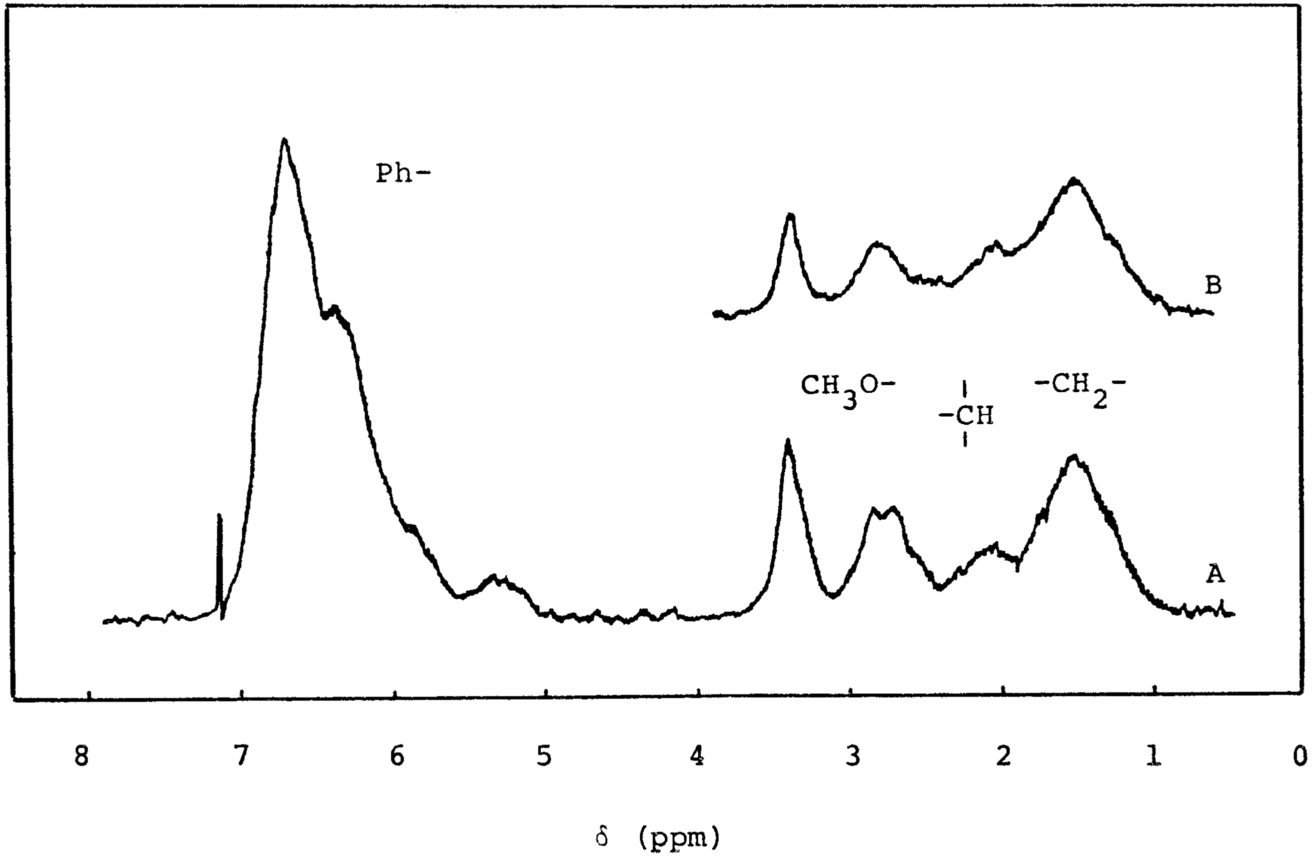


Fig. 1. A: NMR spectrum of the alternating copolymer of *o*-MeOST and DPE.

B: NMR spectrum of the polymer obtained by treating the above copolymer with hydriodic acid. (in $CDCl_3$ at 60°C)

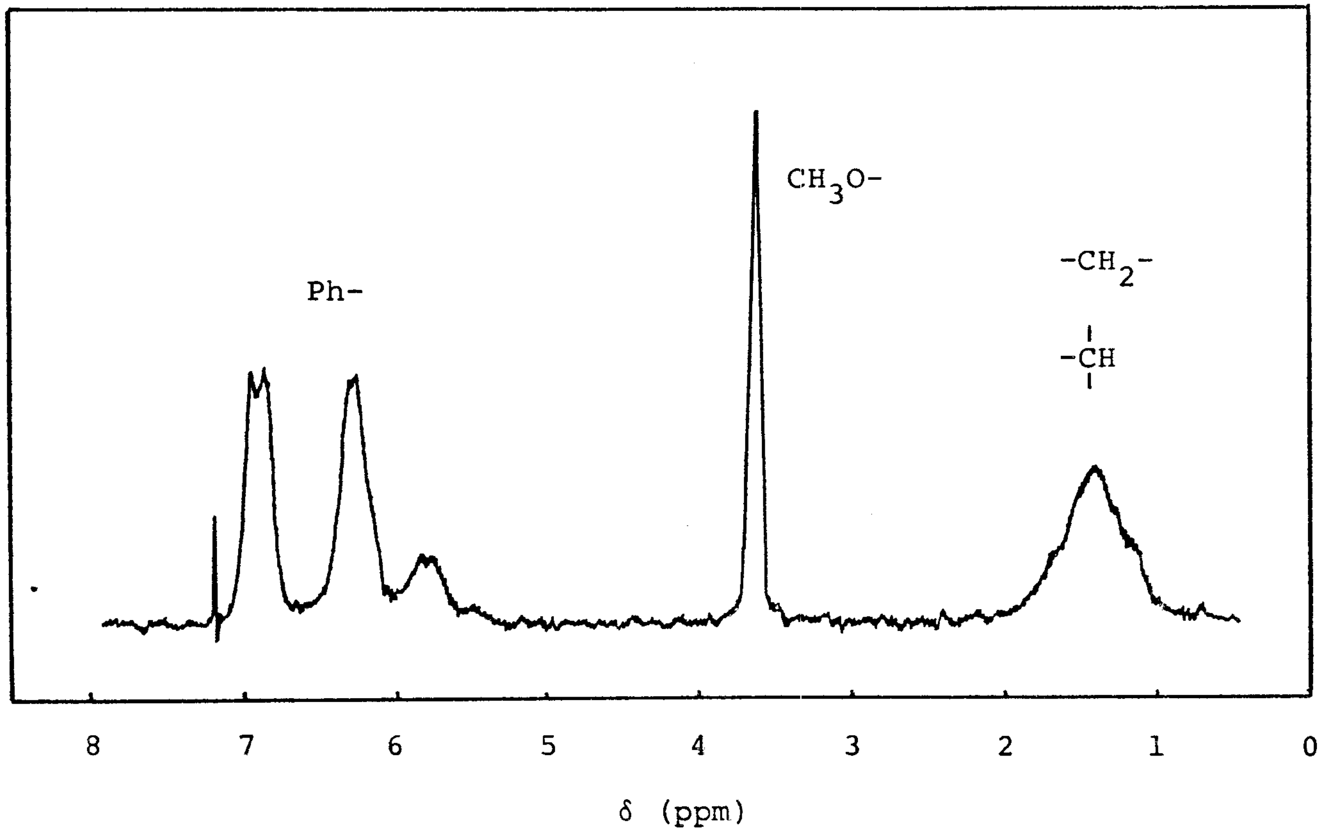


Fig. 2. NMR spectrum of the alternating copolymer of *p*-MeOSt and DPE. (in $CDCl_3$ at 60°C)

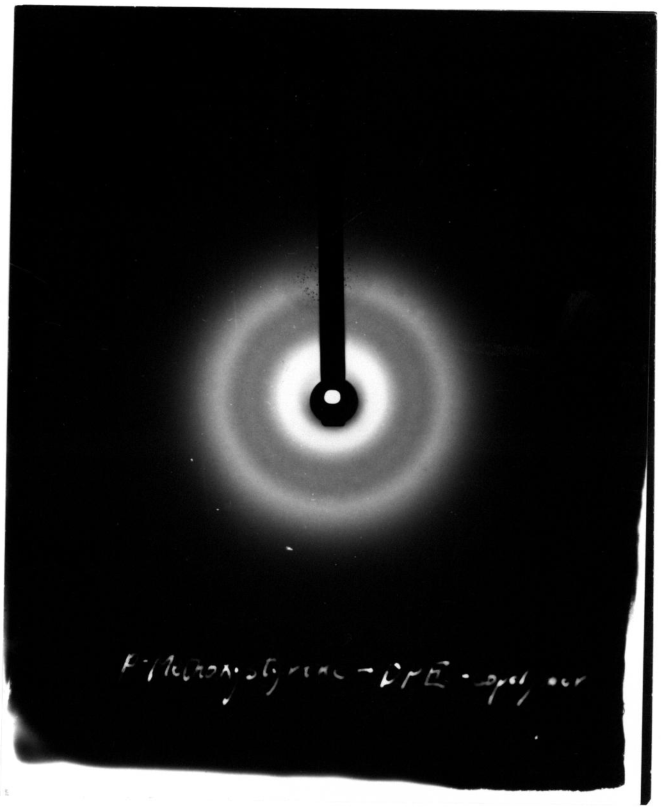


Fig. 3. X-ray diagram of the alternating copolymer of *p*-MeOSt and DPE obtained in THF by n-BuLi.

Chapter 7

Anionic Copolymerization of Styrene and trans-Stilbene with n-Butyllithium

Synopsis

The anionic copolymerization of styrene (M_1) and trans-stilbene (M_2) by n-butyllithium was investigated. trans-Stilbene which can not homopolymerize by itself could be copolymerized with styrene in tetrahydrofuran and benzene by an anionic initiator. The copolymerization in tetrahydrofuran proceeded with a chain-transfer to trans-stilbene, while that in benzene seemed to proceed without the chain-transfer. The monomer reactivity ratio, r_1, was obtained from the copolymer composition at the complete consumption of M_1, assuming that the rate constant, k_{22}, is zero. The r_1 values were 2.3 in tetrahydrofuran at 0°C and 18 in benzene at 30°C. The color of the solution changed from red to purple in tetrahydrofuran, while in benzene no change occurred.

Introduction

It has recently reported that, if a suitable combination of monomers is chosen, an alternating copolymer can be obtained by an anionic mechanism.$^{1)}$ In the previous paper, an investigation of the anionic copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2) was reported in detail.$^{2)}$ The copolymerization proceeded in a living system, and monomer reactivity ratios, r_1 were obtained as 0.2 in tetrahydrofuran

(THF) at 30°C and as 0.4 in benzene at 30°C, assuming that a 1,1-diphenylethylene anion does not add to 1,1-diphenylethylene.

In this paper, a detailed study of the copolymerization of styrene (M_1) and trans-stilbene (M_2) will be described, and the results will be correlated with the results of the copolymerization of styrene and 1,1-diphenylethylene.

Experimental

Materials. Styrene. This was purified by the usual method and was distilled on a vacuum line from calcium hydride.

trans-Stilbene. The monomer synthesized from benzoin$^{3)}$ was re-crystallized from methanol and then twice from n-hexane.

Tetrahydrofuran (THF). The solvent, refluxed over metallic sodium and then over lithium aluminum hydride, was distilled onto sodium-potassium alloy and naphthalene. From the characteristic green solution, it was then distilled on a vacuum line to a reaction vessel.

Benzene. Benzene was purified by the standard method$^{4)}$ and was stored over sodium. Before use, it was transferred to a flask containing n-butyllithium, and then it was distilled on a vacuum system to a reaction vessel.

n-Butyllithium(n-BuLi). According to the method of Ziegler,$^{5)}$ n-BuLi was prepared in n-heptane and the concentration was determined by double titration.$^{6)}$

Polymerization. trans-Stilbene was first placed in a glass ampoule and dried in vacuo. Then, the solvent and styrene were transferred into the ampoule by vacuum distillation. The solution was immersed in a bath at a constant temperature, and n-BuLi was added under dry argon with a syringe. The reaction was terminated by adding methanol, after which the contents of the ampoule were poured into a large amount of methanol. The precipitated polymer was collected by filtration, washed with methanol, dried, and weighed. The mother liquor and the washings of the polymer precipitation were then combined and evaporated at reduced pressure, and the residual unchanged monomer and lithium compounds were weighed.

Measurement. Viscosity. The viscosity of the polymer was measured in a benzene solution (C = 1.0 g/dl) at 30°C.

Electronic Spectrum. The spectrum of a living anion was measured in THF with a Cary 15 Spectrophotometer.

Results

Polymerization in THF. The copolymerization of styrene (M_1) and trans-stilbene (M_2) with n-BuLi was carried out in THF at 0°C, the initial molar ratio of styrene to trans-stilbene, $[M_1]_0/[M_2]_0$, being 1.0/1.5. The results are shown in Fig. 1. The reaction came instantaneously to an end, always giving a copolymer in a 68% yield against the total amount of monomers, regardless of the reaction time measured.

The copolymerization was carried out by varying the ratio, $[M_1]_0/[M_2]_0$, the total amounts of monomers, $[M_1]_0 + [M_2]_0$, being kept constant. The results are summarized in Table 1. Attempts to determine the copolymer composition were made elementary analysis, UV and NMR spectroscopies, but no satisfactory results were obtained because those monomers all have similar structures. On the other hand, the residues recovered from the mother liquor of polymer precipitates were solid and were found to be a mixture of lithium compounds, mainly carbonate, and unchanged trans-stilbene, which was identified by IR and UV spectroscopies. The sum of the amounts of the polymer and the unchanged monomer, $P + M_1$, just balanced the total amounts (weight) of the monomers, $M_1 + M_2$, indicating the complete incorporation of the charged styrene into the copolymer. The amount of unchanged trans-stilbene was also determined by studying the UV spectrum of a part of the reaction mixture; it was found to be nearly equal to the value obtained by gravimetry. Thus, the copolymer composition can be determined from the polymer yield as $M_1/P\text{-}M_1$; this value is converted into the molar ratio of the monomers in the copolymer, $[m_1]/[m_2]$, in Table 1. Below, the composition of the copolymer is always calculated from the polymer yield in the assumption that the charged styrene is completely consumed by the copolymerization. We have found that the polymer yield and the $[m_1]/[m_2]$ ratio decrease with a decrease in the $[M_1]_0/[M_2]_0$ ratio.

The copolymerization at 0°C in THF was investigated by varying the ratio, $[M_1]_0/[M_2]_0$, while the amount of the M_1 monomer was kept constant. The results are listed in Table 2. The polymer yield against the total amount of the monomers, the copolymer composition expressed in the $[m_1]/[m_2]$ ratio, and the viscosity of the polymer all decreased with an increase in the amount of M_2 in the monomers charged, while the softening point rose. The data in Table 2 suggest that a lower monomer composition, $[M_1]_0/[M_2]_0$, than 0.4 may give an essentially alternating copolymer of M_1 and M_2 monomers with a very low molecular weight.

If, in the copolymerization, the M_2 monomer can not add to the $\sim\!\sim M_2^-$ anion, and if the M_1 comonomer is completely incorporated into the copolymer, the monomer reactivity ratio, r_1, can easily be obtained from the polymer yield by assuming that $k_{22}= 0$ and $[M_1] = 0$ in the Mayo-Lewis copolymer composition equation.[2)] The copolymerization in THF at 0°C gave the value, $r_1= 2.3$, as is shown in Fig. 2, the plots in which were obtained from the data in Tables 1 and 2.

Polymerization in Benzene. The reaction rate was investigated in the copolymerization in benzene with n-BuLi at 30°C; the molar ratio of the initial monomer concentrations, $[M_1]_0/[M_2]_0$, was 1.0/3.0. The results are shown in Fig. 3. The reaction proceeded slowly in comparison with that in THF, a constant yield (24%) being obtained after about 24 hr. It was confirmed that, in this case, styrene was also completely incorporated into the copolymer after a sufficient reaction time.

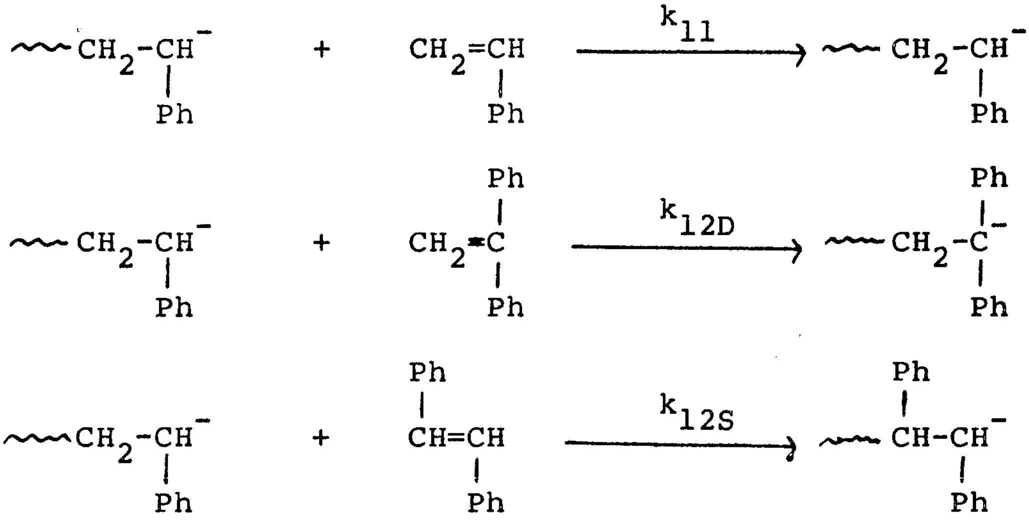
The effects of the initial molar ratio, $[M_1]_0/[M_2]_0$, on the copolymerization in benzene were investigated with a constant concentration of the M_1 monomer. The results are listed in Table 3. The relative reactivity of styrene against trans-stilbene was much greater in benzene than in THF. The solution viscosty of the polymer was constant regardless of $[M_1]_0/[M_2]_0$.

The monomer reactivity ratio, r_1, was calculated from the polymer yield as has been described above, As Fig. 4 shows, r_1 is 18 in the copolymerization in benzene at 30°C.

Electronic Spectrum of the Reaction Mixture. In the copolymerization of styrene and trans-stilbene by n-BuLi in THF, the red color gradually turned purple, even at 0°C. The change in the electronic spectra of the solution was followed; it is shown in Fig. 5. The red color of the solution diminished gradually and an absorption appeared at 555 mμ after about 30 min, by which time the copolymerization reaction had already finished. In the homopolymerization of styrene carried out under the same conditions, the red color of the reaction mixture did not change when it stood for a prolonged period. Therefore, this change in spectra may be attributed to the anion of trans-stilbene. The same spectral change was also observed in the reaction of trans-stilbene with n-BuLi in THF.7) The purple solution initiated the polymerization of styrene to give a polymer quantitatively. On the other hand, in the copolymerization in benzene the orange color of the solution did not change in several hours, even at 30°c.

Discussion

Reactivity of Monomers. The monomer reactivity ratios, r_1, in the copolymerization of styrene (M_1) and trans-stilbene (M_2) or 1,1-diphenylethylene (M_2)2) with n-BuLi are summarized in Table 4. The r_1 values obtained in the copolymerization with 1,1-diphenylethylene were less than unity in THF and also in benzene, while the ratios in the copolymerization with trans-stilbene were more than unity in both the solvents. These results show that, in the following reactions, the order of the rate constants is $k_{12D}>k_{11}>k_{12S}$.



$$\sim CH_2\text{-}\underset{Ph}{CH^-} + \underset{\quad\ \ Ph}{CH_2{=}CH} \xrightarrow{k_{11}} \sim CH_2\text{-}\underset{Ph}{CH^-} \qquad (1)$$

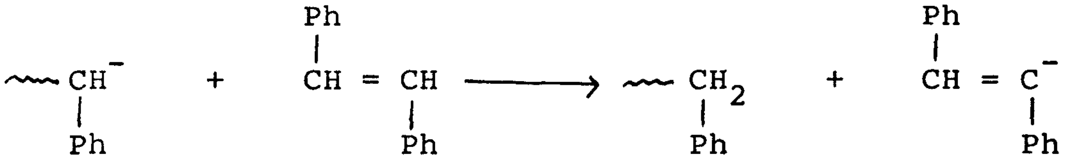
$$\sim CH_2\text{-}\underset{Ph}{CH^-} + CH_2{=}\overset{Ph}{\underset{Ph}{C}} \xrightarrow{k_{12D}} \sim CH_2\text{-}\overset{Ph}{\underset{Ph}{C^-}} \qquad (2)$$

$$\sim CH_2\text{-}\underset{Ph}{CH^-} + \overset{Ph}{CH}{=}\underset{Ph}{CH} \xrightarrow{k_{12S}} \sim \overset{Ph}{CH}\text{-}\underset{Ph}{CH^-} \qquad (3)$$

1,1-Diphenylethylene is the most reactive monomer to a styryl anion, for the monomer reacts with the anion to give a more stable anion conjugating with two benzene rings. On the other hand, trans-stilbene is the least reactive monomer because of its steric hindrance. The copolymerization of styrene and trans-stilbene in THF proceeded rapidly, while the copolymerization of styrene and 1,1-diphenylethylene proceeded so slowly that the reaction finished in 24 hr, even in THF at 0°C.2) This may have been because the trans-stilbene anion produced in the reaction (3) has the same structure as the styryl anion, which is reactive enough to end instantaneously the homopolymerization of styrene, while the 1,1-diphenylethylene anion is very stable and has a big steric hindrance, therefore giving a very small k_{21}.

As Figs 1 and 3 show, the overall rate of the copolymerization is greater in THF than in benzene. This may be because in THF a free ion plays a great part in the chain growth,$^{8)}$ while in benzene living chain ends form ion pairs to associate themselves.$^{9)}$ The $1/r_1$ value (k_{12}/k_{11}) is smaller in benzene than in THF, as is shown in Table 4; this suggests that the relative reactivity of a M_2 monomer toward a $\sim St^{-}Li^{+}$ ion pair is smaller than that toward a styryl free anion, when the reactivities of styrene toward its chain ends are taken as standards

Chain Transfer and Electronic Spectrum of the Living Anion. The viscosity of the copolymer decreased with an increase in the trans-stilbene, as is shown in Table 2. This indicates that a chain transfer to the trans-stilbene occurred in THF. This transfer may proceed as follows:



$$\sim\underset{\displaystyle Ph}{\underset{|}{CH^{-}}} \quad + \quad \overset{\displaystyle Ph}{\overset{|}{CH}} = \underset{\displaystyle Ph}{\underset{|}{CH}} \longrightarrow \sim\underset{\displaystyle Ph}{\underset{|}{CH_2}} \quad + \quad \overset{\displaystyle Ph}{\overset{|}{CH}} = \underset{\displaystyle Ph}{\underset{|}{C^{-}}} \qquad (4)$$

The production of the anion with a λ_{max} at 555 mμ may be connected with the chain transfer reaction shown by the process (4). On the other hand, the copolymerization in benzene (Table 3) seemed to proceed without the chain transfer, for no the change in the red color of the reaction mixture was observed and the solution viscosity of the copolymer did not decrease with an increase in the trans-stilbene charged, although the exact molecular weight of the copolymer could not be determined.

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Table 1. Anionic copolymerization of styrene (M_1) and trans-stilbene (M_2) in THF

$[M_1]_0$ + $[M_2]_0$ 3.4 mmol, [n-BuLi] 5.7×10^{-2}mmol, THF 10 ml, temp. 0°C, time 40-60 min

Monomer, g		$[M_1]_0/[M_2]_0$ a)	Polymer	Unchanged M_2		$[m_1]/[m_2]$ d)
M_1	M_2		P, g	M_1, g b)	M_1, g c)	
0.244	0.187	2.26	0.353	0.080	0.059	3.9
0.206	0.250	1.42	0.338	0.127	0.100	2.7
0.170	0.314	0.94	0.320	0.165	0.118	2.0
0.140	0.374	0.65	0.285	0.235	0.191	1.7

a) Initial molar ratio in monomer mixture.

b) Obtained by gravimetry. Weight (8 mg) of Li-compounds was subtracked from the weight of residue obtained from mother liquor of polymer.

c) Estimated from UV spectrum.

d) Molar ratio of monomers in the copolymer.

Table 2. Anionic copolymerizaton of styrene (M_1) and trans-stilbene (M_2) in THF

$[M_1]_0$ 3.47 mmol, THF 15 ml, [n-BuLi] 5.7×10^{-2} mmol, temp. 0°C, time 2.5 hr

$[M_2]_0$ mmol	$[M_1]_0/[M_2]_0$ a)	Yield %	$[m_1]/[m_2]$ b)	η_{sp}/C c) dl/g	S.P. d) °C
0.41	8.09	85.5	43	0.652	135
0.92	3.76	85.6	6.8	0.391	157
1.26	2.71	87.0	4.2	0.296	160
2.34	1.50	79.6	2.4	0.188	165
3.44	1.00	72.8	1.8	0.126	176
5.28	0.67	62.5	1.4	0.104	190
8.12	0.43	51.1	1.1	0.010	200

a) Initial molar ratio in monomer mixture.

b) Molar ratio of monomers in the copolymer.

c) Benzene solution at 30.0°C.

d) Softening point of the copolymer.

Table 3. Anionic copolymerization of styrene (M_1) and trans-stilbene (M_2) in benzene

$[M_1]_0$ 3.4 mmol, benzene 15 ml, [n-BuLi] 1.14×10^{-1} mmol, temp. 30°C, time 90 hr

$[M_2]_0$ mmol	$[M_1]_0/[M_2]_0$ [a]	Yield %	$[m_1]/[m_2]$ [b]	η_{sp}/C [c] dl/g
0.38	9.00	85.1	99	0.095
0.87	4.00	75.1	19	0.099
1.49	1.90	63.7	13	0.105
2.33	1.44	54.5	9.0	0.093
3.51	0.96	45.2	6.7	0.145
5.26	0.64	36.9	4.9	0.132
7.13	0.47	31.4	3.8	0.101

a) Initial molar ratio in monomer mixture.

b) Molar ratio of monomers in the copolymer.

c) Benzene solution at 30°C.

Table 4. Monomer reactivity ratio, r_1, in anionic copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2)[2] or trans-stilbene (M_2) with n-BuLi

Monomer		r_1 value	
M_1	M_2	in THF	in Benzene
Styrene	1,1-Diphenylethylene	0.13[a]	0.71[a]
Styrene	trans-Stilbene	2.3[b]	18[a]

a) At 30°C. b) At 0°C.

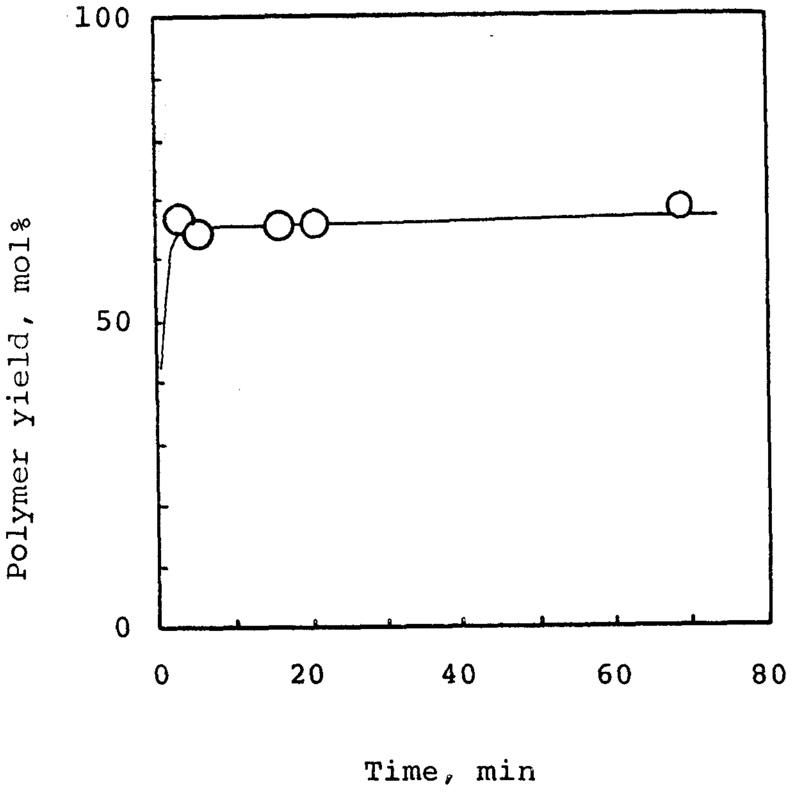


Fig. 1. Anionic copolymerization of styrene (M_1) and trans-stilbene (M_2) in THF.—— Time vs. polymer yield.

$[M_1]_0$ + $[M_2]_0$ 7.0 mmol, $[M_1]_0/[M_2]_0$ 1/1.5, THF 15 ml, Temp. 0°C, n-BuLi 5.8×10^{-2} mmol.

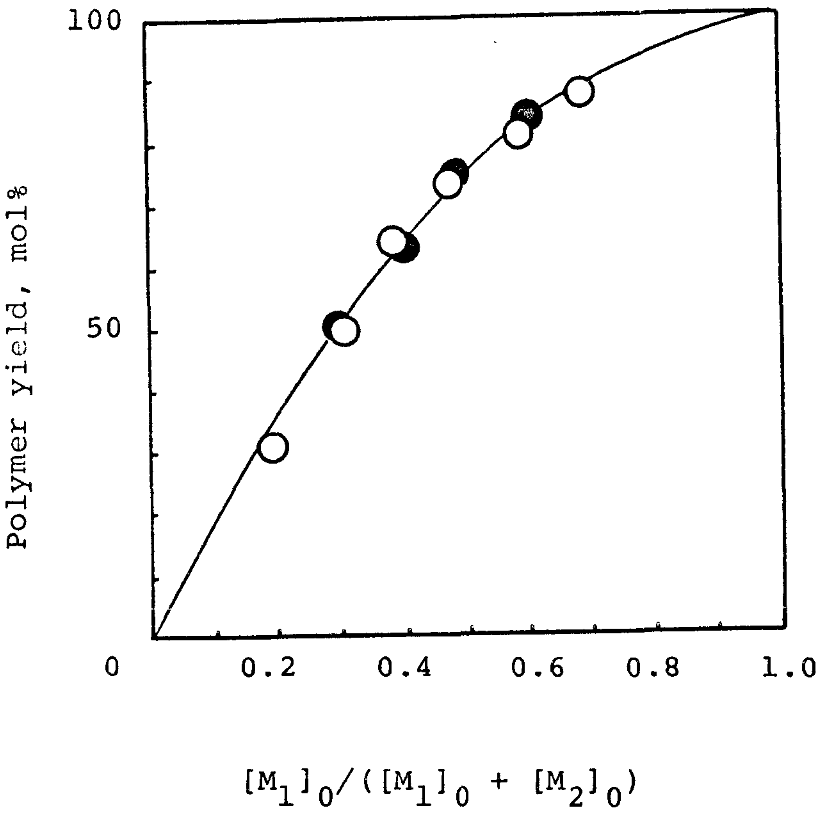


Fig. 2. Anionic copolymerization of styrene (M_1) and trans-stilbene (M_2) in THF.—— Monomer reactivity ratio, r_1.

○: $[M_1]_0$ + $[M_2]_0$ 3.4 mmol, THF 10 ml, Time 40-60 min,

●: $[M_1]_0$ 3.47 mmol, THF 15 ml, Time 2.5 hr, n-BuLi 5.7×10^{-2} mmol, Temp. 0°C.

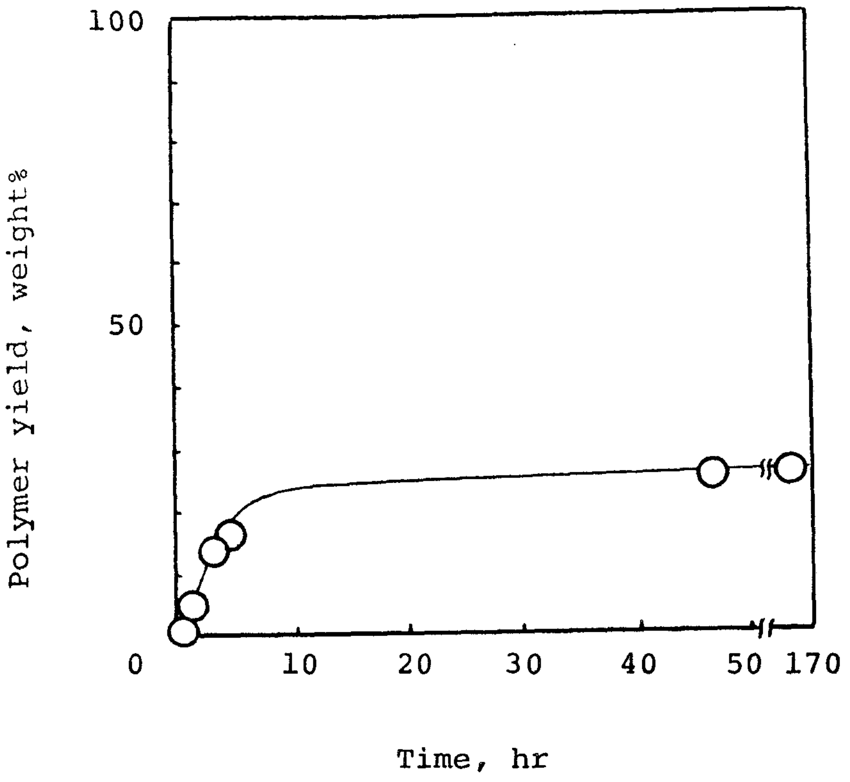


Fig. 3. Anionic copolymerization of styrene (M_1) and trans-stilbene (M_2) in benzene—— Time vs. polymer yield.

$[M_1]_0$ + $[M_2]_0$ 14.8 mmol, $[M_1]_0/[M_2]_0$ 1.0/3.0, Benzene 20 ml, Temp. 30°C, n-BuLi 1.14×10^{-1} mmol.

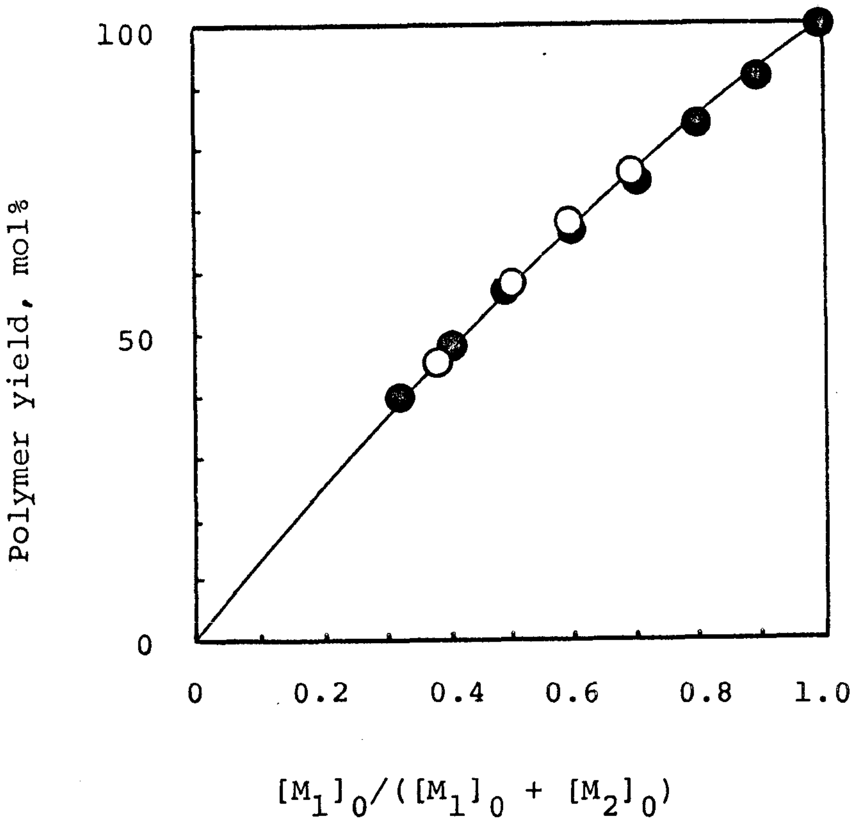


Fig. 4 Anionic copolymerization of styrene (M_1) and trans-stilbene (M_2) in benzene.—— Monomer reactivity ratio, r_1.

○: $[M_1]_0$ + $[M_2]_0$ 8.0 mmol, ●: $[M_1]_0$ 3.4 mmol, Benzene 15 ml, Initiator: n-BuLi, Temp.: 30°C, Time: ○ 40 hr, ● 90 hr.

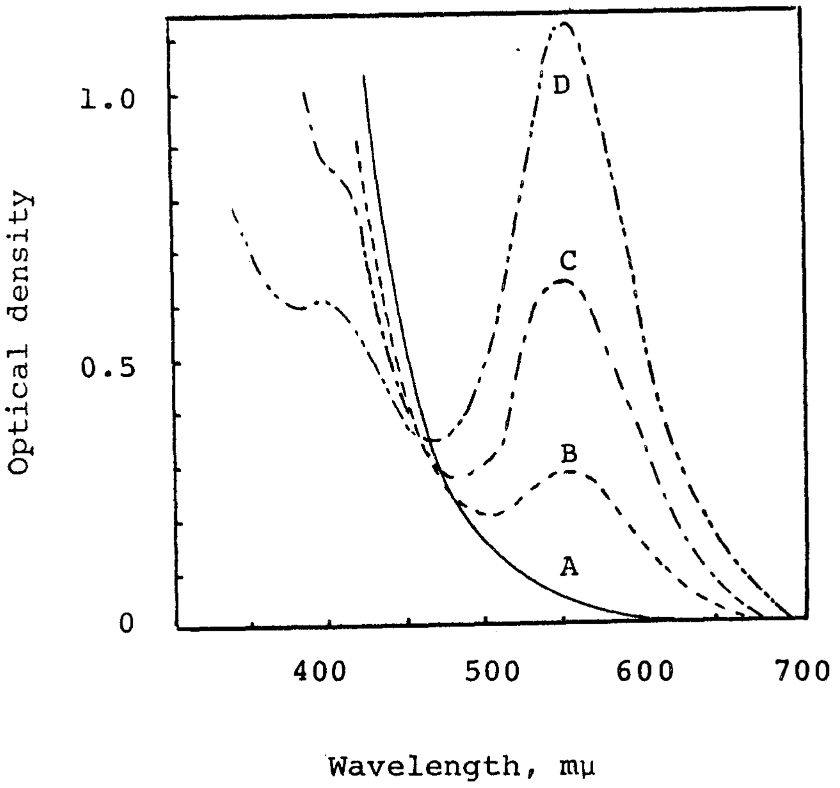


Fig. 5. Anionic copolymerization of styrene (M_1) and trans-stilbene (M_2) in THF—— Electronic spectra of reaction mixture.

$[M_1]_0$ + $[M_2]_0$ 8.8 mmol, Initiator n-BuLi, Temp. 0°C, Time: A 20 min, B 33 min, C 1.6 hr, D 4.8 hr.

Chapter 8

Reaction of trans-Stilbene with n-Butyllithium

Synopsis

The reaction of trans-stilbene with n-butyllithium was investigated in tetrahydrofuran at 0°C. The structures of the products fractionated by column chromatography were determined by elementary analysis, a molecular-weight determination, and a study of the IR, UV, and NMR spectra. The main products were 1,2-diphenylhexane, 1,2-diphenylethane, and 1,2,3-triphenylpropene which was formed by the cleavage of a C-C bond of a product. The reaction mixture showed an ESR signal. The observed results are explained in terms of the anionic copolymerization of trans-stilbene and styrene reported previously.

Introduction

In a previous paper,[1)] a study of the anionic copolymerization of styrene and trans-stilbene by n-butyllithium (n-BuLi) has been reported. The results have shown that in tetrahydrofuran (THF) a chain-transfer reaction to the trans-stilbene occurs, while in benzene the copolymerization proceeds without any chain-transfer. In the copolymerization, the color of the reaction mixture changes in time; it was followed spectrophotometrically.

The work reported here was carried out in order to clarify two points: the reaction mechanism of the chain-transfer and the change in the color in the copolymerization. Wyman and Altares[2) carried out the same reaction in benzene, but their results differ greatly from ours.

Experimental

Reagent. The preparations and purifications of trans-stilbene, n-BuLi, and THF were previously described.[1)

Reaction. The reaction was carried out under dry nitrogen in a glass ampoule equipped with a three-way stopcock. To a solution of trans-stilbene (10.0 g, 5.56×10^{-2} mol) in THF (250 ml), n-BuLi (2.83×10^{-2} mol) was added with a syringe over a three-minute period at 0°C. The color of the reaction mixture changed from red to purple in time. After 48 hr, the reaction was terminated by adding methanol (1.1 ml, 2.6×10^{-2} mol) until the color of the solution disappeared. The solvent was evaporated in vacuo, and then the residue was dissolved in diethyl ether. The ether solution was washed with water and dried over magnesium sulfate; then the ether was removed to give 11.6 g of an oily product.

Fractionation of Product. The fractionation of the above product was carried out by column chromatography with activated alumina, using n-hexane, benzene, and methanol as solvents.

Measurements. The measurements of the molecular weight, the elementary analysis, and the IR, UV, and NMR spectra were made according to methods reported previously.[1) The ESR spectrum was measured with a JES-3BX Spectrometer.

Results

Fractionation of Product. Before the fractionation of the reaction product by column chromatography, the product was submitted to sublimation in order to exclude any unchanged trans-stilbene. However, no trans-stilbene was recovered. The addition of n-hexane to the product gave no precipitate of trans-stilbene, which is almost insoluble in this solvent at 0°C. The results of the fractionation by column chromatography are shown in Table 1. Fraction1, which is not shown in the table, was fractionated by subsequent chromatography, using n-hexane as a solvent, to give two fractions, 1A and 1B.

Characterization of Each Fraction. The results of the elementary analysis, the molecular weight, and the molecular formula of each fraction are listed in Table 1. The characteristics of the IR and UV spectra, and the ratio of the number of aromatic to that of aliphatic protons (H_{ar}/H_{al}) of the fraction are summarized in Table 2.

Compounds Formed in the Reaction Mixture. Table 3 shows the molecular formulae, the structural formulae, the results of the elementary analyses, the molecular weights, and the ratios of the number of aromatic to that of aliphatic protons (H_{ar}/H_{al}) of the compounds which may be supposed to be the reaction products on the basis of the results.

Structure of Each Fraction. Fraction 1A. This fraction was liquid; the results of its elementary analysis and its molecular weight and the molecular formula derived from them were most consistent with those of 1,2-diphenylhexane, I_a, in Table 3. In the NMR spectrum of the fraction 1A (Fig. 1), the chemical shifts of the Ph, $-CH(Ph)CH_2Ph$, $-CH_2-$, and CH_3- protons, and the relative areas of the peaks, 10.0: 2.9: 6.1: 3.0, also support the above structure. The IR spectrum showed the absence of a C=C double bond, as was also speculated on the basis of the UV spectrum.

Fraction 1B. The melting point of the fraction 1B was 50-52°C. Its molecular formula was similar to that of 1,2-diphenylethane, I_b, in Table 3, the melting point of which is 53°C.3) The NMR spectrum of this fraction also completely agreed with that of the authentic sample. The NMR spectrum of the fraction 1 indicated that this fraction contained only I_a and I_b in a molar ratio of 3.3.

Fraction 2. The molecular formula of the fraction 2 was in best accord with 1,2,3-triphenylpropene, II, in Table 3. In the NMR spectrum (Fig. 2), the peaks at 3.65 and 6.29 τ were assigned to the methine and methylene protons, respectively, of the cis-isomer, judging from the NMR spectrum of cis- and trans-stilbene. The peak at 5.96 τ was assigned to the methylene protons of the trans-isomer, while the absorption of its methine proton might overlap with those of aromatic protons near 3 τ. The IR spectrum of the fraction 2 showed an absorption due to a three-substituted olefin at 870 cm^{-1}. A further separation of this fraction by column chromatography gave the cis-isomer as the initial fraction; its melting point was 61-62°C (lit.,$^{4)}$ 62-63°C). The fraction eluted at the later stage of the chromatography was largely composed of the trans-isomer, but it always contained a small portion of the cis-isomer. In the UV spectra, the absorption mixima of cis- and trans-1,2,3-triphenylpropene appeared at 260 mμ (ε_{max} 14200) and 273 mμ (ε_{max} 16100) respectively. The molar ratio of the trans- to the cis-isomer was 1.9; this ratio was calculated from the relative strength of the corresponding absorptions in the NMR spectrum of the fraction 2.

Fraction 3. The molecular weight of the fraction 3 was 345. This rather large value indicates that a compound composed of at least two molecules of trans-stilbene must have been a component of this fraction. The sharp peak at 5.96 τ in the NMR spectrum (Fig. 3) suggests that the tailing of trans-1,2,3-triphenylpropene, which was present in the fraction 2, is incorporated into this fraction. However, 1,2,3,4-tetraphenyloctane, III in Table 3, must be the main component of this fraction, judging from the absorption at 9.1 τ due to the methyl group and absorptions at 7.5-8.9 τ due to methylene and methine groups in the NMR spectrum, and judging from the molecular weight of this fraction.

This fraction also contained a small amount (about 100 mg) of a compound insoluble in petroleum ether at 0°C; this compound was identfied as 1,2,3,4-tetraphenylbutane, V, in Table 3. Its melting point was 181-183°C (lit.,$^{5)}$ 182°C), and the observed

H_{ar}/H_{al} ratio in the NMR spectrum was 3.5. Found: C, 92.76%; H, 7.24%.

Fraction 4. Judging from the elementary analysis, this fraction consisted of a compound containing oxygen. The IR spectrum suggested the presence of an OH group by means of the strong absorption at 3300 cm^{-1}. Although the NMR spectrum was complicated, the H_{ar}/H_{al} ratio was 0.66. This small value means that there were more aliphatic protons than aromatic ones. The reaction of a carbanion with THF must have formed an alcohol containing the greater portion of the aliphatic protons. A compound such as IV in Table 3 may be proposed as one of the alcohols.

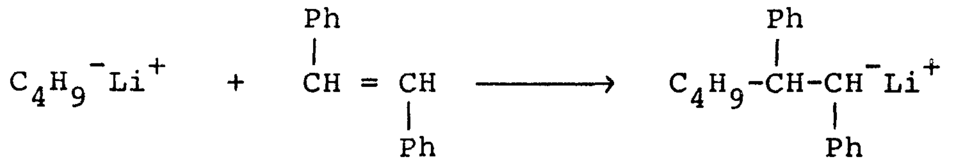
Yields of Product Compounds. The yields of the product compounds identified were calculated from the NMR spectrum of the unfractionated mixture and from the weights of the compounds fractionated by column chromatography. The results are shown in Table 4. The yields of 1,2,3-triphenylpropene (II) and 1,2-diphenylethane (I_b), after reactions of 25 and 180 min carried out under the same conditions as those shown in the Experimental section, were obtained by means of the NMR spectra of the respective reaction mixtures, as are shown in Table 4. The ratios of 1,2,3-triphenylpropene to 1,2-diphenylethane were about 2, regardless of the reaction time.

Electronic Spectrum of Reaction Mixture. The electronic spectra of the reaction mixtures of trans-stilbene and n-BuLi in THF at room temperature are shown in Fig. 4. In the reaction of trans-stilbene with an excess of n-BuLi, the spectrum showed a peak at 332 mμ which was stable for a prolonged time and might be based on a benzyl-type anion, $C_4H_9CH(Ph)-CH(Ph)^-Li^+$. On the other hand, when the molar ratio of trans-stilbene to n-BuLi was 2.0, new peaks appeared at 555 and 420 mμ in time. When n-BuLi was added to the solution of 1,2,3-triphenylpropene in THF, the peaks at 555 and 420 mμ appeared instantaneously in the UV spectrum of the solution. Then, 1,2,3-triphenylpropene-3-d_1, was recovered by terminating the reaction with deuterium oxide. This was confirmed by a study of the NMR spectrum.

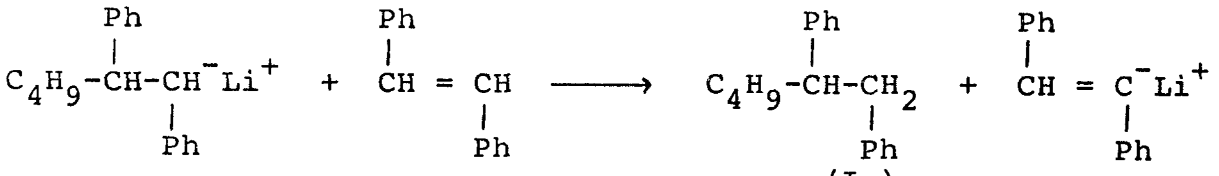
ESR Spectrum of Reaction Mixture. The ESR spectrum of the reaction mixture in THF was measured at room temperature, the molar ratio of trans-stilbene to n-BuLi being 2.0. The spectrum is shown in Fig. 5. In the reaction of 1,2,3-triphenylpropene with n-BuLi in THF, however, no ESR signal was observed.

Discussion

The compounds identified as the main products were 1,2-diphenylhexane (I_a), 1,2-diphenylethane (I_b), and 1,2,3-triphenylpropene (II). It is noteworthy that no trans-stilbene was recovered and that 1,2-diphenylethane and 1,2,3-triphenylpropene were obtained instead. The mechanisms of the formations of these two compounds cannot be explained by simple addition or abstraction reactions of carbanions. The 1,2,3-triphenylpropene can be produced only by the cleavage of a C-C bond because there is no compound with odd carbons in the starting materials. The molar ratio of the yield of 1,2,3-triphenylpropene to 1,2-diphenylethane was two, regardless of the reaction time; this suggests that the formations of these compounds are interrelated. The following processes (1)-(7) constitute our proposed mechanisms for the production of the above compounds.

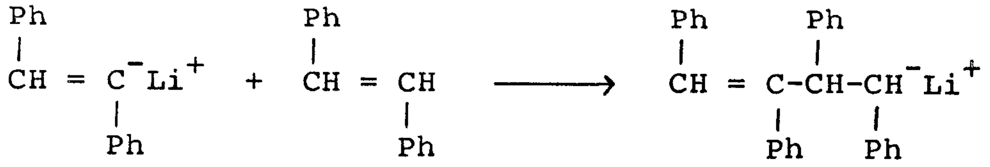


$$\mathrm{C_4H_9{}^-Li^+} + \overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{CH}} \longrightarrow \mathrm{C_4H_9}\text{-}\overset{\mathrm{Ph}}{\mathrm{CH}}\text{-}\underset{\mathrm{Ph}}{\mathrm{CH}^-}\mathrm{Li^+} \qquad (1)$$

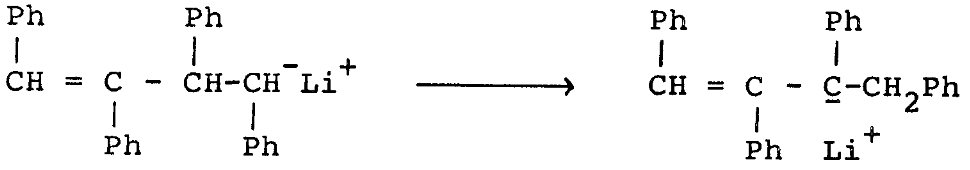


$$\mathrm{C_4H_9}\text{-}\overset{\mathrm{Ph}}{\mathrm{CH}}\text{-}\underset{\mathrm{Ph}}{\mathrm{CH}^-}\mathrm{Li^+} + \overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{CH}} \longrightarrow \underset{(\mathrm{I_a})}{\mathrm{C_4H_9}\text{-}\overset{\mathrm{Ph}}{\mathrm{CH}}\text{-}\underset{\mathrm{Ph}}{\mathrm{CH_2}}} + \overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{C}^-}\mathrm{Li^+} \qquad (2)$$

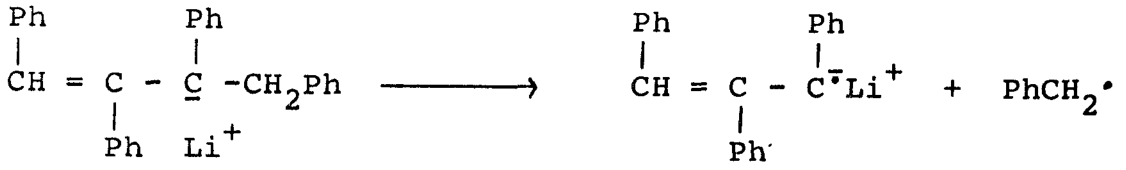
(I$_a$)



$$\overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{C}^-}\mathrm{Li^+} + \overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{CH}} \longrightarrow \overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{C}}\text{-}\overset{\mathrm{Ph}}{\mathrm{CH}}\text{-}\underset{\mathrm{Ph}}{\mathrm{CH}^-}\mathrm{Li^+} \qquad (3)$$



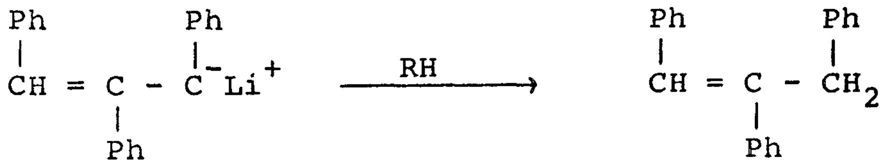
$$\overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{C}} - \overset{\mathrm{Ph}}{\mathrm{CH}}\text{-}\underset{\mathrm{Ph}}{\mathrm{CH}^-}\mathrm{Li^+} \longrightarrow \overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{C}} - \underset{\mathrm{Li^+}}{\overset{\mathrm{Ph}}{\underline{\mathrm{C}}}}\text{-}\mathrm{CH_2Ph} \qquad (4)$$



$$\overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{C}} - \underset{\mathrm{Li^+}}{\overset{\mathrm{Ph}}{\underline{\mathrm{C}}}}\ \text{-}\mathrm{CH_2Ph} \longrightarrow \overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{C}} - \overset{\mathrm{Ph}}{\mathrm{C}^{\bar{\bullet}}}\mathrm{Li^+} + \mathrm{PhCH_2}\bullet \qquad (5)$$

$$2\ \mathrm{PhCH_2}\bullet \longrightarrow \mathrm{PhCH_2CH_2Ph} \qquad (6)$$

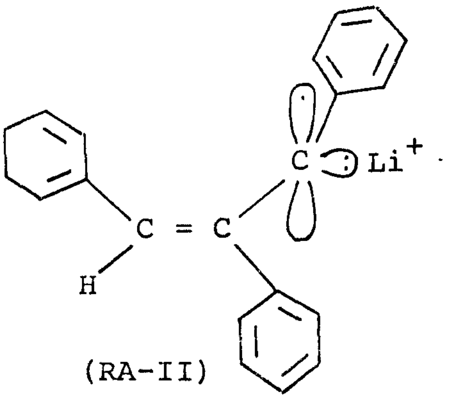
(I$_b$)



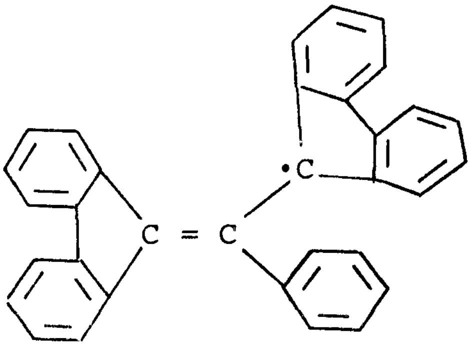
$$\overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{C}} - \overset{\mathrm{Ph}}{\mathrm{C}^{-}}\,\mathrm{Li}^{+} \xrightarrow{\mathrm{RH}} \overset{\mathrm{Ph}}{\mathrm{CH}} = \underset{\mathrm{Ph}}{\mathrm{C}} - \overset{\mathrm{Ph}}{\mathrm{CH_2}} \quad \text{(II)} \qquad (7)$$

The total product yield indicates that the process (1), which is an addition reaction of n-BuLi to trans-stilbene, takes place easily. As may be seen from the electronic spectrum of the reaction mixture, the benzyl-type anion formed in the process (1) is stable, if no excess trans-stilbene is present. However, the acidity of the methine protons of trans-stilbene is rather strong, as is shown by the isomerization of cis-stilbene to the trans-isomer by a base such as potassium tert-butoxide.$^{6)}$ Therefore, if excess trans-stilbene is present, the process (2) will occur. This process must be a chain-transfer reaction in the copolymerization of trans-stilbene and styrene.$^{1)}$

The new anion produced in the process (2) reacts with trans-stilbene to give a dimer anion, which may accompany the cleavage of a C-C bond with the production of the benzyl radical and the 1,2,3-triphenylpropenyl radical anion (the process (5)), via a proton shift reaction in the process (4). This radical anion may be of new type. The structure of the 1,2,3-phenylpropenyl radical anion may be represented as shown by RA-II. This radical anion, if present, can be greatly stabilized by the delocalization of an electron on the benzene rings. It has been estabilished that the 1,3-bis(diphenyl)-2-phenylallyl radical, with a similar structure to that of RA-II, is very stable even in air.$^{7)}$



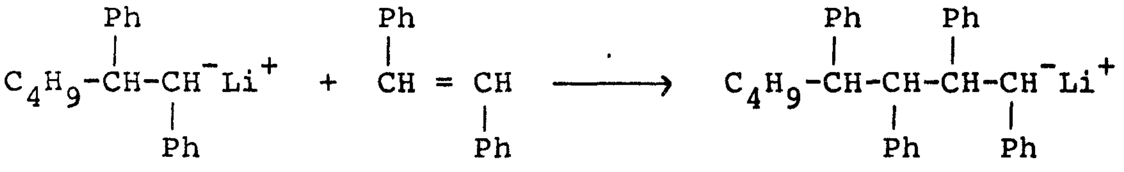
(RA-II)



(1,3-Bis(diphenylene)-2-phenylallyl radical)

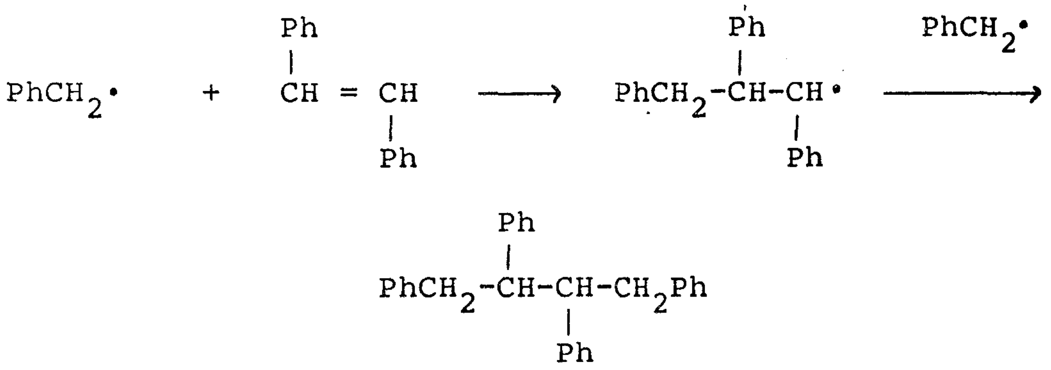
The reaction mixture of trans-stilbene and n-BuLi showed an ESR signal (Fig. 5). This might be because of the mono lithium-adduct of trans-stilbene. However, no absorption maximum at 480 mμ (ε_{max} 62000)$^{8)}$ due to the adduct in THF could be observed in the electronic spectrum of the reaction mixture (Fig. 4). The hyperfine structure of the ESR spectrum observed herein suggests the presence of a radical with a rather complicated structure, although it is not certain at present whether or not the ESR signal is due to the radical anion, RA-II. The coupling of benzyl radicals gives 1,2-diphenylethane, as is shown in the process (6).

Although the yield was rather low, 1,2,3,4-tetraphenyloctane was also obtained. This means that a stilbene anion can add to trans-stilbene to give a dimer, even if the reaction is very slow (the process (8)).



$$C_4H_9\text{-}\overset{\text{Ph}}{\overset{|}{\text{CH}}}\text{-}\underset{\text{Ph}}{\underset{|}{\text{CH}}}^-Li^+ + \overset{\text{Ph}}{\overset{|}{\text{CH}}} = \underset{\text{Ph}}{\underset{|}{\text{CH}}} \longrightarrow C_4H_9\text{-}\overset{\text{Ph}}{\overset{|}{\text{CH}}}\text{-}\underset{\text{Ph}}{\underset{|}{\text{CH}}}\text{-}\overset{\text{Ph}}{\overset{|}{\text{CH}}}\text{-}\underset{\text{Ph}}{\underset{|}{\text{CH}}}^-Li^+ \quad (8)$$

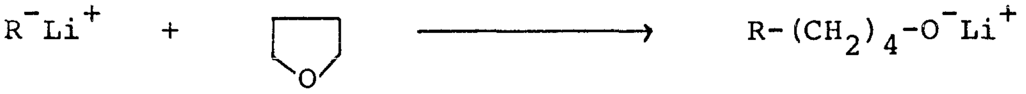
The formation of a small amount of 1,2,3,4-tetraphenylbutane can be explained by the following process:



$$PhCH_2\cdot + PhCH{=}CHPh \longrightarrow PhCH_2\text{-}CH(Ph)\text{-}CH(Ph)\cdot \xrightarrow{PhCH_2\cdot} PhCH_2\text{-}CH(Ph)\text{-}CH(Ph)\text{-}CH_2Ph \qquad (9)$$

(V)

The carbinol in the fraction 4 may be produced through the following process:[9,10)]

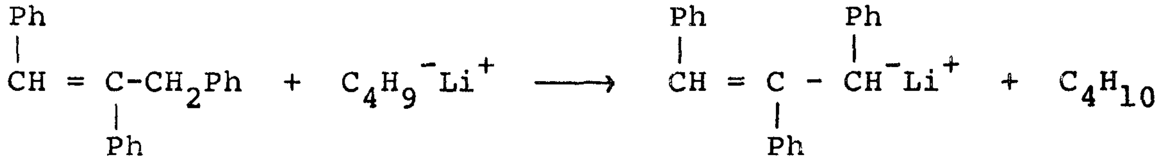


$$R^-Li^+ + \text{THF} \longrightarrow R\text{-}(CH_2)_4\text{-}O^-Li^+$$

Judging from the yield of each compound obtained in this experiment, n-BuLi is considered to be consumed almost quantitatively in the process (1); about 49% of the 1,2-diphenylhexyl anions produced in the process reacted with trans-stilbene to give 1,2-diphenylhexane, 1,2,3-triphenylpropene, and 1,2-diphenylethane. About 10% of the 1,2-diphenylhexyl anions were apparently consumed in the formation of 1,2,3,4-tetraphynyloctane, while about 20% of the anions remained free from the subsequent reactions. The residual 1,2-diphenylhexyl anions and also probably a part of the 1,2,3,4-tetraphenyloctyl anions reacted with THF to yield alcohols. The absence of 1,2,3,4-tetraphenylbutene indicates that the anions produced in the processes (3) and (4) are rather unstable.

The reaction mixtures both of trans-stilbene with n-BuLi and of 1,2,3-triphenylpropene with n-BuLi showed the same absorption maxima, at 555 and 420 mμ. It is likely that the A-II anion, which may be produced from RA-II by the abstraction of a hydrogen from any material in the system, will be present in the reaction mixture of trans-stilbene and n-BuLi. It may be supposed that the radical anion, RA-II, shows the same absorption maxima, at 555 and 420 mμ.

The reaction of 1,2,3-triphenylpropene with n-BuLi proceeds as follows:

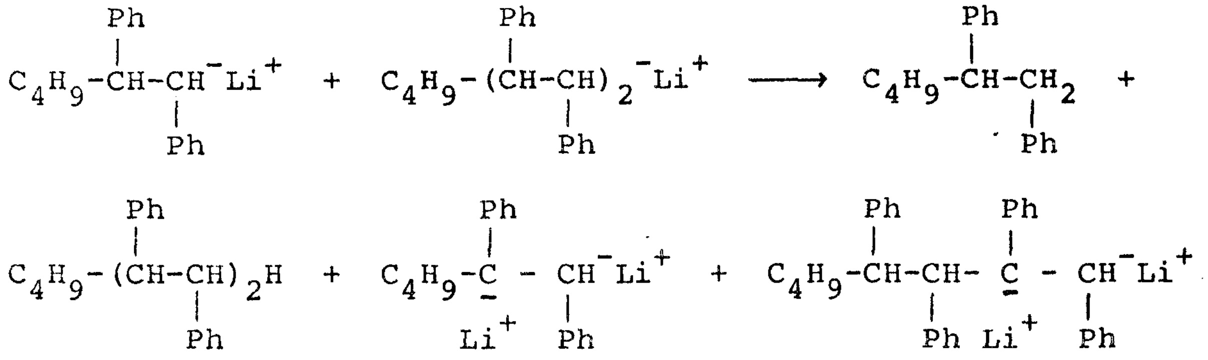


$$\mathrm{PhCH=C(Ph)-CH_2Ph} + \mathrm{C_4H_9^-Li^+} \longrightarrow \mathrm{PhCH=C(Ph)-CH(Ph)^-Li^+} + \mathrm{C_4H_{10}} \qquad (10)$$

(A-II)

since the 1,2,3-triphenylpropene with a deuterium at the methylene position is recovered when the reaction is terminated by deuterium oxide.

A distinct solvent effect exists in the reaction of trans-stilbene and n-BuLi. Wyman and Altares$^{2)}$ have studied the reaction of trans-stilbene and n-BuLi in benzene at 60°C. Contrary to the reaction in THF, the main process (II) was found to follow the processes (1) and (8), thus giving the dianions shown below.



$$\mathrm{C_4H_9\text{-}\overset{\overset{Ph}{|}}{C}H\text{-}\underset{\underset{Ph}{|}}{C}H^{-}Li^{+}} + \mathrm{C_4H_9\text{-}(\overset{\overset{Ph}{|}}{C}H\text{-}\underset{\underset{Ph}{|}}{C}H)_2{}^{-}Li^{+}} \longrightarrow \mathrm{C_4H_9\text{-}\overset{\overset{Ph}{|}}{C}H\text{-}\underset{\underset{Ph}{|}}{C}H_2} +$$

$$\mathrm{C_4H_9\text{-}(\overset{\overset{Ph}{|}}{C}H\text{-}\underset{\underset{Ph}{|}}{C}H)_2H} + \mathrm{C_4H_9\text{-}\overset{\overset{Ph}{|}}{\underset{\underset{Li^{+}}{-}}{C}} - \underset{\underset{Ph}{|}}{C}H^{-}Li^{+}} + \mathrm{C_4H_9\text{-}\overset{\overset{Ph}{|}}{C}H\text{-}\underset{\underset{Ph}{|}}{C}H\text{-}\ \overset{\overset{Ph}{|}}{\underset{\underset{Li^{+}}{-}}{C}} - \underset{\underset{Ph}{|}}{C}H^{-}Li^{+}} \qquad (11)$$

The results obtained in the present study establish that the chain-transfer in the copolymerization of trans-stilbene and styrene occurs by means of the abstraction of a proton from the trans-stilbene, as is shown by the process (2), and that the change in the color observed in the copolymerization is associated with the 1,2,3-triphenylpropenyl anion or the radical anion.

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Table 1. Fractionation of reaction mixture by column chromatography

Fraction	Eluent	Recovery	Elementary analysis		Molecular	Molecular
		Wt%	C%	H%	weight	formula
1A	n-Hexane	38	90.70	9.27	233	$C_{18}H_{21.9}$
1B	n-Hexane	9	92.28	7.72	168	$C_{14}H_{13.9}$
2	H/B(95/5)[a]	19	93.37	6.82	264	$C_{21}H_{18.3}$
3	H/B(50/50)[a]	21	92.46	7.64	345	$C_{27}H_{27.0}$
4	Methanol	6	83.27	8.77	291	$C_{22}H_{27.7}$

a) H: n-hexane, B: benzene.

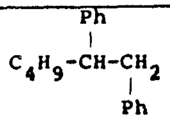
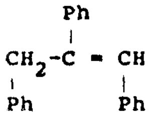
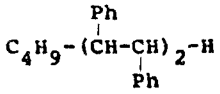
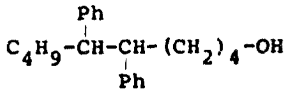
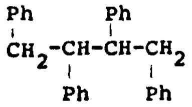
Table 2. Characteristics of IR, UV, and NMR spectra

Fraction	IR(cm^{-1})[a]			UV		NMR[b]
	870	1380	3300	λ_{max} (mμ)	ε_{max}	H_{ar}/H_{al}
1A	–	Medium	–	260	411	0.83
1B	–	Weak	–	260	450	2.4
2	Medium	Weak	–	272	14800	5.1
3	Weak	Weak	–	272	5490	2.4
4	Weak	Medium	Strong	–	–	0.68

a) 870: $R_1R_2C = CHR_3$, 1380: CH_3, 3300: -OH.

b) The ratio of the numbers of aromatic to aliphatic protons.

Table 3. Compounds supposed to be the products in the reaction

Molecular Formula	Structural Formula	Coposition C%	H%	Molecular weight	H_{ar}/H_{al} [a)]	Remarks
$C_{18}H_{22}$	 $C_4H_9\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH_2}$	90.76	9.24	238	0.83	I_a
$C_{14}H_{14}$	$PhCH_2CH_2Ph$	92.31	7.69	182	2.5	I_b
$C_{21}H_{18}$	 $\underset{Ph}{CH_2}\text{-}\overset{Ph}{C}=\underset{Ph}{CH}$	93.33	6.67	270	5.0	II
$C_{32}H_{34}$	 $C_4H_9\text{-}(\overset{Ph}{CH}\text{-}\underset{Ph}{CH})_2\text{-}H$	91.87	8.13	418	1.43	III
$C_{22}H_{30}O$	 $C_4H_9\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH}\text{-}(CH_2)_4\text{-}OH$	85.16	9.68	310	0.5	IV
$C_{28}H_{26}$	 $\overset{Ph}{CH_2}\text{-}\underset{Ph}{CH}\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH_2}$	92.82	7.18	362	3.3	V

a) The ratio of the numbers of aromatic protons to aliphatic protons.

Table 4. Yields of product compounds[a)]

Reaction condition: [stilbene]/[n-BuLi] = 2.0, in THF, at 0°C.

Reaction time	I_a	I_b	II	III	V
25 min	-	6	16	-	-
180 min	-	16	34	-	-
48 hr	62	18	38	10	2

a) Yield was calculated as per cent of the product (mole) per n-BuLi (mole).

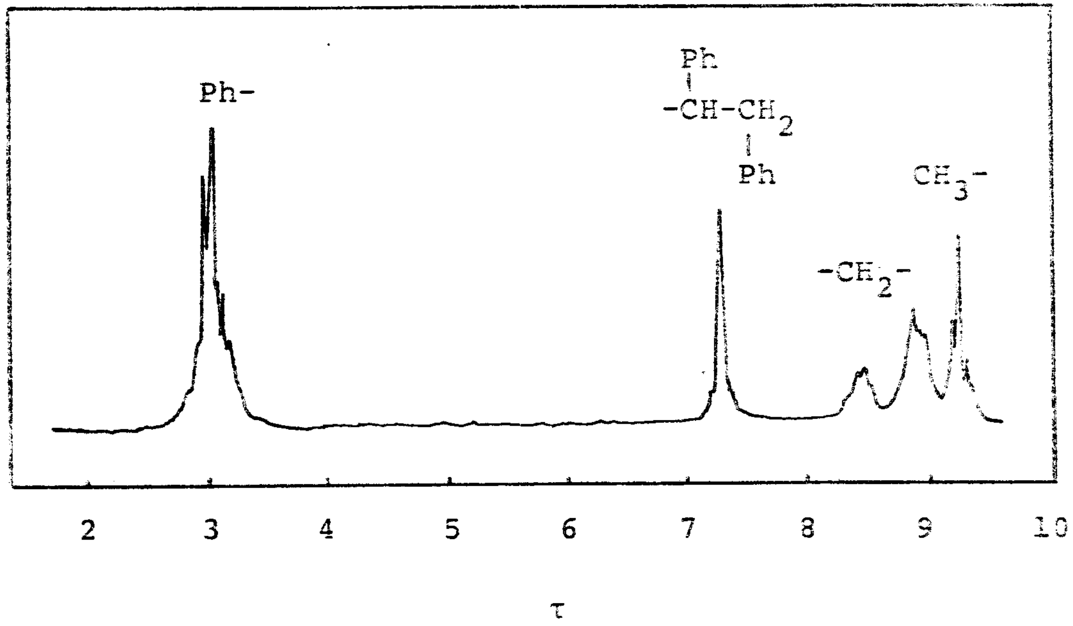


Fig. 1. NMR spectrum of fraction 1A.

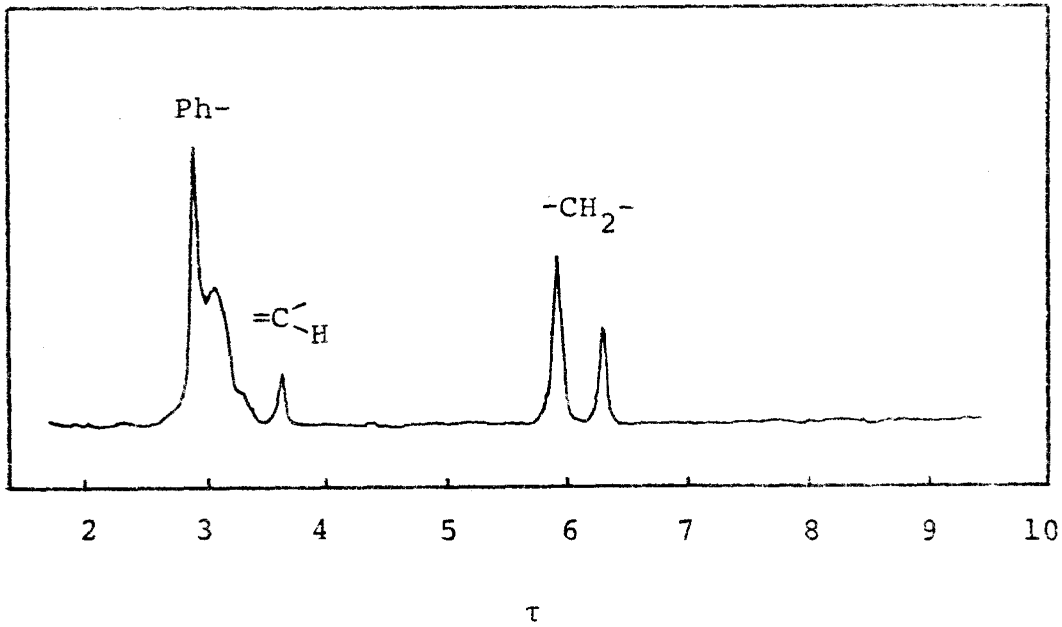


Fig. 2. NMR spectrum of fraction 2.

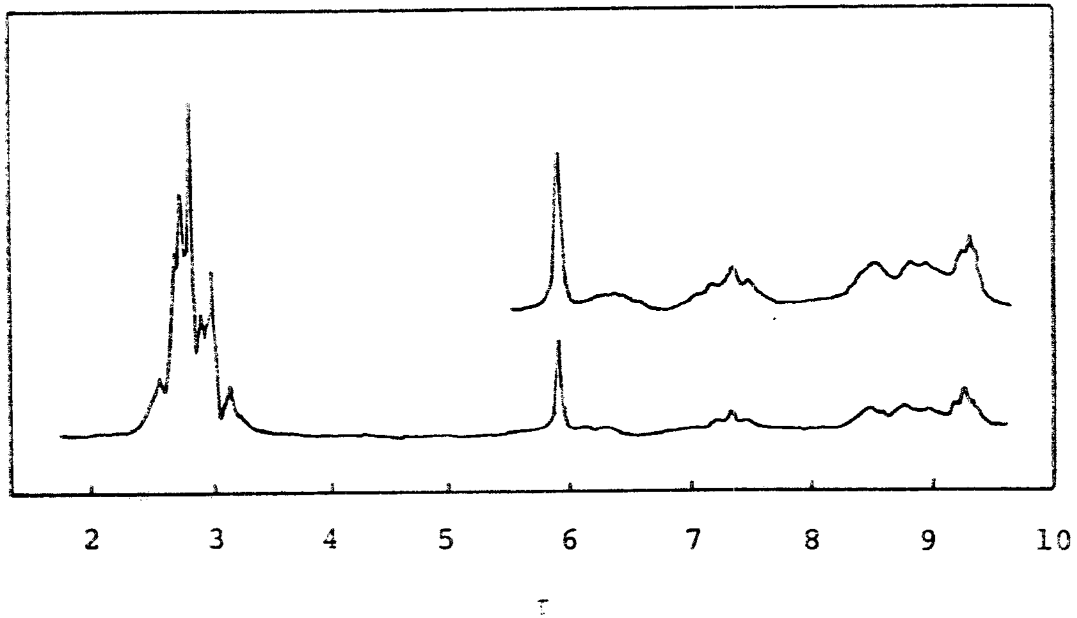


Fig. 3. NMR spectrum of fraction 3.

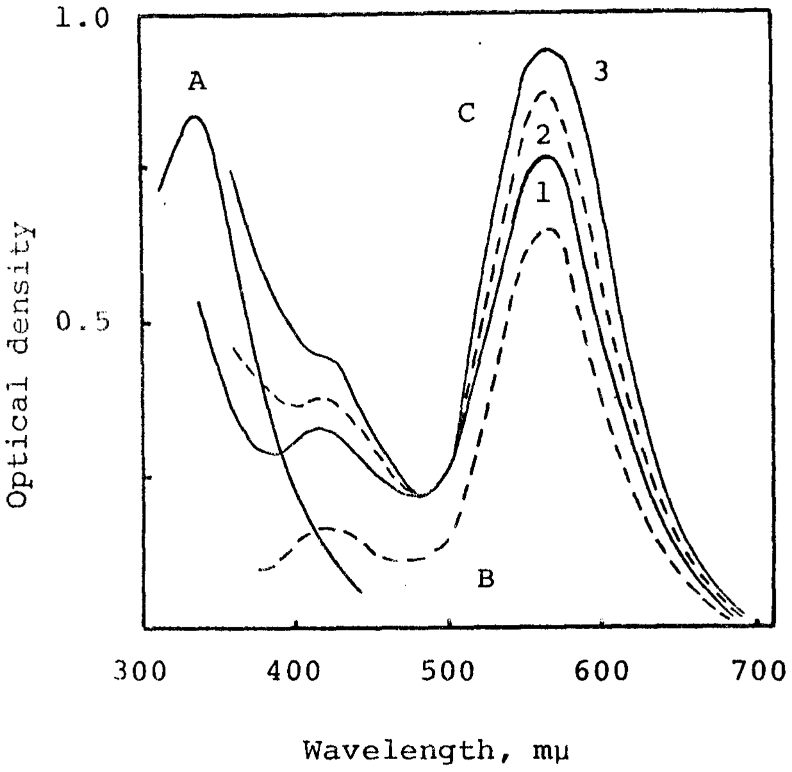


Fig. 4. Electronic spectrum of reaction mixture.

A: [Stilbene]/[n-BuLi] = 0.25

B: 1,2,3-Triphenylpropene + n-BuLi (1:1)

C: [Stilbene]/[n-BuLi] = 6.2

Time: (1) 46 min, (2) 1.4 hr, (3) 2.4 hr.

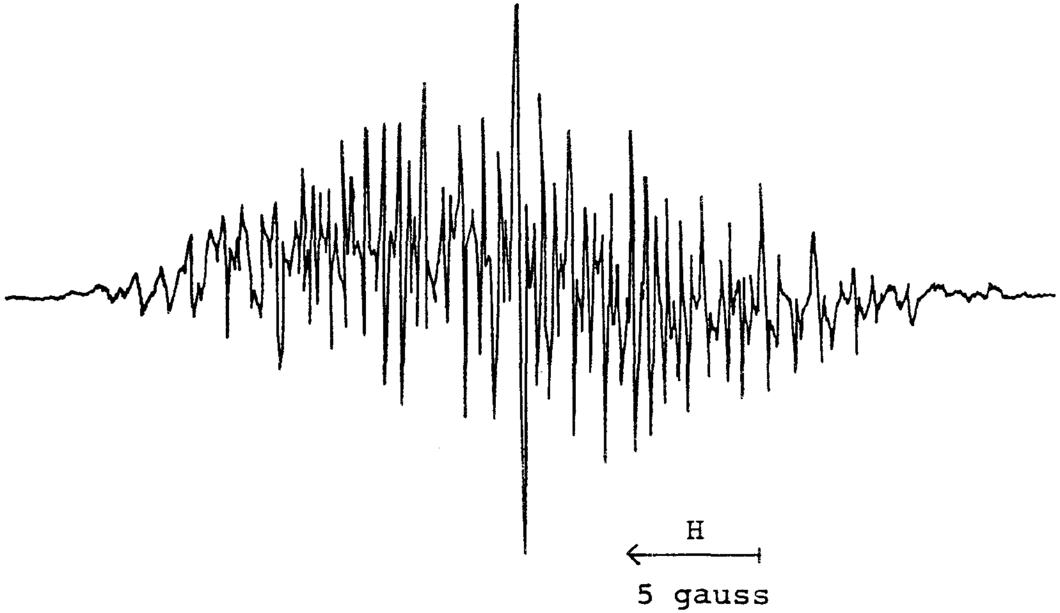


Fig. 5. ESR spectrum of reaction mixture.

[Stilbene]/[n-BuLi] = 2.0, temp. = room temp.

Chapter 9

Anionic Copolymerizations of trans-Stilbene with Butadiene, Isoprene, and 2,3-Dimethylbutadiene

Synopsis

Anionic copolymerizations of trans-stilbene (M_2) with butadiene (M_1), isoprene (M_1), and 2,3-dimethylbutadiene (M_1) were studied in tetrahydrofuran (THF) at 0°C and in benzene at 40°C by means of n-butyllithium (n-BuLi) as an initiator. All the copolymerizations gave alternating copolymers, and the order of the observed rate was butadiene>isoprene>2,3-dimethylbutadiene in THF. In the copolymerizations with isoprene and 2,3-dimethylbutadiene in THF, the reactions were stopped remaining unchanged M_1 monomers when the concentration of n-BuLiwas low, and at the same concentration of n-BuLi the final yield was lower in the copolymerization with 2,3-dimethylbutadiene. In both cases, the final yields increased with an increase in n-BuLi and decreased with increasing $[M_2]_0/[M_1]_0$ ratio. The copolymerization with butadiene was completed without remaining M_1 monomer. All the dienes, however, were completely consumed in the copolymerizations in benzene. In the copolymerizations with butadiene and isoprene, trans-stilbene was little incorporated into the copolymers, but a considerable amount of trans-stilbene was consumed in the copolymerization with 2,3-dimethylbutadiene. All the electronic spectra of the reaction mixtures in THF showed no peak near 540 mμ at the initial stage of the reactions, but new peaks appeared near 540 mμ in time. The order of the optical densities after a prolonged time was 2,3-dimethylbutadiene>isoprene>butadiene. The microstructures of the dienes in the homopolymers and alternating copolymers which were polymerized in THF were determined by NMR spectroscopy. The alternating copolymers had more 1,4-structure than the corresponding homopolymers and the 1,4-content decreased as follows: 2,3-dimethylbutadiene>isoprene>butadiene.

Introduction

Anionic copolymerizations of 1,1-diphenylethylene with other comonomers such as styrene and conjugated dienes proceeded without chain-transfer and termination reactions to give alternating copolymers in THF.1) The copolymerization of trans-stilbene and styrene in THF also gave an alternating copolymer under appropriate reaction conditions, but it brought with chain-transfer,2) the mechanism of which was clarified recently.3)

In this work, using butadiene, isoprene, and 2,3-dimethylbutadiene as comonomers, the copolymerizations of trans-stilbene by means of n-BuLi are investigated in THF and benzene.

Experimental

Materials. trans-Stilbene. The monomer synthesized from benzoin4) was recrystallized three times from methanol and twice from n-hexane. Mp 124°C.

Butadiene. Butadiene (Phillips, polymerization grade) dried over Molecular Sieves was mixed with solvent-free n-BuLi before use. The monomer was then distilled in vacuo to a reaction vessel.

Isoprene. The monomer (Phillips, polymerization grade) dried over Molecular Sieves was transferred onto lithium aluminum hydride, from where it was redistilled under high vacuum before use.

2,3-Dimethylbutdiene. This was synthesized by dehydration of pinacol.[5)] The monomer purified by fractional distillation was stored over lithium aluminum hydride. Before use, it was distilled on the vacuum line.

THF. The solvent was first refluxed over sodium and then over lithium aluminum hydride. This was then distilled onto benzophenone and Na-K alloy to form the blue solution, from which the solvent was distilled on the vacuum system just before use.

Benzene. To the solvent purified in the usual manner, n-BuLi in benzene was added and then the solvent was distilled in vacuo.

n-BuLi. According to the method of Ziegler,[6)] n-BuLi was prepared from n-butyl-chloride and metallic lithium in n-heptane.

n-Butyl Alcohol. A small amount of Na-K alloy was added to the alcohol (spectro grade) under dry nitrogen. The alcohol containing butoxides was then transferred on the vacuum system to a glass ampoule to prepare a standard n-butyl alcohol solution in n-heptane. The solution was used for the colorimetric titration of the colored carbanion solution.

Polymerization. Under the atomphere of dry nitrogen trans-stilbene was placed in a glass ampoule which had been dried by flaming in vacuo, and then the monomer was dried under high vacuum. To the ampoule, a comonomer solution prepared on the vacuum system was added with a hypodermic syringe. n-BuLi was added drpowise until a red color due to a stilbenyl anion was stable; usually ca. 0.04-0.05 mmol of n-BuLi was required. Then an additional n-BuLi was added as an effective initiator. In the case of the reaction in benzene, a yellow color of the anion appeared very slowly. Therefore, the same amount of n-BuLi as that needed in the reaction in THF was added. When the polymerization was terminated, the concentration of the carbanion present in the system was estimated by colorimetric titration with the standard n-butyl alcohol solution and then the reaction mixture was poured into methanol. The polymer precipitated in methanol was filtrated, washed with methanol, and weighed. On the other hand, the mother liquor and the washings of the polymer precipitation was combined and evaporated under reduced pressure to recover unchanged trans-stilbene.

NMR Spectrum. The spectrum of the polymer was taken on a JNM-4H-100 Spectrometer (Japan Electron Optics Laboratory Co. Ltd.) in carbon tetrachloride at 60°C by using tetramethylsilane as an internal standard.

UV Spectrum. The UV spectrum of the reaction solution was measured with a Hitachi 124 Spectrophotometer. The sample solution was prepared in the method as described in the polymerization procedure.

Molecular Weight. The molecular weight of the polymer reprecipitated from toluene-methanol was determined with a Mechrolab Vapor Pressure Osmometer, Model 301 A, using benzene as a solvent.

Viscosity. The solution viscosity of the polymer was measured in toluene at 30.0°C.

Results

Polymerization in THF. The copolymerizations of trans-stilbene (M_2) with butadiene (M_1), isoprene (M_1), and 2,3-dimethylbutadiene (M_1) were investigated at 0°C. The results are shown in Fig. 1. Since these copolymerizations gave alternating copolymers as will be stated later, the percentage of the consumption of the dienes is used as a measure of polymer yield. The order of the observed rate was butadiene>isoprene>2,3-dimethylbutadiene. In the copolymerizations using isoprene and 2,3-dimethylbutadiene as comonomers, the reactions stopped remaining unchanged M_1 monomers. The colors of all reaction mixtures were red in the initial stage, but it gradually turned purple; especially in the copolymerization with 2,3-dimethylbutadiene the change was remarkable. All the copolymers obtained were powder.

The copolymer composition was determined by gravimetry, as is shown in Table 1. The copolymer compositions were nearly unity regardless of the polymer yield. This means that all the copolymers were essentially alternating because the homopolymerizability of trans-stilbene is very poor.

The relationship between monomer composition and polymer yield was investigated in the copolymerizations with butadiene and 2,3-dimethylbutadiene at constant concentration of M_1 monomer.

The results are shown in Fig. 2 and Table 2. In the copolymerization of trans-stilbene and 2,3-dimethylbutadiene, the consumption of the M_1 monomer decreased with an increase in the $[M_2]_0/[M_1]_0$ ratio. With butadiene, the monomer was completely consumed, but the copolymer composition, $[m_1]/[m_2]$, decreased as the $[M_1]_0/[M_2]_0$ decreased. These results indicate that trans-stilbene related to a termination reaction, and that when large excess of trans-stilbene was used, stilbene-stilbene unit must have been formed in the copolymer but would be two at longest.

The effect of initiator concentration on the polymer yield was studied. Fig. 3 shows the results in the copolymerizations with isoprene and 2,3-dimethylbutadiene, in which the reaction time was so long that all the reactions were completed. At low initiator concentration the dienes remained unchanged, but the polymer yield increased with the concentration of n-BuLi.

The molecular weights of the copolymers of trans-stilbene and isoprene which were obtained in the above copolymerizations were almost constant regardless of the initiator concentration, as is shown in Table 3.

The color change of the reaction mixtures was followed spectrophotometrically. The spectra are shown in Fig. 4. The reaction mixtures showed no peak near 540 mμ at the initial stage of the reaction, but new peak appeared at 540 mμ in time. The order of the optical density was 2,3-dimethylbutadiene>isoprene>butadiene after a prolonged reaction time. A pe k was clearly observed at 340 mμ in the copolymerization of trans-stilbene and butadiene, indicating that trans-stilbene was almost completely consumed and a benzyl type anion remained the system. The purple solution formed in the copolymerization employing isoprene and 2,3-dimethylbutadiene as comonomers could not initiated the polymerizations of these monomers and even butadiene.

The microstructures of the dienes in the alternating copolymers and homopolymers were investigated by NMR spectroscopy. The results are summarized in Table 4. The alternating copolymer of trans-stilbene and isoprene showed a very weak absorption due to a vinyl group at 910 cm^{-1} and a rather strong absorption due to a terminal methylene group at 890 cm^{-1}. Therefore, it can be assumed that this copolymer had no 1,2-structure. In all cases, the 1,4-content was higher in the alternating copolymers than in the corresponding homopolymers. The order of the 1,4-content of the dienes was 2,3-dimethylbutadiene>isoprene>butadiene.

Polymerization in Benzene. The copolymerizations of trans-stilbene and the dienes were carried out in benzene at 40°C. The results are shown in Table 5. Although all the dienes were completely consumed, trans-stilbene was little incorporated into the copolymers, except in the copolymerization with 2,3-dimethylbutadiene. The copolymer of trans-stilbene and 2,3-dimethylbutadiene was solid, but the others were viscous liquid.

Discussion

Since the copolymerizations in THF proceeded alternatingly to give the copolymers, $\sim M_1M_2M_1M_2\sim$, we may regared these copolymerizations as homopolymerizations of M_1M_2 or M_2M_1 unit in the kinetic treatment. The first order plots taken for the results in Fig. 1 are shown in Fig. 5. A linear relationship was obtained in the copolymerization of trans-stilbene and butadiene, suggesting that there was no termination reaction which was caused by the transformation of an active chain end to an inactive anion. If the addition reaction of a trans-stilbenyl anion to butadiene is the rate determing step, the rate constant, k_{21}, will be 1.0 l/mol sec. This value seems to be correct because k_{12} should be greater than the k_{11}= 0.59 l/mol sec obtained in the homopolymerization of butadiene in THF by n-BuLi at 0°C.7) The value is greater than k_{21} = 0.27 l/mol sec found in the copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2) carried out under similar reaction conditions,8) but smaller than k_{21} = 32.7 l/mol sec observed in the addition reaction of styryl anion to butadiene (M_1).9) This suggests that 1,1-diphenylethylenyl anion is very stable owing to the conjugation of two benzene rings, and the addition of stilbenyl anion is more sterically hindered than that of styryl anion.

On the other hand, a concave relationship between log $[M_1]/[M_1]_0$ and time was found in the copolymerization of trans-stilbene and 2,3-dimethylbutadiene (Fig. 5). These results indicate that, in the copolymerization with 2,3-dimethylbutadiene, the termination reaction caused by the formation of inactive anion is very important, while less important in the copolymerization with butadiene.

In the reaction of trans-stilbene with n-BuLi in THF,3) we found that α-proton of trans-stilbene was abstracted by a carbanion to give a stilbene anion, $C_6H_5-CH=\bar{C}-C_6H_5$, which then reacted with trans-stilbene to form a stable carbanion, C_6H_5-CH=C(C_6H_5)-$\bar{C}$H-C_6H_5. The stable triphenylpropene anion showed an absorption maximum at 555 mμ and could not initiated the polymerizations of the dienes used in this work. The change of the color of the reaction mixture also suggest the presence of this termination in the copolymerization. The electronic spectra show that the order of the frequency of the occurrence of the termination was 2,3-dimethylbutadiene>isoprene>butadiene, and in the copolymerization with the last comonomer the termination was less important.

If this termination oocures, the final yield will increase with an increase in the concentration of the initiator and the molecular weight of the polymer will be constant regardless of the yield. The results in Fig. 3 and Table 3 support the above consideration.

From the results of the copolymerizations of the dienes (M_1) and trans-stilbene (M_2), the monomer reactivity ratios, r_1, could be derived.1) The values are collected in Table 6. Great differences in the reactivities are found in the copolymerizations in THF and in benzene. Isoprene and butadiene had greater reactivity in benzene than in THF, but 2,3-dimethylbutadiene had rather similar reactivity in THF and benzene. These results are quite in accord with those found in the copolymerization of 1,1-diphenylethylene and the dienes,1) where detailed discussions had been done.

The microstructures of dienes must be controlled mainly by steric factor (Table 4). Although in the homopolymers 1,2- and

3,4-structures were rather favored, in the alternating copolymer 1,4-structure came more important. This may be caused by larger steric hindrances of 1,2- and 3,4-structures in the copolymers than those in the homopolymers. It is obvious that 2,3-dimethylbutadiene has the largest steric hindrance in the dienes. The higher content of 1,4-structure of the dienes were found in the copolymerizations of 1,1-diphenylethylene and the dienes used here.8) This also suggests the importance of steric factor in the copolymer with 1,1-diphenylethylene which has also a large steric hindrance in the reaction.

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Table 1. Anionic copolymerization of trans-stilbene (M_2) and dienes (M_1) by n-BuLi in THF—— Copolymer composition

THF = 15 ml, temp. = 0°C

M_1 [a)	M_1 g	M_2 g	$[M_1]_0/[M_2]_0$ mol/mol	Polymer g	Recovered M_2, g	Copolymer composition m_1, mmol	m_2, mmol
Bd	0.293	1.000	0.977	0.200	0.848	0.89	0.85
Bd	0.293	1.000	0.977	0.791	0.378	3.14	3.45
Bd	0.293	1.000	0.977	1.198	0.075	5.05	5.14
Isp	0.375	0.935	1.057	0.723	0.410	2.91	2.91
Isp	0.375	0.935	1.057	0.964	0.235	3.89	3.89
Isp	0.375	0.935	1.057	1.247	0.032	5.06	5.03
DMB	0.325	0.798	0.893	0.164	0.689	0.73	0.61
DMB	0.325	0.798	0.893	0.358	0.534	1.15	1.46
DMB	0.325	0.798	0.893	0.494	0.453	1.82	1.91

a) Bd = Butadiene; Isp = Isoprene; DMB = 2,3-Dimethylbutadiene.

Table 2. Anionic copolymerization of butadiene (M_1) and trans-stilbene (M_2) by n-BuLi in THF—— Relationship between monomer composition and polymer yield

M_1 = 0.276 (5.10 mmol), THF = 15 ml, n-BuLi = 0.04 mmol, temp. = 0°C
time = 24 hr

M_2 g	$[M_1]_0/[M_2]_0$ mol/mol	Polymer g	Recovered M_2, g	Copolymer composition m_1, mmol	m_2, mmol
0.850	1.08	1.098	0.020	4.58	4.66
1.000	0.92	1.241	0.035	5.10	5.36
1.200	0.76	1.312	0.162	5.10	5.77
1.350	0.68	1.354	0.266	5.00	6.02
1.600	0.57	1.410	0.463	5.05	6.44

Table 3. Anionic copolymerization of isoprene (M_1) and trans-stilbene (M_2) by n-BuLi in THF—— Molecular weight of the copolymer

$[M_1]_0$ = 5.20 mmol, $[M_2]_0$ = 5.03 mmol, THF = 15 ml, temp. = 0°C, time = 40 hr

n-BuLi mmol	Yield %	$\eta_{sp}/C^{a)}$ dl/g	Molecular weight
0.018	9.3	0.13	9000
0.029	23.2	0.15	7300
0.058	72.6	0.16	6000
0.167	94.0	0.14	9600

a) Toluene solution at 30.0°C.

Table 4. Microstructure of the dienes in the alternating copolymers and in the homopolymers$^{a)}$

Diene	Alternating copolymer, %			Homopolymer, %		
	1,2-	1,4-	3,4-	1,2-	1,4-	3,4-
Butadiene	12	88	-	81	19	-
Isoprene	0	90	10	17	22	61
2,3-Dimethyl-butadiene	0	100	-	49	51	-

a) Solvent = THF, initiator = n-BuLi.

Table 5. Anionic copolymerization of trans-stilbene (M_2) and dienes (M_1) by n-BuLi in benzene

Benzene = 15 ml, n-BuLi = 0.07-0.10 mmol, temp. = 40°C, time = 5-7 day

M_1 a)	M_1 g	M_2 g	$[M_1]_0/[M_2]_0$ mol/mol	Polymer g	Recovered M_2, g	Copolymer composition $[m_1]$,mmol	$[m_2]$,mmol
Bd	0.275	1.000	0.92	0.290	0.980	5.10	0.11
Bd	0.275	1.500	0.61	0.270	1.496	5.10	0.02
Bd	0.275	2.000	0.46	0.290	1.985	5.10	0.08
Isp	0.350	1.000	0.92	0.354	1.000	5.10	0.02
Isp	0.350	1.500	0.61	0.353	1.503	5.10	0.02
Isp	0.350	2.000	0.46	0.373	1.990	5.10	0.13
DMB	0.441	1.000	0.97	0.690	0.760	5.36	1.33
DMB	0.441	1.250	0.77	0.730	0.972	5.36	1.54
DMB	0.441	1.500	0.64	0.782	1.162	5.36	1.86

a) Bd = Butadiehe: Lsp = Isoprene; DMB = 2,3-Dimethylbutadiene.

Table 6. Anionic copolymerization of trans-stilbene with dienes by n-BuLi—— Monomer reactivity ratio, r_1

Diene	THF a)	Benzene b)
Butadiene	0	>50
Isoprene	0	>50
2,3-Dimethyl-butadiene	0	8.5

a) At 0°C. b) At 40°C.

Table 7. Microstructures of the dienes in the homopolymers and the alternating copolymers obtained in the polymerization by n-BuLi in THF

Diene	Homopolymer, %			Alternating copolymer, %		
	1,2-	1,4-	3,4-	1,2-	1,4-	3,4-
Butadiene	82	18	-	30	70	-
Isoprene	17	22	61	0	83	17
2,3-Dimethyl-butadiene	49	51	-	0	100	-

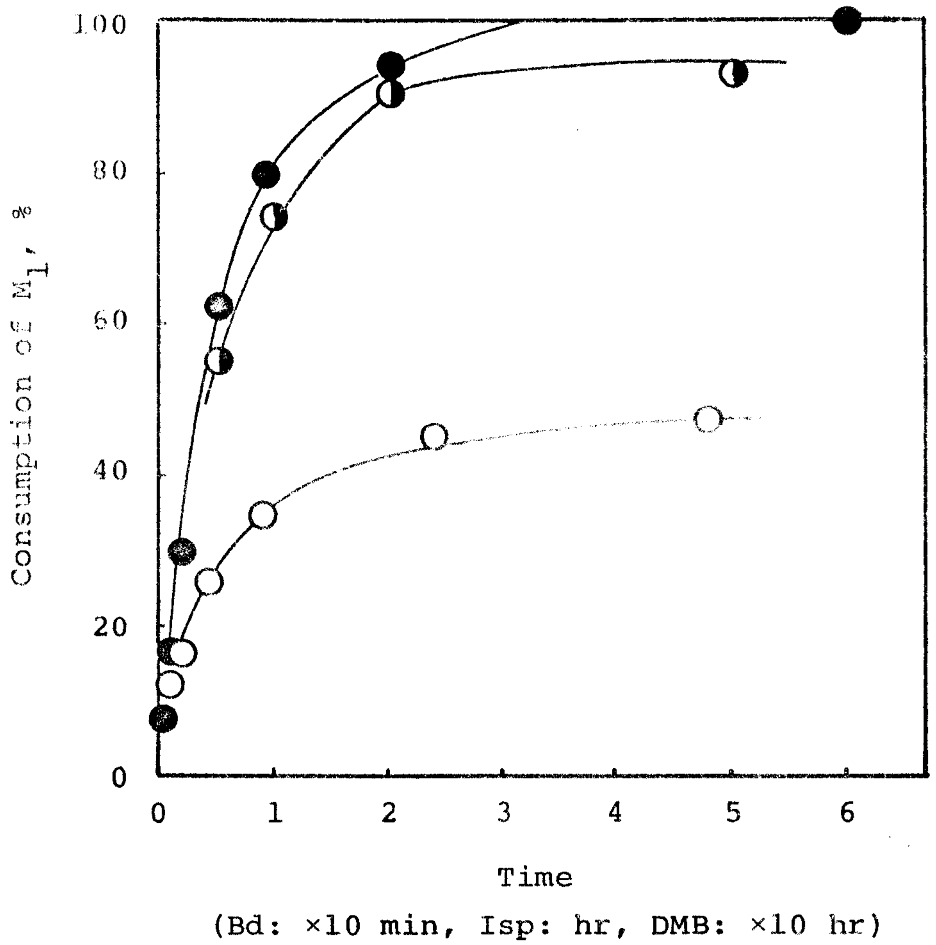

Fig. 1. Anionic copolymerizations of trans-stilbene (M_2) and dienes (M_1) by n-BuLi in THF —— Time vs. polymer yield.

●: Bd = 5.42 mmol, $[M_2]_0$ = 5.55 mmol, [n-BuLi] = 0.047 mmol.

◑: Isp = 5.60 mmol, $[M_2]_0$ = 5.30 mmol, [n-BuLi] = 0.056 mmol.

○: DMB = 3.96 mmol, $[M_2]_0$ = 4.44 mmol, [n-BuLi] = 0.040 mmol.

THF = 15 ml, Temp. = 0°C.

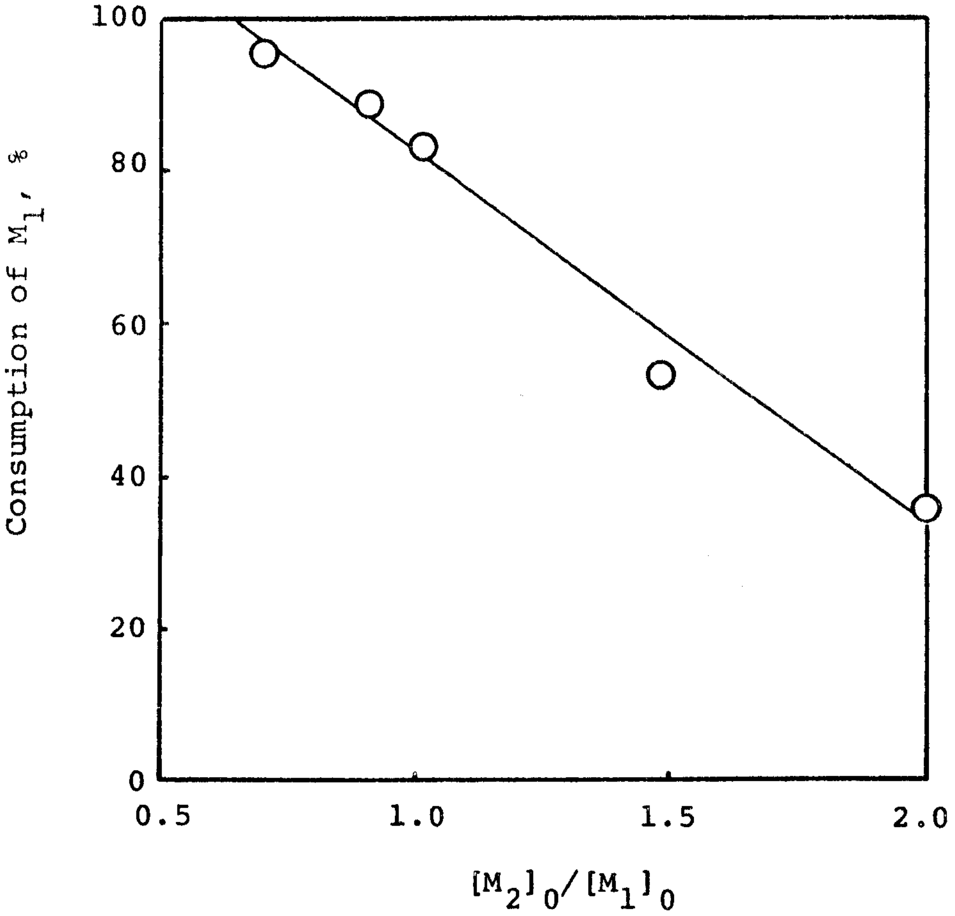

Fig. 2. Anionic copolymerization of 2,3-dimethylbutadiene (M_1) and trans-stilbene (M_2) by n-BuLi in THF —— Relationship between monomer composition and polymer yield.

$[M_1]_0$ = 3.96 mmol, THF = 15 ml, n-BuLi = 0.058 mm01
Temp. = 0°C, Time = 62 hr.

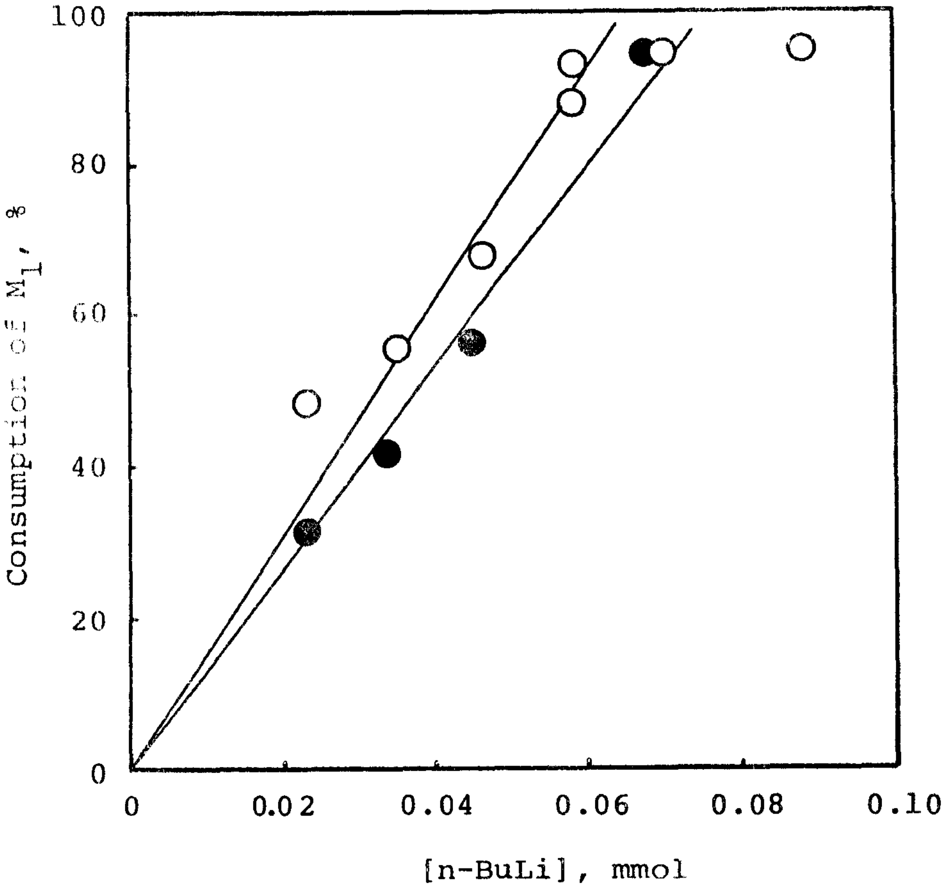

Fig. 3. Anionic copolymerizations of trans-stilbene (M_2) and dienes (M_1) by n-BuLi in THF.

○: Isp = 5.22 mmol, $[M_2]_0$ = 5.02 mmol, time = 40 hr.

●: DMB = 4.42 mmol, $[M_2]_0$ = 4.87 mmol, time = 68 hr.

THF = 15 ml, Temp. = 0°C.

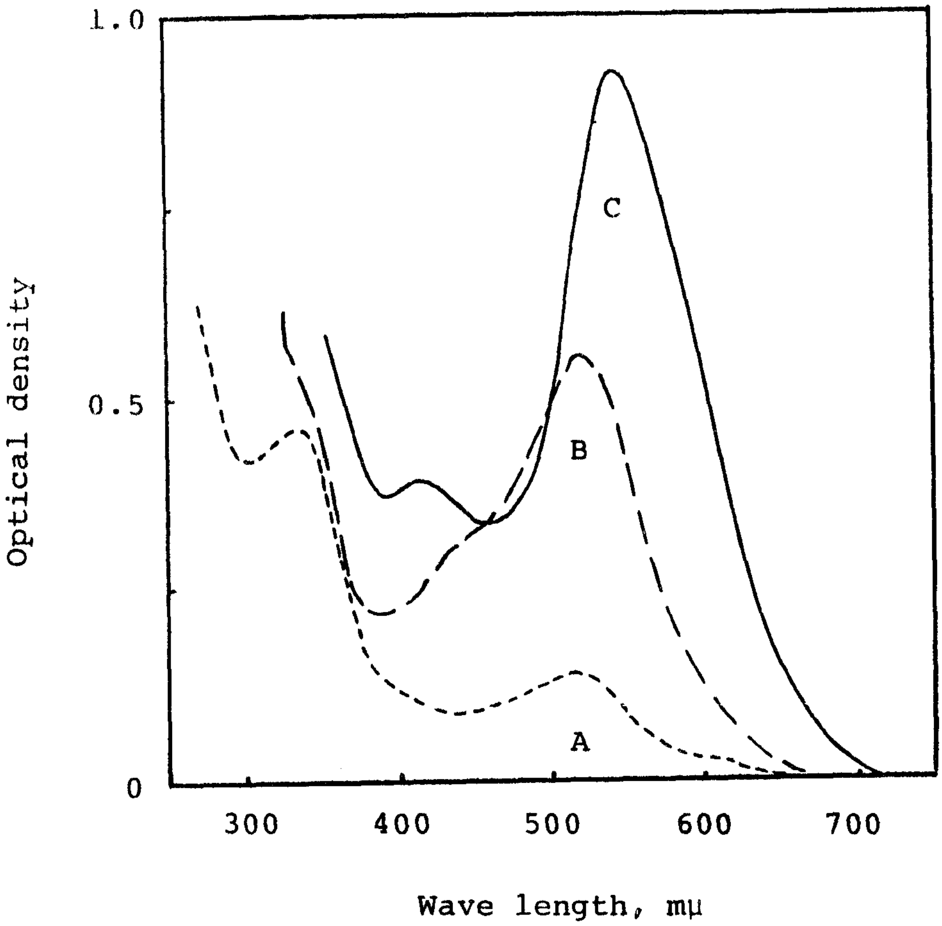

Fig. 4. Anionic copolymerizations of dienes (M_1) and trans-stilbene (M_2) by n-BuLi in THF —— Electronic spectra of reaction mixtures.

A: Bd = 5.42 mmol, n-BuLi = 0.040 mmol

B: Isp = 5.33 mmol, n-BuLi = 0.045 mmol

C: DMB = 5.37 mmol, n-BuLi = 0.055 mmol

$[M_2]_0$ = 5.55 mmol, THF = 15 ml, Temp. = 0°C.

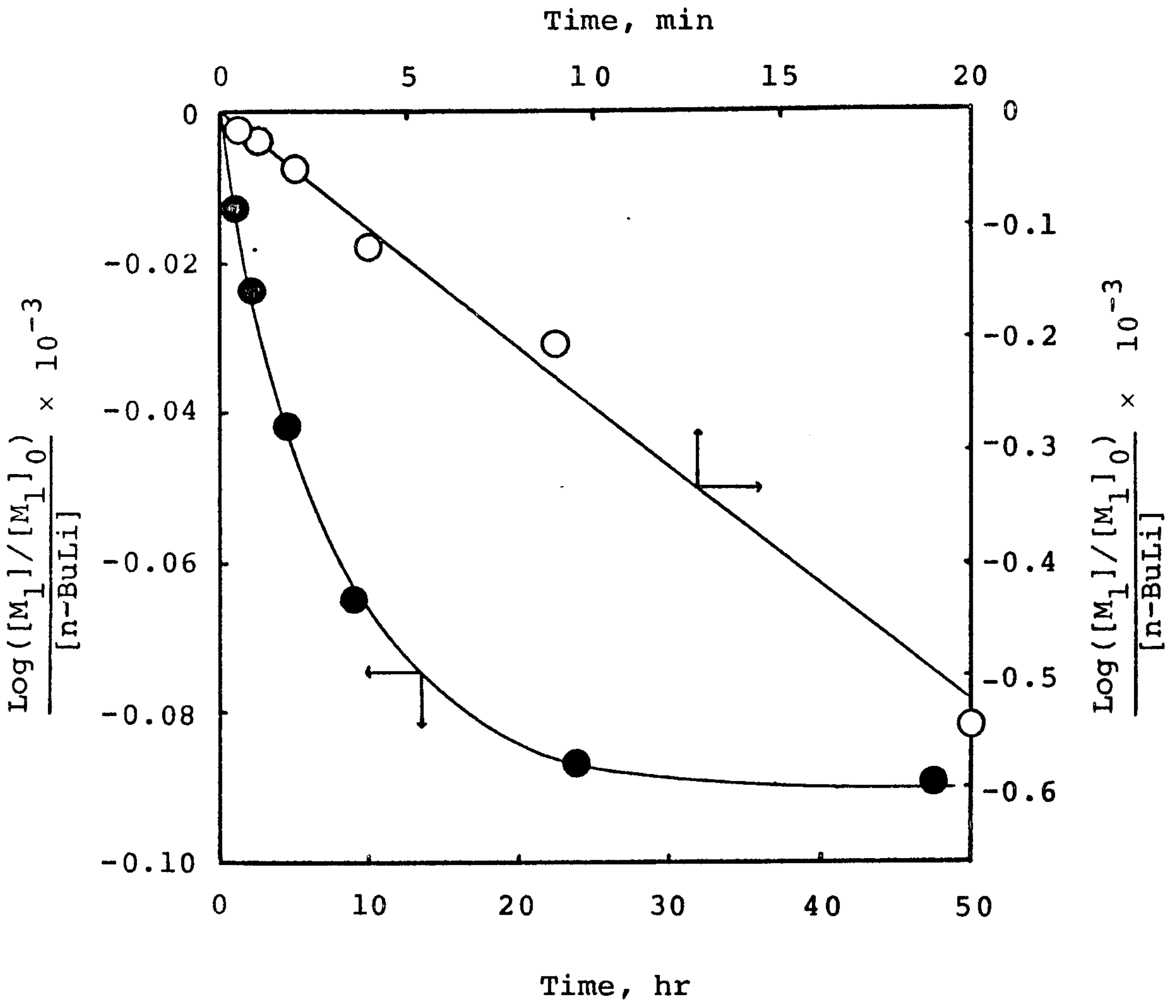

Fig. 5. Anionic copolymerizations of trans-stilbene (M_2) and dienes (M_1) —— First order plots.

○: M_1 = Butadiene, ●: M_1 = 2,3-Dimethylbutadiene. Reaction conditions are shown in Fig. 1.

Summary

The monomer reacitivity ratios, r_1, obtained in the present study are summarized in Tables 1 and 2. From these tables, the following facts may be pointed out.

1) In THF the r_1 value was *not* affected by the initiator, and the alternating copolymer was formed when $[M_2]_0 > [M_1]_0$.

2) In hydrocarbon the order of the r_1 value was Li>Na>K.

3) Butadiene, isoprene, and *o*-methoxystyrene were more reactive in hydrocarbon than in THF, when n-BuLi was employed as an initiaor. However, when Na or K was used, the reactivities were similar in both THF and hydrocarbon.

4) Little effect of the solvent on the r_1 value was found in the copolymerizations in which 2,3-dimethylbutadiene, styrene, and *p*-methoxystyrene were used as comonomers M_1.

5) With Li-initiator, the r_1 values derived in THF were smaller than those in hydrocarbon.

6) The order of the reactivity to styryl anion in both THF and hydrocarbon was 1,1-diphenylethylene>styrene>trans-stilbene.

7) The orders of the reactivities to isoprenyl and butadienyl anions were 1,1-diphenylethylene, trans-stilbene>dienes, in THF, and dienes>>1,1-diphenylethylene>trans-stilbene, in hydrocarbon with n-BuLi.

8) The orders of reactivities against 2,3-dimethylbutadienyl anion were 1,1-diphenylethylene, trans-stilbene>2,3-dimethylbutadiene, in THF, and 1,1-diphenylethylene>2,3-dimethylbutadiene>trans-stilbene, in hydrocarbon.

One of great differences between 1,1-diphenylethylene and trans-stilbene was that the copolymerizations employing 1,1-diphenylethylene were living polymerization, while in those employing trans-stilbene, termination and transfer reactions to to the monomer occurred.

The rate constants, k_{21}, measured in this study are collected in Table 3 togather with those reported by other researchers.[1-4] These results show that the orders of the homopolymerization rates of the dienes and of the addition rates against styryl and 1,1-diphenylethylenyl anions were butadiene>isoprene>2,3-dimethylbutadiene.

The dienes in the alternating copolymers had more content of 1,4-structure than those in the corresponding homopolymers, and the 1,4-content decreased as follows: 2,3-dimethylbutadiene>isoprene>butadiene.

In the course of this study, the author not only obtained great deal of information on the relative reactivities of several monomers in the anionic copolymerization and discussed about them, but also prepared several new alternating copolymers by anionic mechanism.

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Table 1. Monomer reactivity ratio, r_1.

(M_2 = 1,1-Diphenylethylene)

M_1 a)	Solvent	Initiator	Temp.,°C	r_1
Bd	THF	n-BuLi	0	0.13
Bd	THF	Na-Naph.	0	0.09
Bd	THF	K-disp.	0	0.09
Bd	Benzene	n-BuLi	40	54
Bd	Benzene	Na-disp.	40	0.71
Bd	Benzene	K-disp.	40	0.10
Isp	THF	n-BuLi	0	0.11
Isp	THF	Na-Naph.	0	0.12
Isp	THF	K-disp.	0	0.11
Isp	Dioxane	n-BuLi	30	0.50
Isp	Benzene	n-BuLi	40	37
Isp	Benzene	Na-disp.	40	0.38
Isp	Benzene	K-disp.	40	0.05
Isp	n-Hexane	n-BuLi	40	29
DMB b)	THF	n-BuLi	22	~ 0
DMB	Benzene	n-BuLi	40	0.23
St	THF	n-BuLi	30	0.13
St	THF	Na-Naph.	30	0.14
St	Toluene	n-BuLi	30	0.44
o-MeOSt	THF	n-BuLi	0	~ 0
o-MeOSt	Benzene	n-BuLi	40	20
o-MeOSt	Toluene	n-BuLi	0	20
o-MeOSt	Toluene	n-BuLi	−30	28
p-MeOSt	THF	n-BuLi	0	~ 0
p-MeOSt	Benzene	n-BuLi	40	<0.3
p-MeOSt	Toluene	n-BuLi	0	<0.3

a) Bd: butadiene, Isp: isoprene, DMB: 2,3-dimethylbutadiene, *o*- and *p*-MeOSt: *o*- and *p*-methoxystyrene. b) Ref. 1.

Table 2, Monomer reactivity ratio, r_1.

(M_2 = trans-Stilbene)

M_1 [a]	Solvent	Initiator	Temp.,°C	r_1
Bd	THF	n-BuLi	0	0
Bd	Benzene	n-BuLi	40	>50
Isp	THF	n-BuLi	0	0
Isp	Benzene	n-BuLi	40	>50
DMB	THF	n-BuLi	0	0
DMB	Benzene	n-BuLi	40	8.5

a) Bd: butadiene, Isp: isoprene, DMB: 2,3-Dimethylbutadiene.

Table 3. Rate constant.

(Solvent = THF)

M_1	k_{11}, l/mol sec	k_{21}, l/mol sec M_2 = DPE [e]	 M_2 = Styrene
Bd	0.59 [a]	0.27 [b]	3.27×10 [d]
Isp	3.8×10^{-2} [a]	$2,6\times10^{-3}$ [b]	1.7×10 [d]
DMB	1.4×10^{-3} [c]	1.6×10^{-3} [c]	4.8×10^{-1} [d]

a) Li, 0°C, ref. 2,3. b) Li, 0°C, this work.
c) Li, 22°C, ref. 1. d) Na, 25°C, ref. 4.
e) 1,1-Diphenylethylene.

PUBLICATION LIST

Chapter 1. H. Yuki, J. Hotta, Y. Okamoto and S. Murahashi, Bull. Chem. Soc., Japan, 40, 2659 (1967).

Chapter 2. H. Yuki, Y. Okamoto and K. Sadamoto, Bull. Chem. Soc., Japan, in press.

Chapter 3. H. Yuki and Y. Okamoto, Bull. Chem. Soc., Japan, in press.

Chapter 4. H. Yuki and Y. Okamoto, to be published.

Chapter 5. H. Yuki, Y. Okamoto, Y. Kuwae and K. Hatada, J. Polymer Sci. A-1, in press.

Chapter 6. H. Yuki and Y. Okamoto, to be published.

Chapter 7. H. Yuki, M. Kato and Y. Okamoto, Bull. Chem. Soc., Japan, 41, 1940 (1968).

Chapter 8. Y. Okamoto, M. Kato and H. Yuki, Bull. Chem. Soc., Japan, in press.

Chapter 9. H. Yuki, K. tsubota and Y. Okamoto, to be published.

Other publications not included in this thesis

1. Anionic Polymerization of trans-β-Methylstyrene. Y. Okamoto, H. Yuki and S. Murahashi, Bull. Chem. Soc., Japan 41, 197 (1968).
2. Reaction of Allylbenzene with n-Butyllthium in Tetrahydrofuran. Y. Okamoto and H. Yuki, Bull. Chem. Soc., Japan, 41, 677 (1968).