

Polymerization Mechanism in Methyl Methacrylate—9-Fluorenyllithium Initiator System

Yoshio INOUE, Riichirô CHÛJÔ and Atsuo NISHIOKA

Department of Polymer Engineering, Tokyo Institute of Technology, 12-1 Ookayama 2-Chome, Meguro-ku, Tokyo, 152, Japan.

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ABSTRACT: It is confirmed from NMR data on the polymers and the initiator that there are two distinct propagation mechanisms of stereospecific polymerization in the methyl methacrylate—9-fluorenyllithium initiator system.

Various kinds of tactic poly(methyl methacrylate) were prepared by the use of 9-fluorenyllithium under various compositions of the mixed solvents of toluene—THF and at different polymerization temperatures. Their microtacticities estimated from high resolution nuclear magnetic resonance (NMR) spectroscopy were analysed with the aid of the testing formulae for ultimate and penultimate unit effects in propagation step. From these analyses it was found that the microtacticities were remarkably dependent on the composition of solvents and on temperatures. The dependence on the composition of the solvents appearing in the plots of the testing formulae have been interpreted reasonably well by the introduction of two kinds of propagation mechanisms.

NMR spectra of 9-fluorenyllithium and -sodium were also measured. Chemical shifts of protons in these salts varied with the composition of solvents and temperatures. This behavior has been interpreted in terms of two kinds of ion pairs, *i.e.*, solvent-separated ion pairs and contact ion pairs. This difference in the states of the catalyst must influence on the microtacticities of the polymer obtained. It is concluded that the two distinct propagation mechanisms in the stereospecific polymerization must have originated from the two different kinds of catalyst.

KEY WORDS Poly(Methyl Methacrylate) / Propagation Mechanism / 9-Fluorenyllithium / Penultimate Effect / Ultimate Effect / Stereoblock / Stereoblock / Stereocomplex / Solvent-Separated Ion Pair / Contact Ion Pair /

Fox, *et al.*,¹ first reported on the stereospecific polymerization of methyl methacrylate (MMA) using organometallic catalysts. The conditions for obtaining isotactic, syndiotactic, and stereoblock fractions with highly steric purity have become well known through this and other works.²⁻⁵ They obtained three types of poly(methyl methacrylate) (PMMA) from 9-fluorenyllithium initiated polymerization, *i.e.*, syndiotactic PMMA in 1,2-dimethoxyethane at -60°C , isotactic PMMA in toluene at -60°C , stereoblock PMMA in toluene involving a small amount of dioxane at -70°C . They thought that the species of propagating end are free ions in 1,2-dimethoxyethane and ion pairs in toluene. Similar dependence of the microtacticity of the polymer on the solvent has been

reported in isoprene—*n*-butyllithium system,⁶ and in MMA—*n*-butyllithium system.⁷

The phenomenon of stereoblock formation in the polymerization of MMA is hardly acceptable if there is only one kind of active species of catalyst. A possible mechanism of stereoblock formation has been proposed by Coleman and Fox⁸ by the introduction of the concept of anionic polymerization of MMA with two-state mechanism.

On the other hand, Liquori and his co-workers,^{9,10} recently reported the formation of a 2:1 complex of isotactic and syndiotactic PMMA in polar solvent. This complex structure was called a stereocomplex. It was proposed that the stereoblock PMMA could be a stereocomplex between isotactic and syndiotactic

PMMA.

One of the aims of this paper is to clarify the relationship between the polymerization conditions and the microtacticity of PMMA, and to ascertain the possibility of the stereocomplex formation. For this purpose, PMMA's with various tacticities were therefore prepared using 9-fluorenyllithium at various compositions of toluene-THF solvent mixtures and polymerization temperatures. The propagation mechanisms in these stereospecific polymerizations will be discussed by applying the testing formulae for ultimate and penultimate unit effects in the propagation step developed by Chûjô,¹¹ to the data on the microtacticity obtained by NMR. By the use of the Δ and Γ formulae,¹² we can ascertain graphically whether the polymers are stereoblock or not. The physical meaning of the Δ - Γ relation will be shown in a later section.

Another aim is to find out the ionic state of the catalyst, 9-fluorenylcarbanion, and to establish the effect of the catalyst on the polymerization mechanism. For this purpose, the NMR spectra of 9-fluorenyl salts were measured in various compositions of the mixed solvents and at various temperatures. As pointed out by Fox, *et al.*, carbanionic ion pairs exist in more than two different types in a polymerization medium.

At the present time we are unable to ascertain whether each ionic state of the catalyst-solvent system is the same as that at the propagating end in the polymerization medium. However, it may be possible to deduce the ionic state of the propagating end from that of the catalyst.

Finally, the relation between the propagation mechanism and ionic state of the catalyst will be discussed.

EXPERIMENTAL

Material

Methyl methacrylate was purified by washing several times with a 60-% aqueous solution of sodium bisulphite, followed with a 10-% aqueous solution of sodium hydroxide, and then repeated washing with water. It was distilled under vacuum into ampoules after being thoroughly dried over CaH₂.

Fluorene obtained from the Tokyo Kasei Co. was purified by repeated recrystallization from ethyl alcohol and *n*-hexane solution.

Toluene was distilled under vacuum after being thoroughly dried over CaH₂.

Tetrahydrofuran (THF) was refluxed over sodium and distilled on to fresh sodium. A small amount of benzophenone was added to form the benzophenone dianion.

MMA and the solvents used in this experiment were distilled under vacuum into ampoules, using an all-glass apparatus equipped with a breakseal.

The fluorenyl salts (lithium or sodium) were prepared by stirring the THF solutions of fluorene on freshly cut metallic lithium or sodium mirror under vacuum.¹³

The solutions of the salts in other solvents were prepared from the corresponding THF solutions by removing the THF under vacuum and distilling the appropriate solvents on to the dry salt. Since complete removal of THF by this procedure was difficult, a small amount of THF still remained in the fluorenyl salts.

Polymerization

Polymerization was carried out under vacuum. MMA (3 g) was polymerized in an anhydrous solvent (30 ml) with 9-fluorenyllithium (0.009 mol/l) as an initiator. The temperature of the reaction apparatus was maintained at an appropriately set temperature for an hour, and then methyl alcohol (2 ml) was added to terminate the reaction. The polymer was precipitated by pouring the solution into vigorously agitated methyl alcohol (500 ml). The swollen solid separated was dried and dissolved in toluene (50 ml), and the solution was filtered. The polymer was precipitated again by pouring the solution into methyl alcohol (500 ml), recovered and dried.

Measurement of NMR

Microtacticity of PMMA was determined from NMR spectra obtained with a JNM C-60H NMR spectrometer operated at 60MHz. Measurements were carried out at 120°C in nitromethane, the concentration of polymer being 10 wt/vol %.

NMR spectra for the fluorenyl salts were measured at various temperatures controlled by

Polymerization Mechanism in MMA—Fluorenyllithium

Table I. Results of 9-fluorenyllithium-initiated polymerization of methyl methacrylate in toluene—tetrahydrofuran mixtures

Run	%THF by volume	Temp, °C ^a	Tacticity ^b			Conditional probabilities	
			<i>I</i>	<i>H</i>	<i>S</i>	<i>P_{is}</i>	<i>P_{si}</i>
A-1	100	-72.5	0.013	0.253	0.734	0.883	0.147
A-2		-57	0.023	0.296	0.681	0.862	0.178
A-3		-41.8	0.032	0.319	0.649	0.834	0.197
A-4		-25.5	0.041	0.358	0.601	0.810	0.230
B-1	80	-68	0.023	0.264	0.713	0.852	0.156
B-2		-51.5	0.041	0.315	0.644	0.794	0.197
B-3		-38	0.028	0.310	0.662	0.845	0.190
B-4		-23	0.035	0.341	0.624	0.827	0.215
C-1	50	-68	0.027	0.265	0.708	0.828	0.157
C-2		-50	0.026	0.300	0.674	0.850	0.182
C-3		-35	0.040	0.321	0.639	0.800	0.201
C-4		-24	0.044	0.318	0.638	0.781	0.199
D-1	20	-50	0.102	0.275	0.623	0.573	0.180
D-2		-34	0.195	0.262	0.543	0.402	0.195
D-3		-23	0.252	0.284	0.464	0.362	0.235
E-1	10	-71	0.120	0.226	0.654	0.488	0.147
E-2		-51	0.265	0.246	0.489	0.318	0.239
E-3		-36	0.263	0.285	0.452	0.353	0.240
E-4		-19.5	0.298	0.325	0.377	0.353	0.301
F-1	4	-71	0.416	0.211	0.373	0.203	0.221
F-2		-54	0.538	0.214	0.248	0.167	0.301
F-3		-39	0.543	0.230	0.227	0.175	0.336
F-4		-23	0.475	0.295	0.230	0.238	0.392
G-1	0.7	-71	0.760	0.160	0.080	0.096	0.500
G-2		-54	0.916	0.067	0.017	0.036	0.680
G-3		-37	0.921	0.061	0.018	0.033	0.644

^a Set temperature of polymerization.

^b Estimated from the peaks of α -methyl group of PMMA.

a low temperature probe, covering as wide a temperature range as possible, the concentration of the salts being 10 mol%.

RESULTS AND DISCUSSION

Microtacticity of PMMA

PMMA's were prepared in various compositions of mixed solvents of toluene—THF at various temperatures between -78 and -20°C examine the temperature dependence of their microtacticities. The microtacticity was determined from the intensities of the three finely resolved peaks assigned to the α -methyl groups in PMMA. The results of the polymerization are shown in Table I. It is obvious that the

microtacticity of the polymer depended upon the composition of the solvent used in polymerization. The polymers prepared in THF were highly syndiotactic, while those in THF—toluene (0,7/99.3) were highly isotactic. The isotacticities of the polymers increased with an increase in the fraction of toluene in the mixed solvent. The isotacticities increased slightly with an increase in temperature, though the degree of dependence of the overall tacticity on the polymerization temperature was not very clear.

Δ — Γ Plot

In order to learn whether the polymers are stereoblock or not, we used the Δ and Γ

formulae,¹² defined by

$$2\Delta = P_{ii} - P_{si} = P_{ss} - P_{is} \quad (1)$$

$$2\Gamma = P_{ii} + P_{si} = 2 - (P_{ss} + P_{is}) \quad (2)$$

where subscripts i and s for P denote isotactic and syndiotactic dyads, respectively, and P_{xy} 's ($x, y = i$ or s) are the conditional probabilities of y -addition following the x -ultimate dyad. The quantity P_{xy} can be readily calculated from the fraction of triads using the next relations,

$$I = iP_{ii}, \quad S = sP_{ss} \quad (3)$$

$$I + H + S = 1 \quad (4)$$

$$P_{ii} + P_{is} = 1, \quad P_{ss} + P_{si} = 1 \quad (5)$$

$$P_{is} = H/(2I + H) \quad (6)$$

$$P_{si} = H/(2S + H) \quad (7)$$

where I , H , and S are mole fractions of isotactic, heterotactic, and syndiotactic triads, respectively.

Now we must consider the physical meaning of the Δ - Γ plot. It is schematically shown in Figure 1. From the definition of Δ and Γ , each experimental value must fall within the square region surrounded by the solid lines. This region is further separated into four subregions, (I) to (IV), as shown by the broken lines. These are as follows: (I) $P_{is} > 0.5$ and

$P_{si} < 0.5$, which suggest that isotactic sequences tend to form alternative and syndiotactic ones to stereoblock; (II) $P_{is} < 0.5$, $P_{si} < 0.5$, both isotactic and syndiotactic ones to stereoblock; (III) $P_{is} < 0.5$, $P_{si} > 0.5$, isotactic ones to stereoblock and syndiotactic ones to alternative; (IV) $P_{is} > 0.5$, $P_{si} > 0.5$, both isotactic and syndiotactic to alternative. We can immediately distinguish whether the polymers are stereoblock or not from the information on the subregion where the point is located in the Δ - Γ plots of the data.

Our experimental data are plotted in Figure 1. The data for polymerization series A, B, and C fall in the subregion (I); those for D fall in (I) to (II); those for series E and F fall in (II), and those for series G fall in (II) to (III). From these plots, it is obvious that the propagation mechanism varies from that corresponding to the subregion (I) to (III) through (II) with the composition of the solvent. If the propagation mechanism obeys the symmetric single parameter model (Bernoulli trial) proposed by Bovey, *et al.*,¹⁴ the next relation must hold

$$P_{is} + P_{si} = 1 \quad (8)$$

From Table I eq 8 holds satisfactory for the polymerization series A, B, and C, while for series D, E, F, and G the data deviates considerably from the equation. These facts show that the polymerization mechanisms in the A, B, and C series can be specified by the Bernoulli trial but not in the case of the D, E, F, and G series.

Ultimate Unit Effects and Penultimate Unit Effects

From the Δ - Γ plots in last section, we can assume that there are at least two different propagation mechanisms in these polymerizations. We treated these mechanisms with expressions testing the reality of the ultimate and penultimate unit effects. Furukawa¹⁵ has derived an expression which evaluates the magnitude of ultimate unit effects in stereospecific polymerization as follows,

$$\Delta\epsilon_u = -kT \ln(I/S) \quad (9)$$

where $\Delta\epsilon_u$ is the contribution from the ultimate unit to the difference in activated free energy between isotactic and syndiotactic placements; k is the Boltzmann constant and T is the poly-

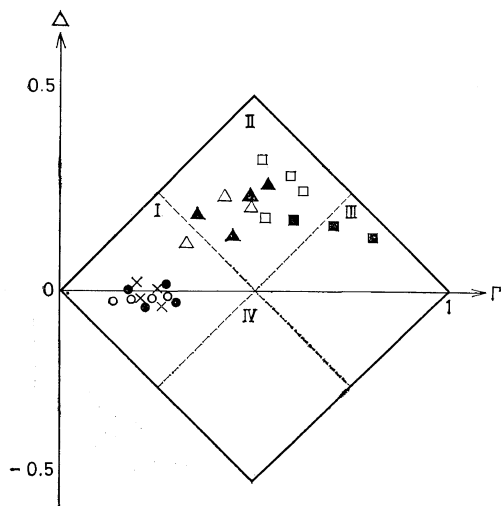


Figure 1. The Δ - Γ plots for PMMA. Symbols reveal the polymerization series as follows: \circ , A; \bullet , B; \times , C; \triangle , D; \blacktriangle , E; \square , F; \blacksquare , G.

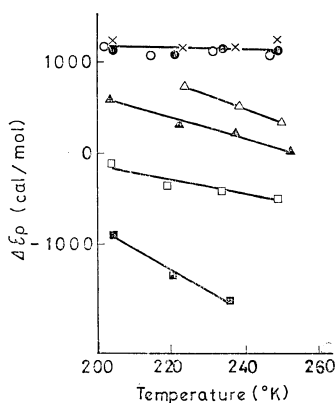


Figure 2. The plot of $\Delta\epsilon_u$ vs. T for PMMA. Symbols reveal the polymerization series as follows: \circ , A; \bullet , B; \times , C; \triangle , D; \blacktriangle , E; \square , F; \blacksquare , G.

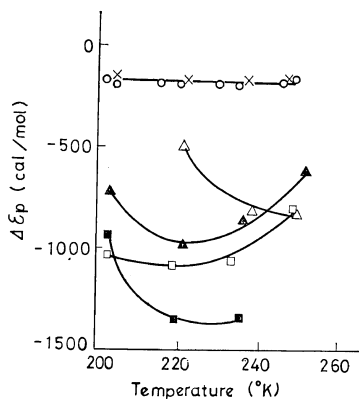


Figure 3. The plot of $\Delta\epsilon_p$ vs. T for PMMA. Symbols reveal the polymerization series as follows: \circ , A; \bullet , B; \times , C; \triangle , D; \blacktriangle , E; \square , F; \blacksquare , G.

merization temperature in Kelvin. $\Delta\epsilon_u$'s are plotted against T in Figure 2. From these plots, it is shown that all the polymerization series had ultimate unit effects, but two different tendencies clearly existed. In series A, B, and C, $\Delta\epsilon_u$'s were kept constant irrespective of temperature. On the other hand, in series D, E, F, and G, $\Delta\epsilon_u$'s were linearly dependent on the temperature.

Next, the contribution from the penultimate unit to the propagation mechanism is considered, with the aid of the following expression, to test the reality of such a contribution proposed by Chûjô,¹¹

$$\Delta\epsilon_p = -kT \ln(4IS/H^2) \quad (10)$$

where $\Delta\epsilon_p$ is the contribution from the penultimate unit to the difference in activated free energy between isotactic and syndiotactic placements. The quantities, $\Delta\epsilon_p$'s, are plotted against polymerization temperatures for our samples in Figure 3. Two different tendencies are apparent in the figure. In series A, B, and C, $\Delta\epsilon_p$'s were kept constant irrespective of temperature and their values almost vanished. This indicates there were little penultimate unit effects and thus the propagation mechanisms could be specified roughly by Bernoulli trial as described in the last section. However in series D, E, F, and G, $\Delta\epsilon_p$'s were rather complex functions of polymerization temperatures, so that polymerization mechanisms could not be specified by either Bernoullian or simple Markovian statistics. The features of these curves are similar and therefore, we cannot regard these tendencies as experimental errors. As to the causes of $\Delta\epsilon_p$ - T plots not being linear, we can point out the following two possibilities, (i) There are contributions to $\Delta\epsilon_p$'s from the units farther than the penultimate unit. (ii) There are more than two different propagation mechanisms in the stereospecific polymerization.

From the facts that the different tendencies between series A, B, and C, and series D, E, F, and G are seen both in Figure 1 and 2, cause (ii) may be reasonable. That is, in the polymerization medium of series A, B, and C, there is only one propagation mechanism, while in those of series D, E, F, and G, at least two propagation mechanisms coexist and existing ratios of each mechanism depend on the composition of the solvent and the polymerization temperatures.

NMR Spectra of Alkali Salts of Fluorene

As mentioned above, it is obvious that there were at least two different propagation mechanisms in the stereospecific polymerization. To clarify in detail the relation between the results of polymerization and the state of the catalyst, the change in the state of the catalyst was also investigated with the aid of the NMR spectra of the catalyst itself.

The NMR spectra of the fluorene and 9-fluo-

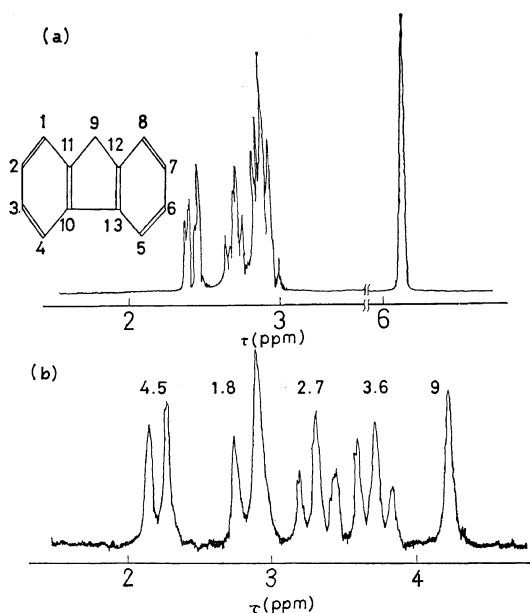


Figure 4. NMR spectra of (a) fluorene in tetrachloroethylene (at 30°C, 100MHz) and (b) 9-fluorenyllithium in THF (at 30°C, 60MHz). The values of chemical shifts is in reference to TMS.

renyllithium are depicted in Figure 4. In the spectrum of fluorene, the peaks with complex structure at the lower field were assigned to the aromatic ring protons, and the sharp peak at the higher field was assigned to the 9th proton. On the other hand, in the spectrum of 9-fluorenyllithium, the signals of aromatic ring protons were much simpler and first order analyses of the spectrum were possible. The assignment for every peak in the spectrum is also shown in Figure 4. The assignment was made due to the intensity and the spin-coupling patterns, but there are some ambiguities, between protons 2,7 and 3,6 and between protons 1,8 and 4,5. It must be noted that the signal of the 9th proton of fluorenyllithium shifts to lower field than that of fluorene. This large shift is due to the aromatic nature of the 9th carbon. From these assignments, the electron density distribution in aromatic rings could be estimated. It has been recognized that the proton resonance shift in aromatic molecules tends to reflect the π -electron density of the carbon atom to which the proton is bonded.¹⁶⁻¹⁹ There is a well known, simple

Table II. The chemical shifts of 9-fluorenyllithium (9-FILi) and 9-fluorenylsodium (9-FINa) in THF at 30°C, from benzene^a

	4, 5	1, 8	2, 7	3, 6	9
δ_{ppm} (9-FILi)	-0.615	-0.01	0.46	0.865	1.355
δ_{ppm} (9-FINa)	-0.775	-0.20	0.295	0.68	1.20

^a Positive values indicate higher field shifts.

linear correlation between the proton chemical shifts, δ , and the local excess charge, $\Delta\rho$, in aromatic systems, such as

$$\delta = c\Delta\rho \quad (11)$$

where the constant c is found empirically to have a value about 10 ppm/electron. The change in ionic state must appear in the proton chemical shifts in the NMR spectrum. The chemical shifts of fluorenyl salts from benzene in THF at 30°C were measured, and are shown in Table II.

Hogen-Esch, *et al.*,²⁰ have found direct evidence for the existence of two kinds of ion pairs, namely, a contact (or intimate) ion pair and a solvent-separated ion pair, from the absorption spectra. From their studies, it is thought that in THF at 25°C, fluorenyllithium exists predominantly as solvent-separated ion pairs whereas fluorenylsodium exists mainly as contact ion pairs.

If there is a solvent molecule between the counter cation and the anionic center, the effect of the cationic field on the carbanion must be reduced. Therefore, in the solvent separated fluorenyl carbanion and the lithium cation, more of the charge must reside in the carbanion.

Hence the protons will be more shielded in fluorenyllithium than in fluorenylsodium. The results of the NMR, shown in Table II, therefore support the results of the absorption spectra described above. However, we are unable, purely from the results of NMR spectra, to designate the ionic state directly, *i.e.*, whether it is solvent-separated ion pair, contact ion pair, or some other species.

Next, NMR spectra of fluorenyllithium were measured in mixed solvents comprising THF as a polar component and toluene as a non-polar one. No structural changes in spectra were observed. The changes in chemical shifts from benzene are shown in Figure 5. The

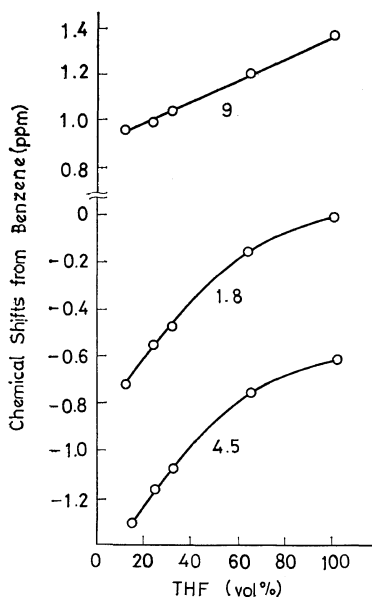


Figure 5. The plot of the chemical shifts of 9-fluorenyllithium from benzene vs. solvent composition. The numbers in the figure show the position of carbons in 9-fluorenyllithium.

data for the 2,3,6 and 7th protons are not shown, because their peaks were not clearly separated from the peak from toluene. The magnitude of lower field shifts of the peaks in 9-fluorenyllithium increased as the fraction of toluene increased (the concentration of the salt was kept constant). As to the causes of the lower shifts, two possibilities are assumed: (i) A decreasing fraction of solvent-separated ion pairs with an decrease in the fraction of THF and (ii) a paramagnetic anisotropic effect of solvent toluene. Ledaal²¹ considered that the solvent toluene is oriented to the aromatic solute in a study of the solvent effect on NMR spectra. The orientation is of such a form that the methyl group in toluene is perpendicular to the plane constituted by the aromatic carbons of the solute. He called this orientational form a "solvent—solute collision complex." If this complex model is accepted, 9-fluorenyllithium can take the state of contact ion pair easily due to the access between ions. Because toluene is in a state of hyperconjugation, the methyl group has a positive charge. Thus the counteranion lies more and more close

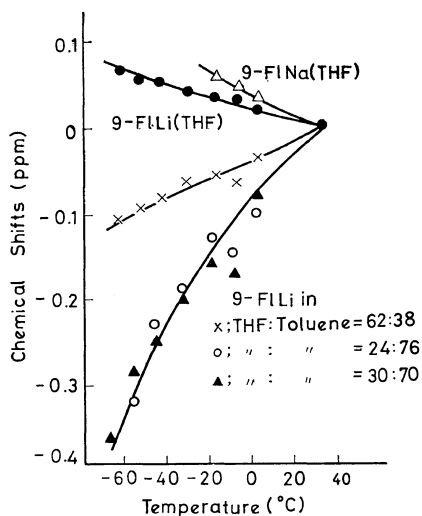


Figure 6. The plot of changes in the chemical shifts of the 9th proton in 9-fluorenyl salt vs. temperature. The value of the chemical shifts at 30°C is taken as a reference.

to the anionic center. Causes (i) and (ii) therefore are compatible.

Finally, the changes in chemical shifts from the peak assigned to benzene are plotted against temperatures, as shown in Figure 6. The values of the chemical shifts at 30°C were taken as a reference, that is, to be zero. In THF, both peaks due to 9-fluorenyllithium and 9-fluorenyl-sodium shift to a higher field with a decrease in temperature. On the other hand, in the mixtures of toluene and THF, they shift to a lower field with a decrease in temperature, and the magnitude of lower shifts become greater with an increase in toluene. From these shifts we believe that in THF the fraction of solvent-separated ion pairs increases, and in the mixed solvents the fraction of contact ion pairs increases with a decrease in temperature. However in the latter case, there is a considerable contribution to lowering the shift from the paramagnetic solvent effect. The contribution to the chemical shifts from the paramagnetic solvent effect and that from the charge density cannot be separately estimated. Recently, Cox²² reported on the effect of the cation on the NMR spectrum of fluorenyl carbanion, and arrived at a conclusion similar to ours.

Table III. Correspondence between the results of polymerization of PMMA and the ionic state of 9-fluorenyllithium

	Polarity of solvent		
	Polar	Intermediate	Weak or nonpolar
Ionic state of 9-fluorenyllithium	Dominant solvent-separated ion pair (increase with a decrease in temperature)	Coexistence of both ion pairs	Dominant contact ion pair
Polymerization of PMMA	Highly syndiotactic and increase in syndiotacticity with a decrease in temperature (Bernoullian)	Stereoblock (non-Bernoullian)	Highly isotactic

CONCLUSION

From the facts described above, it is concluded that there are at least two distinct propagation mechanisms in the stereospecific polymerization of MMA—9-fluorenyllithium system. The remarkable changes in the microtacticity, $\Delta\text{—}\Gamma$ plots, $\Delta\epsilon_u$, and $\Delta\epsilon_p$ of PMMA with changes in the solvent or temperature correspond to the changes in the state of 9-fluorenyllithium. It must be mentioned here that we have not investigated the ionic state of the catalyst under the existence of polar monomer, that is, MMA, because there is no way to investigate it directly. Nevertheless we proceeded with the discussion on the assumption of the similarity between the active species of the catalyst with and without the polar monomer.

The correspondence between the results of polymerization of PMMA and the ionic state of 9-fluorenyllithium is shown in Table III. From this it is concluded that the two different propagation mechanisms may originate from the two different types of catalyst, *i.e.*, solvent-separated ion pairs and contact (or intimate) ion pairs. However, we cannot conclude at present whether each of these ion pairs are maintained at the propagating end in the polymerization medium. Further, we cannot conclude whether these mechanisms are of the Coleman—Fox type,⁸ stereocomplex type,¹⁰ or some other unknown type. The existence of two kinds of propagation mechanism is one of the bases for Liquori's belief that stereoblock PMMA may be the stereocomplex formed through the polymerization. Because the so-called "stereocomplex" state does not always lead to a so-called "stereoblock" polymer, and since we have no information as to whether

isotactic and syndiotactic parts belong to the same or different chains, we will call the polymer examined in the paper "stereoblend."

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Polymerization Mechanism in MMA—Fluorenyllithium

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