Slow Growth Polymerization of Methyl Methacrylate in Toluene by Butyllithium

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ABSTRACT: In this paper, a new method of ionic polymerization is described and designated as "slow growth polymerization." An initiator solution was slowly added to a monomer solution to enable it to rest on top as a separate liquid phase and the polymerization was allowed to proceed without stirring. The initiation occurs at the interface between the solutions of initiator and monomer, and the polymerization proceeds from top to bottom. When methyl methacrylate was polymerized by this method, using butyllithium as initiator in toluene, the molecular weight and isotacticity of the polymer formed were much higher than those of the polymer obtained by the ordinary method. The mechanism for the increase in the isotacticity is discussed in some detail.

KEY WORDS   Anionic Polymerization without Stirring / Anionic Slow Growth Polymerization / Methyl Methacrylate / Butyllithium / 1,1-Diphenylhexyllithium / Lithium Methoxide / Isotactic Poly(methyl methacrylate)

In our previous communications,[1-3] we briefly reported on the polymerization and copolymerization of methyl methacrylate by the slow growth method. Slow growth polymerization is a special method for ionic polymerization, wherein the initiator solution is placed on the monomer solution so as to rest on top of it as a separate liquid phase and the polymerization is allowed to proceed without stirring (Figure 1). In this polymerization, the initiation occurs at the interface between the initiator and monomer solutions, and the polymerization reaction proceeds from top to bottom. By this method we can obtain polymers and copolymers of different tacticity, molecular weight or composition from those obtained by ordinary method. For instance, poly(methyl methacrylate) prepared by slow growth polymerization initiated by butyllithium had a higher isotacticity and molecular weight than the polymer obtained by the ordinary method.[1]

In this paper, slow growth polymerizations of undeuterated and perdeuterated methyl methacrylates by butyllithium were studied in detail in toluene and the number of the initiator fragments

in the polymer and oligomer chains was measured according to the method shown in a previous publication.[4] Diffusion of isotactic and syndiotactic oligomers of methyl methacrylate into the solution of an isotactic polymer was studied by using ^{1}H NMR spectroscopy. On the basis of these results, the
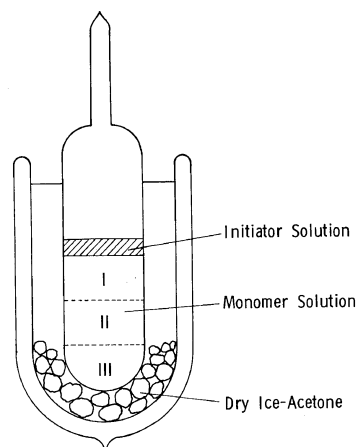

Figure 1. Slow growth polymerization.

mechanism of slow growth polymerization is discussed in some detail.

EXPERIMENTAL

Methyl methacrylate was purified by fractional distillation under nitrogen pressure. The monomer thus purified was distilled over calcium dihydride under high vacuum just before use.

Perdeuterated methyl methacrylate was prepared from acetone cyanohydrin-d_7 and methanol-d_4 according to the method of Crawford[5] and purified in the same way as undeuterated methyl methacrylate.

Toluene was dried by adding a small amount of a solution of butyllithium in toluene and was then distilled under high vacuum.

Butyllithium was prepared from 1-chlorobutane and metallic lithium in heptane.

1,1-Diphenylhexyllithium was synthesized by the reaction of equimolar amounts of butyllithium and 1,1-diphenylethylene in toluene.

Slow growth polymerization was carried out in the following way. The monomer solution was cooled to a desired polymerization temperature in the reaction vessel under nitrogen atmosphere and the initiator solution was slowly added on to the monomer solution as a separate liquid phase; and then, the polymerization was allowed to proceed without stirring. After a desired period, the polymerization vessel was cooled in liquid nitrogen and carefully broken. The reaction mass was sliced into three portions, and designated as I, II, and III from top to bottom. Each portion of the reaction mass was put into a large amount of methanol to precipitate the polymer formed. After standing overnight, the precipitated polymer was collected by filtration, washed with methanol and dried *in vacuo* at room temperature.

The concentration of butyllithium in the initiator layer of the slow growth polymerization was estimated in the following way by Fourier-transform NMR spectroscopy. The spectrometer used was JNM-FX100 (JEOL) and was operated at 100 MHz. An aliquot amount (0.11 ml) of 0.9 mol l^{-1} solution of methyl methacrylate in toluene-d_8 was put into a 5 mm NMR sample tube under nitrogen atmosphere and a 0.12 ml solution of butyllithium in heptane-d_{16} (1.2 mol l^{-1}) was carefully placed at $-78°C$ on the monomer solution as a separate liquid phase. The

sealed tube was immediately set in the probe of the spectrometer at $-78°C$ so that the butyllithium solution layer was located just at the centre of the irradiation coil. The Fourier-transform NMR spectra of the butyllithium solution were measured at $-78°C$ without spinning the sample tube, and the concentration of butyllithium was followed with time by the intensity measurement of the signal from the protons of methylene group adjacent to the lithium atom, which appeared 3.03 ppm upfield from the resonance of the remaining methyl protons in the solvent toluene-d_8.

In the polymerization of perdeuterated methyl methacrylate, the filtrate and the washings were combined and evaporated to dryness under reduced pressure. The residue was redissolved in benzene and a small amount of insoluble material was removed by filtration. The methanol-soluble oligomer was recovered from the benzene solution by freeze-drying technique. Polymerization was also done by the ordinary method in a glass ampoule under dry nitrogen. The polymer and oligomer were isolated in a way similar to that of the slow growth polymerization.

The isotactic polymer of methyl methacrylate with a deuterated methoxyl group was prepared in the polymerization in toluene by phenylmagnesium bromide at 0°C. The triad tacticity of the polymer is as follows: I, 96%; H, 4%; S, 0%. The monomer was obtained from methacryloyl chloride and perdeuterated methanol at room temperature in ether in the presence of triethylamine.

The isotactic ($M_n = 2657$, I, 85%; H, 8%; S, 7%) and syndiotactic ($M_n = 2576$, I, 3%; H, 10%; S, 87%) oligomers of methyl methacrylate were obtained as the methanol-soluble fractions of the products formed in the polymerizations of this monomer in toluene by phenylmagnesium bromide at 0°C and by bis(pentamethylenimino)-magnesium at $-78°C$, respectively.

The triad tacticity of poly(methyl methacrylate) was determined from the α-methyl proton resonances in the ^1H NMR spectrum measured in chloroform-d_1 at 55°C. The spectrum was taken on a JNM-MH-100 (JEOL) spectrometer at 100 MHz, using tetramethylsilane as the internal standard.

The diffusion of oligo(methyl methacrylate) through the solution of isotactic poly(methyl methacrylate) with a deuterated methoxy group in toluene was investigated by using a Fourier-

Table I. Slow growth polymerization of methyl methacrylate in toluene
by butyllithium at $-78°C$ for 24 h[a]

	Yield	Tacticity/%			$M_n \times 10^{-3}$	Li compd[c]
	%	I	H	S		mmol
I	19.5	84	11	5	29.3	0.48
II	9.9	82	11	7	35.2	0.01
III	23.3	83	11	6	52.1	0.01
O[b]	72	70	19	11	21.1	—

[a] Monomer, 10 mmol; butyllithium, 0.5 mmol; toluene, 10 ml.
[b] Polymerization by ordinary method.
[c] Amount of lithium compound contained in each layer after the polymerization.

transform NMR spectrum at 27°C. In a 5 mm NMR sample tube was placed a 0.29 ml solution of the poly(methyl methacrylate-d_3) in toluene-d_8 (0.05 g ml^{-1}), and on this a 0.1 ml solution of isotactic or syndiotactic oligo (methyl methacrylate) in a mixture of toluene and toluene-d_8 (0.05 g ml^{-1}) was carefully added. The tube was transferred to the probe of the NMR spectrometer so that the half-height position of the polymer solution was located at the center of the coil. The spectra of the polymer solution were measured without spinning the sample tube. The amount of the oligomer diffused into the polymer solution was determined by the intensity measurement of the signal of methoxy methyl protons in the oligomer. The degree of diffusion is represented by the proportion in percent of the intensity of the methoxy methyl resonance to that of the completely mixed solutions of oligomer and polymer in the tube.

The number-average molecular weights of polymer and oligomer were measured by a Hitachi 117 vapor-pressure osmometer in benzene at 42°C.

RESULTS AND DISCUSSION

Slow growth polymerization of methyl methacrylate was carried out in toluene at $-78°C$ by butyllithium for 24 h.* The results are shown in Table I together with the results of the polymerization by the ordinary method. The

* In our previous communication,[1] the polymerization was carried out for 429 h and the reaction mixture was sliced into four portions instead of three after the polymerization. However, the results were substantially the same as those obtained in this work.

isotacticity and the molecular weight of the polymer prepared by the slow growth method were much higher than those of the polymer obtained by the ordinary method. The molecular weight depended on the position in the reaction mixture, increasing from top to bottom.

The amount of lithium compound existing in each portion of the reaction mixture after the polymerization was determined by acid-titration using methyl orange as an indicator. The results indicate that the lithium compound originated from the initiator remained mostly in the upper portion even after the polymerization proceeded over 50% (Table I). The change in the concentration of butyllithium in the layer of the initiator solution was followed during the polymerization in an NMR sample tube by the Fourier-transform NMR method mentioned in the experimental section. The results

Table II. Concentration of remaining butyllithium in the layer of initiator solution in the course of the slow growth polymerization of methyl methacrylate in toluene at $-78°C$

Time	Concentration of butyllithium/%
h	
0	100
0.28	100
0.55	97
0.78	93
1.15	93
2.23	93
24.0	91

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Table III. Effect of polymerization time on the slow growth polymerization of methyl methacrylate by butyllithium in toluene at $-78°C$[a]

Polymerization time	Yield	$M_n \times 10^{-3}$	Amount of polymer chain $\times 10^3$/mmol	Tacticity/%		
h	%			I	H	S
1	1.6	18.7	0.9	74	17	9
2	3.6	23.2	1.5	76	16	8
4	16.9	43.1	3.9	83	12	5
24	23.3	52.1	4.5	83	11	6
168	32.7	73.5	4.5	85	11	4

[a] Monomer, 10 mmol; butyllithium, 0.5 mmol; toluene, 10 ml. The data are concerned with the polymer formed in the third portion (bottom) of the reaction mixture.

are given in Table II. Over 90% of the butyllithium used was found to exist unchanged in the layer even after 24 h, during which over a half of the monomer changed into the polymer. These facts indicate that only a small fraction of the added butyllithium was used for the initiation of methyl methacrylate, resulting in the formation of a polymer of higher molecular weight than that of the polymer prepared by the ordinary method.

The effect of the polymerization time is shown in Table III. The data in the Table are concerned with the polymers isolated from the third portions of the reaction masses, whose weights were almost the same. The yield and molecular weight of the polymer increased with increasing polymerization time. The amount in mmoles of the polymer molecule formed, calculated from the yield and the molecular weight of the polymer, also increased with increasing polymerization time, especially in the initial stage of the polymerization. The isotacticity of the polymer increased with an increase in the polymerization time. A similar tendency was also observed in ordinary polymerization.[6]

From the results mentioned above, the following conclusions can be drawn on the slow growth polymerization by butyllithium in toluene: The initiation occurs at the interface between the initiator and monomer solutions and the active species thus formed gradually diffuse from top to bottom, growing into the polymer chain of higher molecular weight. As a result of this, the molecular weight of the formed polymer increased from top to bottom. Though the apparent rate of the initiation is slow, it is continuous and the number of polymer chains in the reaction mixture increases during the polymerization.

One of the characteristic features of this slow growth polymerization is the formation of a polymer of higher isotacticity than that of the polymer prepared by ordinary polymerization. In order to clarify the mechanism for this increase in the isotacticity, the rate of diffusion of the isotactic or syndiotactic oligomer of methyl methacrylate into the solution of isotactic poly(methyl methacrylate) in toluene was measured by using the Fourier-transform NMR. This method was described in the experimental section and the results are shown in Figure 2. The isotactic oligomer slowly diffused through the solution of the isotactic polymer. The syndiotactic oligomer did not diffuse into the polymer solution, although the toluene molecules added to the oligomer solution diffused gradually. The formation of a stereocomplex may occur between the isotactic polymer and the syndiotactic oligomer at the interface, and this may prevent the diffusion of the oligomer molecules.

In our previous paper[7] it was shown that there exist isotactic and syndiotactic active species in the polymerization of ethyl methacrylate by butyllithium in toluene. It may be true in the polymerization of methyl methacrylate. The increase of the isotacticity in the slow growth polymerization may thus be explained in the following way. In the slow growth polymerization in toluene, the isotactic and syndiotactic active species simultaneously form at the interface between the solutions of initiator and monomer, where the isotactic species are predominant in a nonpolar solvent such as toluene. The diffusion of syndiotactic species into the reaction mixture is interfered with by a larger amount of the
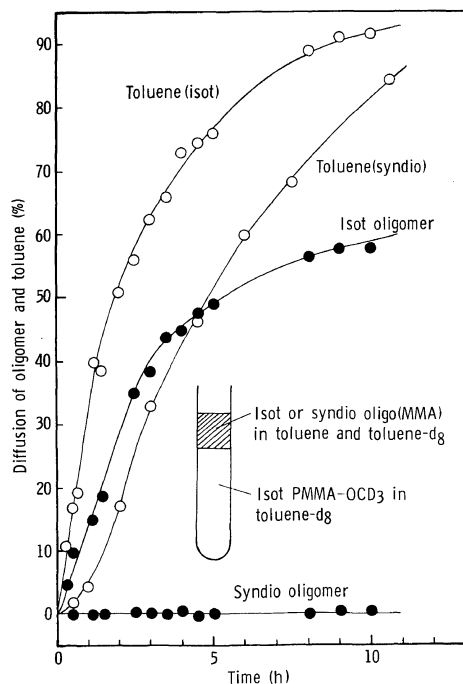
Figure 2. Diffusion of isotactic or syndiotactic oligomer of methyl methacrylate into the solution of isotactic poly(methyl methacrylate) in toluene-d_8 at room temperature.

Table IV. Number of butyl group per a molecule of polymer and oligomer obtained in the polymerization of perdeuterated methyl methacrylate in toluene by butyllithium for 24 h

Polymn[a]		C_4H_9 (total)[b]	C_4H_9CO
SG[c]	Polymer	1.51	0.61
	Oligomer	1.67	0.67
O[d]	Polymer	2.04	0.99
	Oligomer	1.80	0.77

[a] Monomer, 4.97 mmol; butyllithium, 0.25 mmol; toluene, 10 ml.
[b] Total sum of the contents of terminal butyl and butyl carbonyl groups.
[c] Slow growth polymerization.
[d] Polymerization by ordinary method.

isotactic species, owing to the formation of the stereocomplex. This results in the predominance of isotactic species in the monomer solution, where the species grow to high polymers. This leads to an increase in the isotacticity of the polymer formed in the reaction mixture. The long period of time butyllithium remains in the layer of initiator solution may be caused by the gradual formation of the gel of the stereocomplex at the interface.

Another reason to be considered for this increase in isotacticity is the contribution of lithium methoxide formed in the reaction mixture during the polymerization. Wiles and Bywater[8] reported that in the polymerization of methyl methacrylate by butyllithium in toluene, the initiator first reacted more easily with the carbonyl group of the monomer to produce lithium methoxide and butyl isopropenyl ketone rather than with the vinyl bond at low temperatures. They related the resultant methoxide to the formation of syndiotactic blocks in the polymer chain.

The butyl isopropenyl ketone described above should be incorporated into the polymer chain as a comonomer. When perdeuterated methyl methacrylate is polymerized by undeuterated butyllithium, the butyl isopropenyl ketone unit contained in the polymer and oligomer can be analyzed by ^1H NMR spectroscopy.[4] It has a characteristic signal at 2.40 ppm in the ^1H NMR spectrum, due to the methylene protons of the butyl group adjacent to the carbonyl group. Perdeuterated methyl methacrylate was polymerized by the slow growth method with butyllithium in toluene at $-78°C$ and the resultant methanol-insoluble polymer and methanol-soluble oligomer were subjected to analysis. These results are shown in Table IV, comparing them with the results for the polymer of perdeuterated methyl methacrylate prepared by the ordinary method. The number of butyl carbonyl groups in a polymer, and in oligomer molecules prepared by the slow growth method were lower than those in the polymer and oligomer obtained by the ordinary method; still, they contained appreciable amounts of butyl carbonyl. This indicates that in the slow growth polymerization the formation of lithium methoxide through the reaction of the initiator with the carbonyl group still occurred, but to a limited extent.

The amount of the lithium compound existing in each portion of the reaction mixture after the polymerization was compared with the total amount of the polymer and oligomer molecules formed in the

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Table V. Slow growth polymerization of perdeuterated methyl methacrylate in toluene by butyllithium at $-78°C$ for 24 h[a]

	Polymer		Oligomer		N[b]	Li compd[c]
	Yield	$M_n \times 10^{-3}$	Yield	$M_n \times 10^{-3}$	mmol	mmol
	mg		mg			
I	109.5	33.4	32.2	0.60	0.057	0.23
II	75.7	45.0	10.7	0.99	0.013	0.01
III	75.7	46.0	10.2	1.23	0.010	0.01

[a] Monomer, 4.97 mmol; butyllithium, 0.25 mmol; toluene, 10 ml.
[b] Total amounts in mmol of polymer and oligomer molecules formed during the polymerization.
[c] Amount of lithium compound in the reaction mixture after the polymerization.

corresponding portion. Both were in good agreement with each other, except for the top portion (I) where unreacted butyllithium also existed (Table V).

The results mentioned here suggest that in the slow growth polymerization, the extent of the carbonyl attack by butyllithium is lower than in the ordinary polymerization and the lithium methoxide formed does not enter into the reaction mixture, probably owing to a complex formation with the remaining butyllithium so that the propagation reaction occurs almost free from the methoxide to enhance the formation of the highly isotactic polymer.

The slow growth polymerization of methyl methacrylate was carried out in toluene with 1,1-diphenylhexyllithium at $-78°C$. In this case, the polymerization was initiated by adding slowly the monomer solution onto the initiator solution because of the higher density of the latter solution. The deep red color of the initiator remained almost unchanged during the polymerization, and after 24 h, the polymer was obtained only in the bottom portion (III). The results are shown in Table VI, together with those of ordinary polymerization. The polymer prepared by the slow growth method was similar in stereoregularity to those prepared by the ordinary method and also by the slow growth polymerization initiated with butyllithium in toluene. In the polymerization by 1,1-diphenylhexyllithium in toluene, the amount of lithium methoxide formed was found to be much less than with butyllithium.[8] The less lithium methoxide and, accordingly, the low level of the syndiotactic active species are the reasons as to why the increase in the isotacticity cannot be observed in the slow

Table VI. Slow growth polymerization of methyl methacrylate in toluene by 1,1-diphenyl-hexyllithium at $-78°C$[a]

	Yield	Tacticity/%		
	%	I	H	S
I	0.0	—	—	—
II	0.0	—	—	—
III	19.4	86	11	3
O[b]	94.1	83	13	4

[a] Monomer, 10 mmol; initiator, 0.5 mmol; toluene, 10 ml.
[b] Polymerization by ordinary method.

growth polymerization by 1,1-diphenylhexyllithium.

In conclusion, the formation of a stereocomplex between isotactic and syndiotactic active species, together with the reduced amount of lithium methoxide in the reaction mixture, may contribute to the increase in the isotacticity in the slow growth polymerization of methyl methacrylate in toluene by butyllithium. It is rather difficult at the present to decide which contributes predominately. It may depend on the structure of the monomer and an extensive study is now under way on the slow growth polymerization of alkyl methacrylates other than methyl methacrylate.

preparing this manuscript.

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