

Radical Polymerization of Highly Isotactic and Syndiotactic Poly(methyl methacrylate) Macromonomers

Eiji MASUDA, Shigeki KISHIRO, Tatsuki KITAYAMA,
and Koichi HATADA*

Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan

(Received October 12, 1990)

ABSTRACT: Highly isotactic (*iso*-) and syndiotactic (*syn*-) poly(methyl methacrylate) (PMMA) macromonomers having styrene end group were prepared by the reaction of the corresponding PMMA living anions with *p*-vinylbenzyl bromide and their polymerizations were studied in toluene using 2,2'-azobisisobutyronitrile as an initiator. The rate of polymerization (R_p) of *iso*-PMMA macromonomer was slightly higher than that of *syn*-macromonomer. A similar tacticity dependence of the reactivity was also observed in the radical copolymerization of the macromonomers with styrene. Propagation rate constant (k_p) for the homopolymerization of macromonomers was estimated from R_p , termination rate constant (k_t) determined by ESR spectroscopy [K. Hatada *et al.*, *Makromol. Chem., Rapid Commun.*, **11**, 101 (1990)] and initiator efficiency (f) determined from end group analysis of polymacromonomer by means of NMR spectroscopy [T. Kitayama *et al.*, *Polym. Bull.*, **25**, 205 (1991)]. Both the k_t and k_p values were much smaller than those for styrene polymerization, and the decrease of k_t of the macromonomer was much more evident than the decrease of k_p . The k_p and k_t values for *iso*-macromonomer were much larger than the corresponding values for the *syn*-one. The results suggest that the higher segmental mobility of *iso*-PMMA chain than that of *syn*-PMMA chain brings about the larger rate constants for propagation and termination reactions.

KEY WORDS PMMA Macromonomer / Stereoregularity / Tacticity / Propagation / Termination / Monomer Reactivity Ratio / Initiator Efficiency /

Many papers have been published on the syntheses and applications of macromonomers.¹⁻⁵ Especially, macromonomers of high purity and narrow molecular weight distribution (MWD) have been desired for the syntheses of graft or comb-like polymers which have well-defined structures. Characteristic features of the radical polymerization of macromonomers have been studied by kinetic experiments.⁶⁻¹⁴ However, little attention has been paid to the tacticity of the macromonomers.¹⁵⁻¹⁷

Poly(methyl methacrylate) (PMMA) is one of the typical polymers whose tacticity can be

widely varied by changing the reaction conditions and whose properties in bulk and in solution depend strongly on the tacticity.^{18,19} Glass transition temperature (T_g) of PMMA is much lower for the *iso*-PMMA than for the *syn*-PMMA.^{19,20} The ¹³C NMR spin-lattice relaxation times of the carbons in *iso*-PMMA are larger than those of the corresponding carbons in *syn*-PMMA, indicating that the *iso*-polymer chains have greater segmental mobility than the *syn*-ones.²¹ Therefore, control of stereoregularity of PMMA macromonomer will provide another means for controlling the properties of graft

* To whom correspondence should be addressed.

and comb-like polymers.

Recently, we found isotactic^{22,23} and syndiotactic^{24,25} living polymerizations of methyl methacrylate (MMA) which give highly stereoregular PMMAs with the same chemical structure and narrow MWD. By utilizing these living anionic polymerization systems, highly *iso*- and *syn*-PMMA macromonomers having the same chemical structure were prepared. The preliminary results of the radical homopolymerization and copolymerization of these macromonomers were reported in the previous communication.²⁶ We also briefly reported on the observation of the propagating radicals in the polymerization of *syn*-PMMA macromonomer with 2,2'-azobisisobutyronitrile (AIBN) in benzene, which allowed us to directly determine termination rate constant (k_t) for the macromonomer polymerization.²⁷

In the present work the effect of tacticity of macromonomer on the kinetic data was studied in detail for the radical polymerization of the stereoregular PMMA macromonomers.

EXPERIMENTAL

Materials

iso-PMMA macromonomer was prepared through the end-capping reaction of living isotactic PMMA, which was formed with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C ,^{22,23} with *p*-vinylbenzyl bromide in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene. The detailed procedure was described in the previous communication.²⁶

syn-PMMA macromonomers were prepared through the end-capping reaction of living syndiotactic PMMA, which was formed with $t\text{-C}_4\text{H}_9\text{Li}-(n\text{-C}_4\text{H}_9)_3\text{Al}$ (1 : 3 mol mol⁻¹) in toluene at -78°C ,^{24,25} in the presence of *N,N,N',N'*-tetramethylethylenediamine according to the previous communication.²⁶

2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol and dried *in vacuo*.

Toluene, purified in a usual manner and stored over sodium metal, was mixed with a

small amount of $n\text{-C}_4\text{H}_9\text{Li}$ and then vacuum-distilled.

Toluene- d_8 was dried over calcium dihydride and vacuum-distilled.

Polymerization Reaction

Polymerization was carried out in a glass ampule or in an NMR sample tube under dry nitrogen. The reaction mixture was poured into a large amount of hexane to collect the polymacromonomer and the starting macromonomer. The unchanged macromonomer was removed from the reaction product by reprecipitation from toluene solution to methanol.

Measurement

¹H NMR spectra were measured on JEOL JNM-FX100 (100 MHz), GSX400 (400 MHz), and GX500 (500 MHz) spectrometers.

Gel permeation chromatography (GPC) for the characterization of macromonomer was performed on a JASCO FLC-A10 chromatograph equipped with Shodex GPC columns 802.5 and A-80M using tetrahydrofuran as an eluent. The GPC-LALLS (low-angle laser light scattering) experiment for polymacromonomer was performed on a Tosoh HLC-801A chromatograph equipped with a LALLS detector, LS-8, which was operated with two Tosoh GMH_{x1} columns using chloroform as an eluent at 39°C.

RESULTS AND DISCUSSION

Effect of Tacticity of PMMA Macromonomer on the Radical Polymerization

(i) Homopolymerization

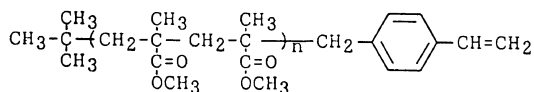
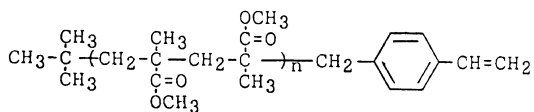
Both the highly *iso*- and *syn*-PMMA macromonomers, prepared according to the procedures reported in the previous communication,²⁶ have the same chemical structure from left end (*t*-butyl group) to right end (*p*-vinylbenzyl group) as follows:

Table I. Characteristics of *iso*- and *syn*-PMMA macromonomers

Tacticity/%			M_n^a	M_w/M_n^b	CH ₂ =CH- per chain ^a	T_g °C
<i>mm</i>	<i>mr</i>	<i>rr</i>				
95	4	1	2900	1.12	0.96	21
1	10	89	2720	1.18	0.97	95
0	9	91	5380	1.15	0.96	105

^a Determined by ¹H NMR.

^b Determined by GPC.

 Highly *iso*-PMMA macromonomer

 Highly *syn*-PMMA macromonomer


The characteristics of macromonomers used in this work are summarized in Table I.

Polymerization of *iso*- or *syn*-PMMA macromonomer with AIBN in toluene-*d*₈ was carried out in an NMR sample tube at 60 and 80°C. The spectral change for the polymerization mixture of *iso*-PMMA macromonomer at 80°C is shown in Figure 1. As the polymerization proceeded, the signal intensity of the vinyl group decreased, and the signals of methoxy and *t*-butyl group became broader. The amount of macromonomer consumed was determined from the relative intensity of vinyl methylene proton signals (5.03–5.05 ppm and 5.52–5.56 ppm) to *t*-butyl signal (0.90 ppm). Figures 2 and 3 show the first order plots of monomer consumption of the *iso*- and *syn*-macromonomers at 60 and 80°C, respectively. These plots clearly indicate that the initial rate of polymerization (R_p) of the *iso*-PMMA macromonomer is high than that of the *syn*- one.

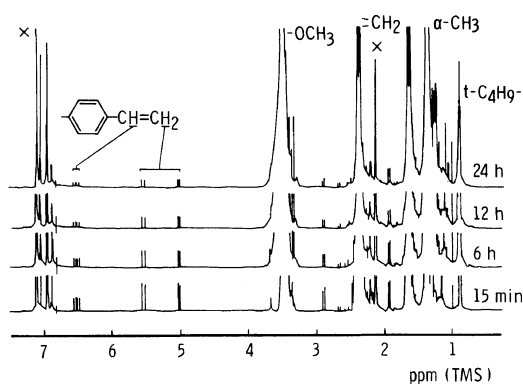


Figure 1. 400 MHz ¹H NMR spectra of polymerization mixture of *iso*-PMMA macromonomer ($M_n = 2900$) with AIBN in toluene-*d*₈ at 80°C. $[M]_0 = 0.05 \text{ mol l}^{-1}$; $[M]_0/[I]_0 = 20 \text{ mol mol}^{-1}$. ×, solvent signals. 30° pulse, 5 s × 32 scans.

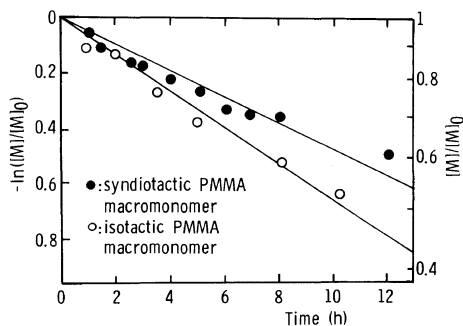


Figure 2. Effect of tacticity on the polymerization of PMMA macromonomer with AIBN in toluene-*d*₈ at 60°C. $[M]_0 = 0.05 \text{ mol l}^{-1}$; $[M]_0/[I]_0 = 20 \text{ mol mol}^{-1}$.²⁶

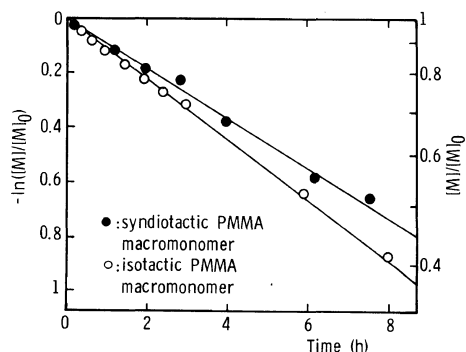


Figure 3. Effect of tacticity on the polymerization of PMMA macromonomer with AIBN in toluene-*d*₈ at 80°C. $[M]_0 = 0.05 \text{ mol l}^{-1}$; $[M]_0/[I]_0 = 20 \text{ mol mol}^{-1}$.

Table II. Polymerization of *iso*- and *syn*-PMMA macromonomers in toluene-*d*₈ for 48 h^a

Macro- monomer	Temp °C	Conv./%		M_n^b	M_w/M_n^b	DP ^b
		GPC ^b	NMR ^c			
<i>iso</i> - ^d	60	69	75	65300	1.42	22.5
	80	73	80	39800	1.79	13.7
<i>syn</i> - ^e	60	59	67	51900	1.38	19.1
	80	64	68	33200	1.71	12.8

^a $[M]_0 = 0.05 \text{ mol l}^{-1}$, $[I]_0 = 0.0025 \text{ mol l}^{-1}$.^b Determined by GPC-LALLS.^c Determined by ¹H NMR.^d $M_n = 2900$.^e $M_n = 2720$.

Table II summarizes the results of the polymerization with AIBN in toluene-*d*₈ at 60 and 80°C for 48 h. The conversions determined by ¹H NMR as described above were slightly higher than those determined by GPC curves of the reaction mixtures. The results might be due to the formation of unimer of macromonomer which formed by the attack of the initiator radical but failed to propagate. The degree of polymerization (DP) was determined by GPC-LALLS, which is very useful for the determination of accurate molecular weight of branched polymer. Both DP and the conversion for *iso*-PMMA macromonomer were higher than the corresponding values for *syn*-one.

We have already found from ESR spectroscopic study²⁷ that the termination reaction of the PMMA macromonomers is bimolecular process as in the case of ordinary radical polymerization of low molecular monomers. The result suggests that the following equations 1 and 2 for R_p and kinetic chain length (ν), respectively, for the ordinary radical polymerization are applicable to our present case.

$$R_p = (k_p/k_t^{0.5})(f \cdot k_d)^{0.5}[I]^{0.5}[M], \quad (1)$$

$$\nu = (k_p/k_t^{0.5})(1/2)(f \cdot k_d)^{-0.5}[I]^{-0.5}[M] \quad (2)$$

where f , k_d , and k_p are initiator efficiency and the rate constants for decomposition of initiator and for propagation, respectively. $[I]$ and $[M]$ represent concentrations of initiator and monomer, respectively.

The kinetic orders with respect to macromonomer and initiator have been discussed from kinetic measurement by several research groups. The reported values for macromonomers scatter largely depending on the structure of macromonomers (1.36–1.49^{6,7} and 2.5–3.1⁸), while the values for initiators were only slightly lower than 0.5. R_p was determined at different $[M]_0$ for the polymerizations of *iso*- and *syn*-macromonomers by ¹H NMR spectroscopy. For *syn*-macromonomer (number average molecular weight, M_n , of 5380), R_p was $5.30 \times 10^{-7} \text{ l mol}^{-1} \text{ s}^{-1}$ at $[M]_0 = 0.05 \text{ mol l}^{-1}$, and was $2.61 \times 10^{-7} \text{ l mol}^{-1} \text{ s}^{-1}$ at $[M]_0 = 0.025 \text{ mol l}^{-1}$. For *iso*-macromonomer (M_n of 2900), R_p was $7.40 \times 10^{-7} \text{ l mol}^{-1} \text{ s}^{-1}$ at $[M]_0 = 0.05 \text{ mol l}^{-1}$, and was $3.52 \times 10^{-7} \text{ l mol}^{-1} \text{ s}^{-1}$ at $[M]_0 = 0.025 \text{ mol l}^{-1}$. The results indicate that eq 1 and 2 can actually describe the polymerization process and the kinetic rate constants can be estimated based on eq 1.

(ii) Copolymerization with Styrene

Copolymerization of macromonomer (M_1) with low molecular weight monomer (M_2) is a facile method to examine the reactivity of macromonomers. For the analysis of copolymerization of macromonomer, Jaacks' single point experiment method²⁸ has been widely applied.^{4,9-14} In this method copolymerization is carried out under the condition, $[M_1] \ll [M_2]$, and one of the reactivity ratios can be determined as follows:

$$r_2 = \frac{\log([M_2]_t/[M_2]_0)}{\log([M_1]_t/[M_1]_0)} \quad ([M_1] \ll [M_2]). \quad (3)$$

Then, the reactivity of M_1 (macromonomer) can be estimated by $1/r_2 = k_{21}/k_{22}$, which represents the relative addition rate of M_1 and M_2 to M_2 radical. The reason why the Jaacks's

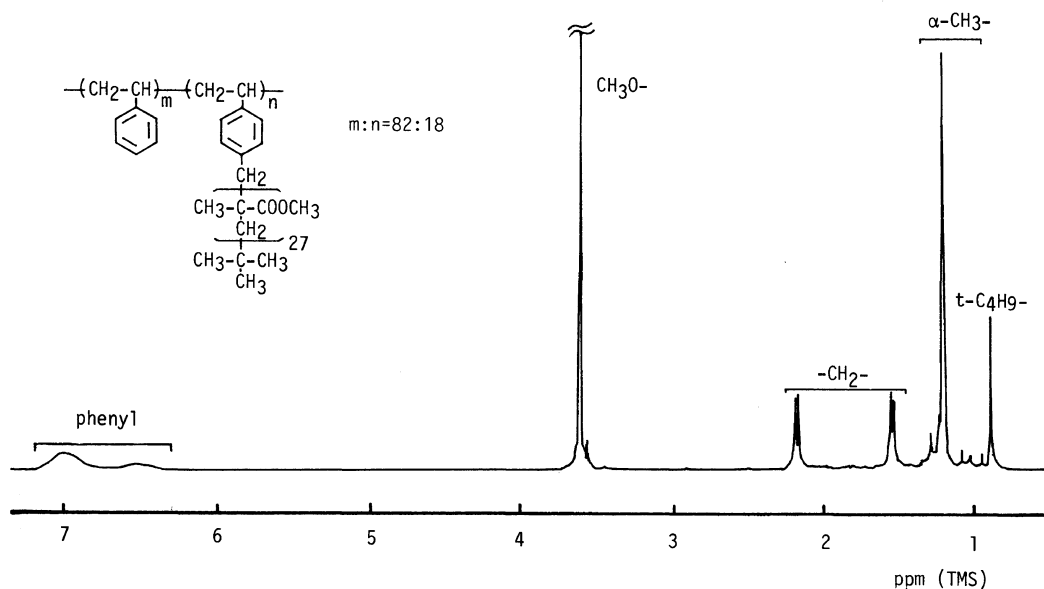


Figure 4. 500 MHz ¹H NMR spectrum of poly[styrene-*co*-(*iso*-PMMA macromonomer)] observed in CDCl₃ at 55°C.

method has been widely used instead of standard copolymerization procedure, which gives both r_1 and r_2 , is that the analysis of the molar copolymer composition is very difficult for the copolymers formed under the conditions, $[\text{M}_1] \geq [\text{M}_2]$, because of the large difference between molecular weights of macromonomer and low molecular weight comonomer.

The stereoregular PMMA macromonomers used in this work have one *t*-butyl group per molecule at the left end of the chain, the ¹H NMR signal of which is observed separately from those of the monomeric units. For copolymers with styrene, from the intensity measurements of the ¹H NMR signals due to the *t*-butyl group in the macromonomer units and the phenyl groups of both monomer units allow the molar fraction in the copolymer to be accurately and easily determined over a wide range of copolymer composition. Therefore, both r_1 and r_2 for the copolymerization of these macromonomers with styrene could be determined based on the Mayo-Lewis' ordinary copolymerization theory. The data should give

us more profound knowledge on the copolymerization of macromonomer.

The copolymerization of *iso*- or *syn*-PMMA macromonomer (M_1) with styrene (M_2) was carried out in toluene at 60°C with AIBN. The reactions were terminated before the conversions of macromonomer and styrene reached 10%. Both the starting macromonomers were soluble in methanol and could be easily removed from the reaction mixtures by reprecipitation from toluene solution into methanol. Figure 4 shows ¹H NMR spectrum of poly(*iso*-PMMA macromonomer-*co*-styrene) obtained at the initial monomer ratio $[\text{M}_1]_0/[\text{M}_2]_0$ of 21/79 mol mol⁻¹. The broad peaks observed at 6.30–7.15 ppm were attributed to the phenyl groups of styrene and macromonomer units. The peak at 0.87 ppm was due to *t*-butyl group of the macromonomer unit. Molar ratio of the macromonomer unit to styrene unit in this copolymer was determined as 18 : 82 from the signal intensity ratio of *t*-butyl group to the phenyl groups (1 : 2.98).

Copolymer composition curves are shown in Figure 5. Each curve is not much far from the

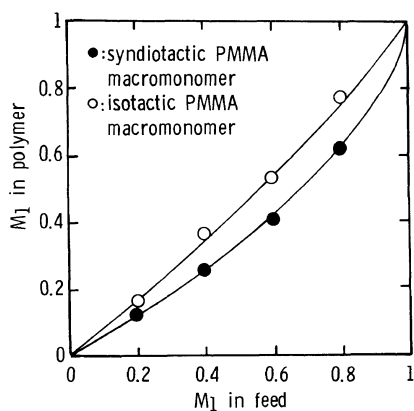


Figure 5. Copolymer composition curves for radical copolymerization of PMMA macromonomer (M_1) with styrene (M_2) by AIBN in toluene at 60°C. $[M_1]_0 = 0.07 \text{ mol l}^{-1}$; $[M_1 + M_2]_0/[I]_0 = 100 \text{ mol mol}^{-1}$.²⁶

azeotrope line, indicating that the difference between the apparent reactivities of each macromonomer and styrene in the copolymerization is rather small. Table III summarizes the values of r_1 and r_2 together with those of $1/r_2$. The values of r_1 and r_2 for both copolymerizations mean $k_{11} < k_{12}$ and $k_{21} < k_{22}$, indicating that styrene has higher reactivity than the macromonomers toward both the macromonomer radical ($M_1\cdot$) and styrene radical ($M_2\cdot$). Then the macromonomer units in the copolymers tend to be isolated in styrene unit sequences. Since the values of $1/r_2$ ($=k_{21}/k_{22}$) correspond to the relative reactivity of the macromonomers to styrene toward styrene radical, the larger value of $1/r_2$ for the *iso*-PMMA macromonomer than that for the *syn*- one indicates the higher reactivity of *iso*-macromonomer; k_{21} for the *iso*-macromonomer is 1.26 times as large as k_{21} for the *syn*-macromonomer. In the above discussion, only the reactivity in the propagation process should be concerned, and thus the higher mobility of *iso*-PMMA chain²¹ than that of *syn*-PMMA chain may be related to the higher reactivity of the *iso*-macromonomer.

Comparison of r_1 values for *iso*- and *syn*-macromonomers may not lead to simple

Table III. Reactivity ratio in the radical copolymerization of PMMA macromonomer (M_1) and styrene (M_2)

M_1	r_1^a	r_2^a	$1/r_2 = k_{21}/k_{22}$
<i>Iso</i> -PMMA Macromonomer ^b	0.79	1.29	0.775
<i>syn</i> -PMMA Macromonomer ^c	0.40	1.62	0.617

^a Cited from ref 26.

^b $M_n = 2900$.

^c $M_n = 2720$.

conclusion on the reactivities of the macromonomer radicals because any rate constants included in r_1 does not represent the common addition steps to both copolymerizations. However, if one assumes that the effect of tacticity of the macromonomer on the rate constants for cross propagations, k_{12} and k_{21} , are the same, that is,

$$\frac{(k_{12})_{iso}}{(k_{12})_{syn}} = \frac{(k_{21})_{iso}}{(k_{21})_{syn}} \quad (4)$$

the ratio $(r_1/r_2)_{iso}/(r_1/r_2)_{syn}$ is described as follows:

$$\begin{aligned} \frac{(r_1/r_2)_{iso}}{(r_1/r_2)_{syn}} &= \frac{(k_{11} \cdot k_{21}/k_{12} \cdot k_{22})_{iso}}{(k_{11} \cdot k_{21}/k_{12} \cdot k_{22})_{syn}} \\ &= \frac{(k_{11})_{iso}}{(k_{11})_{syn}} \\ &= 2.5 \end{aligned} \quad (5)$$

Then the rate constant of homopropagation of *iso*-macromonomer is estimated to be 2.5 times as large as that of *syn*-macromonomer. The results mean that the effect of tacticity of PMMA macromonomer is more evidently observed in the homopropagation (the addition process of macromonomer to macromonomer radical) than in cross propagation (the addition to styrene radical). This may be due to the fact that in the homopropagation process both the PMMA chain in the propagating chain end and

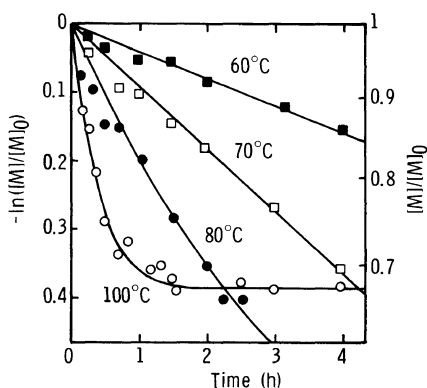


Figure 6. Effect of temperature on the polymerization of *syn*-PMMA macromonomer ($M_n=5380$) with AIBN in toluene- d_8 . $[M]_0=0.05 \text{ mol l}^{-1}$; $[M]_0/[I]_0=20 \text{ mol mol}^{-1}$.

that in the incoming monomer mutually interact to affect the reaction process.

Effect of Temperature on the Polymerization of PMMA Macromonomer

Figure 6 shows the first order plots of monomer consumption in the polymerization of *syn*-PMMA macromonomer ($M_n=5380$) in toluene- d_8 with AIBN at various temperatures. The R_p 's were determined from the slope of the plots at the time of zero, and the values are shown in Table IV. Half-life times of AIBN were calculated using the literature data²⁹ and also shown in Table IV. The deviation of the plots from the linearity at 80 and 100°C was explained by fast loss of AIBN at these temperatures. The Arrhenius plot of the R_p values gave a linear relationship as shown in Figure 7 and the activation energy for the overall process of polymerization (E_{overall}) was determined to be 68 kJ mol^{-1} . E_{overall} is expressed as follows;

$$E_{\text{overall}} = E_p - E_t/2 + E_d/2, \quad (6)$$

where E_p , E_t , and E_d represent the activation energies for propagation, termination, and decomposition of the initiator, respectively. The value of E_t for this macromonomer was determined to be 66 kJ mol^{-1} by ESR spectroscopy,

Table IV. Initial rate of polymerization (R_p) for *syn*-PMMA macromonomer with AIBN in toluene- d_8 at various temperatures^a

Temp °C	$R_p \times 10^6$ $\text{l mol}^{-1} \text{s}^{-1}$	$-\ln R_p$	Half-life of AIBN ^b h
60	0.530	14.5	19.8
70	1.06	13.8	5.11
80	1.96	13.1	1.42
100	7.21	11.8	0.14

^a Macromonomer: $M_n=5380$, $[M]_0=0.05 \text{ mol l}^{-1}$, $[M]_0/[I]_0=20 \text{ mol mol}^{-1}$.

^b Calculated by the equation of $\ln 2/[1.58 \times 10^{15} \exp(-128.9 \text{ kJ RT}^{-1})]$ according to the ref 29.

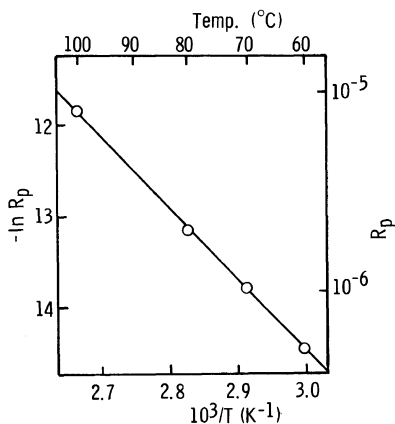


Figure 7. Arrhenius plot of R_p in the polymerization of *syn*-PMMA macromonomer ($M_n=5380$) with AIBN in toluene- d_8 . $[M]_0=0.05 \text{ mol l}^{-1}$; $[M]_0/[I]_0=20 \text{ mol mol}^{-1}$.

copy,²⁷ which is much larger than that for styrene polymerization (10 kJ mol^{-1}),³⁰ indicating that the termination reaction in the polymerization of macromonomer was highly restricted. From the E_t and E_d for AIBN ($128.9 \text{ kJ mol}^{-1}$),²⁹ E_p of *syn*-PMMA macromonomer ($M_n=5380$) was determined as 36 kJ mol^{-1} , which is slightly larger than that for styrene polymerization (33 kJ mol^{-1}).³⁰ The result indicates that propagation reaction of macromonomer is also restricted as compared with that of styrene, although the extent of the restriction in propagation reaction

Table V. Comparison of the DP of poly(*syn*-PMMA macromonomer) prepared with AIBN in toluene-*d*₈^a with the DP calculated for the polystyrene prepared under the same conditions^b

Temp °C	Macromonomer DP ^c	DP ^b	Styrene		AIBN
			k_p^d	k_t^d	k_d^e
			l mol ⁻¹ s ⁻¹	l mol ⁻¹ s ⁻¹	l mol ⁻¹ s ⁻¹
60	21.9	11.4	176	3.6×10^7	9.54×10^{-6}
70	18.6	7.33	236	4.0×10^7	3.70×10^{-5}
80	15.2	4.98	315	4.3×10^7	1.33×10^{-4}
100	11.2	2.37	532	5.1×10^7	1.41×10^{-3}

^a Macromonomer: $M_n = 5380$, $[M]_0 = 0.05 \text{ mol l}^{-1}$, $[M]_0/[I]_0 = 20 \text{ mol mol}^{-1}$.

^b Calculated from the following equation; $DP = 2 \cdot \nu = k_p \cdot [M] / (f \cdot k_d \cdot k_t \cdot [I])^{0.5}$, $f = 0.7$.

^c Determined by GPC-LALLS.

^d Taken from ref 30.

^e Taken from ref 29.

is less remarkable than that in termination reaction.

Table V shows the DP's of the poly-macromonomers and polystyrenes prepared at various temperatures. The DP's for the polystyrene formed under the same conditions as those for the macromonomer were calculated by using rate constants taken from a literature³⁰ on the assumption that DP is $2 \cdot \nu$, even though a part of polystyrene radicals terminate through disproportionation reaction.³¹ The DP's of polymacromonomers were higher than those of polystyrene, indicating the value of $k_p/k_t^{0.5}$ for the polymerization of macromonomer was higher than that for styrene polymerization (*cf.*, eq 2). Figure 8 shows the plot of log DP against the reciprocal of temperature. A linear relationship was obtained as in the case of radical polymerization of usual monomers.

Kinetics of Radical Polymerization of Stereoregular PMMA Macromonomer

As mentioned previously, the mobility of PMMA chain strongly depends on its tacticity in bulk¹⁸⁻²⁰ and in solution,^{18,19,21} and *iso*-PMMA chain has higher mobility than *syn*-PMMA chain. The mobility of the macromonomer should affect each reaction process

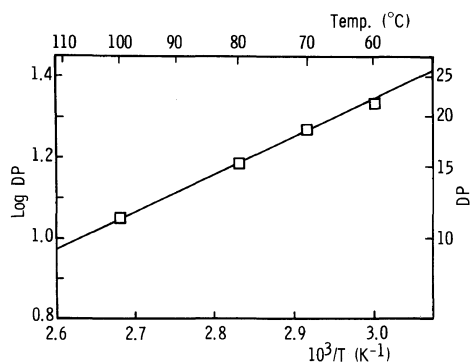


Figure 8. Plots of log DP of the poly(*syn*-PMMA macromonomer) against the reciprocal of polymerization temperature. The polymerizations were carried out in toluene-*d*₈ for 48 h. $[M]_0 = 0.05 \text{ mol l}^{-1}$; $[M]_0/[I]_0 = 20 \text{ mol mol}^{-1}$.

in the polymerization. Thus the difference of R_p and DP in the polymerizations of *iso*- and *syn*-macromonomers should be caused by the difference of their mobilities. However, eq 1 and 2 mean that both R_p and DP are proportional to the value of $k_p/k_t^{0.5}$, and thus the larger R_p and ν do not necessarily mean the larger values of both k_p and k_t , since these constants act in opposite ways on R_p and ν . Then, in order to clarify the effects of stereoregularity of the PMMA macromonomers on their radical polymerization, further

Table VI. Kinetic parameters for the polymerization of PMMA macromonomers or styrene in toluene at 60°C with AIBN^a

Macromonomer		$R_p \times 10^6$	f^b	k_p	k_t^c	ν^d	DP ^e
Tacticity	M_n	$\text{mol l}^{-1} \text{s}^{-1}$		$\text{l mol}^{-1} \text{s}^{-1}$	$\text{l mol}^{-1} \text{s}^{-1}$		
<i>iso</i> -	2900	0.74	0.28	50	7000 ^f	58	22.5
<i>syn</i> -	2720	0.66	0.22	4.7	670 ^f	63	19.1
<i>syn</i> -	5380	0.53	0.18	3.9	590	61	21.9
Styrene monomer		0.19 ^g	0.7 ^h	176 ⁱ	3.6×10^{7i}	5.7	—

^a $[M]_0 = 0.05 \text{ mol l}^{-1}$, $[M]_0/[I]_0 = 20 \text{ mol mol}^{-1}$.

^b Initiator efficiency taken from the ref 36.

^c Taken from the ref 27 and 33.

^d Kinetic chain length estimated from eq 2.

^e Determined by GPC-LALLS for the polymacromonomer formed in the polymerization for 48 h.

^f Estimated by extrapolation of the data obtained at lower temperatures.³³

^g Calculated from the literature data and eq 1.

^h Taken from the ref 34.

ⁱ Taken from the ref 30.

information such as the rate constants for the elementary processes is required. For this purpose, we determined k_t values by ESR spectroscopy^{33,34} as well as initiator efficiencies (f 's) by ²H NMR spectroscopy,³⁶ and estimated k_p values for the radical polymerization of macromonomers as described below.

ESR spectroscopy is the most promising way for the study on the nature of propagating radicals³² and was recently applied to the radical polymerization of macromonomer.^{27,33,34} We reported that the propagating radicals in the polymerization of *syn*-PMMA macromonomer ($M_n = 5380$) could be observed by using ESR spectroscopy, and k_t values in the temperature range from 30 to 60°C were determined from the decay of the ESR signal.²⁷ Lately, ESR signals of propagating radicals of *iso*-PMMA macromonomer ($M_n = 2900$) could also be observed successfully at and below 30°C, and the k_t values were determined in the temperature range from 10 to 30°C.³³ Since an Arrhenius plot of the k_t gave a linear correlation, k_t value at 60°C was estimated by extrapolation of the k_t 's at lower temperatures. The values of k_t for *syn*-macromonomer with M_n of 2720 could be determined similarly in the temperature range

from 20 to 50°C,³³ and the k_t at 60°C was estimated by extrapolation as in the case of *iso*-macromonomer. The values are summarized in Table VI.

The PMMA macromonomers were polymerized in toluene at 60°C using AIBN-*d*₁₂ and the initiator fragments in the resultant polymacromonomers were analyzed by ²H NMR spectroscopy to determine the f values.^{35,36} The f values thus obtained are listed in Table VI, all of which are lower than that for bulk or solution polymerization of styrene (0.5—0.7).³⁷ The results suggest that a large amount of the primary radicals fail to initiate the polymerization of macromonomer as compared with the case of the polymerization of ordinary monomer owing to high viscosity of the reaction media from the initial stage of polymerization.

From eq 1 and the value of k_d available from the literature,²⁹ the k_p 's for the polymerization of PMMA macromonomers were estimated from the values of R_p , f , k_t , and k_d . The results are summarized in Table VI.

Although both k_p 's and k_t 's for the PMMA macromonomers are smaller than the corresponding values of styrene, the R_p for the macromonomers were larger than that for styrene

(Table VI). This means that, even though k_p 's for the macromonomers are smaller than that for styrene, extremely smaller k_t values for the macromonomers than that for styrene bring about the larger R_p 's for the macromonomers than styrene.

The R_p for *iso*-PMMA macromonomer is higher than that for *syn*-PMMA macromonomer. The k_t value for the *iso*-macromonomer was about 100 times as large as that for the *syn*-macromonomer of a similar M_n . The k_p for the *iso*-macromonomer is about 10 times as large as that for the *syn*-macromonomer. Effect of tacticity of the macromonomer is much greater on the termination reaction than on the propagation reaction. This is probably because the termination process involves the reaction between two propagating radical centers both of which should be surrounded by many PMMA segments while the propagation process involves the reaction of one propagating radical with a macromonomer which consists of a single PMMA chain. The difference between R_p 's for *iso*- and *syn*-macromonomers is not so remarkable since R_p is proportional to $k_p/k_t^{0.5}$ and thus the increases of k_p and k_t affect R_p in opposite ways. The difference in R_p is mostly accounted for the difference in f values as seen in Table V, that is, $(f_{iso}/f_{syn})^{0.5} = 1.12$. However, the larger k_p and k_t values for the *iso*-PMMA macromonomer than those for the *syn*-one indicate that the higher segmental mobility of *iso*-PMMA chain contributes to increase these kinetic parameters.

The ratio of k_p for the *iso*-macromonomer to that for *syn*-macromonomers (~ 10) (see Table VI) is larger than the ratio of $(k_{11})_{iso}/(k_{11})_{syn}$ in the copolymerization with styrene as M_2 monomer (~ 2.5) (see eq 5). The smaller tacticity effect in the copolymerization may be ascribed to the lower density of PMMA segments around the propagating radicals due to the incorporation of styrene units. Thus, the monomer sequence distribution around the propagating radical may be an important

factor to determine the rate of propagation, that is, the penultimate effect should be taken into consideration in the strict sense. Monomer reactivity ratio r_2 , however, may be a good measure for the relative reactivity of macromonomer toward styrene radical. The ratio of reactivities of *iso*- and *syn*-PMMA macromonomers toward styrene radical could be estimated as 1.26 from r_2 values (see Table III). Therefore, the tacticity effect increased in the following order.

$$\begin{array}{cccc} & k_{21} & <k_{11} & <k_p & <k_t \\ iso-/syn- & 1.26 & \sim 2.5 & \sim 10 & \sim 100 \end{array}$$

The order is consistent with the increasing number of PMMA chains involved in each process, indicating that the mutual interaction between the PMMA chains plays an important role in determining the rate constant for propagation process.

The ν value for the polymerization of PMMA macromonomers at 60°C was calculated using the kinetic parameters obtained in this work and eq 2. The ν values and the observed DP's of the polymacromonomer are listed in Table VI. In all the cases, the DP's are apparently smaller than the calculated ones, indicating the chain transfer reaction to occur. A number of initiator fragment in the polymacromonomer molecule, N , was found to be less than unity (0.50—0.72) from the end group analysis.³⁶ The result also confirms the occurrence of the chain transfer reaction. Thus, in the radical polymerization of macromonomers, high segmental density around the propagating radicals not only decreases the rates of elementary processes (k_t and k_p) but also changes the reaction pathway. The N values for *syn*-macromonomers (0.50—0.65) were smaller than that for *iso*-macromonomer (0.72), indicating the higher frequency of the chain transfer reaction for the *syn*-macromonomer, probably because the termination reaction between polymacromonomer radicals is more strongly restricted for the *syn*-macromonomer than for the *iso*- one. Therefore, the stereo-

regularity of PMMA macromonomer affects not only the rates of elementary processes but also the frequency of the transfer reaction.

Acknowledgments. The authors are grateful to Professor M. Kamachi of Osaka University for his helpful discussion. They thank Professor T. Kotaka and Dr. K. Adachi of Osaka University for the use of GPC-LALLS equipments. They are also indebted to Mr. T. Iijima for his experimental support. A part of this work was financially supported by a Grant-in-Aid for Scientific Research (C) (No. 01550717) from the Ministry of Education, Science, and Culture of Japan, and by Kurata Foundation (1989—1990).

REFERENCES

1. R. Milkovich and M. T. Chiang, U.S. Patent, 3,786,116 (1974); R. Milkovich, *Polym. Prepr., Polym. Chem. Div., Am. Chem. Soc.*, **21**, 40 (1980).
2. P. F. Rempp and E. Franta, *Adv. Polym. Sci.*, **58**, 1 (1984).
3. Y. Yamashita, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **36**, 193 (1981).
4. R. Asami and M. Takaki, *Makromol. Chem., Rapid Commun.*, **12**, 163 (1985).
5. K. Ito, *Kobunshi Kako (Polymer Applications)*, **35**, 262 (1986).
6. Y. Tsukahara, K. Mizuno, S. Segawa, and Y. Yamashita, *Polym. Prepr. Jpn.*, **37**, 336 (1988); *Macromolecules*, **22**, 1546 (1989).
7. K. Tanaka, K. Ito, and E. Yamada, *Polym. Prepr. Jpn.*, **37**, 337 (1989).
8. M. Takaki and R. Asami, *Polym. Prepr. Jpn.*, **37**, 335 (1988).
9. G. Schulz and R. Milkovich, *J. Polym. Sci.*, **22**, 1633 (1984).
10. P. Rempp, P. Lutz, P. Masson, and E. Franta, *Makromol. Chem., Suppl.*, **13**, 471 (1985).
11. J. P. Kennedy and M. Hiza, *J. Polym. Sci.*, **21**, 1033 (1983); J. P. Kennedy and C. Y. Lo, *Polym. Bull.*, **13**, 343 (1985).
12. K. Ito, H. Tsuchida, A. Hayashi, T. Kitano, W. Yamada and T. Matsumoto, *Polym. J.*, **17**, 827 (1985); K. Ito, H. Tsuchida, and T. Kitano, *Polym. Bull.*, **15**, 425 (1986).
13. G. G. Cameron and M. S. Chisholm, *Polymer*, **26**, 437 (1985).
14. K. Muehlbach and V. Percec, *J. Polym. Sci., Polym. Chem.*, **25**, 2605 (1987).
15. K. Ute and K. Hatada, *Kobunshi Kako (Polymer Applications)*, **36**, 366 (1986).
16. K. Hatada, H. Nakanishi, K. Ute, and T. Kitayama, *Polym. J.*, **18**, 581 (1986).
17. K. Hatada, T. Shinozaki, K. Ute, and T. Kitayama, *Polym. Bull.*, **19**, 231 (1988).
18. H. Yuki and K. Hatada, *Adv. Polym. Sci.*, **31**, 1 (1979).
19. K. Hatada, T. Kitayama, and K. Ute, *Adv. Polym. Sci.*, **13**, 189 (1988).
20. E. V. Thompson, *J. Polym. Sci., A-2*, **4**, 199 (1966).
21. K. Hatada, T. Kitayama, Y. Okamoto, K. Ohta, Y. Umemura, and H. Yuki, *Makromol. Chem.*, **179**, 485 (1978).
22. K. Hatada, K. Ute, K. Tanaka, T. Kitayama, and Y. Okamoto, *Polym. J.*, **17**, 977 (1985).
23. K. Hatada, K. Ute, K. Tanaka, Y. Okamoto, and T. Kitayama, *Polym. J.*, **18**, 1037 (1986).
24. T. Kitayama, T. Shinozaki, E. Masuda, M. Yamamoto, and K. Hatada, *Polym. Bull.*, **20**, 505 (1988).
25. T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto, and K. Hatada, *Macromol. Chem., Suppl.*, **15**, 167 (1989).
26. K. Hatada, T. Kitayama, K. Ute, E. Masuda, T. Shinozaki, and M. Yamamoto, *Polym. Bull.*, **21**, 165 (1989).
27. K. Hatada, T. Kitayama, E. Masuda, and M. Kamachi, *Makromol. Chem., Rapid Commun.*, **11**, 101 (1990).
28. V. Jaacks, *Makromol. Chem.*, **161**, 161 (1972).
29. J. P. Van Hook and A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 779 (1958).
30. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, **73**, 1700 (1951).
31. K. Hatada, T. Kitayama, and E. Masuda, *Polym. J.*, **17**, 985 (1985).
32. M. Kamachi, *Adv. Polym. Sci.*, **82**, 207 (1987).
33. E. Masuda, T. Kitayama, K. Hatada, and M. Kamachi, *Polym. J.*, to be submitted.
34. Y. Tsukahara, K. Tsutsumi, Y. Yamashita, and S. Shimada, *Macromolecules*, **22**, 2869 (1989).
35. K. Hatada, T. Kitayama, E. Masuda, M. Yamamoto, and T. Shinozaki, *Polym. Prepr. Jpn.*, **37**, 1487 (1988).
36. T. Kitayama, S. Kishiro, E. Masuda, and K. Hatada, *Polym. Bull.*, **25**, 205 (1991).
37. J. C. Bevington, *Trans. Faraday Soc.*, **51**, 1392 (1955).