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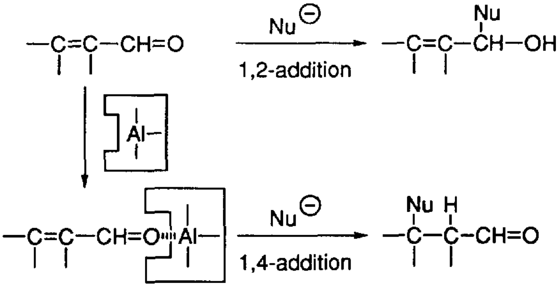
Remarkable Effect of Structure of Bulky Aluminum Phenoxides on Stereospecificity of Methacrylate Polymerization

Tatsuki Kitayama*, Tomohiro Hirano, and Koichi Hatada
Department of Chemistry, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka 560, Japan

Abstract: Polymerizations of methyl methacrylate and ethyl methacrylate with combinations of *t*-butyllithium and several bulky alkylaluminum bisphenoxides were carried out in toluene at −78°C. Methylaluminum bisphenoxide derivatives gave heterotactic polymers which comprise an alternating sequence of *meso* and *racemo* diads. On the other hand, ethyl or isobutylaluminum bis(2,6-di-*t*-butylphenoxide) exhibited syndiotactic-specificity. The effect of structure of bulky aluminum phenoxide on stereospecificity of polymerization was discussed based on the stereochemical analysis of the polymers.

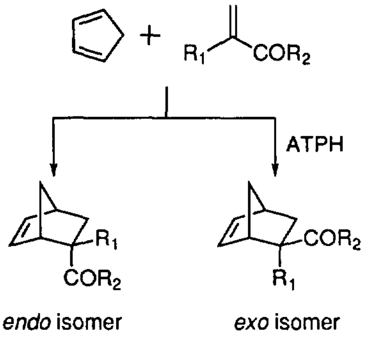
Introduction

Bulky organoaluminum reagents such as methylaluminum bis(2,6-di-*t*-butyl-4-methylphenoxide) (MAD) and aluminum tris(2,6-diphenylphenoxide) (ATPH) have been recognized as promising Lewis acids in selective organic synthesis. The unique character of the bulky aluminum reagents is essentially related to the remarkable ability as a Lewis-acid receptor to recognize oxygen-containing organic molecules and activate certain functionalities. For example, ATPH facilitates selective 1,4-addition of nucleophiles to α,β-unsaturated carbonyl substrates due to efficient stabilization of carbonyls by coordination of the aluminum reagent[1,2], providing the chemoselectivity, while 1,2-addition occurs predominantly in the absence of the aluminum reagent (1).



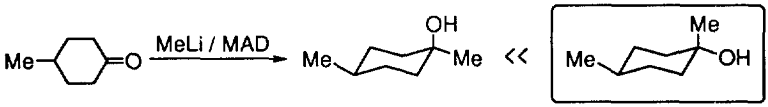
(1)

ATPH has also been utilized in *exo*-selective Diels-Alder reaction of α,β-unsaturated carbonyl compounds owing to steric repulsion of coordinating ATPH[3] (2).



(2)

MAD facilitates the formation of *equatorial* alcohol in the alkylation reaction of cyclohexanone derivatives with methyllithium (MeLi), while the reaction with the nucleophile alone produces predominantly *axial* alcohol (3)[4,5].



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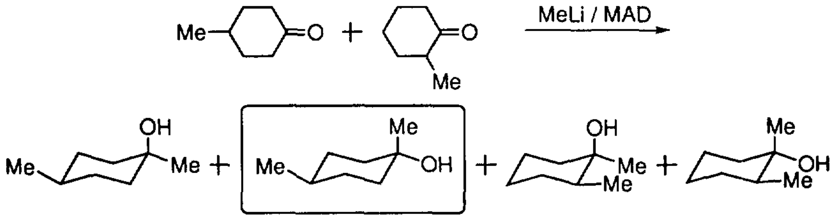
Treatment of the equimolar mixture of 2- and 4-methylcyclohexanones and MAD with a nucleophile gives mainly an *equatorial* alcohol derived from the less hindered ketone, exhibiting substrate selectivity and stereoselectivity at the same time[4,5] (4).



(4)

These examples demonstrate that the bulky aluminum reagents are able to provide stereoselectivity, substrate selectivity, and chemoselectivity in organic synthesis through coordination to carbonyl groups to activate or protect the functionalities.

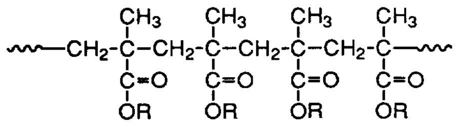
In the field of polymer chemistry, bulky aluminum phenoxides have been used as a Lewis-acid activator in the polymerizations of polar vinyl monomers such as methacrylates[6,7] and heterocyclic monomers such as lactones[8] and oxetane[9]. The polymerization of methyl methacrylate (MMA) with an aluminum tetraphenylporphyrin complex is initiated with visible-light irradiation, the following propagation being very slow. When 3 equiv. of a bulky aluminum phenoxide such as MAD with respect to the propagating species are added to the reaction mixture, a strikingly vigorous reaction takes place with heat evolution to attain 100% conversion within only 3 seconds[6,7]. The polymerization is termed "high-speed living polymerization", where the bulky aluminum phenoxides are assumed to activate the monomer through coordination. More recently, Maruoka *et. al.* claimed that ATPH is a more efficient Lewis acid in this polymerization to give narrower molecular weight distributions (MWDs)[10]. Miyamoto *et al.* reported that enamines can initiate the polymerization of methacrylate in combination with bulky aluminum phenoxides which activate the monomer enough to be attached by the weak Lewis base[11].

On the other hand, Ballard *et al.* reported that an initiator comprising *t*-butyllithium (*t*-BuLi) and (2,6-di-*t*-butylphenoxy)diisobutylaluminum [i-$Bu_2Al(ODBP)$] gave predominantly syndiotactic PMMA with narrow MWD in a living manner. They claimed that i-$Bu_2Al(ODBP)$ coordinates with the propagating species to stabilize them and the bulkiness of the phenoxide "screened" the polymer anion from possible side reactions to afford the living polymerization at ambient temperature[12].

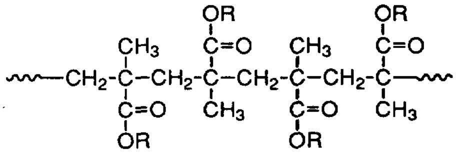
Among living radical polymerizations developed recent years, Sawamoto *et al.* reported the living polymerization of MMA with a combination of alkyl halide, ruthenium(II) chloride tris(triphenyphosphine) complex, and Lewis acids such as methylaluminum bis(2,6-di-*t*-butylphenoxide) [$MeAl(ODBP)_2$][13]. In this system, the Lewis acids are assumed to coordinate to the carbonyl oxygen of terminal monomeric unit of propagating species to facilitate the reversible homolytic cleavage of carbon-halogen bond.

Although these examples demonstrate the versatile utility of bulky Lewis acids in polymer synthesis, the examples which illustrate the potential of bulky Lewis acids in the control of selectivity in polymerization have scarcely been reported.

In 1980's, we found two stereospecific living polymerizations of methacrylate; one is isotactic-specific, initiated with *t*-butylmagnesium bromide[14,15], and the other syndiotactic-specific, initiated with *t*-BuLi / trialkylaluminum[16,17].



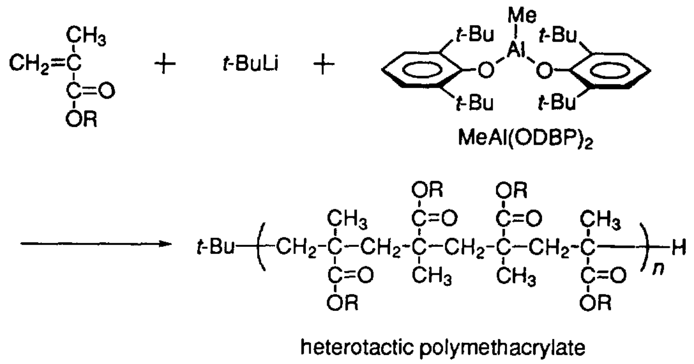
isotactic polymethacrylate



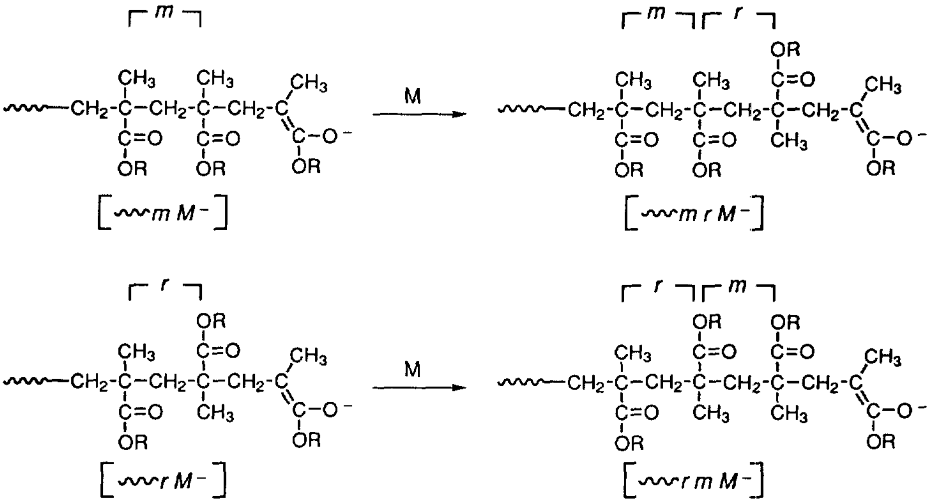
syndiotactic polymethacrylate

More recently, we found heterotactic-specific living polymerization of certain alkyl methacrylates with a combination of *t*-BuLi and $MeAl(ODBP)_2$ in toluene at low temperature[18,19] (Scheme 1). Heterotactic polymer is one kind of stereoregular polymer that comprises an alternating sequence of meso (*m*) and racemo (*r*) diads. The formation of heterotactic sequence requires two different types of stereoregulation, *m*- and *r*-additions, to occur in an alternate manner. This means that the diad configuration at the propagating chain-end should affect the stereospecificity drastically; the chain end with *m* diad ($\sim\!\sim\!\sim mM^-$) prefers *r*-addition and that with *r* diad ($\sim\!\sim\!\sim rM^-$) prefers *m*-addition (Scheme 2). This obviously requires a higher-order stereoregulation than those

Scheme 1

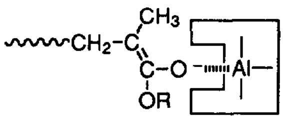


Scheme 2



for isotactic and syndiotactic polymerizations; for the latters the control of configurational relationship between neighboring constitutional repeating units is sufficient in principle.

The existence of an excess amount of $MeAl(ODBP)_2$ over *t*-BuLi is essential for the formation of the heterotactic polymer. In fact, at the ratio of Al / Li = 1, where most of the aluminum phenoxide might coordinate with the propagating species, a syndiotactic polymer forms in low yields[19]. The result suggests that the propagating species is stabilized by the coordination with the bulky aluminum phenoxide, becomes less reactive, and favors *r*-addition with the monomer free from the coordination by the aluminum phenoxide. At higher Al / Li ratios, the excess $MeAl(ODBP)_2$ may activate the monomer through coordination, and the less reactive propagating species preferentially add the activated monomer. In this process, the steric interaction between the sterically crowded active-end (5) and the bulky monomer–$MeAl(ODBP)_2$ complex (6) might be an important factor for



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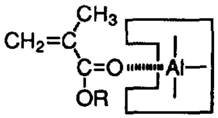
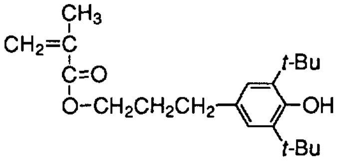


(6)

the heterotactic propagation. Thus $\mathrm{MeAl(ODBP)_2}$ in this polymerization plays roles of the stabilization of the propagating species and of the activation of the monomer, thereby providing not only livingness but also the unique stereospecificity.

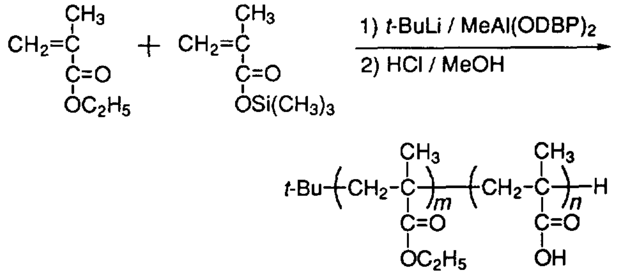
The stabilization given by $\mathrm{MeAl(ODBP)_2}$ has been successfully utilized for anionic living polymerization of a methacrylate monomer (7) having an unprotected phenolic group[20]; the polymerization of the monomer (7) with *t*-BuLi / $\mathrm{MeAl(ODBP)_2}$ in toluene gives a polymer with narrow MWD, while *t*-BuLi alone is quenched with the hydroxyl group of the monomer so that no polymer forms.



(7)

On the other hand, the monomer activation mechanism is used to facilitate monomer-selective copolymerization. The copolymerization of ethyl methacrylate (EMA) and trimethylsilyl methacrylate (TMSMA) with *t*-BuLi / $\mathrm{MeAl(ODBP)_2}$ proceeds in a monomer-selective manner, giving a stereoregular block copolymer that comprises heterotactic poly(EMA) block and syndiotactic poly(TMSMA) block; the second block is easily converted to syndiotactic poly(methacrylic acid) block[21] (Scheme 3).

Scheme 3



Characteristic feature of the polymerization of alkyl methacrylates with *t*-BuLi / $\mathrm{MeAl(ODBP)_2}$ is that bulkiness of the alkyl group affects drastically the stereospecificity of the polymerization. Both the primary and secondary alkyl methacrylates give heterotactic polymers. Heterotactic triad content of PMMA, the simplest polymethacrylate, was 68%. On the other hand, the content of poly(EMA) prepared under the same conditions is 87% and reaches 92% by lowering polymerization temperature to –95°C. In sharp contrast, tertiary alkyl methacrylates give syndiotactic polymers[18]; particularly, TMSMA gives polymers with syndiotactic triad content of over 96% at –78°C and 98% at –95°C[22]. These results imply that the stereospecificity in the polymerization with *t*-BuLi / $MeAl(ODBP)_2$ is very sensitive to steric factors.

Another important factor that affects the stereospecificity of the polymerization should be the structure of aluminum phenoxide. In the present paper, polymerizations of MMA and EMA with *t*-BuLi and several aluminum phenoxides are reported and the effects of the structure of the aluminum compounds on the stereocontrol in the polymerization are discussed based on the stereochemical sequence analysis of the obtained polymers.

Results

Polymerization with Combinations of t-BuLi and Several Methylaluminum Bisphenoxides

To examine the effects of the structure of aluminum phenoxides on the polymerization, MMA and EMA were polymerized in toluene at –78°C with *t*-BuLi in the presence of several aluminum phenoxides having *t*-butyl groups at 2- and 6-positions of the phenoxy groups.

As reported previously[18,19], when polymerizations of MMA and EMA were carried out with *t*-BuLi / $MeAl(ODBP)_2$, heterotactic polymers with narrow MWD were obtained (runs 1 and 5). When methylaluminum bisphenoxides with *p*-substituents such as *p*-methyl, *p*-*t*-butyl, and *p*-bromo groups were employed in the polymerization of MMA, heterotactic-rich PMMA with narrow MWD were also obtained almost quantitatively (runs 2, 3, and 4). The heterotactic triad (*mr*) contents were lower than that for the polymer obtained with

Table 1 Polymerization of MMA and EMA with *t*-BuLi / methylaluminum bisphenoxide (1 / 3 mol / mol) in toluene at –78°C for 24h[a]

Run	Monomer	*p*-Substituent	Yield (%)	Tacticity (%)[b]			$\overline{M}n$[c]	$\overline{M}w$[c] / $\overline{M}n$
				mm	*mr*	*rr*		
1[d]	MMA	H	100	11.6	67.8	20.6	11640	1.14
2	MMA	Me	90	13.7	59.1	27.3	6010	1.27
3	MMA	*t*-Bu	99	14.7	60.9	24.4	6300	1.12
4	MMA	Br	100	19.4	65.1	15.5	6410	1.10
5[d]	EMA	H	100	7.7	88.6	3.7	7010	1.07
6	EMA	Me	97	6.9	67.5	25.6	6040	1.12
7	EMA	*t*-Bu	100	6.2	84.3	9.5	8170	1.10
8	EMA	Br	100	13.2	82.7	4.1	6360	1.08

[a] Monomer 10mmol, toluene 10ml, *t*-BuLi 0.2mmol, methylaluminum bisphenoxide 0.6mmol.
[b] Determined by ^1H NMR or ^{13}C NMR. [c] Determined by GPC. [d] $MeAl(ODBP)_2$ 1.0mmol.

$MeAl(ODBP)_2$. The decrease in *mr* content in runs 2 (*p*-methyl) and 3 (*p*-*t*-butyl) is accompanied by the increase in *mm* and *rr* contents. In run 4 (*p*-bromo), however, the *mm* content increases but the *rr* content decreases. The results indicate that these *p*-substituents of the aluminum bisphenoxide affect the stereospecificity of the polymerization in different ways.

The effect of *p*-substituent on tacticity is more remarkable in the case of the polymerization of EMA. The polymers obtained are all heterotactic and have narrow MWD (runs 5 - 8). The unsubstituted derivative, $MeAl(ODBP)_2$, gives the highest *mr* content (run 5) as in the case of the polymerization of MMA. It is evident that in the cases of *p*-methyl (run 6) and *p*-*t*-butyl (run 7) derivatives, the decrease in *mr* content is accompanied by the increase in *rr* content. Contrastingly, the introduction of *p*-bromo group (run 8) gives rise to the increase in *mm* content while *rr* content being unchanged from the case of $MeAl(ODBP)_2$ (run 5). Since the *p*-methyl and *p*-bromo groups are sterically almost identical, the results indicate that the main factor that governs the change of stereospecificity is not the steric but electronic features of the aluminum bisphenoxides. The most probable cause is the change in their Lewis acidity; the presence of the electron-withdrawing bromo group at *para* position of the aluminum phenoxide may increase the Lewis acidity of the aluminum center while the electron-donating alkyl groups may decrease it. Therefore, the structural change even at the position away from the aluminum center affects coordination ability of the aluminum compounds to the propagating chain-ends and thus alters the stereospecificity in the polymerization.

As described in the Introduction, $\sim\sim rM^-$ and $\sim\sim mM^-$ anions coexist in the heterotactic polymerization, which should have opposite stereospecificity, *i.e.*, *m*-addition and *r*-addition, respectively. Thus it is reasonable to expect that the effect of the Lewis acidity of the aluminum phenoxides on stereospecificity differs in these two types of propagating anions. Stereochemical sequence in the main chain of heterotactic poly(EMA) prepared with t-$BuLi/MeAl(ODBP)_2$ almost obeys first-order Markovian statistics[18,23]. The conditional probability of *m*-addition by *r*-ended anion ($\sim\sim rM^-$), $P_{r/m}$, and that of *r*-addition by *m*-ended anion ($\sim\sim mM^-$), $P_{m/r}$, were determined from the triad values for the poly(EMA)s obtained with several aluminum phenoxides as shown in Table 2. In the polymerization with $MeAl(ODBP)_2$ (*p*-substituent = H), $P_{r/m}$ is greater than $P_{m/r}$, indicating the higher heterotactic selectivity of $\sim\sim rM^-$ than that of $\sim\sim mM^-$. In the polymerization with aluminum phenoxide having electron-donating *p*-methyl (run 6) or *p*-*t*-butyl group (run7), $P_{r/m}$ decreases greatly and becomes smaller than $P_{m/r}$. On the other hand, in the case of *p*-bromo derivative (run 8), $P_{m/r}$ decreases drastically while $P_{r/m}$ is the same as that with $MeAl(ODBP)_2$. The ratios, $P_{m/r} / P_{m/m}$ and $P_{r/m} / P_{r/r}$, are shown in the table as the measure of the heterotactic selectivity of $\sim\sim mM^-$ and $\sim\sim rM^-$, respectively, which express the effects of the *p*-substituent more evidently.

Table 2 also includes second-order Markovian parameters estimated from tetrad fractions determined from methylene carbon NMR signals, which show hexad-level splittings as illustrated in Figure 1. In most cases

Table 2 Parameters of first-order and second-order Markovian statistics in heterotactic polymerizations of EMA

Run[a]	*p*-Substituent	First-order parameter				Second-order parameter			
		$P_{m/r}$	$P_{r/m}$	$\frac{P_{m/r}}{P_{m/m}}$	$\frac{P_{r/m}}{P_{r/r}}$	$P_{mm/r}$	$P_{rm/r}$	$P_{mr/m}$	$P_{rr/m}$
5	H	0.85	0.92	$5._8$	$12._0$	0.90	0.86	0.94	0.86
6	Me	0.83	0.57	$4._9$	$1._3$	0.90	0.88	0.73	0.70
7	*t*-Bu	0.87	0.82	$6._8$	$4._4$	0.90	0.89	0.85	0.93
8	Br	0.76	0.91	$3._1$	$10._1$	0.90	0.73	0.94	(1.00)[b]

[a] See Table 1.

[b] Due to low content of *rrr* tetrad, the value could not be estimated at sufficient accuracy.

except run 8, the difference in the second diad from the terminal (ante-penultimate diad) of $\sim\sim mM^-$ affects the parameters only slightly, *i.e.* $P_{mm/r} \doteqdot P_{rm/r}$. This seems to mean that the first-order Markovian treatment is adequate. However, the difference between $P_{mm/r}$ and $P_{rm/r}$ is quite evident for the case of *p*-bromo derivative (run 8). This implies that the ante-penultimate diad configuration affects the stereoselectivity of $\sim\sim mM^-$, probably due to stronger penultimate coordination of *p*-bromo derivative.

The stereochemical defect in the heterotactic poly(EMA)s is either —*mm*— or —*rr*— sequence. In the ^{13}C NMR spectra of poly(EMA)s obtained with *p*-methyl derivative (Figure 1b), $mrm\underline{rr}$ hexad peak is evidently strong, while in the spectrum of heterotactic poly(EMA) obtained with *p*-bromo derivative, the main defect is —*mm*— as in $r\underline{mm}rm$ and $\underline{mm}rmr$ hexads. These

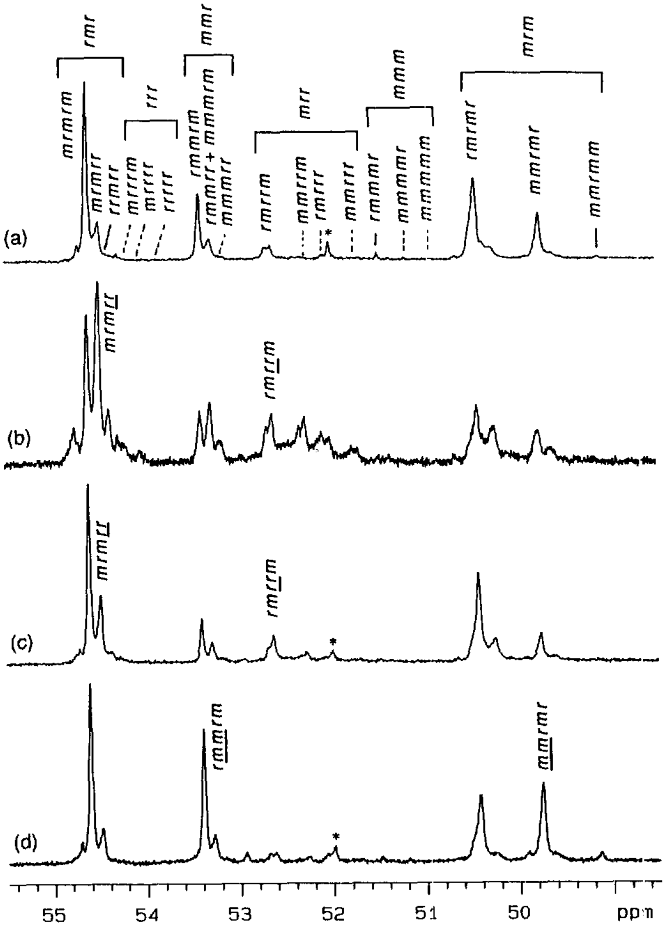


Figure 1 ^{13}C NMR spectra of methylene carbon in heterotactic poly(EMA)s prepared with *t*-BuLi / methylaluminum bisphenoxide; *p*-substituent (a) -H, (b) -Me, (c) -*t*-Bu and (d) -Br.
* A signal due to chain-end unit.

reflect the lower heterotactic-selectivity of ~~~ rM^- anion formed with *p*-methyl derivative and lower heterotactic-selectivity of ~~~ mM^- anion formed with *p*-bromo derivative.

The effects of *p*-substituent of the aluminum phenoxides are also observed on the stereoregularity at the initiating chain-ends of the poly(EMA)s. Stereochemical structures at the chain ends relate to the initiation reaction and the analysis often provides important information on the stereospecificity of initiating species. We have reported the ^{13}C NMR analysis of heterotactic poly(EMA) for the stereoregularity at and near the initiating chain-end and revealed the stereospecificity of the dimer and trimer anions[23]. Figure 2 shows the ^{13}C NMR spectra of methyl carbons of *t*-butyl group at the initiating chain-end of the heterotactic poly(EMA)s obtained with several aluminum phenoxides. The methyl carbon resonances show splittings due to triad tacticity at the initiating chain-end as indicated in Figure 2. The assignments were made by the comparison with the spectra of isotactic and syndiotactic poly(EMA)s of the same chemical structure[23].

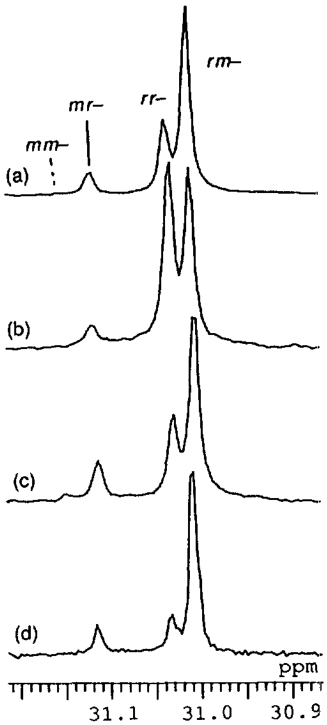


Figure 2 Expanded spectra of methyl carbon NMR signals of *t*-butyl group at the initiating chain-end of heterotactic poly(EMA)s obtained with four different methylaluminum phenoxides; *p*-substituent (a) –H, (b) –Me, (c) –*t*-Bu and (d) –Br.

The relative intensities of four peaks provides the *r* / *m* ratio of the first diad, as determined from the ratio [*rr*+ *rm*] / [*mm* + *mr*], and the *m* / *r* ratio at the second diad following the first *r* diad, as estimated from the triad ratio of ***r m*** / ***r r***. The results of the analysis are shown in Table 3. In all the cases, the first diads are predominantly *r*. However, the second diad after the first *r*-diad strongly depends on the kind of aluminum phenoxide used; as compared with the case of MeAl(ODBP)$_2$ (*p*-substituent = H), ***r m*** / ***r r*** increases for the case of *p*-bromo derivative and decreases for the cases of *p*-methyl and *p*-*t*-butyl derivatives. The results are consistent with those obtained from the main-chain sequence analysis; that is, heterotactic selectivity of ~~~ rM^- anion as represented by $P_{r/m}$ / $P_{r/r}$ is in the order of *p*-Br > *p*-H > *p*-*t*-Bu > *p*-Me. A similar analysis for ~~~ mM^- anion was difficult due to the low content of ***mm*** triad at the initiating chain-end.

Table 3 Stereoselectivities of dimer and trimer anions in heterotactic EMA polymerization estimated from the first (*r* / *m*) and the second diads (*r m* / *r r*) at the initiating chain-end

Run[a]	*p*-Substituent	First diad	Second diad
		r / *m*	*r m* / *r r*
5	H	92 / 8	72 / 28
6	Me	93 / 7	46 / 54
7	*t*-Bu	85 / 15	68 / 32
8	Br	91 / 9	85 / 15

[a] See Table 1.

Polymerization with Combinations of t-BuLi and Alkylaluminum Bis(2,6-di-t-butylphenoxide)

Ethyl- and isobutylaluminum bis(2,6-di-*t*-butylphenoxide)s were prepared and used for the polymerizations of MMA and EMA with *t*-BuLi in toluene at –78°C. The results are shown in Table 4 together with those with MeAl(ODBP)$_2$. The replacement of methyl group in MeAl(ODBP)$_2$ with ethyl or isobutyl group drastically alters the stereospecificity in the polymerization from heterotactic to syndiotactic. On the other hand, the living character is retained as evidenced by narrow MWD of the polymers obtained. This result indicates that the change in steric structure around the aluminum center drastically affects the stereospecificities of the propagating anions. Furthermore, the yields decreased in the polymerizations using *i*-BuAl(ODBP)$_2$ (runs 10 and 12), suggesting that the bulkiness around the aluminum center hinders propagation reaction.

Table 4 Polymerization of MMA and EMA with *t*-BuLi / alkylaluminum bis(2,6-di-*t*-butylphenoxide) (1 / 5 mol / mol) in toluene at –78°C for 24h[a]

Run	Monomer	Alkyl group	Yield (%)	Tacticity (%)[b]			$\overline{M}n^c$	$\overline{M}w^c / \overline{M}n$
				mm	*m r*	*r r*		
1	MMA	Me	100	11.6	67.8	20.6	11640	1.14
9	MMA	Et	82	0.0	10.9	89.1	4450	1.10
10	MMA	*i*-Bu	20	0.0	16.2	83.8	1920	1.38
5	EMA	H	100	7.7	88.6	3.7	7010	1.07
11	EMA	Et	100	0.0	8.1	91.9	6490	1.09
12	EMA	*i*-Bu	30	0.3	17.5	82.2	4990	1.14

[a] Monomer 10mmol, alkylaluminum bis(2,6-di-*t*-butylphenoxide) 1.0mmol, *t*-BuLi 0.2mmol, toluene 10ml. [b] Determined by ^{1}H NMR or ^{13}C NMR. [c] Determined by GPC.

As described in the Introduction, we have proposed that in the heterotactic polymerization, MeAl(ODBP)$_2$ coordinates with the propagating species to stabilize them [*cf.* structure (5)], and the excess of MeAl(ODBP)$_2$ coordinates to the monomers to activate them [*cf.* structure (6)]. In the process that the monomer coordinated with MeAl(ODBP)$_2$ reacts with the propagating species, there is a possibility that MeAl(ODBP)$_2$ stays at the newly formed chain-end unit and the MeAl(ODBP)$_2$ having coordinated to the propagating end is kept coordinated to the newly formed penultimate unit after the addition of the monomer (Scheme 4). If this is the case, an exchange between MeAl(ODBP)$_2$ molecule coordinating to the propagating species and that to the monomers should take place. Based on the finding that MeAl(ODBP)$_2$ and EtAl(ODBP)$_2$ exhibit quite different stereospecificity (*cf.* Table 4), the following two-step polymerizations were examined to investigate the possibility of the exchange (Table 5), where the tacticity of the obtained polymer should be diagnostic of the occurrence of the exchange.

First, EMA was polymerized with *t*-BuLi / MeAl(ODBP)$_2$ at the ratio = 1, where all of the aluminum compound is expected to coordinate to propagating anions. After 1 hour, two times EtAl(ODBP)$_2$ as much as

Scheme 4

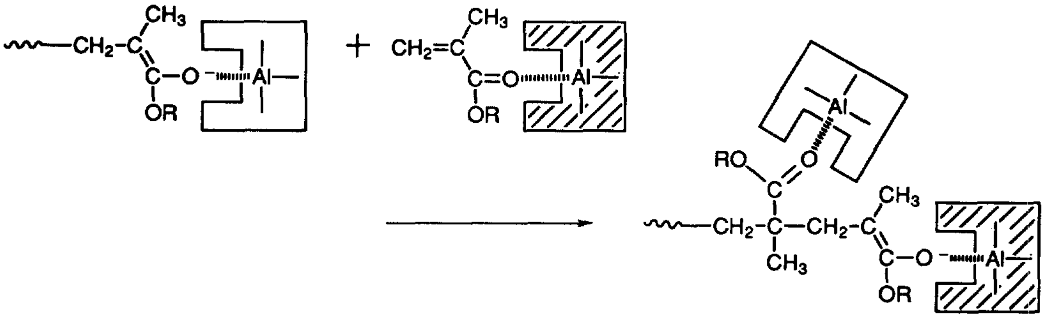


Table 5 Polymerization of EMA with *t*-BuLi and two kinds of aluminum phenoxide in toluene at -78°C for 24hr[a]

Run	Aluminum phenoxide	$\frac{\text{Al}}{\text{Li}}$	Time (h)	Yield (%)	Tacticity (%)[b]			$\bar{M}_n$[c]	$\frac{\bar{M}_w}{\bar{M}_n}$[c]
					mm	*m r*	*r r*		
13	$MeAl(ODBP)_2$	1	1	4.2	-	-	-	-	-
14	$MeAl(ODBP)_2$ $EtAl(ODBP)_2$	1 +2	1 +23	80	0.8	25.7	73.5	6220	1.16
15	$MeAl(ODBP)_2$ $MeAl(ODBP)_2$	1 +2	1 +23	100	7.0	74.6	18.4	7340	1.14

[a] Monomer 10mmol, *t*-BuLi 0.2mmol, toluene 10ml. [b] Determined by ^{13}C NMR.
[c] Determined by GPC.

t-BuLi was added to the polymerization mixture and the reaction was continued for further 23 hours. The yield for the first 1 hour was very low (run 13) because of the absence of activated monomers, and thus most of the polymer obtained in this two-step polymerization (run 14) should form after the second aluminum phenoxide, $EtAl(ODBP)_2$, was added. If the exchange of the aluminum compounds does not occur and the stereospecificity of polymerization is controlled by $MeAl(ODBP)_2$ which coordinates to the propagating anion, the resulting polymer should be heterotactic. On the other hand, if the exchange occurs and $EtAl(ODBP)_2$, which coordinates to the monomer, stays at the chain end as shown in Scheme 4 and controls the stereospecificity, the polymerization should give a syndiotactic polymer.

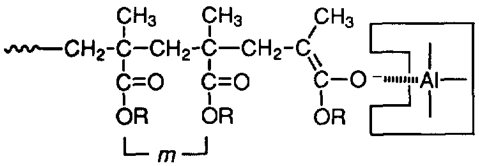
The obtained polymer is syndiotactic, although the syndiotactic triad content is lower than that of the polymer obtained by the polymerization with *t*-BuLi / $EtAl(ODBP)_2$ (*cf.* Table 4, run 11). This results suggest the occurrence of the exchange of the aluminum compounds during the propagation process. When $MeAl(ODBP)_2$ was added in the second stage, the resulting polymer was heterotactic (run 15), though the heterotacticity was slightly lower than that of the polymer obtained by the usual polymerization (run 5 in Table 1).

Discussion

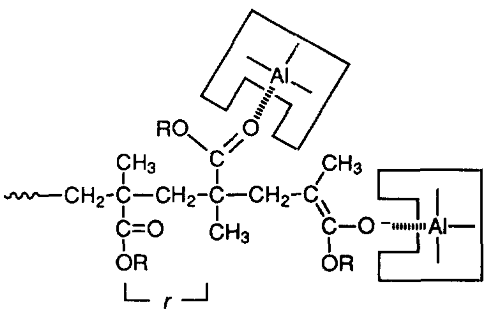
When the polymerization with *t*-BuLi / $MeAl(ODBP)_2$ is carried out at the Al/Li ratio = 1, a syndiotactic polymer forms in low yield[18,19]. The result suggests the formation of syndiotactic-specific species with low activity, which may be stabilized through the coordination by the bulky aluminum phenoxide as suggested by Ballard *et al.* for the polymerization of MMA with *t*-BuLi / *i*-$Bu_2Al(ODBP)$[11]. If all the $MeAl(ODBP)_2$ coordinates to the propagating chain-end, there exists no excess $MeAl(ODBP)_2$ in the polymerization system. Under these conditions where most of the incoming monomers are free from the coordination by $MeAl(ODBP)_2$, the syndiotactic polymer is formed probably due to the intrinsic syndiotactic-specific nature of the propagating species coordinated with $MeAl(ODBP)_2$ as in the cases of other aluminum-assisted methacrylate polymerizations[12,16,17,24-29].

Heterotactic poly(EMA)s with narrow MWD are obtained in high yields at Al/Li≥2, where excess $MeAl(ODBP)_2$ existing in the polymerization system may activate the monomer through coordination[6,7]. As depicted in Scheme 4, the less reactive propagating species, stabilized through the coordination by $MeAl(ODBP)_2$, should react preferentially with the activated monomer carrying the bulky $MeAl(ODBP)_2$. The mechanism implies the possibility that two aluminum phenoxides coordinate at the terminal and penultimate units.

In order to explain the different stereospecificity of $\sim\sim\sim mM^-$ and $\sim\sim\sim rM^-$ anions, we assume that the difference in the terminal diad configuration affects the stability of the coordination of the aluminum phenoxide to the penultimate unit. Based on this assumption, we have proposed the structure models of the two types of propagating species; $\sim\sim\sim mM^-$ anion coordinates one aluminum phenoxide at the terminal unit, and $\sim\sim\sim rM^-$ anion bears two phenoxides at the terminal unit and the penultimate ester group[30]. The models explain the higher stability and higher stereospecificity of $\sim\sim\sim rM^-$ anion than $\sim\sim\sim mM^-$ anion[23,30]. The *r*-selectivity of $\sim\sim\sim mM^-$ anion seems consistent with syndiotactic-specific nature of the species formed at *t*-BuLi / $MeAl(ODBP)_2$ = 1, which should carry one $MeAl(ODBP)_2$. The *m*-selectivity of $\sim\sim\sim rM^-$ anion can be explained as follows. When $\sim\sim\sim rM^-$ anion, bearing two bulky aluminum phenoxides, adds the monomer coordinated with the



$\sim\sim\sim mM^-$

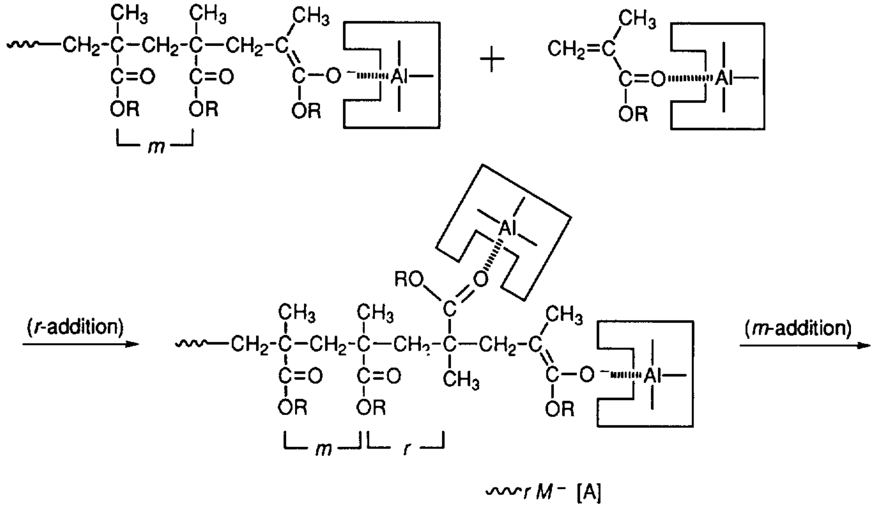


$\sim\sim\sim rM^-$

phenoxide, which can be regarded as a temporarily bulky monomer, the situation is similar to the polymerization of exceedingly bulky triarylmethyl methacrylates such as triphenylmethyl methacrylate, which undergoes in an isotactic-specific manner regardless of polymerization conditions[31]. The result of two-step polymerization (run 14), where $EtAl(ODBP)_2$ was added to the polymerization mixture formed with *t*-BuLi / $MeAl(ODBP)_2 = 1$, suggests the exchange between the aluminum phenoxide coordinated to the propagating species and that to the monomer during the propagation. The exchange can occur through the mechanism shown in Scheme 4.

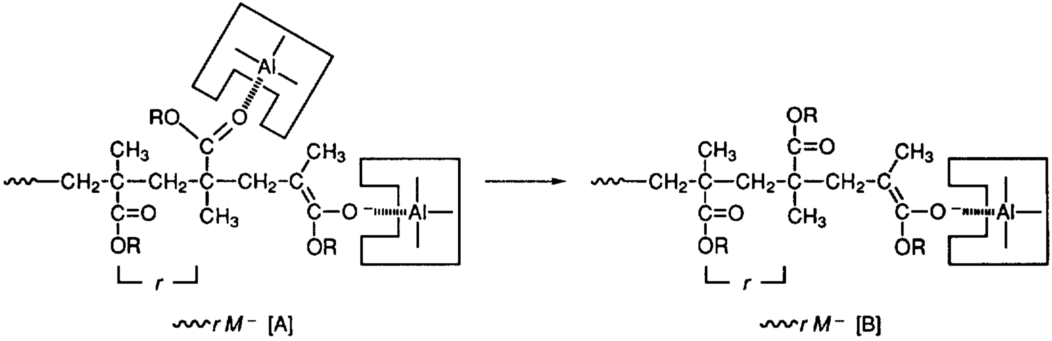
Starting from ∼∼∼ mM^- anion, which carries one aluminum phenoxide and favors *r*-addition, the addition of a monomer carrying $MeAl(ODBP)_2$ gives an intermediate species bearing two aluminum phenoxides, ∼∼∼ rM^- [A] (Scheme 5), which favors *m*-addition:

Scheme 5



When the aluminum phenoxide of lower Lewis acidity such as *p*-methyl derivative is used, the coordination to the penultimate unit becomes weaker and the ∼∼∼ rM^- [A] tends to release the phenoxide at the penultimate unit and become the species having one aluminum phenoxide, ∼∼∼ rM^- [B] (Scheme 6). The released phenoxide

Scheme 6

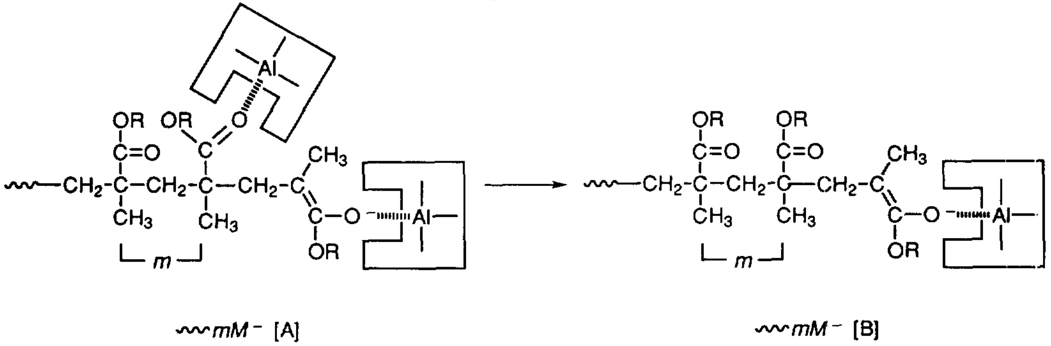


may coordinate with the monomer, and be involved again in the process depicted in Scheme 5.

The structure of $\sim\sim rM^-$ anion [B] is similar to $\sim\sim mM^-$ anion and expected to exhibit *r*-selectivity. This explains the lower $P_{r/m}$ values for the polymerization with *p*-methyl and *p*-*t*-butyl derivatives (*cf.* Table 2, runs 6 and 7).

We postulate that $\sim\sim mM^-$ anion has one aluminum phenoxide. As depicted in Scheme 4, however, immediately after it is formed from $\sim\sim rM^-$ anion, the aluminum phenoxide having coordinated to the $\sim\sim rM^-$ anion may stay at the newly formed penultimate monomer unit to generate $\sim\sim mM^-$ [A] shown in Scheme 7. The Lewis acidity of the aluminum phenoxide is again the key that determines whether the phenoxide coordinated the penultimate unit is released before or kept until the monomer addition takes place. In the case of $MeAl(ODBP)_2$ the phenoxide at the penultimate unit is expected to be removed easily to form $\sim\sim mM^-$ [B] as depicted in Scheme 7, which exhibits *r*-selectivity to form *mr* sequence.

Scheme 7



If an aluminum phenoxide with higher Lewis acidity such as *p*-bromo derivative is used, it tends to stay at the penultimate unit ($\sim\sim mM^-$ [A]) and makes the species *m*-selective as in the case of $\sim\sim rM^-$ [A] (*cf.* Scheme 5). Thus $P_{m/r}$ value for the polymerization with *p*-bromo derivative is smaller than other cases (*cf.* Table 2).

In the cases of $EtAl(ODBP)_2$ and *i*-$BuAl(ODBP)_2$, the coordination to the penultimate unit may be sterically unfavorable, leading to the formation of syndiotactic-specific species like $\sim\sim rM^-$ [B] (Scheme 6).

As a whole, the results obtained in this work suggest that the control of the coordination of the aluminum phenoxide to the penultimate unit is the key to the stereospecificity of the polymerization. Since an increase or a decrease of Lewis acidity affects the degree of stereospecificity of $\sim\sim mM^-$ and $\sim\sim rM^-$ anions in opposite ways, it seems difficult to increase heterotacticity of the polymer by changing the Lewis acidity of the aluminum phenoxide. So far the highest heterotacticity is obtained with $MeAl(ODBP)_2$, which is in a good balance of Lewis acidity. However, it is noteworthy that we could change the stereospecificity of particular types of propagating anions, $\sim\sim mM^-$ and $\sim\sim rM^-$, by proper selection of Lewis acidity as well as steric factors of the aluminum phenoxide.

The lower heterotactic-specificity of $\sim\sim mM^-$ anion is still the problem to be solved for attaining higher heterotacticity. The key process may be smooth and selective removal of the aluminum phenoxide coordinated to the penultimate unit of $\sim\sim mM^-$. For this purpose, we are now investigating the effects of some ester compounds which competitively coordinates with the aluminum phenoxide to remove it from the polymer chain-end[32]. The results will be reported elsewhere.

Experimental

Materials

MMA and EMA were purified by fractional distillation under reduced nitrogen pressure, dried over calcium dihydride and vacuum-distilled just before use. Toluene and heptane were purified in the usual manners, mixed with a small amount of *n*-BuLi, and distilled under high vacuum. Benzene was distilled, and dried over sodium.

2,6-Di-*t*-butylphenol, obtained commercially, was fractionally distilled, dried over Molecular Sieves (MS) 4A, and used as a toluene solution. 2,6-Di-*t*-butyl-4-methylphenol, 2,4,6-tri-*t*-butylphenol, and 4-bromo-2,6-di-*t*-butylphenol were recrystallized from heptane, dried over MS 4A, and used as toluene solutions.

t-BuLi in pentane (Aldrich Co. Ltd.) was used as a heptane solution. The concentration was determined by titration with butan-2-ol[33]. Trimethylaluminum, triethylaluminum, and triisobutylaluminum (Nippon Aluminum Alkyls) were used as toluene solutions.

Preparation of alkylaluminum bisphenoxide[34]

A solution of substituted phenol (2,6-di-*t*-butylphenol, 2,6-di-*t*-butyl-4-methylphenol, 2,4,6-tri-*t*-butylphenol, or 4-bromo-2,6-di-*t*-butylphenol) in toluene (2 equiv.) was added slowly to a toluene solution of trialkylaluminum (1 equiv.) at 0°C. The resulting mixture was stirred at room temperature for 20h and used for the polymerization reaction without further purification. $MeAl(ODBP)_2$ was recrystallized in the following procedure. The solvent was removed under vacuum to leave a yellowish solid. The product was recrystallized three times by dissolving it in hot heptane and cooling to –78°C. After most of heptane was removed by a syringe and the residual heptane was evaporated under vacuum to dryness, the solid residue was dissolved in toluene and used for the polymerization reactions.

Polymerization

All the polymerization were carried out in a glass ampoule filled with dried nitrogen passed through MS 4A cooled at –78°C. A heptane solution of *t*-BuLi was added to an aluminum phenoxide in toluene at –78°C. The polymerization reaction was initiated by adding the monomer slowly to this mixture at –78°C. The reaction was terminated by adding methanol containing HCl at the polymerization temperature. The reaction mixture was concentrated to dryness under reduced pressure, and the residue was dissolved in benzene. Insoluble materials were removed by centrifugation, and the polymer was recovered from the solution by freeze-drying and dried under vacuum.

Measurements

Tacticities of PMMAs were determined from α-methyl hydrogen signals in ^{1}H NMR spectra measured in $CDCl_3$ at 55°C on a JEOL JNM GX270 spectrometer operated at 270MHz. Tacticities of poly(EMA)s were determined from carbonyl carbon signals in ^{13}C NMR spectra measured in nitrobenzene-d_5 at 110°C or $CDCl_3$ at 55°C on a Varian Unity Inova 500 spectrometer operated at 125MHz. Molecular weight and its distribution of the polymers were determined by gel permeation chromatography (GPC) using a JASCO 880-PU chromatograph equipped with Shodex GPC columns KF-80M (30cm x 0.8cm) and KF-802.5 (30cm x 0.8cm) using tetrahydrofuran as an eluent at 40°C. The GPC chromatogram was calibrated against standard polystyrene samples.

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