Chain-End Stereostructure of Heterotactic Poly(ethyl methacrylate) Prepared with *t*-Butyllithium/Bis(2,6-di-*t*-butylphenoxy)methylaluminum as Studied by ^{13}C NMR Spectroscopy

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(Received September 11, 1995)

ABSTRACT: Heterotactic poly(ethyl methacrylate)s [poly(EMA)s] were prepared with *t*-butyllithium/bis(2,6-di-*t*-butylphenoxy)methylaluminum in toluene at -78°C and -95°C . The end-group signals in ^{13}C NMR spectra of the poly(EMA) were assigned in terms of triad configurations near the initiating and terminating chain-ends. The analysis for the initiating chain-end revealed that (1) the dimer anion preferentially undergoes *racemo* addition to form a trimer anion with *racemo* (*r*) diad ($t\text{-Bu-M-M}^- \longrightarrow t\text{-Bu-r-M}^-$), (2) the trimer anion with *r* diad favors *meso* (*m*) addition ($t\text{-Bu-r-M}^- \longrightarrow t\text{-Bu-r-m-M}^-$), and (3) the *m*-selectivity is much enhanced by lowering the polymerization temperature. The analysis of the terminating chain-end showed that (1) living polymer having *r* diad at the chain end ($\sim\text{rM}^-$) exists more than that with *m* diad ($\sim\text{mM}^-$), suggesting the higher stability of the *r*-ended anion, and (2) the living anion favors *r*-addition in their termination reaction with alcohol, indicating the inherently *r*-specific nature of the propagating species. Based on these structural analyses the mechanism of stereospecificity in the heterotactic polymerization is discussed.

KEY WORDS Heterotactic Living Polymerization / Polymethacrylate / Stereospecific Polymerization / Stereoregularity / End Group /

End-group analysis of polymers by NMR spectroscopy often provides important information for the understanding of polymerization mechanism.¹ In particular, stereochemical structures near the initiating and terminating chain-ends relate to stereospecificity of initiating and propagating species.

Methacrylate is one of the most intensively investigated monomers in regard of stereospecificity of polymerization.^{2,3} During the last decade stereospecific living polymerization of methacrylate has become possible.^{4–8} We have reported stereospecific living polymerizations of methyl methacrylate (MMA) with *t*-butylmagnesium bromide ($t\text{-BuMgBr}$)^{4,5} and *t*-butyllithium (*t*-BuLi)/trialkylaluminum,^{6,7} which give highly isotactic and syndiotactic polymers, respectively, with narrow molecular weight distribution (MWD). These stereoregular PMMAs have the same chemical structure from initiating chain-end (*t*-butyl group) to terminating chain-end (methine hydrogen). The diad tacticities of both the initiating and terminating chain-ends have been studied by ^1H NMR spectroscopy and by the analysis of the distribution of stereoisomeric oligomers by means of chromatographic separation.^{9–13}

Recently we found that polymerizations of certain alkyl methacrylates with *t*-BuLi/bis(2,6-di-*t*-butylphenoxy)methylaluminum [MeAl(ODBP)_2] in toluene at low temperature proceeds in a living manner and give highly heterotactic polymers with narrow MWD.^{14–16} Heterotactic polymer is one kind of stereoregular polymer that comprises an alternating sequence of *meso* (*m*) and *racemo* (*r*) diads. It is obvious that the formation

of heterotactic polymer requires a higher order of stereoregulation than those for isotactic and syndiotactic polymers; for the formation of heterotactic sequence, two different types of stereoregulation, *m*- and *r*-additions,*¹ should occur in an alternate manner. In fact, there have been few publication on the formation of heterotactic polymers.^{17–23} Exceptionally high heterotacticity was reported for an alternating copolymer of methyl methacrylate (MMA) and styrene obtained by a radical copolymerization in the presence of BCl_3 at $-95 \sim -100^\circ\text{C}$, the cotacticity of MMA-centered triad being $mm:mr:rr=9:89:2$ and that of styrene-centered triad $mm:mr:rr=9:88:3$.²³ The highest heterotacticity so far reported for homopolymer was that for poly(triisopropylsilyl vinyl ether) prepared with $\text{C}_2\text{H}_5\text{AlCl}_2$ in toluene at -78°C ($mm:mr:rr=26:69:8$).¹⁹ The heterotactic triad content of certain poly(alkyl methacrylate)s including poly(ethyl methacrylate) [poly(EMA)] prepared with *t*-BuLi/ MeAl(ODBP)_2 at -78°C reached 87%, and, in particular, that of poly(EMA) obtained at -95°C was 91%.^{*2} Thus the heterotactic specificity of the polymerization with *t*-BuLi/ MeAl(ODBP)_2 is the highest one ever reported.

The structural feature of heterotactic polymer, *i.e.*, the alternation of *m* and *r* diads in the chain, $\cdots mrmrmr \cdots$, raises the question whether the polymer chain starts with *m* or *r* diad and ends with *m* or *r* diad. Thus the end-group analysis of heterotactic polymer in regard of stereochemistry is particularly interesting.

In this work, the stereostructure near the chain ends of heterotactic poly(EMA) was investigated by ^{13}C

*¹ *Meso* (*racemo*) addition means the process of monomer addition through which the configuration of the penultimate unit of the propagating chain-end is fixed to form a *meso* (*racemo*) diad at penultimate and antepenultimate monomer units.

*² The previous communication (ref 14) reports *mr* triad content for poly(EMA) obtained at -95°C to be 87.6%. The value for the polymer obtained under similar conditions (see Table I) is 91.6%. The difference in polymerization conditions was monomer concentration; for the previous work, monomer/solvent = 10 mmol/5 ml, and for the present work, monomer/solvent = 10 mmol/10 ml. The relatively large concentration dependence of stereospecificity is interesting for the understanding of polymerization mechanism and further investigation is under way.

NMR spectroscopy. Poly(EMA) was selected because it has the highest heterotacticity among the heterotactic poly(alkyl methacrylate)s obtained with *t*-BuLi/MeAl(ODBP)₂. The structure of the polymer is depicted as follows.

The end-group structure is identical to those of isotactic and syndiotactic poly(EMA)s obtained with the respective stereospecific living polymerizations mentioned above.⁴⁻⁷ Thus ¹³C NMR spectra of the isotactic and syndiotactic polymers could be used as good references for the spectral assignments of the chain-end signals of the heterotactic poly(EMA).

EXPERIMENTAL

Materials

Ethyl methacrylate (EMA) was 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 manner, mixed with a small amount of *n*-BuLi, and distilled under high vacuum.

Methanol was fractionally distilled and dried over Molecular Sieves 4A. Phenol, *t*-butyl alcohol, and 2,6-di-*t*-butylphenol, obtained commercially, were fractionally distilled, dried over Molecular Sieves 4A, and used as toluene solutions.

t-BuLi in pentane, obtained commercially, was used as a heptane solution. The concentration was determined by titration with *s*-butyl alcohol.²⁴ *t*-BuMgBr was prepared in diethyl ether from *t*-butyl bromide and magnesium.⁵ The amounts of *t*-BuMg-group, total magnesium (Mg²⁺) and total bromide (Br⁻) ions were determined by acid-base titration, chelatometric titration and Fajans' method, respectively. Trimethylaluminum (Me₃Al) and tributylaluminum (*n*-Bu₃Al) were purchased from Nippon Aluminum Alkyls and used as toluene solutions.

Preparation of MeAl(ODBP)₂²⁵

A solution of 2,6-di-*t*-butylphenol in toluene (2 equiv.) was added slowly to a toluene solution of Me₃Al (1 equiv.) at 0°C. The resulting mixture was stirred at room temperature for 20 hours. 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 polymerizations were carried out in a glass

ampoule filled with dried nitrogen. The polymerization reaction was initiated by adding the monomer slowly to the initiator solution in toluene at polymerization temperature. In the case of two component initiators, *t*-BuLi/*n*-Bu₃Al and *t*-BuLi/MeAl(ODBP)₂, each component was mixed at the polymerization temperature. The reaction was terminated by adding methanol, *t*-butyl alcohol, or phenol at the polymerization temperature. Then methanol containing a small amount of HCl was added to neutralize this mixture. 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. In the case of the heterotactic-specific polymerization the product contained 2,6-di-*t*-butylphenol, which was removed by gel permeation chromatography (GPC) using a JASCO TRI ROTAR-II chromatograph equipped with Shodex GPC column K-2003 (30 cm × 2.0 cm) using CHCl₃ as an eluent at room temperature.

Measurement

Tacticities of the polymers were determined from carbonyl carbon signals in ¹³C NMR spectra measured in CDCl₃ at 55°C on a JEOL JNM GX500 spectrometer operated at 125 MHz. Molecular weight of the polymers and its distribution were determined by GPC using a JASCO TRI ROTAR-V chromatograph equipped with Shodex GPC columns KF-80M (30 cm × 0.8 cm) and KF-802.5 (30 cm × 0.8 cm) using tetrahydrofuran (THF) as an eluent at 40°C. The GPC chromatogram was calibrated against standard polystyrene samples.

RESULTS AND DISCUSSION

Initiating Chain-End

The polymerization of EMA in toluene was carried out at -78°C and/or -95°C with three initiators, *t*-BuMgBr,^{5,26} *t*-BuLi/*n*-Bu₃Al,⁶ and *t*-BuLi/MeAl(ODBP)₂,¹⁴⁻¹⁶ which are known to promote isotactic, syndiotactic, and heterotactic polymerizations, respectively. Based on the knowledge that kinds of alcohol used as a terminating agent affect the stereospecificity in the terminating reaction, phenol, *t*-butyl alcohol, and methanol were used as terminating agent depending on the polymerization system. The results are shown in Table I. All the polymers have a *t*-butyl group at the initiating chain-end and methine carbon at the terminating chain-end.

Figure 1 shows the ¹³C NMR resonances of *t*-butyl group at the initiating chain-end of the isotactic, syndiotactic, and heterotactic poly(EMA)s. In all the spectra, the methyl carbon resonances split into principally two groups of peaks reflecting the stereochemical structure of the initial diad of the chains.

Table I. Polymerization of EMA with several initiators in toluene at -78°C for 24 h, terminated with several alcohols

Initiator	Terminating agent	Yield	Tacticity/% ^a			$\bar{M}_n^b$	$\bar{M}_w^b$
		%	<i>mm</i>	<i>mr</i>	<i>rr</i>		$\bar{M}_n$
<i>t</i> -BuMgBr ^c	MeOH	100	91.8	8.2	0	2400	1.82
	PhOH + dioxane	100	91.8	8.2	0	2560	1.20
<i>t</i> -BuLi/ <i>n</i> -Bu ₃ Al ^d (1/3)	MeOH	100	0	10.4	89.6	3000	1.06
	<i>t</i> -BuOH	100	0	9.5	90.5	2900	1.05
<i>t</i> -BuLi/MeAl(ODBP) ₂ ^e (1/5)	MeOH	100	7.7	87.2	5.1	5680	1.08
	<i>t</i> -BuOH	100	7.6	87.6	4.8	6220	1.08
	PhOH	100	8.0	87.2	4.8	6230	1.08
	MeOH ^f	100	7.1	91.6	1.3	8100	1.11

^a Determined by ¹³C NMR signals due to carbonyl carbon. ^b Determined by GPC. ^c EMA, 10 mmol; *t*-BuMgBr, 0.5 mmol; toluene, 10 ml. ^d EMA, 5 mmol; *t*-BuLi, 0.25 mmol; *n*-Bu₃Al, 0.75 mmol; toluene, 5 ml. ^e EMA, 10 mmol; *t*-BuLi, 0.2 mmol; MeAl(ODBP)₂, 1.0 mmol; toluene, 10 ml. ^f Polymerization temperature, -95°C.

Figure 1. 125 MHz ^{13}C NMR spectra of *t*-butyl group at the initiating chain-end of three types of stereoregular poly(EMA)s prepared with (a) *t*-BuMgBr, (b) *t*-BuLi/*n*-Bu $_3$ Al, and (c) *t*-BuLi/MeAl(ODBP) $_2$ in toluene at -78°C (CDCl_3 , 55°C).

The isotactic and syndiotactic poly(EMA)s show the major signals at 31.16 and 30.99 ppm, respectively. Isotactic and syndiotactic PMMAs obtained under similar conditions are known to contain predominantly *m* and *r* diads, respectively, at the beginning of the chain.^{9–13} Since the stereoregularities of PMMA and

poly(EMA) obtained with *t*-BuMgBr or *t*-BuLi/*n*-Bu₃Al are almost identical, the predominant initial diads of the isotactic and syndiotactic poly(EMA)s are safely assumed to be *m* and *r*, respectively. Thus the major signal at 31.16 ppm observed in the spectrum of the isotactic poly(EMA) should be assigned to initial *m* diad, and the signal at 30.99 ppm in the spectrum of the syndiotactic poly(EMA) to initial *r* diad.

In the spectrum of heterotactic poly(EMA) (Figure 1c) the major signal is observed in the same region as that of the syndiotactic poly(EMA), along with a smaller signal in the region for *m* diad signal (*cf.* Figure 1a). The results indicate that the initial diad in the heterotactic poly(EMA) is predominantly syndiotactic, the *m/r* ratio being 1/9. The stereostructure of the initial diad relates to the stereospecificity of the dimer anion. These results indicate that the dimer anion prefers *r*-addition rather than *m*-addition.

In the spectrum of the heterotactic poly(EMA), the major signal around 31.0 ppm due to the *r* diad splits further into two peaks, reflecting the difference in the second diad configuration following the initial *r* diad. Thus the chemical shift of *t*-butyl methyl signal is sensitive to the initial triad configuration. In this respect, the two methyl carbon signals of the isotactic poly(EMA) (31.16 and 31.02 ppm) should be assigned to *mm* and *rm* triads because the interior sequence of the polymer mostly comprises *m* diad. Similarly, the two signals of the syndiotactic poly(EMA) (30.99 and 31.08 ppm) should be ascribed to the initial *rr* and *mr* triads. The minor shouldered signal at 30.99 ppm in the spectrum of the heterotactic poly(EMA) is close to the *rr* triad signal of the syndiotactic poly(EMA). Thus the major signal at 30.97 ppm is assignable to *rm* triad at the initiating chain-end and the minor one at 30.99 ppm to *rr* triad.

Table II. Assignment of ^{13}C NMR signals of methyl carbon of *t*-butyl group of three types of stereoregular poly(EMA)s measured in CDCl_3 at 55°C

Poly(EMA)	Chemical shift/ppm	Assignment
Isotactic	31.16 ₄	<i>mm</i>
	31.02 ₅	<i>rm</i>
Syndiotactic	31.08 ₄	<i>mr</i>
	30.98 ₉	<i>rr</i>
Heterotactic	31.07 ₃	<i>mr</i>
	30.99 ₂	<i>rr</i>
	30.96 ₇	<i>rm</i>

The chemical shifts of the methyl carbon signals for three types of stereoregular poly(EMA)s are summarized in Table II. The values for the heterotactic poly(EMA) are not in complete agreement with the corresponding values for the isotactic and syndiotactic poly(EMA)s. The fact suggests that the chemical shifts depend on longer sequences than triad. The most remarkable difference is observed in *rm* triad signals of the heterotactic polymer and isotactic polymer. The *rm* signal of the heterotactic poly(EMA) resonates at slightly lower magnetic field than that of the isotactic polymer. This is most likely due to the difference in the third diad from the initiating chain-end. Since the interior sequence of the isotactic poly(EMA) comprises *m* diad, the *rm* signal of the isotactic poly(EMA) can be ascribed to the tetrad sequence *rmmm*. Therefore the *rm* signal of the heterotactic poly(EMA) is due to *rmr* tetrad, indicating the formation of heterotactic sequence at the beginning of the chain.

Figure 2 shows the methyl carbon signals of *t*-butyl group of poly(EMA)s prepared at -78 and -95°C , respectively. The *rr* triad signal at 30.99 ppm is much smaller for the polymer obtained at -95°C than for the polymer formed at -78°C . The polymer obtained at -95°C has higher heterotacticity (*mm*:*mr*:*rr* = 7.1:91.6:1.3) than that formed at -78°C (*mm*:*mr*:*rr* = 7.6:87.2:5.2). The fact that syndiotacticity is reduced and heterotacticity is enhanced by lowering the polymerization temperature seems consistent with the higher fraction of the initial *rm* triad in the polymer obtained at -95°C and thus supports the present assignments. Another signal due to initial *m* diad at 31.07 ppm is closer in its chemical shift to the signals of the syndiotactic poly(EMA) rather than that of the isotactic polymer, and thus can be assigned to *mr* triad. The *mm*

Figure 2. Expanded spectra of methyl carbons of *t*-butyl group in heterotactic poly(EMA)s prepared at (a) -78°C and (b) -95°C .**Table III.** Triad sequence distribution near the initiating chain-end of stereoregular poly(EMA)s

Poly(EMA)	Terminating agent	Triad tacticity/%				[<i>mm</i> -] + [<i>mr</i> -] [<i>rm</i> -] + [<i>rr</i> -]
		<i>mm</i> -	<i>mr</i> -	<i>rm</i> -	<i>rr</i> -	
Isotactic	MeOH	89	—	11	—	89/11
Isotactic	PhOH	90	—	10	—	90/10
Syndiotactic	MeOH	—	9	—	91	9/91
Syndiotactic	<i>t</i> -BuOH	—	13	—	87	13/87
Heterotactic	MeOH	—	8	66	26	8/92
Heterotactic	<i>t</i> -BuOH	—	9	66	25	9/91
Heterotactic	PhOH	—	8	62	30	8/92
Heterotactic ^a	MeOH	—	7	83	10	7/93

^a Polymerization temperature, -95°C .

triad signal to be observed at around 31.16 ppm (*cf.* Figure 1a) is hardly observable. Though the lower intensity of the signal does not allow a decisive conclusion, the initial *m* diad mostly follows *r* diad.

Table III shows the triad sequence distribution at the initiating chain-end of isotactic, syndiotactic, and heterotactic poly(EMA)s. The values for each set of tactic poly(EMA)s are expectedly in good agreement irrespective of terminating agent used. The fraction of the initial diad in the heterotactic poly(EMA) indicates that the dimer anion forms *r*-trimer anion as described before. For the heterotactic poly(EMA) obtained at -78°C , the fraction of the second diad following the initial *r* diad suggests that *r*-trimer favors *m*-addition three times as much as *r*-addition, leading to the preferential formation of heterotactic triad even in the early stage of polymerization. The *m*-selectivity by the *r*-trimer anion is much enhanced at -95°C , the ratio *rm*/*rr* being 9/1. The signals due to initial *m*-diad does not change evidently with the polymerization temperature, suggesting that the stereospecificity of the *m*-diad trimer anion is less sensitive to the polymerization temperature.

Stereochemical sequence of the main-chain tacticity almost obeys first-order Markovian statistics.^{14,15,27} The conditional probability of *m*-addition by *r*-ended anion ($\sim\text{rM}^-$), $P_{r/m}$, and that of *r*-addition by *m*-ended anion ($\sim\text{mM}^-$), $P_{m/r}$, were determined as follows;

Table IV. Stereoselectivity of dimer anion and *r*-ended trimer anion

Temp/°C	Dimer anion			<i>r</i> -Ended trimer anion		
	P_r^*	P_m^*	$\frac{P_r^*}{P_m^*}$	$P_{r/m}^*$	$P_{r/r}^*$	$\frac{P_{r/m}^*}{P_{r/r}^*}$
-95	0.93	0.07	13	0.90	0.10	9
-78	0.92	0.08	11.5	0.75	0.25	3

$$P_{r/m} = 0.972 \quad P_{m/r} = 0.866 \quad \text{at } -95^\circ\text{C}$$

$$P_{r/m} = 0.926 \quad P_{m/r} = 0.833 \quad \text{at } -78^\circ\text{C}$$

It is evident that the *r*-ended propagating species has higher stereospecificity than the *m*-ended anion. Moreover, the *m*-selectivity of $\sim rM^-$ ended anion, as expressed by the ratio, $P_{r/m}/P_{r/r}$, is improved by lowering the temperature with much greater extent than *r*-selectivity of $\sim mM^-$ ended anion ($P_{m/r}/P_{m/m}$):

$$P_{r/m}/P_{r/r} = 34.7, \quad P_{m/r}/P_{m/m} = 6.5 \quad \text{at } -95^\circ\text{C}$$

$$P_{r/m}/P_{r/r} = 12.5, \quad P_{m/r}/P_{m/m} = 5.0 \quad \text{at } -78^\circ\text{C}$$

Table IV shows stereoselectivity of dimer anion and *r*-trimer anion. Comparing the *m*-selectivity of the *r*-trimer anion and the *r*-ended polymer anion, one can find a similar tendency of temperature dependence, though the selectivity itself is much lower for the trimer anion. The selectivity of the dimer anion, which has no antepenultimate unit, was almost invariable at -78°C and -95°C . The results suggest the important role of penultimate and antepenultimate units in the heterotactic propagation step, *r*-addition by *m*-ended anion.

Terminating Chain-End

Configuration of terminal methine carbon is fixed upon protonation by the addition of alcohol as a terminating agent, forming a terminal diad. For the isotactic and syndiotactic living polymerizations of MMA, the terminal diad configuration is known to depend on the kind of alcohol used for termination.¹³ In the isotactic-specific polymerization of MMA with *t*-BuMgBr, the termination with phenol preferentially forms terminal *m* diad. On the other hand, *t*-butyl alcohol terminates the syndiotactic-specific polymerization of MMA with *t*-BuLi/*n*-Bu₃Al to form terminal *r* diad preferentially.¹³ In both systems, methanol was found to be a non-stereospecific terminator.¹³

The heterotactic living polymer may be either

Figure 3. 125 MHz ¹³C NMR spectra of methine carbon at the terminating chain-end of stereoregular poly(EMA)s prepared with (a) *t*-BuMgBr, (b) *t*-BuLi/*n*-Bu₃Al, and (c) *t*-BuLi/MeAl(ODBP)₂, respectively, in toluene at -78°C terminated with methanol (CDCl₃, 55°C).

$\sim rM^-$ ended anion or $\sim mM^-$ ended one. By quenching the living anions with a terminating agent, the chain-end diad configurations are fixed to form the terminal triads as follows:

Thus the information on the triad tacticity at the terminating chain-end is particularly important in the case of the end-group analysis of heterotactic polymers.

Figure 3 shows ¹³C NMR signals due to the terminal methine carbons of isotactic, syndiotactic, and heterotactic poly(EMA)s formed by the termination with methanol. The assignments shown in the figure were made as follows based on the knowledge about the stereospecificity of the alcohols in the termination reaction mentioned above.¹³ The isotactic poly(EMA), obtained by the termination with methanol, shows two signals, one at 36.88 ppm and the other at 36.05 ppm (Figure 3a). The polymer formed by protonation with phenol, which is an isotactic-specific terminator,¹³ showed a strong signal at 36.93 ppm and a very weak one at 36.05 ppm. Thus the peak at 36.88 ppm is assignable to $\sim mm$ terminal and the other at 36.05 ppm to $\sim mr$ terminal. Two major signals of syndiotactic poly(EMA) (Figure 3b) were also assigned similarly as shown in Figure 3b based on the fact that *t*-butyl alcohol preferentially forms *r* diad in the termination reaction of the syndiotactic living polymerization with *t*-BuLi/*n*-Bu₃Al¹³; the signal at 35.42 ppm ($\sim rr$) was the major one and the signal at 35.72 ppm ($\sim rm$) the minor one

Table V. Triad sequence distribution at the terminating chain-end of stereoregular poly(EMA)s

Poly(EMA)	Terminating agent	Triad tacticity/%				[-mm] + [-mr]
		-mm	-mr	-rm	-rr	
Isotactic	MeOH	36	64	—	—	100/~0
Isotactic	PhOH	90	10	—	—	100/~0
Syndiotactic	MeOH	—	—	44	56	~0/100
Syndiotactic	<i>t</i> -BuOH	—	—	—	100	~0/100
Heterotactic	MeOH	—	35	15	50	35/65
Heterotactic	<i>t</i> -BuOH	—	37	15	48	37/63
Heterotactic	PhOH	12	23	27	38	35/65
Heterotactic ^a	MeOH	10	22	22	46	32/68

^a Polymerization temperature, -95°C.

in the spectrum of syndiotactic poly(EMA) obtained by termination with *t*-butyl alcohol. Based on these assignments the signals of methine carbon of heterotactic poly(EMA) were assigned in terms of triad as shown in Figure 3c, though the resonances show further splittings due to the longer tactic sequences near the terminating chain-end.

The triad sequence distribution at the terminating chain-end are shown in Table V. The fractions of the second diad from the terminal correspond to the fractions of two kinds of anions, $\sim mM^-$ ended and $\sim rM^-$ ended anions having existed in the polymerization system before termination reaction. The ratio could be determined from the terminal triad fractions as $(-mm + -mr)/(-rm + -rr) = \sim mM^- / \sim rM^- = 1/2$. The values for the poly(EMA)s obtained by termination with different alcohols are quite consistent with each other, confirming the reproducibility of the *m/r* ratio at the second diad from the terminating chain-end. The ratio means that the *r*-ended anion $\sim rM^-$ is more abundant than the *m*-ended one $\sim mM^-$ in this polymerization system. The dominant population of $\sim rM^-$ anion suggests its higher stability than $\sim mM^-$ anion, which might bring about the higher stereoselectivity of $\sim rM^-$ ended anion.

The *m/r* ratios at the terminal diad of heterotactic poly(EMA)s were also analyzed to examine stereospecificity of protonation of the propagating anion with methanol, *t*-butyl alcohol, and phenol. The methine carbon resonances of the heterotactic poly(EMA)s formed by termination with these alcohols are shown in Figure 4. Table VI shows the stereoselectivity in the protonation reaction by these alcohols with the heterotactic living polymer. The chain-end diad of the heterotactic poly(EMA)s are predominantly *r*, when the polymerization was terminated with *t*-butyl alcohol or even with methanol which is known as a non-stereospecific terminator in both the isotactic and syndiotactic living polymerizations of MMA.¹³ Even in the case of phenol, which has high *m*-selectivity in the isotactic-specific polymerization and moderate *m*-selectivity in the syndiotactic-specific polymerization,¹³ exhibited moderate *r*-selectivity. The results suggest that both $\sim mM^-$ and $\sim rM^-$ anions in the heterotactic polymerization have an intrinsically syndiotactic-specific nature.

In conclusion, the analysis for the initiating chain-end

Figure 4. 125 MHz ¹³C NMR spectra of methine carbon at the terminating chain-end of heterotactic poly(EMA)s formed by termination with (a) methanol, (b) *t*-butyl alcohol, and (c) phenol (CDCl₃, 55°C).**Table VI.** Stereospecificity in protonation of heterotactic poly(EMA) anion with several alcohols

Alcohol	(meso Addition)/(racemo Addition)		
	Poly(EMA) anion in average ^a	-mM ⁻ ended anion ^b	-rM ⁻ ended anion ^c
MeOH	15/85	~0/100	23/77
<i>t</i> -BuOH	15/85	~0/100	24/76
PhOH	39/61	34/66	41/59
MeOH ^d	32/68	31/69	32/68

^a Determined from the triad fractions at the terminating chain-end (see Table IV) as $([-mm] + [-rm])/([-mr] + [-rr])$. ^b Determined by $[-mm]/[-mr]$. ^c Determined by $[-rm]/[-rr]$. ^d Polymerization temperature, -95°C.

revealed that (1) the dimer anion (*t*-Bu-M-M⁻), which does not have an antepenultimate monomer unit, preferentially undergoes *r*-addition to form the *r*-trimer anion (*t*-Bu-*r*-M⁻), (2) the *r*-trimer anion favors *m*-addition, and (3) the *m*-selectivity of the *r*-trimer anion is much enhanced by lowering the polymerization temperature. On the other hand, the analysis of the terminating chain-end showed that (1) living polymer having *r* diad ($\sim rM^-$) is more stable than that having *m* diad ($\sim mM^-$), and (2) the living anion favors *r*-addition in their termination reaction with alcohol, indicating the intrinsically syndiotactic-specific nature of the propagating species.

As reported previously,¹¹ when the polymerization with *t*-BuLi/MeAl(ODBP)₂ is carried out at the Al/Li ratio of 1, a syndiotactic polymer formed in low yield.^{14,15}

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/iso-Bu₂Al(ODBP).²⁸ If all the MeAl(ODBP)₂ coordinates to the propagating chain-end, there exist no excess MeAl(ODBP)₂ in the polymerization system. Under the conditions, most of the incoming monomers are free from the coordination with MeAl(ODBP)₂, giving rise to the formation of the syndiotactic polymer probably due to the intrinsic syndiotactic-specific nature of the propagating species coordinated with MeAl(ODBP)₂. Heterotactic poly(EMA)s with narrow MWD were obtained in high yields at Al/Li ≥ 2, where excess MeAl(ODBP)₂ existing in the polymerization system may activate the monomer through coordination.^{29–31} The less reactive propagating species, stabilized by the coordination with MeAl(ODBP)₂, should react preferentially with the activated monomer carrying the bulky MeAl(ODBP)₂. The steric restriction due to the sterically bulky active end and also bulky monomer complex might be an important factor for the heterotactic propagation. In this regard it may be worth noting that exceedingly bulky methacrylates such as triphenylmethyl methacrylate favor *m*-addition irrespective of polymerization conditions.³² If this is the case, the polymerization may involve two opposite tendencies of stereoregulation, *m*- and *r*-additions.

As described above, the propagating species coordinated with MeAl(ODBP)₂ exhibit intrinsically *r*-selectivity. However, $\sim rM^-$ ended anion favors *m*-addition toward the monomer carrying MeAl(ODBP)₂. One of the possible explanation for the *m*-selectivity by $\sim rM^-$ ended anion is that the penultimate and antepenultimate units in *r* diad configuration coordinate with MeAl(ODBP)₂ so that the anion becomes more stable and the surrounding of the chain end becomes bulkier than $\sim mM^-$ ended anion. The bulkiness around the chain end may be the reason for the *m*-addition of the temporarily bulky monomer carrying MeAl(ODBP)₂ as in the case of polymerization of triphenylmethyl methacrylate. Such a coordination near the chain end might be strengthened at lower temperature and be responsible for the large temperature-dependence of *m*-selectivity of $\sim rM^-$ ended anion. On the other hand, if the penultimate and antepenultimate units in $\sim mM^-$ ended anion disfavor the coordination with MeAl(ODBP)₂, the propagating species coordinated with MeAl(ODBP)₂ exhibit intrinsic *r*-selectivity. Since the coordination of MeAl(ODBP)₂ to the propagating chain-end is strong enough not to be affected by the polymerization temperature, the *r*-selectivity of the $\sim mM^-$ ended anion is much less dependent on the temperature.

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