Polymer Bulletin 32, 439–446 (1994)

Polymer Bulletin

Preparation of heterotactic-rich poly(methyl methacrylate) with narrow molecular weight distribution by *tert*-butyllithium/bis(2,6-di-*tert*-butylphenoxy)methylaluminum

Tatsuki Kitayama, Yajun Zhang, and Koichi Hatada*

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

SUMMARY

Polymerization of methyl methacrylate (MMA) with *tert*-butyllithium (t-C_4H_9Li) in toluene in the presence of aluminum alkoxides such as ethoxide, *tert*-butoxide and 2,6-di-*tert*-butylphenoxide, were examined at various Al/Li ratios. In the cases of ethoxide and *tert*-butoxide, predominantly isotactic polymers with broad molecular weight distribution were obtained. Combinations of t-C_4H_9Li and bis(2,6-di-*tert*-butylphenoxy)methylaluminum [MeAl(ODBP)$_2$] were found to be an efficient initiating system for heterotactic polymerization of MMA, which gives PMMA rich in heterotactic triads up to 68% with narrow molecular weight distribution ($\overline{M}w/\overline{M}n$ =1.09-1.17). End group analysis by ^{1}H NMR indicated that t-C_4H_9Li initiates the polymerization and MeAl(ODBP)$_2$ works as a stereospecific modifier. From stereosequence analysis of the heterotactic PMMA by ^{13}C NMR, it was found that the calculated pentad fractions from the first-order Markovian statistics ($P_{m/r}$=0.742, $P_{r/m}$=0.627) fitted the observed ones better than those from Bernoullian statistics. The glass transition temperature of the heterotactic PMMA was 13°C lower than that of syndiotactic PMMA, and the intrinsic viscosity in tetrahydrofuran was close to that of isotactic PMMA with a similar molecular weight but higher than that of syndiotactic PMMA.

INTRODUCTION

Many papers have been published on the stereospecific polymerization of methacrylates [1, 2]. However, there have been a few publications concerning the formation of heterotactic polymers [3-7]. A polymer containing more than 50% heterotactic triads should be defined as a heterotactic polymer, or heterotactic-rich polymer in a more strict sense, since the heterotactic triad content can attain at most 50% even when the polymerization is nonstereospecific.

For the formation of heterotactic sequence, two different types of stereoregulation, meso and racemo additions, should occur in an alternate manner. Methacrylic anhydride is known to undergo cyclopolymerization by inter- and intramolecular propagation steps [8-12], and thus there exists some possibility that PMMA derived from the poly(methacrylic anhydride) shows a tendency toward alternation of meso and racemo diads, giving a heterotactic polymer. However, the fraction of heterotactic triads was at most 50% [12]. Hydrolysis and re-esterification of cyclopolymerized 2,2'-methylene-bis(4-methyl-1,2-phenylene) dimethacrylate was reported to give a PMMA rich in heterotactic triads (mr=52%) [13].

Another possibility of generation of heterotactic sequence is a copolymerization in which stereospecificities of the addition processes of two monomers are opposite. This was partly realized in the radical copolymerization of MMA (M_1) and triarylmethyl methacrylates (M_2) [14]. By the use of a deuterated monomer (MMA-d_8) as M_1, the M_2 centered $M_1M_2M_1$ triad in the copolymers of MMA-d_8 and triphenylmethyl, diphenyl-2-pyridylmethyl or phenyl-2-

---

*Corresponding author

pyridyl-*o*-tolylmethyl methacrylate is rich in heterotactic triads (>60%). Based on these results, radical copolymerization of MMA and diphenyl-2-pyridylmethyl methacrylate was carried out. However, heterotactic triad content of the whole copolymer of MMA and diphenyl-2-pyridylmethyl methacrylate is at most 51.6% at the MMA content of 50%, due to lower heterotacticity of triad comonomer sequences other than $M_1M_2M_1$.

Higher coheterotacticity has been attained by alternating copolymerization of MMA and styrene. The radical copolymerization in the presence of boron trichloride excess to MMA below -60°C gives coheterotactic alternating copolymer, the highest coheterotacticity being 89% at -95°C [15].

Heterotactic-rich PMMA has been prepared with octylpotassium in tetrahydrofuran (THF) and with fluorenylcesium in toluene at -78°C [9]; the heterotactic triad contents were 50% and 53%, and molecular weight distributions (MWD) were 1.90 and 1.92, respectively. Other methacrylic esters also gave heterotactic polymers under the same conditions. In particular, secondary esters such as isopropyl, cyclohexyl, α-methylbenzyl and diphenylmethyl methacrylates gave polymers with higher heterotactic contents with octylpotassium in THF [3], although their MWD's were broad.

We have reported that combinations of t-C_4H_9Li and trialkylaluminums are efficient initiating systems for highly syndiotactic-specific living polymerization of methacrylate[16, 17]. Combinations of trialkyl- or triphenylphosphine and trialkylaluminum give highly syndiotactic polymethacrylate [18]. Diethylaluminum diphenylamide, which itself is a syndiotactic-specific initiator [19, 20], also works as an additive in the polymerization of MMA in toluene with t-C_4H_9Li, giving a syndiotactic PMMA [17]. These suggest that aluminum compounds play an important role in the syndiotactic-specific polymerization of methacrylate.

This communication describes a study on the effects of aluminum alkoxides, instead of trialkylaluminum, on the stereoregulation in the polymerization of MMA in toluene with t-C_4H_9Li. Among the aluminum alkoxides examined, we found that a combination of t-C_4H_9Li and bis(2,6-di-*tert*-butylphenoxy)methylaluminum gives PMMA rich in heterotactic triads (up to 68%) with narrow MWD ($\overline{M}w/\overline{M}n$ =1.09-1.17).

EXPERIMENTAL

Materials MMA was purified by fractional distillation, dried over calcium dihydride and vacuum-distilled just before use. Toluene was purifed in the usual manner, mixed with a small amount of n-C_4H_9Li, and distilled under high vacuum.

Ethanol, 2-methylpropan-2-ol (*tert*-BuOH) and 2,6-di-*tert*-butylphenol, obtained commercially, were fractionally distilled and dried over Molecular Sieves 4A.

t-C_4H_9Li in pentane, obtained commercially, was used as a heptane solution. The concentration was determined by titration with butan-2-ol [21].

Trimethylaluminum (Me_3Al) was purchased from Aldrich as a solution in hexane or toluene and used as received.

Preparation of aluminum alkoxides [22, 23] To a solution of alcohol (1-3 equiv.) in toluene was added at room temperature a hexane or toluene solution of Me_3Al (1 equiv.). The resulting mixture was stirred at room temperature for 16 hr and used for polymerization without further purification.

Polymerization Polymerization was carried out in a glass ampoule filled with dried nitrogen. t-C_4H_9Li was added to an organoaluminum compound in toluene at -78°C. The polymerization reaction was initiated by adding the monomer slowly to this mixture. The reaction was terminated by the addition of methanol containing HCl at the polymerization temperature. The reaction mixture was poured into a large amount of hexane to precipitate the polymeric product.

The precipitate was collected by filtration, washed with hexane, dilute HCl and water, successively, and dried under vacuum.

Measurement ^1H and ^{13}C NMR spectra of the polymers were measured in nitrobenzene-d_5 at 110°C on a JEOL JNM GX500 spectrometer at 500 MHz and 125 MHz, respectively.

The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a JASCO TRI ROTAR-V chromatograph equipped with Shodex GPC columns KF-80M (30cmX0.8cm) and KF-802.5 (30cmX0.8cm) using THF as an eluent at 40°C. The GPC chromatogram was calibrated against standard polystyrene samples.

Glass transition temperature (Tg) was measured on a Rigaku 8230 differential scanning calorimeter at a heating rate of 10°C/min.

Intrinsic viscosity was measured in THF at 40°C using a VISCOTEK differential viscometer MODEL 110-02 connected to the GPC (sample concentration 1.0mg/ml, injection volume 0.5ml, flow rate 1.0 ml/min).

RESULTS AND DISCUSSION

The polymerization of MMA with t-$C_4H_9Li/Me_{(3-n)}Al(OR)_n$ (n=1, 2) in toluene was carried out at -78°C. OR was ethoxy, *tert*-butoxy or 2,6-di-*tert*-butylphenoxy group. The results of polymerization are shown in Table 1. Polymerization with t-C_4H_9Li alone gives a predominantly isotactic PMMA with a broad MWD [16, 17]. When aluminum ethoxides and dimethylaluminum *tert*-butoxide were used as additives, predominantly isotactic polymers with broad MWD's were also obtained. In contrast to trialkylaluminums [16, 17], these aluminum alkoxides do not exhibit remarkable effects on the stereospecificity of the polymerization with t-C_4H_9Li, although slight increases of isotactic triad content are evident, particularly in the case of $MeAl(OEt)_2$.

Table 1 Polymerization of MMA with t-C_4H_9Li in the presence or absence of various aluminum alkoxides in toluene at -78°C for 24h[a]

Aluminum alkoxide	Al/Li	Yield (%)	$\overline{M}_n$ (GPC)	$\overline{M}_w/\overline{M}_n$	Tacticity (%)		
					mm	mr	rr
—	0	100	18900	5.31	81.2	13.0	5.8
Me_2AlOEt	3	100	17640	3.50	84.5	10.9	4.6
$MeAl(OEt)_2$	3	100	33770	2.61	87.3	9.7	3.0
$Al(OEt)_3$	3	100	29570	4.36	83.9	11.6	4.5
$Me_2Al(O^tBu)$	3	100	19470	3.67	82.6	12.4	5.0
$Me_2Al(ODBP)$[b]	1	100	33880	2.84	83.9	12.5	3.6
	2	87	5580	1.13	1.4	26.7	71.9
$MeAl(ODBP)_2$	1	11	2480	1.02	5.9	24.0	70.1
	2	62	12480	1.14	9.7	63.5	26.8
	3	100	11460	1.17	11.6	65.1	23.3
	5	100	11640	1.14	11.6	67.8	20.6
	7	100	8870	1.14	12.5	66.2	21.3
	10	100	5310	1.20	12.8	64.8	22.4
$MeAl(ODBP)_2$+DBPOH[c]	5	100	21470	1.16	11.7	66.9	21.4

[a] MMA 10mmol, t-C_4H_9Li 0.2mmol, toluene 10ml.

[b] ODBP=2,6-di-*tert*-butylphenoxy.

[c] A reaction mixture of Me_3Al and 2,6-di-*tert*-butylphenol (DBPOH) in 1:3 molar ratio.

Aluminum phenoxides bearing bulky substituents have been widely used in organic chemistry [22, 23] and recently in polymer chemistry [24-28]. Ballard *et al.*[27] reported that an initiator comprising *t*-C_4H_9Li and (2,6-di-*tert*-butylphenoxy)diisobutylaluminum [*i*Bu_2Al-(ODBP)] gave predominantly syndiotactic PMMA with narrow MWD in a living manner. They claimed that the bulkiness of the phenoxide "screened" the polymer anion from possible side reactions to afford the living polymerization at ambient temperature. Polymerization of MMA was carried out in toluene at -78°C using *t*-C_4H_9Li and aluminum alkoxides derived from Me_3Al and one or two equivalents of 2,6-di-*tert*-butylphenol; (2,6-di-*tert*-butylphenoxy)dimethylaluminum [Me_2Al(ODBP)] or bis(2,6-di-*tert*-butylphenoxy)methylaluminum [MeAl$(ODBP)_2$] (Table 1). In the case of Me_2Al(ODBP) at the Al/Li ratio of 1, an isotactic PMMA with broad MWD was obtained as in the case of the polymerization with *t*-C_4H_9Li alone. A predominantly syndiotactic PMMA with narrow MWD was obtained at the ratio of 2 with high initiator efficiency. Thus, the stereochemical effect of Me_2Al(ODBP) seems almost the same as that of *i*Bu_2Al(ODBP) [27], though Me_2Al(ODBP) is known to exist in solution as an equilibrium mixture of several aluminum compounds [29a]. Contrastingly, *t*-C_4H_9Li/MeAl$(ODBP)_2$ gave a PMMA rich in heterotactic triads with narrow MWD at the Al/Li ratio of 2 and higher than 2. The heterotactic triad content and polymer yield increased with an increase in the Al/Li ratio, and the highest heterotactic content of 68% was attained at the Al/Li ratio of 5. Further increase of the Al/Li ratio to 7 and 10 gave rise to an increase of initiator efficiency, probably because the aluminum phenoxide promotes dissociation of *t*-C_4H_9Li aggregated in toluene, while the heterotactic triad content decreased slightly. As far as we are aware, this is the first example of preparation of heterotactic PMMA with narrow MWD whose heterotactic triad is higher than 65%.

It has been claimed that synthesis of three-coordinate aluminum aryloxides has been unsuccessful and only the bis(aryloxide) compounds could be isolated [29, 30], although Healy and Barron recently succeeded in preparing $Al(OAr)_3$ (OAr: 2,6-di-*tert*-butyl-4-methylphenoxy) from $LiAlH_4$ and the phenol [31]. However, we examined the polymerization of MMA by *t*-C_4H_9Li with a reaction mixture of Me_3Al and three equivalents of 2,6-di-*tert*-butylphenol, which was found by ^1H NMR spectroscopy to be a 1:1 mixture of MeAl$(ODBP)_2$ and the unreacted phenol. As shown in Table 1, a heterotactic PMMA with narrow MWD was obtained at the ratio of Al/Li=5 even in the presence of the unreacted phenol, whose amount would be 5 times as large as that of *t*-C_4H_9Li used. The initiator mixture (Al/Li=5) prepared in toluene-d_8 was examined by ^1H NMR spectroscopy and it was confirmed that *t*-C_4H_9Li and the unreacted

Table 2 Polymerization of MMA with *t*-C_4H_9Li and bis(2,6-di-*tert*-butylphenoxy)-methylaluminum [MeAl$(ODBP)_2$] in toluene at various temperatures[a]

Temp. (°C)	Time (hr)	Yield (%)	$\overline{Mn}$ (GPC)	$\overline{Mw}/\overline{Mn}$	Tacticity (%) mm	mr	rr
-95	48	21	3300	1.09	9.3	60.9	29.8
-78	24	62	12480	1.14	9.7	63.5	26.8
-60	5	100	7900	1.34	3.0	44.0	53.0
-40	5	100	19710	1.24	0.5	23.1	76.4
-20	5	100	9080	1.23	0.7	22.2	77.1
0	5	100	10530	1.32	1.2	26.4	72.4
30	5	100	15720	1.37	2.1	27.5	70.4

[a] MMA 15mmol, toluene 15ml, *t*-C_4H_9Li 0.3mmol, Al/Li=2.
t-C_4H_9Li and MeAl$(ODBP)_2$ were mixed at -78°C, regardless of polymerization temperature.

phenol still existed at least at -60°C. The lower initiator efficiency is probably due to a partial quenching of *t*-C_4H_9Li with the phenol.

Table 2 shows the effects of temperature on the polymerization of MMA by *t*-C_4H_9Li/MeAl(ODBP)$_2$ in toluene at the Al/Li ratio of 2. The polymer yield increased with increasing temperature and reached 100% in the polymerization at -60°C for 5h. The tacticity was greatly affected and changed from heterotactic to syndiotactic with increasing temperature, while the MWD became a little broader.

Figure 1a shows ^{1}H NMR spectrum of the PMMA prepared with *t*-C_4H_9Li/MeAl(ODBP)$_2$ (Al/Li=5), α-methyl proton signals of which apparently indicate the high heterotacticity of the polymer. The spectrum also shows a characteristic singlet peak at 0.811ppm due to the *t*-C_4H_9 group at the initiating end of the chain but no signals due to 2,6-di-*tert*-butylphenoxy or methyl group in the chain. The $\overline{M}$n value estimated from the intensity ratio of OCH_3 and *t*-C_4H_9 protons, assuming that the polymer molecule contains one *t*-C_4H_9 group in a chain, agreed well with that obtained by GPC ($\overline{M}$n=12900 from NMR and $\overline{M}$n=11640 from GPC). These results suggest that the polymerization is initiated by *t*-$C_4H_9^-$ anion and MeAl(ODBP)$_2$ itself does not initiate polymerization of MMA. Therefore, MeAl(ODBP)$_2$ may work as a stereospecific modifier in this polymerization.

The mechanism of heterotactic growth is of great interest. Statistical analysis of stereochemical sequence distribution may provide information on the stereoregulation. In Figure 1b is shown ^{13}C NMR spectrum of the carbonyl carbon resonances of the heterotactic PMMA prepared by *t*-C_4H_9Li/MeAl(ODBP)$_2$ (Al/Li=5) in toluene at -78°C. The triad and pentad sequence distributions were calculated assuming Bernoullian statistics and the pentad one assuming first-order Markovian statistics. The results are shown in Table 3 and compared with the observed values. The triad and pentad sequence distributions apparently do not obey

Table 3 Tactic sequence distribution in heterotactic PMMA prepared with *t*-C_4H_9Li/MeAl(ODBP)$_2$ (1:5) in toluene at -78°C

Sequence		Observed	First-order Markovian statistics[a]	Bernoullian statistics[b]
Triad (quaternary carbon)	mm	0.118 (0.116[c])	0.118	0.210
	mr	0.680 (0.678[c])	0.680	0.496
	rr	0.202 (0.206[c])	0.202	0.294
Pentad (C=O)	mmmm	0.009	0.008	0.044
	mmmr	0.022	0.045	0.104
	rmmr	0.086	0.065	0.062
	mmrm	0.183	0.110	0.104
	mmrr	0.088	0.065	0.123
	rmrm	0.278	0.316	0.123
	rmrr	0.128	0.188	0.146
	mrrm	0.063	0.079	0.062
	mrrr	0.107	0.095	0.146
	rrrr	0.036	0.029	0.086

[a] Calculated using parameters Pm/r=0.742 and Pr/m=0.627, the values of which were obtained from the triad tacticities.

[b] Calculated using parameter Pm=0.458, the value of which was derived from the triad tacticities.

[c] From α–methyl proton signals.

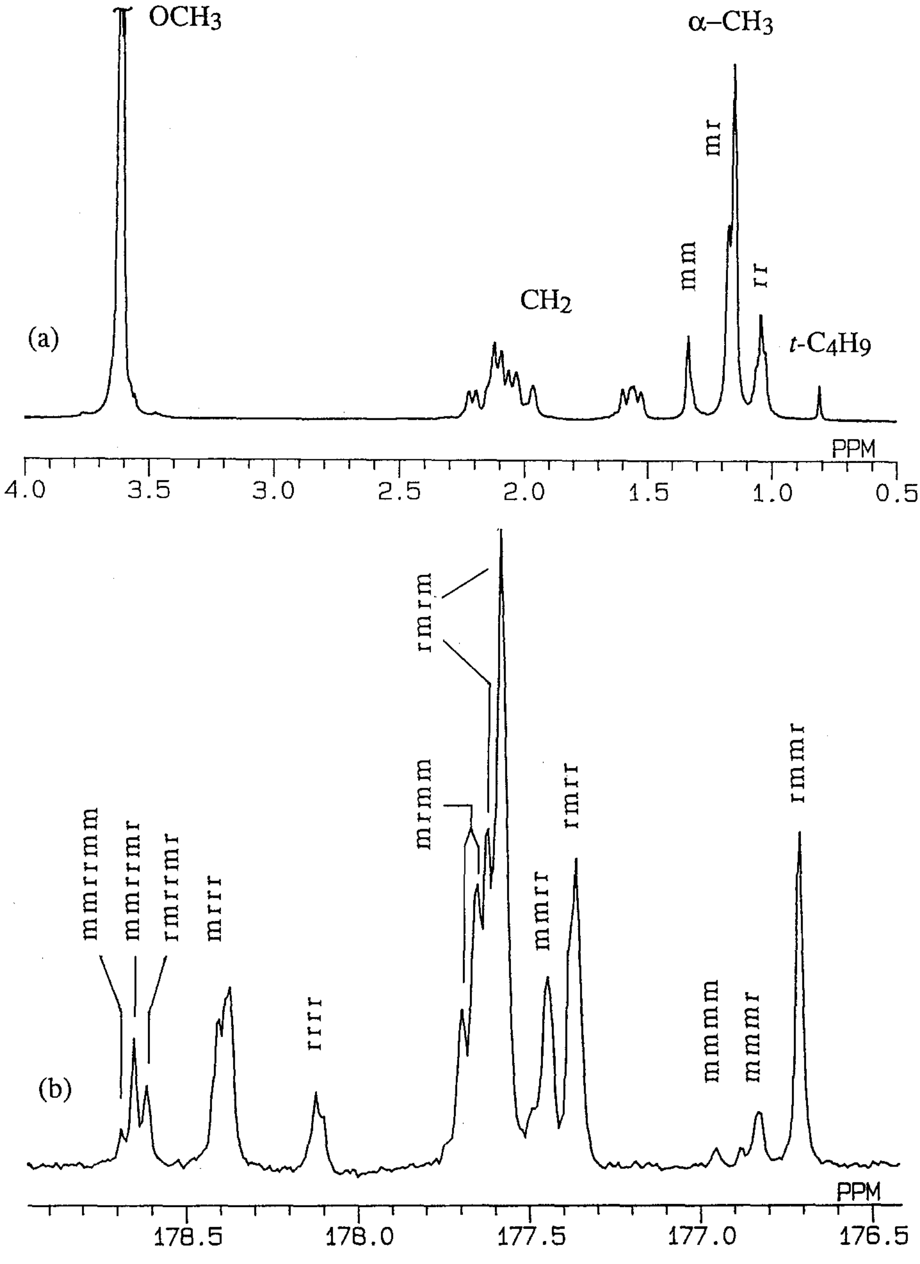

Figure 1. 500MHz ^1H (a) and 125MHz ^{13}C (b) NMR spectra of heterotactic PMMA prepared in toluene at -78°C with t-C_4H_9Li/ MeAl(ODBP)$_2$ (1/5) measured in nitrobenzene-d_5 at 110°C.

Bernoullian statistics (Pm=0.458). The calculated pentad fractions from the first-order Markovian statistics (Pm/r=0.742, Pr/m=0.627) fitted the observed ones better than those from Bernoullian statistics. The first-order Markovian parameters Pm/r and Pr/m are both larger than 0.5, demonstrating the principal feature of the heterotactic propagation, that is, alternating tendency of meso and racemo additions. There still exists a large discrepancy, however, especially in mmrm and rmrr pentads, suggesting that the configurational sequences in the heterotactic polymer obeys the second-order or higher-order Markovian statistics.

Even though the initiator efficiency of the heterotactic-specific polymerization is less than unity, $\overline{M}n$ of the polymer was almost proportional to the initiator-to-monomer ratio (Figure 2). Combined with the narrow MWD observed, the results suggest that the present polymerization system is likely a living system. The livingness of the polymerization is now being examined. Polymerization of other methacrylates is also being extensitively studied and some of alkyl methacrylates including ethyl methacrylate were found to give polymers of much higher heterotacticity with narrow MWDs [32].

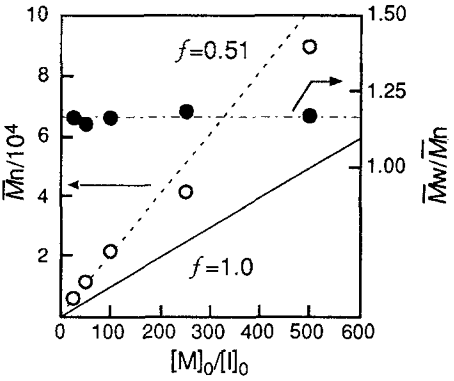

Figure 2. Polymerization of MMA by t-C_4H_9Li /$MeAl(ODBP)_2$ (1/5) in toluene at -78°C. Polymerization time were 1-26 days, depending on $[M]_0/[I]_0$, and the yields were 100% in all the cases. Solid and broken lines indicate the expected $\overline{M}n$ for the initiator efficiencies (f) of 1.0 and 0.51, respectively, the latter being the average value of the five runs.

Table 4 summarizes the glass transition temperature (Tg) and intrinsic viscosity ([η]) of several stereoregular PMMA samples with a similar molecular weight. The Tg value of the heterotactic PMMA lies between those of isotactic and syndiotactic PMMAs as expected and rather close to the Tg of the syndiotactic PMMA. The intrinsic viscosity of the heterotactic PMMA measured in tetrahydrofuran is close to the isotactic PMMA rather than to the syndiotactic PMMA.

Table 4 Glass transition temperature (Tg) and intrinsic viscosity ([η]) of three types of stereoregular PMMAs

PMMA	Tacticity (%)			$\overline{M}n$	$\overline{M}w/\overline{M}n$	Tg[a] (°C)	[η][b] (dl/g)
	mm	mr	rr				
Isotactic[c]	97.0	2.0	1.0	10130	1.12	44.7	0.108
Heterotactic[d]	11.6	67.8	20.6	11640	1.14	102.2	0.101
Syndiotactic[e]	1.2	9.5	89.3	10280	1.24	115.2	0.087

[a] Heating rate 10°C/min.

[b] Determined in tetrahydrofuran at 40°C.

[c] Obtained with t-C_4H_9MgBr in toluene at -60°C.

[d] Obtained with t-$C_4H_9Li/MeAl(ODBP)_2$ (1/5) in toluene at -78°C.

[e] Obtained with t-$C_4H_9Li/(n$-$C_4H_9)_3Al$ (1/3) in toluene at -78°C.

REFERENCE

1. H. Yuki and K. Hatada, *Adv. Polym. Sci.*, **31**, 1 (1979).
2. K. Hatada, T. Kitayama, and K. Ute, *Prog. Polym. Sci.*, **13**, 189 (1989).

3. K. Hatada, H. Sugino, H. Ise, T. Kitayama, Y. Okamoto, and H. Yuki, *Polym. J.*, **12**, 55 (1980).
4. S. Nozakura, T. Okamoto, K. Toyora, and S. Murahashi, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 1043 (1973).
5. S. Nozakura, S. Ishihara, Y. Inaba, K. Matsumura, and S. Murahashi, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 1053 (1973).
6. E. G. Brame, Jr. and O. Vogl, *J. Macromol. Sci., Chem.* **A1**, 277 (1967).
7. M. Goodman and J. Brandrup, *J. Polym. Sci.*, **A3**, 327 (1965).
8. M. Reinmoller and T. G. Fox, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, **7**, 999 (1966).
9. W. T. Gibbs and J. T. Murray, *J. Polym. Sci.*, **58**, 141 (1962).
10. J. C. H. Hwa, *J. Polym. Sci.*, **60**, S12 (1962).
11. G. Smets, P. Hous, and N. Deval, *J. Polym. Sci.*, **A2**, 4825 (1964).
12. M. Reinmoller and T. G. Fox, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **7**, 1005 (1966).
13. H. Kammerer, *Weyerhaeuser Sci. Symp.* Volume Data 1979, **2** (Phenolic Resins: Chem. Appl.), 17 (1980).
14. K. Hatada, T. Kitayama, T. Ochi, and H. Yuki, *Polym. J.*, **19**, 1005 (1987).
15. a) Y. Gotoh, T. Iihara, N. Kanai, N. Toshima and H. Hirai, *Chem. Lett.*, 2157 (1990); b) Y. Gotoh, M. Yamashita, M. Nakamura, N. Toshima, and H. Hirai, *Chem. Lett.*, 53 (1991).
16. T. Kitayama, T. Shinozaki, E. Masuda, M. Yamamoto, and K. Hatada, *Polym. Bull.*, **20**, 505 (1988).
17. T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto, and K. Hatada, *Makromol. Chem., Supplement.* **15**, 167 (1989).
18. T. Kitayama, E. Masuda, M. Yamaguchi, T. Nishiura, and K. Hatada, *Polym. J.*, **24**, 817 (1992).
19. S. Murahashi, T. Niki, T. Obokata, H. Yuki, and K. Hatada, *Kobunshi Kagaku*, **24**, 198 (1967).
20. S. Murahashi, T. Obokata, H. Yuki and, K. Hatada, *Kobunshi Kagaku*, **24**, 309 (1967).
21. S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1965).
22. K. Maruoka and H. Yamamoto, *Angew. Chem., Int. Ed. Engl.*, **24**, 668 (1985).
23. K. Maruoka, T. Itoh, M. Sakura, K. Nonoshita, and H. Yamamoto, *J. Am. Chem. Soc.*, **110**, 3588 (1988).
24. M. Kuroki, T. Watanabe, T. Aida , and S. Inoue, *J. Am. Chem. Soc.*, **113**, 5903 (1991).
25. T. Adachi, H. Sugimoto, T. Aida, and S. Inoue, *Macromolecules*, **25**, 2280 (1992).
26. H. Sugimoto, M. Kuroki, T. Watanabe, C. Kawamura, T. Aida, and S. Inoue, *Macromolecules*, **26**, 3403 (1993).
27. D. G. H. Ballard, R. J. Bowles, D. M. Haddleton, S. N. Richards, R. Sellens, and D. L. Twose, *Macromolecules*, **25**, 5907 (1992).
28. M. Miyamoto, N. Miwa, and K. Hasegawa, *Polym. Prep. Jpn.*, **40**, 1855 (1991).
29. a) M. D. Healy, D. A. Wierda, and A. R. Barron, *Organometallics*, **7**, 2543 (1988); b) M. D. Healy, J. W. Ziller, and A. R. Barron, *J. Am. Chem. Soc.*, **112**, 2949 (1990).
30. a) M. Skowronska-Ptasinska, K. B. Starowieyski, S. Pasynkiewicz, and M. Carewska, *J. Organomet. Chem.*, **160**, 403 (1978); b) A. P. Streve, R. Mulhaupt, W. Fultz, J. Calabrese, W. Robbins, and S. D. Ittel, *Organometallics*, **7**, 409 (1988); c) R. Benn, E. Janssen, H. Lehmkuhl, A. Rufinska, K. Augermund, P. Betz, R. Goddard, and C.Kruger, *J. Organomet. Chem.*, **411**, 37 (1991).
31. M. D. Healy and A. R. Barron, *Angew. Chem. Int. Ed. Engl.*, **31**, 921 (1992).
32. T. Kitayama, Y. J. Zhang, and K. Hatada, *to be submitted to Polym. J.*

Accepted February 13, 1994 S