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Preparation of highly syndiotactic block copolymers of methyl methacrylate and lauryl methacrylate and their characterization

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Summary

Highly syndiotactic diblock and triblock copolymers comprising lauryl methacrylate (LMA) and methyl methacrylate (MMA) with narrow molecular weight distributions were prepared by the living anionic polymerization with t-$C_4H_9Li/(C_2H_5)_3Al$ in toluene at low temperature. The block copolymers were soluble in acetone which is a non-solvent for poly(lauryl methacrylate) (PLMA). ^1H NMR and vapor pressure osmometric analyses of the block copolymers indicated the aggregation of the copolymer in acetone through the interaction between PLMA blocks. Stereocomplex formation between the triblock copolymer and isotactic poly(methyl methacrylate) (PMMA) took place more effectively in solution than in the solid state.

Introduction

Block copolymers comprising polymer blocks of different properties, such as solubility and glass transition temperature (Tg), have received much attention from the viewpoint of polymeric material applications including compatibilizer in polymer blend and thermoplastic elastomer1). Living polymerization is a method of choice for the preparation of block copolymers of well defined molecular structure and various kinds of block copolymers have been prepared by this method. However, little attention has been paid on the stereoregularity of block copolymers.

Control of stereoregularity of vinyl polymers has been well recognized as an important factor for the control of polymer properties. We have demonstrated that the polymerizations of methacrylate monomers with t-C_4H_9MgBr2,3) and t-C_4H_9Li/R_3Al4,5) proceed in a living manner to give highly isotactic(*it*-) and syndiotactic(*st*-) PMMAs, respectively. These living polymerizations have been used to prepare stereoregular block copolymers of methacrylates3,5-7). Recently we also reported the preparation of triblock copolymers comprising flexible polyisobutylene block and stereoregular PMMA blocks by anionic polymerization with the polymeric initiator8,9).

PLMA has long alkyl side chains which provide the polymer with high flexibility (low Tg) and lipophilicity. Preparation of block copolymers comprising PMMA blocks and PLMA block by group transfer polymerization has been already reported by Sogah and his coworkers10). Although their stereoregularities were not reported, it should be similar to that of radically prepared polymers. This communication reports the preparation of highly

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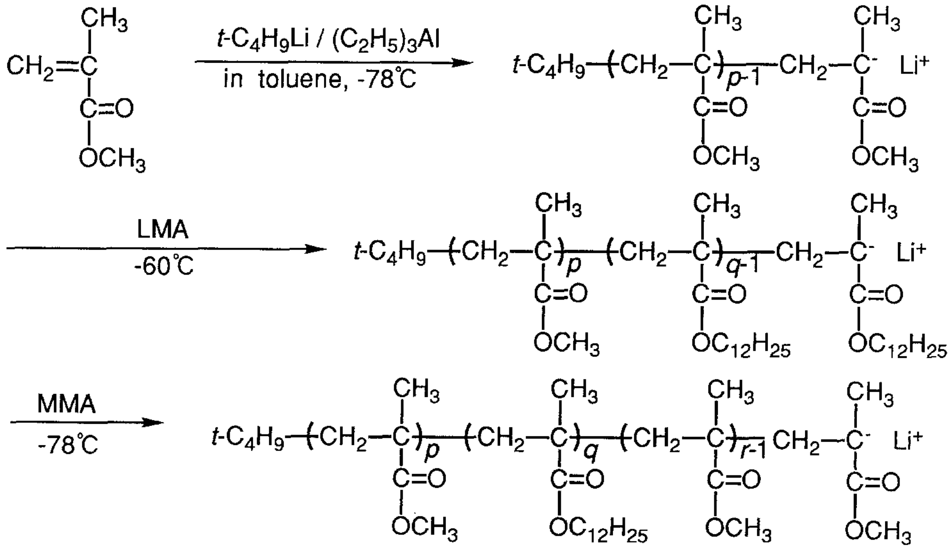
syndiotactic diblock and triblock copolymers of MMA and LMA by the living anionic polymerization with t-$C_4H_9Li/(C_2H_5)_3Al$ in toluene at low temperature. Some solution properties of the block copolymers were investigated by ^1H NMR spectroscopy and vapor pressure osmometry (VPO). Stereocomplex formation of the syndiotactic triblock copolymer with *it*-PMMA is also reported.

Experimental

Toluene, purified in the usual manner, was mixed with a small amount of n-C_4H_9Li and distilled under vacuum. MMA was purified by distillation and then distilled over calcium dihydride under vacuum just before use. LMA was purified by distillation, dried over calcium dihydride, distilled again and then dried over molecular sieves 4A at 0°C. t-C_4H_9Li obtained commercially was used as a heptane solution (1.05M). The concentration was determined by titration with butan-2-ol[11]. $(C_2H_5)_3Al$ was used as a heptane solution (0.959M).

Polymerization was carried out in a glass ampoule filled with dry nitrogen. t-C_4H_9Li was added to a solution of $(C_2H_5)_3Al$ in toluene cooled to the reaction temperature. Homopolymerizations of MMA and LMA were initiated by adding the monomers slowly to the initiator mixture at −78°C and −60°C, respectively. In the case of polymerization of LMA, the monomer was added as a toluene solution containing a small amount of $(C_2H_5)_3Al$. $(C_2H_5)_3Al$ has been used for the purification of methacrylates.[12] The $(C_2H_5)_3Al$ added to the LMA solution can avoid the unintentional quenching of the anion without changing the reactivity and stereoregularity. After the completion of the polymerization the reaction mixture was quenched with a small amount of methanol containing HCl. In the case of polymerization of MMA the mixture was poured into a large amount of hexane, and the precipitated polymer was collected by filtration, washed successively with hexane, diluted aqueous HCl solution, water and hexane, and dried under vacuum at 40°C. The polymerization mixture of



LMA was poured into a large amount of methanol. The precipitated PLMA was redissolved in benzene and recovered from the benzene solution by freeze-drying after removing a small amount of undissolved materials by centrifugation.

PMMA-*block*-PLMA was prepared by adding a toluene solution of LMA containing a small amount of $(C_2H_5)_3Al$ to the living PMMA anion at -60°C. The anion was prepared at -78°C as mentioned above. The diblock copolymer formed was recovered by the same method as in the case of PLMA. PMMA-*block*-PLMA-*block*-PMMA was prepared by polymerizing MMA with PMMA-*block*-PLMA anion at -78°C similarly to the case of the diblock copolymer and the resulting triblock copolymer was poured into a large amount of methanol, and the precipitated polymer was recovered by filtration, washed with methanol, diluted aqueous HCl solution, water and methanol successively, and dried under vacuum at 40°C.

^1H NMR spectra of the polymers were recorded on a JNM MH100 spectrometer (JEOL) at 100MHz or on a JNM GSX270 NMR spectrometer (JEOL) at 270MHz. ^{13}C NMR spectra of the polymers were measured on the JNM GSX270 spectrometer at 67.8MHz. Proton spin-lattice relaxation time (^1H-T_1) was measured at 35°C on a JNM FX100 spectrometer (JEOL) at 100MHz by inversion recovery method.

Gel permeation chromatography (GPC) was performed on a JASCO TRI ROTAR-V chromatograph equipped with Shodex GPC columns KF-80M (30 cm x 0.80 cm) and KF-802.5 (30 cm x 0.80 cm) with maximum porosities of 2×10^7 and 2×10^4, respectively, using tetrahydrofuran as an eluent. The chromatograms were calibrated against standard polystyrene samples.

VPO mesurements were made on a Hitachi 117 vapor pressure osmometer in toluene at 59.9°C and in acetone at 41.0°C.

Differential scanning calorimetric analysis was performed on a Rigaku DSC 8230 calorimeter at a heating rate of 10°C/min.

Results and Discussion

The block copolymers of PMMA and PLMA were prepared by the initiation with t-$C_4H_9Li/(C_2H_5)_3Al$ in toluene at low temperatures as mentioned in the experimental section. The results are shown in Table 1 together with the results of homopolymerizations. The polymerization of MMA was carried out at -78°C, but that of LMA at -60°C because of the low solubility of LMA and the small rate of polymerization of LMA at -78°C. The GPC curves of the block copolymers are shown in Figure 1 together with that of PMMA obtained in the control experiment. These GPC curves indicate that the block copolymers were prepared successfully and the molecular weight distributions were narrow. The number average molecular weights ($\overline{Mn}$'s) of the block copolymers determined by GPC and VPO agreed fairly well with each other and are also close to the calculated values (Table 1). All the homopolymers and block copolymers are highly syndiotactic as shown in Table 1.

The PMMA is soluble in chloroform and in acetone. The PLMA is also soluble in chloroform but not in acetone. Both the diblock and triblock copolymers were dissolved in acetone, probably due to the presence of long sequences of PMMA.

The 270MHz ^1H NMR spectra of the block copolymers were measured in chloroform-d and in acetone-d_6 at 35°C. Signals of $-OCH_3$ protons of MMA units and $-OCH_2-$

protons of LMA units are shown in Figure 2. The absolute intensities were calculated from the intensity ratios of the signals of interest to the signal due to the remaining protons in chloroform-d or acetone-d_6 used as solvent for the measurements. The contents of the remaining protons in the deuterated solvents were determined using a precision coaxial tubing method[13]. The signals of the block copolymers are properly sharp in chloroform-d and the intensities of the signals are very close to the theoretical values (1.00) as indicated in the figure. In acetone-d_6 NMR peaks became broader and the intensities decreased as compared with the theoretical values, particularly for the peaks due to the $-OCH_2-$ protons

Table 1. Block Copolymerization of MMA and LMA with $t-C_4H_9Li/(C_2H_5)_3Al$ (Al/Li=3) in Toluene[a]

MMA	LMA	MMA	Yield	$\overline{M}n$			$\overline{M}w^c$	Tacticity/%[d]		
mmol	mmol	mmol	%	GPC	VPO	Calcd	$\overline{M}n$	*mm*	*mr*	*rr*
10.0	——	——	100	5690	5660	5060	1.21	3	8	89
——	10.2[b]	——	100	11200	12300	13000	1.16	0	14	86
10.0	10.5[b]	——	98	18600	17800	18400	1.18	1	12	87
10.0	10.5[b]	9.6	100	27900	21800	23200	1.21	1	12	87

[a] $t-C_4H_9Li$ 0.2mmol, polymerization time; 24hr and 168hr for the first and second stages of MMA polymerization, respectively, and 96hr for LMA polymerization Temperature; -78°C for polymerization of MMA, and -60°C for that of LMA

[b] LMA was added as a toluene solution containing a small amount of $(C_2H_5)_3Al$.

[c] Determined by GPC

[d] Determined by 100MHz ^1H NMR in the case of PMMA and by 67.9MHz ^{13}C NMR in other cases

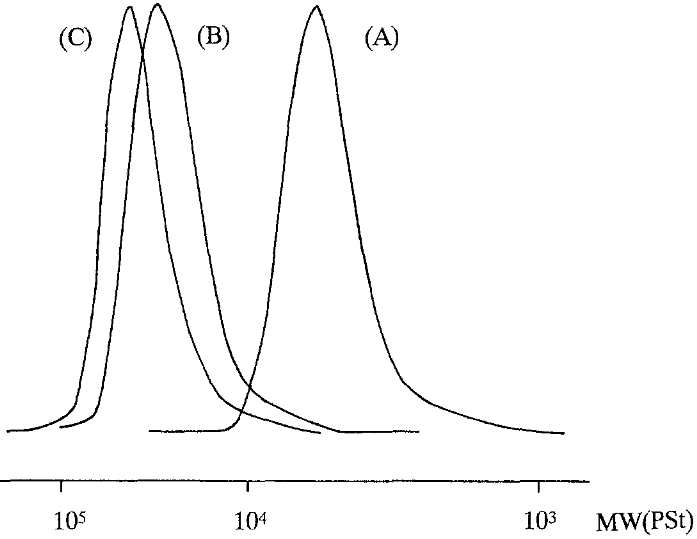


Figure 1. GPC chromatograms of PMMA (A), PMMA-*block*-PLMA (B) and PMMA-*block*-PLMA-*block*-PMMA (C) prepared with $t-C_4H_9Li/(C_2H_5)_3Al$ in toluene

of LMA units. The $\overline{Mn}$'s of the block copolymers determined by VPO in toluene and in acetone are shown in Table 2. The $\overline{Mn}$'s measured in toluene agreed with the calculated values while those measured in acetone were larger than the calculated ones, particularly in

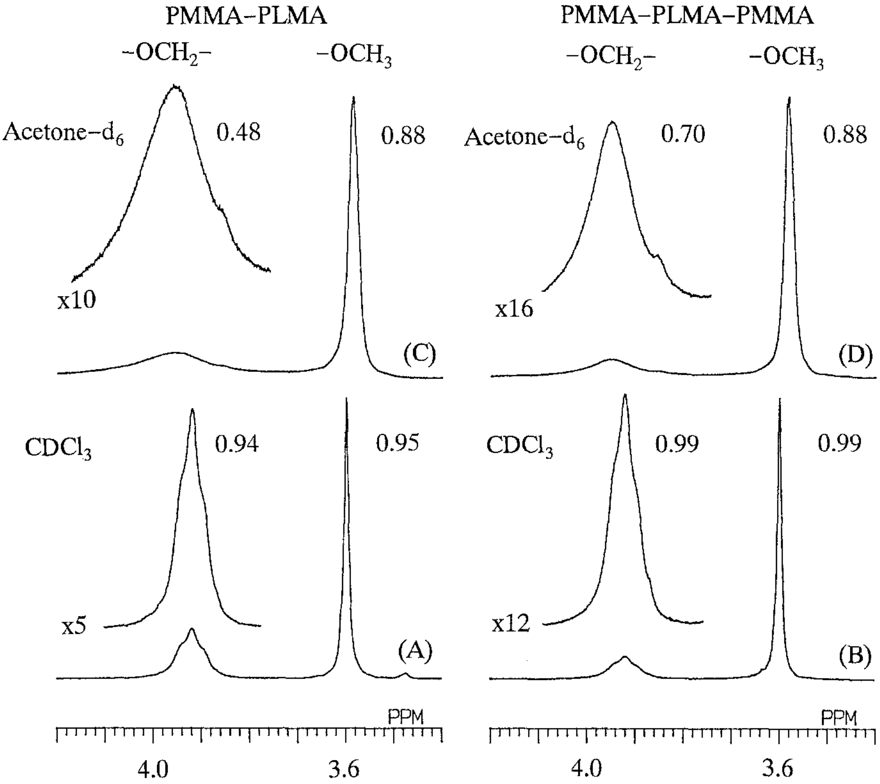


Figure 2. 270MHz ^1H NMR spectra and the absolute intensities of $-OCH_2-$ protons (PLMA) and $-OCH_3$ protons (PMMA) measured in chloroform-d (A,B) and acetone-d_6 (C,D) at 35°C.
(A) and (C): PMMA-*block*-PLMA , (B) and (D): PMMA-*block*-PLMA-*block*-PMMA. Numbers shown in the figures indicate peak intensities; the theoretical values to be 1.00

Table 2. Number Average Molecular Weight of PMMA-*block*-PLMA and PMMA-*block*-PLMA-*block*-PMMA Determined by VPO

Polymer	Solvent		Calcd
	Toluene[a]	Acetone[b]	
PMMA-PLMA	17800	30300	18400
PMMA-PLMA-PMMA	21800	26400	23200

[a] At 59.9°C [b] At 41.0°C

the case of the diblock copolymer. These results suggest that the PLMA blocks of the block copolymers are forced to be dissolved in acetone by good solubility of PMMA blocks linked to the PLMA block and that the block copolymers exist as aggregates or micelles formed through the interaction between PLMA sequences. The diblock copolymer molecules seem to aggregate more tightly than the triblock copolymer molecules.

$^1H-T_1$'s for the block copolymers were measured in chloroform-d and acetone-d_6 at 35°C. The results are shown in Table 3. $^1H-T_1$'s for all the methylene protons of main chain and side chain of PLMA block were much smaller in acetone-d_6 than in chloroform-d while the $^1H-T_1$'s for the $-OCH_3$ protons of PMMA blocks showed no solvent dependence. The results clearly indicate that the block copolymers aggregate through the interaction between the PLMA blocks and the aggregation decreases the segmental mobility of the PLMA block.

Table 3. $^1H-T_1$'s (sec) Measured at 100MHz and 35°C of PMMA-*block*-PLMA and PMMA-*block*-PLMA-*block*-PMMA in Chloroform-d and Acetone-d_6[a]

Unit	Proton	PMMA-PLMA		PMMA-PLMA-PMMA	
		$CDCl_3$	Acetone-d_6	$CDCl_3$	Acetone-d_6
LMA	$-CH_2-$	0.21	0.11	0.18	0.088
	$-OCH_2-$	0.20	0.16	0.18	0.15
	$-\underline{(CH_2)_{10}}-CH_3$	0.52	0.34	0.45	0.35
MMA	$-CH_2-$	0.082	——	0.071	——
	$-OCH_3$	0.31	0.29	0.27	0.30

[a] Conc. 10 wt/v%

Table 4. Absolute ^1H NMR Signal Intensities[a] for $-OCH_2-$ (PLMA) and $-OCH_3$ (PMMA) Measured in Chloroform-d and in Acetone-d_6

Solvent	Temp.	PMMA-PLMA		PMMA-PLMA-PMMA	
	°C	$-OCH_2-$	$-OCH_3$	$-OCH_2-$	$-OCH_3$
Acetone-d_6	35	0.48	0.88	0.70	0.88
	41	0.59	0.87	0.72	0.89
	50	0.86	0.94	0.95	0.92
$CDCl_3$	35	0.94	0.95	0.99	0.99
	41	1.02	1.02	1.06	1.05
	50	0.96	0.96	1.03	1.03

[a] Theoretical value should be unity

The absolute ^{1}H NMR signal intensities for $-OCH_2-$ and $-OCH_3$ protons of the block copolymers in chloroform-d and acetone-d_6 were determined at several temperatures (35–50°C) and the results are shown in Table 4. In chloroform-d the intensities at 35°C and 50°C were almost the same and very close to the theoretical value. In acetone-d_6, however, the intensities increased with increasing temperature and the values observed at 50°C were close to those observed in chloroform-d. These show that the block copolymers exist as aggregates in acetone below 41°C but are almost dissolved as molecules at 50°C. The intensities of $-OCH_2-$ protons of the diblock copolymer in acetone-d_6 were always smaller than those of the triblock copolymer even at 50°C, indicating the stronger aggregation of the diblock copolymer.

It is well known that *it*-PMMA and *st*-PMMA form a crystalline polymer complex named "stereocomplex" [14]. When the triblock copolymer and an *it*-PMMA were mixed in toluene or in acetone at room temperature, or when the solid mixture recovered from chloroform solution was annealed at certain temperatures for 24hr, formation of stereocomplex between the *st*-PMMA block of the copolymer and *it*-PMMA occurred as evidenced by their DSC thermograms shown in Figure 3. The complexes formed in solution showed much larger endothermic peak at 180°C (Figures 3A and 3B) than the complex formed in the solid state (Figure 3C), while the complexes between *it*- and *st*-PMMAs formed in acetone (Figure 3D) and in the solid state (Figure 3E) showed the endothermic peaks of similar intensities.

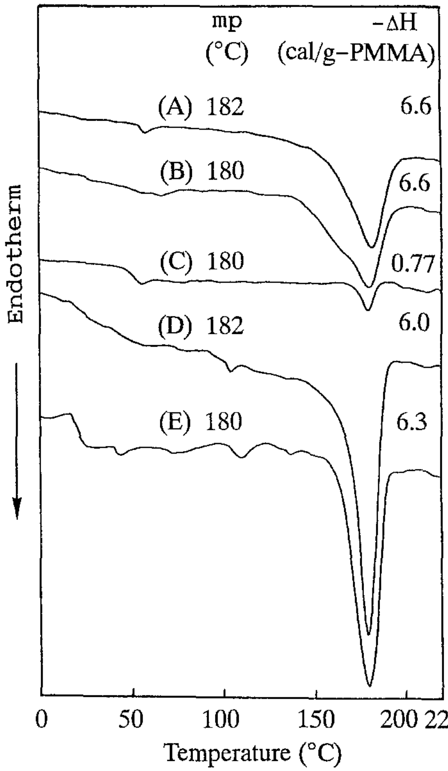


Figure 3. DSC thermograms of stereocomplexes between *it*-PMMA[a] and *st*-PMMA-*block*-PLMA-*block*-PMMA (A,B,C) or *st*-PMMA[b] (D,E).

(A): The complex formed in toluene.

(B,D): The complexes formed in acetone.

(C,E): The complexes formed in solid state by annealing at 150°C.

[a] *it*-PMMA; $\overline{Mn}$=33000, $\overline{Mw}/\overline{Mn}$=1.25, *mm*:*mr*:*rr*=97:2:1

[b] *st*-PMMA; $\overline{Mn}$=5700, $\overline{Mw}/\overline{Mn}$=1.21, *mm*:*mr*:*rr*=3:8:89

The complex formation between the triblock copolymer and *it*-PMMA in the solid state with annealing was studied in the temperature range of 120–150°C. Annealing at 150°C, which is a proper condition for the stereocomplex formation between *it*- and *st*- PMMAs (Figure 3E), resulted in much smaller heat of fusion (Figure 3C, 0.77cal/g-PMMA) as compared with PMMA stereocomplex (Figure 3E, 6.3cal/g-PMMA). The heat of fusion increased with decreasing annealing temperature and reached a maximum value of 3.3cal/g–PMMA at 125°C. The results suggest that higher flexibility of the PLMA block affects the mobility of PMMA blocks to interrupt the stereocomplex formation at 150°C. Thus the lower annealing temperature gave higher extent of the complex formation between the triblock copolymer and *it*–PMMA. A similar tendency was observed in the case of stereocomplex formation between *it*–PMMA and triblock copolymer, *st*–PMMA-*block*—polyisobutylene—*block*-*st*-PMMA$^{15)}$. Hogen–Esch and his coworkers reported the stereocomplex formation between *st*–PMMA-*block*-polybutadine and *it*–PMMA.$^{16)}$ They also observed that the heat of fusion increased with decreasing annealing temperature (110–140°C).

On the other hand, the heat of fusions of the complexes between the triblock copolymer and *it*–PMMA formed in solution were almost the same as that of stereocomplex between *it*– and *st*– PMMAs formed in solution (Figure 3A, 3B and 3D) after normalization by weight of MMA unit in the mixtures. The results indicate that higher segmental mobility of PLMA block is not a limiting factor for the complex formation in solution. DSC curves of the complexes of the triblock copolymer formed in toluene and in acetone did not differ evidently. Though PLMA block aggregates in acetone but not in toluene and chloroform, the aggregation hardly supresses the mobility of PMMA blocks as evidenced from ^{1}H–T$_1$ values for the PMMA blocks measured in chloroform–d and acetone–d$_6$ (Table 3). The aggregation of the triblock copolymer in acetone did not affect stereocomplex formation.

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References

1. G. Riess, G. Hurtrez, P. Bahadur, *Encyclopedia Polym. Sci. Eng.*, **Vol. 2**, 324, A Wiley–Interscience Publication, New York (1985)
2. K. Hatada, K. Ute, K. Tanaka, T. Kitayama, and Y. Okamoto, *Polym. J.*, **17**, 977 (1985)
3. K. Hatada, K. Ute, K. Tanaka, Y. Okamoto, and T. Kitayama, *Polym. J.*, **18**, 1037 (1986)
4. T. Kitayama, T. Shinozaki, E. Masuda, M. Yamamoto, and K. Hatada, *Polym. Bull.*,**20**, 505 (1988)
5. T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto, and K. Hatada, *Makromol. Chem., Supplement* **15**, 167 (1989)
6. T. Kitayama, K. Ute, M. Yamamoto, N. Fujimoto, and K. Hatada, *Polym. J.*, **22**, 386 (1990)
7. T. Kitayama, K. Ute, and K. Hatada, *Brit. Polym. J.*, **23**, 5 (1990)
8. T. Kitayama, T. Nishiura, and K. Hatada, *Polym. Bull.*, **26**, 513 (1991)
9. T. Nishiura, T. Kitayama, and K. Hatada, *Polym. Bull.*, **27**, 615 (1992)
10. D. Y. Sogah, W. R. Hertler, O. W. Webster, and G. M. Cohen, *Macromolecules*, **20**, 1473 (1987)
11. S. C. Watson, J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967)
12. R. D. Allen, T. E. Long, and J. E. McGrath, *Polym. Bull.*, **15**, 127 (1986)
13. K. Hatada, Y. Terawaki, and H. Okuda, *Org. Magn. Res.*, **9**, 518 (1977)
14. A. M. Liquori, G. Anzuino, V.M. Corio, M. D'Alagni, P. de Santis, and A. Savino, *Nature* (London), **206**, 358 (1965)
15. T. Kitayama, O. Nakagawa, T. Nishiura and K. Hatada, unpublished results
16. T. E. Hogen–Esch, B. J. Ladd and J. P. Mason, *Polym. Prep., ACS, Div. Polym. Chem.*, **31(2)**, 405 (1990)

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