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SHORT COMMUNICATIONS

Heterotactic Polymerization of Methacrylates Having C-3 Ester Group

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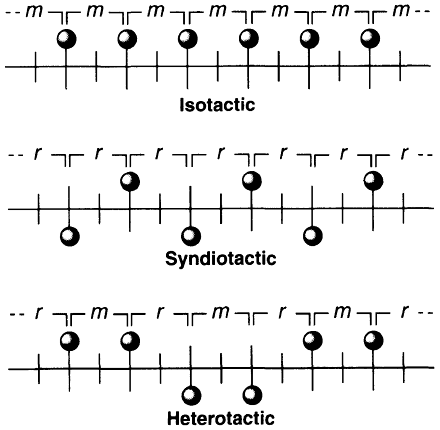
Isotactic and syndiotactic polymers are two typical stereoregular polymers, which comprise, respectively, contiguous *meso* (*m*) and *racemo* (*r*) diads. For isotactic and syndiotactic polymerizations the control of configurational relationship between neighboring constitutional repeating units is sufficient in principle. Heterotactic polymer is another kind of stereoregular polymers that comprises an alternating sequence of *m* and *r* diads. Formation of heterotactic polymer requires two different types of stereoregulation, *m*- and *r*-additions, to occur in an alternate manner. Thus in heterotactic polymerization the diad configuration at the propagating chain-end should specifically affect the stereospecificity of propagating species; the chain end with *m* diad prefers *r*-addition and that with *r* diad prefers *m*-addition. It is obvious that the formation of heterotactic polymer requires a higher level of stereoregulation than those for isotactic and syndiotactic polymers (eq 1).



(1)

Nozakura *et al.* reported cationic polymerization of triisopropylsilyl vinyl ether with dichloroethylaluminum in toluene at $-78°C$, which gave a heterotactic poly(vinyl alcohol) after treatment with hydrofluoric acid.[1] The triad heterotacticity (*mr* content) determined by ^{13}C NMR spectroscopy was 68%. Since then, heterotactic polymer has attracted occasional interest, but the regularity had been scarcely improved. A sole exception was an alternating copolymer, with coheterotacticity of 90%, of methyl methacrylate (MMA) and styrene prepared by photopolymerization in the presence of BCl_3 at $-90 \sim -100°C$.[2] We reported in 1994 the successful preparation of highly heterotactic homopolymers by living polymerization of several primary and secondary alkyl methacrylates with *t*-butyllithium (*t*-BuLi)/bis(2,6-di-*t*-butylphenoxy)methylaluminum [MeAl(ODBP)$_2$] in toluene at low temperatures.[3,4] The highest *mr* content of 92% has been attained for ethyl methacrylate (EMA). More recently, Nakahama *et al.* reported heterotactic polymerization of *N*,*N*-diethylacrylamide, which gave a polymer with $mr = 92\%$.[5]

In the polymerization of methacrylates with a combination of *t*-BuLi and bulky aluminum bisphenoxides, the stereospecificity of the polymerization strongly depends on the structure of the aluminum phenoxides. For instance, use of bis(2,6-di-*t*-butylphenoxy)ethylaluminum or bis(2,6-di-*t*-butylphenoxy)isobutylaluminum, instead of MeAl(ODBP)$_2$, changes the stereospecificity from heterotactic to syndiotactic, while the living character of the polymerization is retained.[6] The bulkiness of the ester group also affects drastically the stereospecificity of the polymerization with *t*-BuLi/MeAl(ODBP)$_2$; both primary and secondary alkyl methacrylates give heterotactic polymers,[3] and, in sharp contrast, tertiary alkyl methacrylates such as *t*-butyl[3] and trimethylsilyl methacrylates[7] give syndiotactic polymers. Even in the polymerization of a series of primary alkyl methacrylates, the length of alkyl group slightly affects the stereoregularities of the obtained polymers (*cf.* Table I). These results mean that the stereospecificity in the polymerization with *t*-BuLi/MeAl(ODBP)$_2$ is very sensitive to steric factors, implying the possibility that even a small change in steric bulkiness of the monomer may improve the stereospecificity in the heterotactic polymerization. In this communication are described the polymerizations of propyl (PrMA), allyl (AlMA), and propargyl methacrylate, which have C-3 ester group.

PrMA was prepared from MMA and propan-1-ol by transesterification with tetrabutyl titanoate as a catalyst.[8] Propargyl methacrylate was prepared by the reaction of methacryloyl chloride and propargyl alcohol in the presence of triethylamine. PrMA, AlMA which was obtained commercially, and propargyl methacrylate 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*-butyllithium, and distilled under high vacuum. *t*-BuLi in pentane, obtained commercially, was used as a heptane solution. MeAl(ODBP)$_2$ was prepared as described elsewhere.[9]

All the polymerization were carried out in a glass

Table I. Polymerization of primary alkyl methacrylate with *t*-BuLi/MeAl(ODBP)$_2$ in toluene at −78°C or −95°C[a]

Run	Alkyl	Temp	Time	Yield	$\bar{M}_n$[b]	$\bar{M}_w$[b]	Tacticity/%[c]		
		°C	h	%		$\bar{M}_n$	*mm*	*mr*	*rr*
1[d]	$-CH_3$	−78	24	100	8330	1.18	11.6	67.8	20.6
2[d]	$-CH_2CH_3$	−78	24	100	7010	1.07	7.7	88.6	3.7
3[d]		−95	48	100	11100	1.07	7.0	92.0	1.0
4	$-CH_2CH_2CH_3$	−78	24	100	7650	1.07	6.1	91.2	2.7
5		−95	48	100	7680	1.09	5.7	93.3	1.0
6	$-CH_2CH=CH_2$	−78	24	94	8070	1.06	5.8	89.8	4.4
7		−95	48	85	11200	1.08	3.1	95.8	1.1
8	$-CH_2C\equiv CH$	−78	24	26	4170	1.15	8.4	52.0	39.6
9		−95	48	18	3410	1.18	10.4	79.4	10.2
10[e]	$-(CH_2)_3CH_3$	−78	24	98	9300	1.07	8.4	87.1	4.5
11	$-(CH_2)_5CH_3$	−78	24	100	13460	1.41	12.0	83.7	4.3

[a] Monomer 10 mmol, *t*-BuLi 0.2 mmol, MeAl(ODBP)$_2$ 1.0 mmol, toluene 10 ml. [b] Determined by GPC. [c] Determined by ^{13}C NMR. [d] Taken from ref 9. [e] Taken from ref 3.

ampoule filled with dried nitrogen passed through molecular sieves 4A cooled at −78°C. A heptane solution of *t*-BuLi was added to MeAl(ODBP)$_2$ in toluene at polymerization temperature. The polymerization reaction was initiated by adding the monomer slowly to this mixture at polymerization temperature. The reaction was terminated by adding methanol containing HCl at polymerization temperature. In the case of PrMA polymerization, 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. When AlMA was used as a monomer, the reaction mixture was poured into a large amount of methanol to precipitate the polymeric product. The polymeric product was precipitated by cooling the methanol to 0°C and organic impurities such as the monomer and 2,6-di-*t*-butylphenol derived from MeAl(ODBP)$_2$ were removed by repeated decantation. The product was redissolved in acetone and the solution was poured into a large amount of water to reprecipitate the polymeric product. The precipitate was collected by filtration, washed with water, and dried under vacuum. In the case of polymerization of propargyl methacrylate, 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 and water, successively, and dried under vacuum.

Tacticities of the polymers were determined from carbonyl carbon signals in ^{13}C NMR spectra measured in CDCl$_3$ at 55°C on a Varian Unity Inova 500 spectrometer operated at 125 MHz. Molecular weight and its distribution of the polymers were determined by gel permeation chromatography (GPC) using a JASCO 880-PU chromatograph equipped with two Shodex GPC columns [KF-806L (30 cm × 0.8 cm) × 2] using tetrahydrofuran as an eluent at 40°C. The GPC chromatogram was calibrated against standard PMMA samples. Differential scanning calorimetry (DSC) was performed on a Rigaku DSC-8230.

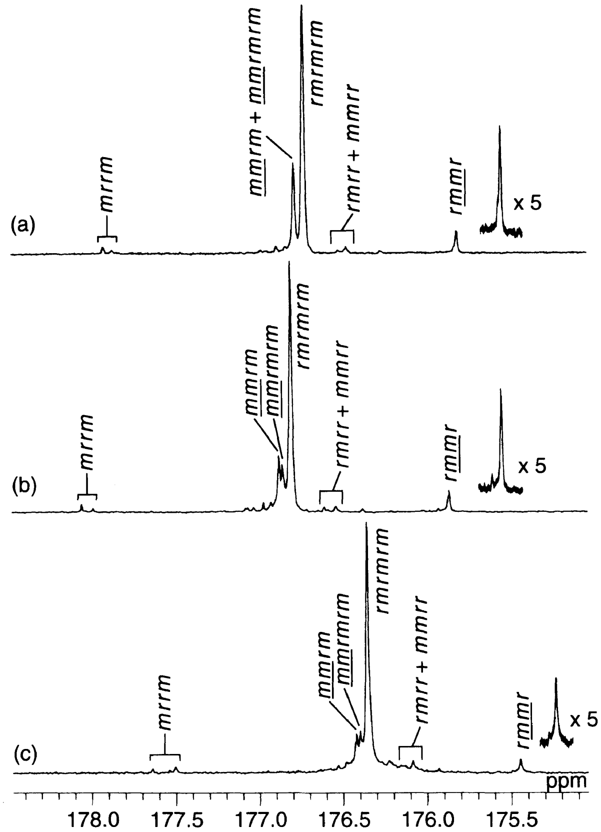
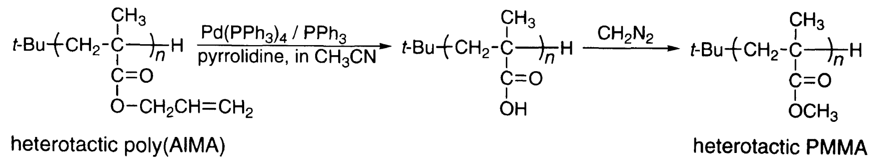


Figure 1. Carbonyl carbon NMR signals of heterotactic polymers of (a) EMA, (b) PrMA, and (c) AlMA prepared with *t*-BuLi/MeAl(ODBP)$_2$ (1 : 5, mol/mol) in toluene at −95°C. (125 MHz, CDCl$_3$, 55°C).

In Table I are summarized the results of the polymerizations of several primary alkyl methacrylates with *t*-BuLi/MeAl(ODBP)$_2$ in toluene at −78°C and/or −95°C. When the simplest ester, MMA, is used as a monomer, the polymer with *mr* = 67.8% is obtained at −78°C (run 1), while the *mr* content of poly (EMA) prepared under the same conditions is 88.6% (run 2) and reaches 92.0% by lowering polymerization temperature to −95°C (run 3). *n*-Butyl methacrylate, a C-4 ester, gave a heterotactic polymer with almost the same *mr* value, *mr* = 87.1% (run 10), as in the case of EMA, and hexyl methacrylate, C-6 ester, gave the polymer whose *mr* content decreases to 83.7% (run 11). These results imply the possibility that the stereospecificity in heterotactic polymerization reaches the maximum between C-2 and C-4 esters. Thus we examined the polymerizations of PrMA, AlMA, and propargyl methacrylate.



Scheme 1.

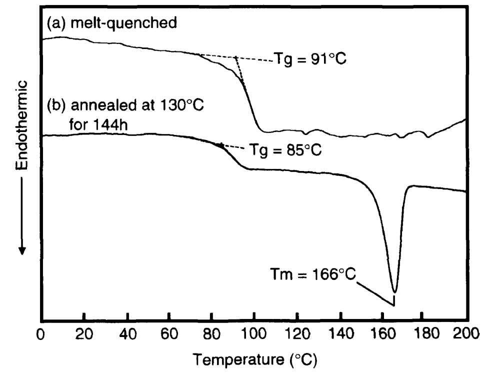


Figure 2. DSC curves of heterotactic PMMA derived from heterotactic poly(AlMA) (run 7 in Table I), recorded at a heating rate of 10°C min^{-1}. (a) melt-quenched; (b) annealed at 130°C for 144 h.

The polymerizations of PrMA at -78°C and -95°C gave heterotactic polymers whose *mr* contents were 91.2 and 93.3%, respectively, with narrow molecular weight distributions (MWDs) (runs 4 and 5). The polymerizations of AlMA gave the polymers with narrow MWDs, which are soluble in common organic solvents such as toluene and chloroform (runs 6 and 7). ^{1}H NMR spectra of the polymers confirm that all the allyl groups are retained without being involved in any side reactions. The heterotacticities of the polymers obtained at -78°C and -95°C were 89.8 and 95.8%, respectively. The heterotacticity of the latter is the highest among those of the heterotactic polymers so far reported.

On the other hand, propargyl methacrylate also gave polymers soluble in common organic solvents with narrow MWD, though the initiator efficiencies were lower than 0.4 probably due to partial quenching of the highly basic *t*-BuLi with the acetylenic hydrogen (runs 8 and 9). The peak intensity ratios in ^{1}H NMR spectra of the poly(propargyl methacrylate) agree well with the values expected from the structures. In addition to the narrow MWD, the result indicates that no side reaction involving the acetylenic groups takes place during the propagating reaction. However, the polymer yield and heterotacticity of the polymers obtained were much lower than those for PrMA and AlMA.

Figure 1 shows carbonyl carbon region of ^{13}C NMR spectra of poly(EMA), poly(PrMA), and poly(AlMA). All the spectra show a strong peak due to *rmrmrm* heptad and small peaks due to several defective sequences including *mm* triad, such as *rmmr*, *mmrm* and *mmrmrm*. The peak intensity in the *rmmr* region decreases in the order of poly(EMA), poly(PrMA), and poly(AlMA), while that of the *mrrm* region is kept almost constant. These results suggest that the stereoselectivity of *m*-ended anions is slightly improved by the small change in steric bulkiness of the monomer without sacrificing high stereoselectivity of *r*-ended anions.

The heterotactic poly(AlMA) with $mr = 95.8\%$ was converted to heterotactic PMMA through the reaction with pyrrolidine in acetonitrile in the presence of $\mathrm{Pd(PPh_3)_4}$,[10,11] followed by methylation with diazomethane[12] (Scheme 1). The DSC curve of the heterotactic PMMA annealed at 130°C for 144 h showed a melting endotherm at 166°C (Figure 2). The melt-quenched PMMA showed a glass transition at 91°C. The results prove the high regularity of this new stereoregular PMMA.

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11. To an ice-cooled solution of $\mathrm{Pd(PPh_3)_4}$ (0.04 mmol), $\mathrm{PPh_3}$ (0.08 mmol), and pyrrolidine (2 mmol) in acetonitrile (2.5 ml) was added a solution of poly(allyl methacrylate) (180 mg, 1.5 mmol of monomeric units) in acetonitrile (2.5 ml). After stirring at 60°C for 24 h, the mixture was poured into acetone and insoluble materials were isolated by centrifugation. The resulting precipitate was reacted with $\mathrm{CH_2N_2}$ to convert it into PMMA. The conversion of allyl ester units into carboxylic acid units was approximately 90%, and it was necessary to repeat the reaction twice for the complete conversion. The appropriate conditions for this conversion reaction are now under examination to attain complete conversion through a single procedure.
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