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Stereospecific Polymerization of Benzyl α-(Methoxymethyl)acrylate

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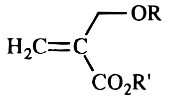
α-(Hydroxymethyl)acrylate derivatives are monomers which have two different types of polar substituents on an olefin. Effects of polar groups on the reactivity and stereoregularation in anionic polymerization are of great interest from the viewpoints of the intramolecular coordination to a countercation by the functional groups. Although atactic polymers have been obtained in the radical polymerization of α-(alkoxymethyl)acrylates,[1] little data are available about the tacticity of the polymers obtained by anionic polymerization. In this study, a novel monomer, benzyl α-(methoxymethyl)acrylate (BMMA), was synthesized,[2,3] and its reactivity and the stereoregularity of obtained polymers in radical and anionic polymerizations were investigated.

The anionic polymerization of methyl α-(phenoxymethyl)acrylate (MPMA)[4] was first examined with lithium reagents. However, the polymer was obtained in a few percent yield in toluene,[5] probably due to side reactions, 1,2-addition (carbonyl attack), and elimination of a phenoxide anion. Wulff et al. also carried out the anionic polymerization of methyl α-((trityloxy)methyl)acrylate,[6] but no polymer was obtained, probably because of the bulky alkoxy group. Therefore, we designed BMMA as a monomer.



MPMA : R = Ph, R' = Me
BMMA : R = Me, R' = Bn

Table 1 lists the results of the radical and anionic polymerizations of BMMA. The radical polymerization with diisopropyl peroxycarbonate (Perloyl) in toluene at 30 °C afforded a polymer quantitatively (entry 1), and the anionic polymerization with lithium reagents at −78 or +30 °C proceeded moderately, giving a polymer in 20−77% yields (entries 2−6). The complex of *n*-BuLi with (−)-sparteine also gave a polymer in a low yield without any significant chiral induction (entry 7). Ethylmagnesium bromide provided no polymer at −78 °C in toluene (entry 8).

Table 1. Radical and Anionic Polymerization of BMMA[a]

entry	initiator	solvent	temp (°C)	time (h)	yield (%)	DP[b]	M_w/M_n[b]
1	(i-PrOCO$_2$)$_2$	toluene	30	48	100	55	3.10
2	*n*-BuLi	toluene	−78	96	77	110	5.61
3	*n*-BuLi	THF	−78	96	70	37	14.9
4	*n*-BuLi	toluene	30	48	43	26	1.40
5	*t*-BuLi	toluene	−78	96	29	102	3.35
6	*t*-BuLi	THF	−78	96	20	145	8.34
7	*n*-BuLi-(−)-Sp[c]	toluene	−78	96	15[d]	74	9.40
8	EtMgBr	toluene	−78	96	0		

[a] [Monomer]/[initiator] = 10. [b] Determined by GPC (polystyrene standard). [c] (−)-Sparteine. [d] $[\alpha]^{25}_{365}$ = 0° (in CHCl$_3$).

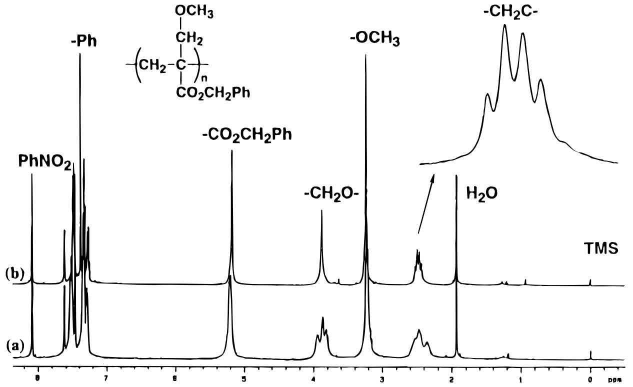


Figure 1. 500 MHz ^{1}H NMR spectra of poly(BMMA), obtained by the radical method at 30 °C (entry 1) (a) and with *t*-BuLi in toluene at −78 °C (entry 5) (b) (Varian VXR-500S, nitrobenzene-d_5, 110 °C).

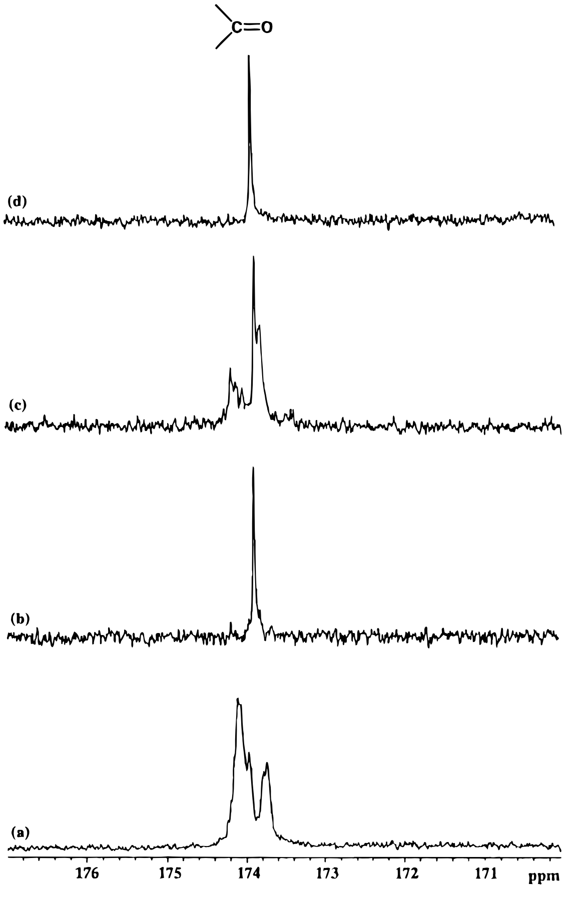


Figure 2. 125 MHz ^{13}C NMR spectra of the carbonyl carbon in poly(BMMA) obtained by the radical method at 30 °C (entry 1) (a), with *t*-BuLi in toluene at −78 °C (entry 5) (b), with *n*-BuLi in toluene at 30 °C (entry 4) (c), and with *t*-BuLi in THF at −78 °C (entry 6) (d) (Varian VXR-500S, CDCl$_3$, 60 °C).

In the ^{1}H NMR spectra of the poly(BMMA)s obtained by the radical (entry 1) and anionic (entry 5) polymerizations in toluene (Figure 1), the spectral patterns of the α-methylene (CH_2O) and β-methylene (CH_2C) protons are quite different between the two polymers. The α-methylene protons of the anionically obtained poly(BMMA) show a sharp singlet, whereas three broad peaks are observed for the radically obtained polymer. The spectral pattern of the β-methylene protons of a main chain looks like an AB quartet for the former polymer. This was confirmed by the measurement of a *J*-resolved spectrum of the β-methylene resonance. The four peaks are assigned to an AB quartet with a coupling constant of 15.0 Hz. The 600 MHz ^{1}H NMR of the same sample also showed an AB quartet of the

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β-methylene resonance. These results indicate that the poly(BMMA) obtained by the anionic polymerization in toluene possesses a high isotacticity, while the polymer obtained by the radical method may be atactic.

Figure 2 shows the ^{13}C NMR spectra of the carbonyl carbon of poly(BMMA)s. A sharp peak is observed for the anionically prepared poly(BMMA) (Figure 2b), and multiple peaks for the polymer obtained by the radical method (Figure 2a). This observation also supports that the anionic polymerization of BMMA in toluene proceeds in a highly isotactic-specific manner. Furthermore, the polymerization with *n*-BuLi at 30 °C in toluene (entry 4) also gave a polymer rich in the same tacticity (Figure 2c). It is noteworthy that the polymers produced with lithium reagents in the presence of a diamine (entry 7) and even in THF (entries 3 and 6) also showed a sharp peak assigned to highly isotactic sequences (Figure 2d). These results were also confirmed by ^{1}H NMR analysis and are in contrast to those of the anionic polymerization of (α-alkyl)acrylates, which usually afford polymers rich in syndiotacticity under the above conditions.[7]

In conclusion, the anionic polymerization of BMMA by lithium reagents provided a polymer with a high isotacticity regardless of the polarity of the solvent. The strong intra-[8] and intermolecular coordination powers of the polar groups of a growing polymer chain end and BMMA monomer to the countercation (Li^{+}) may be the main factor in controlling the stereochemistry in the polymerization.

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(2) Benzyl α-(methoxymethyl)acrylate (BMMA) was synthesized according to the literature[3] from benzyl 2-bromoacetate and triethyl phosphite in four steps. Bp 83−84 °C/0.2 mmHg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.40 (s, 3H, CH_3), 4.17 (s, 2H, CH_2Ph), 5.22 (s, 2H, OCH_2), 5.89 (d, 1H, $J = 1.5$ Hz, vinyl), 6.36 (d, 1H, $J = 1.5$ Hz, vinyl), 7.3−7.4 (m, 5H, aromatic). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.90; H, 6.88.

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(5) Although it has been reported that nearly atactic polymer was obtained in a good yield in the anionic polymerization of MPMA with *n*-BuLi as well as in the radical polymerization,[1b] we could not get an atactic polymer by anionic polymerization, and the obtained polymers were highly isotactic. Our results were confirmed repeatedly.

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