SHORT COMMUNICATIONS

Stereocontrol in Radical Polymerization of Benzyl α-(Methoxymethyl)acrylate Using Zinc Salts

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Stereocontrol in the radical polymerization of vinyl monomer is a most important goal in synthetic polymer chemistry. Although numerous works have been reported on stereospecific polymerization based on anionic and coordination mechanisms, little is known concerning the stereocontrol in radical method.[1,2] We recently reported that the anionic polymerization of α-(alkoxymethyl)acrylates with lithium reagent proceeds in a highly isotactic-specific manner regardless of the polarity of solvents,[3] while the radical polymerization generally gives an atactic polymer.[4] Strong intra- and intermolecular coordination of the polar substituents of the growing polymer chain and monomers to the counter-cation (Li^+) may be the main factor controlling stereochemistry. Therefore, stereocontrol in radical polymerization using benzyl α-(methoxymethyl)acrylate (BMMA)[3] as a monomer in the presence of various metal salts, which may coordinate growing polymer and monomers, was investigated.

OCH_3
|
CH_2
|
H_2C=C
|
CO_2CH_2—⟨benzene ring⟩

BMMA
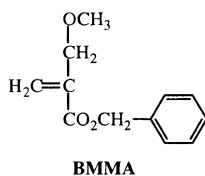
EXPERIMENTAL

^1H and ^{13}C NMR spectra were measured on a Varian Gemini-2000 (400 MHz for ^1H) or UNITY-INOVA (500 MHz for ^1H) spectrometer in $CDCl_3$ or nitrobenzene-d_5 with tetramethylsilane as the internal standard. Size exclusion chromatographic analysis (SEC) was performed on a JASCO 880-PU chromatograph equipped with a JASCO 830-RI refractive index detector. Two commercial columns (TSK G5000H 60 × 0.72 (i.d.) cm, Shodex AC 802.5 50 × 0.72 (i.d.) cm) were connected in series and chloroform was used as eluent. Calibration was performed using standard polystyrenes.

Solvents, toluene and tetrahydrofuran (THF), were distilled from Na wire, and distilled again from butyllithium (n-BuLi) for toluene and $LiAlH_4$ for THF under high vacuum just before use. Dichloromethane was distilled from CaH_2. A radical initiator diisopropyl per-

oxycarbonate $[(iso\text{-}PrOCO_2)_2]$ was generously donated by NOF Co. and used as a toluene solution. BMMA was synthesized from benzyl α-(bromomethyl)acrylate[5] according to the procedure previously reported.[3] Commercially available hydrates of metal salts (LiCl, $MgCl_2$, $ZnCl_2$, and $ZnBr_2$) were dried by heating under reduced pressure for use in the polymerization.

Polymerization was typically carried out using a metal salt (2.25 mmol), BMMA (1.50 mmol), a solvent (1.2 mL), and $(iso\text{-}PrOCO_2)_2$ (0.05 mmol) with stirring of heterogeneous mixture at 30°C. Reaction products were diluted with chloroform, precipitated into methanol and freeze-dried from benzene after filtration.

RESULTS AND DISCUSSION

The results of the radical polymerization of BMMA with various metal salts at 30°C for 48 h are listed in Table I. Figure 1 demonstrates the ^1H NMR spectrum of the polymer obtained with $ZnBr_2$ in CH_2Cl_2 (entry 6). Each peak is assigned as shown in the figure. Elemental analysis of the polymer also supports the structure of poly(BMMA) as follows:

Calcd for $(C_{12}H_{14}O_3)_n$: C, 69.88%; H, 6.84%; Found: C, 69.87%; H, 6.82%.

The spectral pattern of main chain methylene protons around 2.1 ppm seems to exhibit splitting due to stereoregularity.

Table I. Radical polymerization of BMMA at 30°C for 48 h[a]

Entry	Additive	Solvent	Yield[b] %	DP (M_w/M_n)[c]
1	—	CH_2Cl_2	96[d]	63 (2.5)
2	LiCl	Toluene	>99	50 (4.0)
3	$MgCl_2$	Toluene	97	54 (2.6)
4	$ZnCl_2$	Toluene	>99	37 (4.2)
5	$ZnBr_2$	Toluene	88	82 (3.2)
6	$ZnBr_2$	CH_2Cl_2	87	40 (1.5)
7	$ZnBr_2$[e]	THF	>99	63 (4.5)

[a] $[BMMA]/[(iso\text{-}PrOCO_2)_2] = 30$, $[additive]/[BMMA] = 1.5$, $[BMMA] = 1 M$, polymerization was carried out with stirring. [b] MeOH insoluble part. [c] Determined by SEC (polystyrene standard). [d] Hexane insoluble part. [e] $[Additive]/[BMMA] = 1.1$.
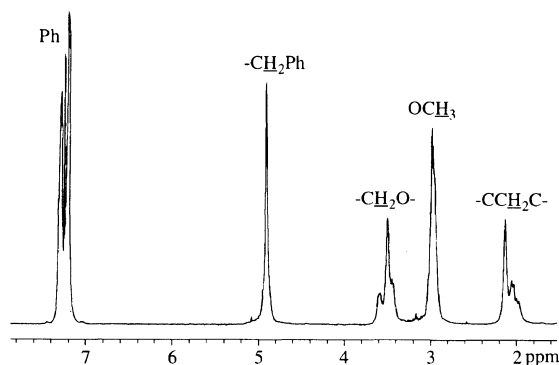
Figure 1. 500 MHz ^{1}H NMR spectrum of poly(BMMA) (entry 6) in CDCl$_3$ at 60°C.
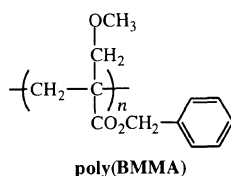

poly(BMMA)

Figure 2(b) shows the expanded ^{1}H NMR spectrum of the main chain methylene protons of poly(BMMA) (entry 6), together with those of the polymers prepared without ZnBr$_2$ in CH$_2$Cl$_2$ (entry 1) (a) and with n-BuLi in toluene at -78°C ($m > 99\%$)[3] (c) for comparison. The spectral pattern of the polymer obtained in the presence of ZnBr$_2$ is quite different from that prepared without a salt, indicating that some stereocontrol takes place in the radical polymerization with ZnBr$_2$. While little change was observed on the stereoregularity of the polymers obtained with LiCl (entry 2) and MgCl$_2$ (entry 3), the polymerization using zinc salts (ZnCl$_2$ and ZnBr$_2$, entries 4—6) gave the polymers having different tacticity from that prepared in the absence of metal salt. However, a polar solvent, THF, greatly reduced the effect of the stereocontrol by ZnBr$_2$ judging from the spectral pattern of ^{1}H NMR (entry 7), suggesting that the coordination of zinc salts to the growing polymer and the monomer is important in this system.

The ^{13}C NMR spectra of the main chain quaternary carbon in poly(BMMA)s are depicted in Figure 3. The polymer obtained with ZnBr$_2$ has a quite different stereoregularity from that of anionically prepared highly isotactic-poly(BMMA)[3a] as well as that of the polymer obtained by a normal radical method.

As reported previously,[3a] the ^{1}H NMR spectrum of the main chain methylene protons of isotactic-poly-(BMMA) anionically prepared shows a typical AB quartet in nitrobenzene-d_5 at 110°C (Figure 4(c)), although peak splitting was not observed in CDCl$_3$ at 60°C as shown in Figure 2(c). ^{1}H NMR of the polymer radically obtained with ZnBr$_2$ in CH$_2$Cl$_2$ (entry 6) was measured in nitrobenzene-d_5 at 110°C (Figure 4(b)). The spectral pattern of the main chain methylene was similar to that shown in Figure 2(b), and the four peaks in the area A seem assignable to an AB quartet with a coupling constant of about 16 Hz due to the diastereotopic meso-protons. Therefore, a peak in the region B may be due to the protons of racemo-diad. However, since the chemical shifts for the former four peaks are
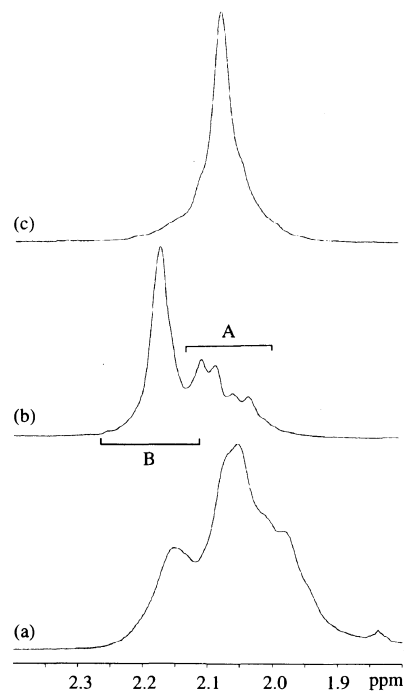
Figure 2. 500 MHz ^{1}H NMR spectra of the main chain methylene protons in poly(BMMA) (entry 1) (a), obtained with ZnBr$_2$ (entry 6) (b), and with n-BuLi in toluene at -78°C[3a] (c) (CDCl$_3$, 60°C).
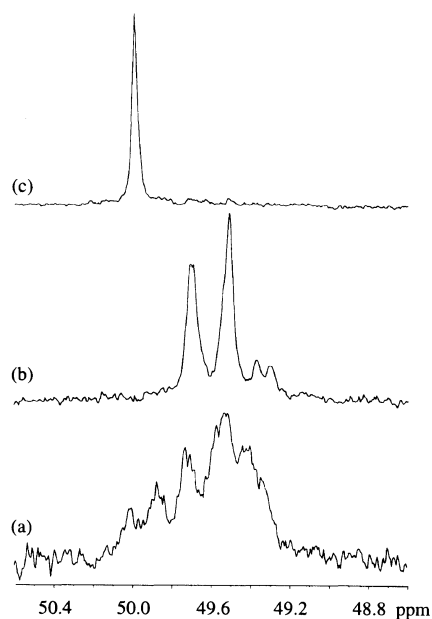

Figure 3. 125 MHz ^{13}C NMR spectra of the main chain quaternary carbon in poly(BMMA) (entry 1) (a), obtained with ZnBr$_2$ (entry 6) (b), and with n-BuLi in toluene at -78°C[3a] (c) (CDCl$_3$, 60°C).

different from those for the protons of the isotactic-poly(BMMA), the higher order (tetrad) tacticity should be considered the spectral pattern for the main chain methylene protons of poly(BMMA). Supposing that the peaks from 2.3 to 2.4 ppm are ascribed to one of the protons of meso-diad, diad tacticity of the polymer prepared using ZnBr$_2$ is estimated to be $r : m = 67 : 33$, while that of the radically obtained polymer in its absence (entry 1) is nearly $r \approx m$ (≈ 0.5) (estimated from the ^{1}H NMR spectrum in nitrobenzene-d_5 at 150°C) (Figure 4(a)). The diad tacticities of other poly(BMMA)s were
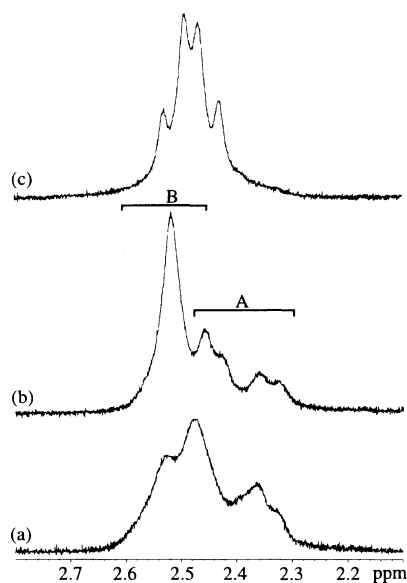
Figure 4. 400 MHz ^{1}H NMR spectra of the main chain methylene protons in poly(BMMA) (entry 1) (a) (nitrobenzene-d_5, 150°C), obtained with ZnBr$_2$ (entry 6) (b), and with n-BuLi in toluene at $-78°$C^{3a} (c) (nitrobenzene-d_5, 110°C).

evaluated to be $r:m = 65:35$ (entry 4)[6] and $70:30$ (entry 5).[7]

The addition of zinc chloride accelerates the polymerization rate of methacrylates,[8] and tacticity is hardly changed during the polymerization, while an increase of isotacticity was observed in radical bulk polymerization of the complexes of methacrylate with zinc chloride.[9] The radical polymerization of benzyl methacrylate (BnMA) with ZnBr$_2$ was also carried out by the same procedure as that for the polymerization of BMMA. The polymer was obtained using ZnBr$_2$ (1.5 eq.) in CH$_2$Cl$_2$ in 97% yield (DP = 59, $M_w/M_n = 2.0$) with a triad tacticity, $mm:mr:rr = 3:34:63$, while poly(BnMA) (96% yield, DP = 120, $M_w/M_n = 4.8$) prepared in its absence showed a tacticity, $3:33:64$. These results indicate that the zinc salts characteristically affect the stereoregularity of poly(BMMA) in the radical polymerization, and a polar α-substituent on an acrylate is important in the stereocontrol of this system.

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6. Elemental analysis: Calcd for (C$_{12}$H$_{14}$O$_3$)$_n$: C, 69.88%; H, 6.84%; Found: C, 69.87%; H, 6.91%.

7. Elemental analysis: Found: C, 69.86%; H, 6.89%.

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