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Stereospecific Radical Polymerization of α-(Alkoxymethyl)acrylates Controlled by a Catalytic Amount of Zinc Halides

Shigeki Habaue, Takahiro Uno, Hideo Baraki, and Yoshio Okamoto*

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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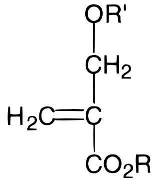
ABSTRACT: The stereospecific radical polymerization of α-(alkoxymethyl)acrylates—benzyl α-(methoxymethyl)acrylate, benzyl α-(ethoxymethyl)acrylate, and ethyl α-(ethoxymethyl)acrylate—in the presence of a catalytic amount of zinc halides ($ZnCl_2$ and $ZnBr_2$) was attained, and the obtained polymers had very different tacticities, rich in syndiotacticity (up to $r = 0.71$), from that prepared in the absence of a zinc salt (atactic). In contrast, no change was observed in the stereoregularity of the polymethacrylates radically obtained in the presence of $ZnBr_2$ as an additive. The coordination of zinc salts to polar α-substituents on the ω-end of the propagating polymer and the monomer must play an important part in this system.

Introduction

The control of the stereochemistry during the radical polymerization of vinyl monomers has been a longstanding concern and is still one of the most important topics in synthetic polymer chemistry. Although numerous studies have been reported on the radical polymerization of vinyl monomers, limited data are available about the stereospecific polymerization.[1,2] It has been known that the radical polymerization of α-(alkoxymethyl)acrylates generally affords atactic polymers,[3] whereas the anionic polymerization with lithium reagents proceeds in a highly isotactic-specific manner regardless of the solvent polarity.[4] Strong intra- and intermolecular coordination of the α-substituents of a propagating polymer chain and a monomer to the countercation (Li^+) should be the main factors controlling the stereochemistry during the anionic polymerization. We recently reported that zinc salts ($ZnCl_2$ and $ZnBr_2$) significantly change the stereoregularity during the radical polymerization of benzyl α-(methoxymethyl)acrylate (BMMA) in comparison with that of the polymer prepared without salts.[5] The coordination of zinc salts to the polar substituents, especially the methoxy groups, of the growing polymer chain and the monomer is important for the stereocontrol of this system, since no change was observed in the stereoregularity of the poly(benzyl methacrylate) radically obtained in the presence of $ZnBr_2$ as an additive. This system can provide a novel method for controlling the stereochemistry during the radical polymerization of vinyl monomers. Here, a further investigation of the stereospecific radical polymerization of BMMA and two other α-(alkoxymethyl)acrylates, benzyl α-(ethoxymethyl)acrylate (BEMA) and ethyl α-(ethoxymethyl)acrylate (EEMA), using zinc salts is discussed.

Experimental Section

Materials. The solvents, toluene and tetrahydrofuran (THF), used in the polymerization 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 and 1,2-dichloroethane were distilled from CaH_2. A radical initiator, diisopropyl peroxycarbonate [$(i\text{-}PrOCO_2)_2$], was kindly supplied by the NOF Co. and used as a toluene solution. Methyl methacrylate (MMA) was first purified by fractional distillation from CaH_2 and then distilled under high vacuum from CaH_2 just before use. The commercially available hydrates of metal salts (ZnF_2, $ZnCl_2$, $ZnBr_2$, etc.) were dried by heating under reduced pressure for use in the polymerization. *n*-BuLi was prepared from 1-chlorobutane and lithium powder in heptane. Monomers were synthesized from α-(bromomethyl)acrylate[6] according to the previously reported procedure.[3,4]



$H_2C{=}C(CH_2OR')CO_2R$

R = Bn R' = Me : **BMMA**
Bn Et : **BEMA**
Et Et : **EEMA**

Benzyl α-(ethoxymethyl)acrylate (BEMA): ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, 3H, $J = 6.8$ Hz, $-CH_3$), 3.55 (q, 2H, $J = 6.8$ Hz, $-OCH_2-$), 4.21 (s, 2H, $-OCH_2-$), 5.22 (s, 2H, $-OCH_2-$), 5.90 (m, 1H, vinyl), 6.35 (m, 1H, vinyl), 7.30−7.40 (m, 5H, aromatic). IR (neat) 2976, 1719, 1637, 1456, 1383, 1300, 1267, 1158, 1106, 952 cm^{-1}. MS (EI) *m/z* 220 (M^+).

Radical Polymerization Procedure. Polymerization was typically carried out using a metal salt (2.25 mmol), a monomer (1.50 mmol), a solvent (1.2 mL), and $(i\text{-}PrOCO_2)_2$ (0.05 mmol) with stirring of a heterogeneous mixture for 48 h at 30 °C. Radical copolymerization of BMMA and MMA was performed using $ZnBr_2$ (0.3 mmol), BMMA (1.4 mmol), MMA (1.4 mmol), toluene (1.1 mL), and $(i\text{-}PrOCO_2)_2$ (0.05 mmol) with stirring at 30 °C. Reaction products were diluted with chloroform, precipitated into methanol for poly(BMMA), poly(EBMA), and a copolymer or a mixture of methanol with H_2O (4/1 (v/v)) for poly(EEMA) and freeze-dried from benzene after filtration.

Measurements. ^1H NMR spectra were measured using a Varian Gemini-2000 (400 MHz for ^1H) or UNITY-INOVA (500 MHz for ^1H) spectrometer in nitrobenzene-d_5 or $CDCl_3$ with tetramethylsilane as the internal standard. Infrared (IR) spectra were recorded on a JASCO FT/IR-550 spectrometer. Mass spectra were taken on a JEOL LMS-AX505HA mass spectrometer. Size exclusion chromatographic analysis (SEC) was performed on a JASCO 880-PU chromatograph equipped with a JASCO RI-930 refractive index detector using two commercial columns (TSK G5000H and Shodex AC 802.5) connected in series with chloroform as the eluent. Calibration was performed using standard polystyrenes.

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* To whom all correspondence should be addressed.

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Table 1. Radical Polymerization of BMMA with (i-$PrOCO_2$)$_2$ in the Presence of Variety of Metal Salts at 30 °C for 48 h[a]

entry	additive	solvent	yield[b] (%)	DP (M_w/M_n)[c]
1		toluene	>99[d]	55 (3.1)
2	$LaCl_3$[e]	toluene	>99	62 (3.8)
3	$ZrCl_4$	CH_2Cl_2	78	40 (1.7)
4	$FeCl_3$	CH_2Cl_2	0	
5	$CuCl_2$	CH_2Cl_2	0	
6	$HgCl_2$	CH_2Cl_2	>99	48 (3.4)
7	ZnF_2[e]	CH_2Cl_2	>99	53 (4.9)
8[f]	$ZnCl_2$[e]	toluene	>99	36 (4.2)
9[f]	$ZnBr_2$[e]	toluene	88	82 (3.2)
10	$Zn(EtCO_2)_2$	CH_2Cl_2	89	56 (2.5)

[a] [Additive]/[BMMA] = 1. [b] MeOH insoluble part. [c] Determined by SEC (polystyrene standard). [d] Hexane insoluble part. [e] [Additive]/[BMMA] = 1.5. [f] Reference 5.

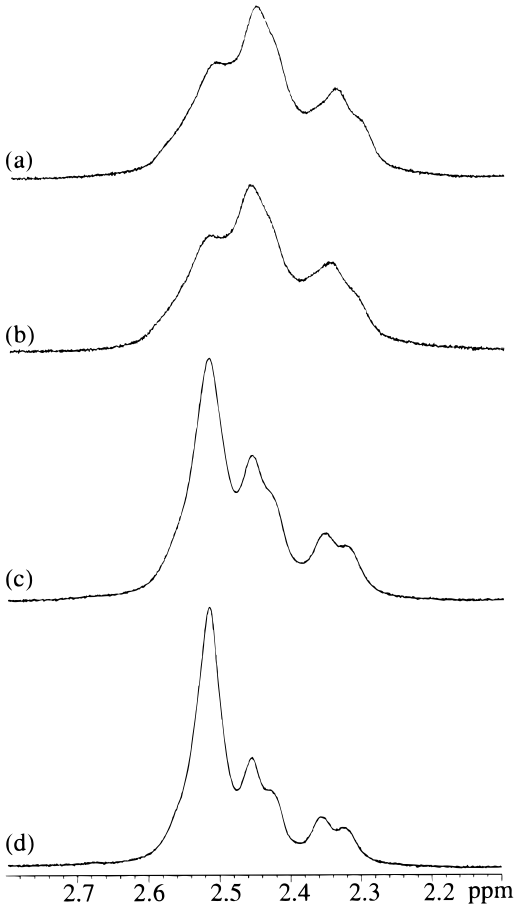

Figure 1. The 400 MHz ^{1}H NMR spectra of the main chain methylene protons in poly(BMMA) (entry 1, Table 1) (a), obtained with ZnF_2 (entry 7, Table 1) (b), with $ZnCl_2$ (entry 8, Table 1) (c), and with $ZnBr_2$ (entry 9, Table 1) (d) (nitrobenzene-d_5, 110 °C).

Table 2. Radical Polymerization of BMMA with (i-$PrOCO_2$)$_2$ in the Presence of $ZnBr_2$ at 30 °C for 48 h[a]

entry	solvent	yield[b] (%)	DP (M_w/M_n)[c]
1	d	>99	210 (9.3)
2[e]	toluene[f]	88	82 (3.2)
3[g]	toluene[f]	10	28 (1.2)
4[e]	CH_2Cl_2[f]	87	40 (1.5)
5	$ClCH_2CH_2Cl$	>99	52 (3.0)
6[e]	THF	>99	63 (4.5)

[a] [$ZnBr_2$]/[BMMA] = 1. [b] MeOH insoluble part. [c] Determined by SEC (polystyrene standard). [d] Bulk. [e] Reference 5. [f] [$ZnBr_2$]/[BMMA] = 1.5. [g] Initiator = AIBN; temp = 60 °C.

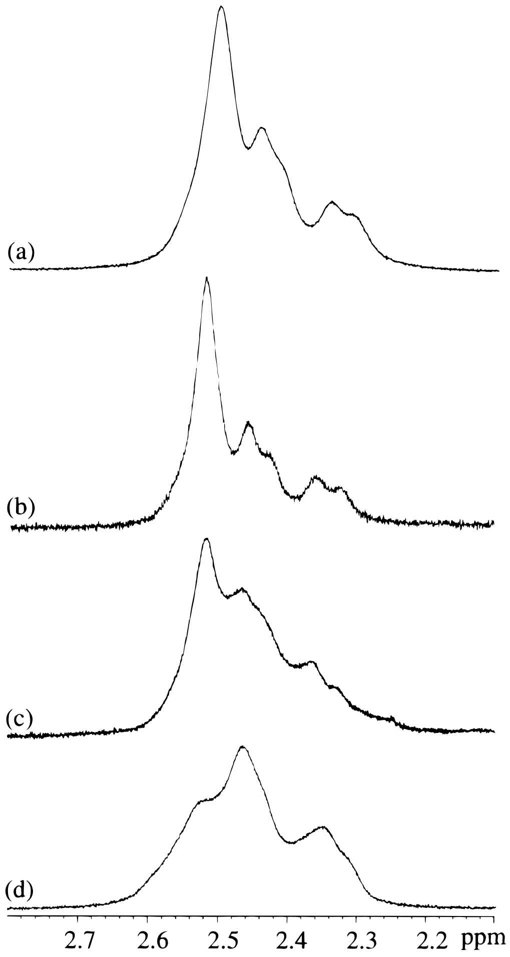

Figure 2. The 400 MHz ^{1}H NMR spectra of the main chain methylene protons in poly(BMMA) prepared in bulk (entry 1, Table 2) (a), obtained with $ZnBr_2$ in CH_2Cl_2 (entry 4, Table 2) (b),[5] in toluene at 60 °C (entry 3, Table 2) (c), and in THF (entry 6, Table 2) (d) (nitrobenzene-d_5, 110 °C).

Results and Discussion

A previous paper reported that little change was observed in the stereoregularlity of the polymers obtained in the presence of LiCl and $MgCl_2$, while the polymerization of BMMA using zinc salts ($ZnCl_2$ and $ZnBr_2$) as an additive gave the polymers having a different tacticity, probably rich in syndiotacticity compared with that prepared in the absence of a metal salt.[5] A further investigation on the effect of various metal salts as an additive (1−1.5 equiv) for the radical polymerization of BMMA was carried out. These results are summarized in Table 1, together with the previous data on the polymerization in the presence of $ZnCl_2$ and $ZnBr_2$ in toluene (entries 8 and 9).

The metal salts listed in Table 1 except $ZnCl_2$ and $ZnBr_2$ showed no effects on the stereocontrol. In the ^{1}H NMR spectrum of poly(BMMA), the spectral pattern for the main chain methylene protons provides information on the higher order (tetrad) tacticity, although a detailed assignment has not been made.[5] Figure 1 demonstrates the expanded ^{1}H NMR spectra of the main chain methylene protons of the polymers prepared by a normal radical method (Table 1, entry 1) and in the presence of zinc salts (Table 1, entries 7−9). Interestingly, the spectral pattern of the polymers obtained with $ZnCl_2$ and $ZnBr_2$ (Figure 1c and d) is quite different from that prepared without a salt (Figure 1a), although little change was observed for the polymer obtained with ZnF_2

Table 3. [$ZnBr_2$]/[BMMA] Effect for Radical Polymerization of BMMA with (i-$PrOCO_2$)$_2$ at 30 °C for 48 h in Toluene

entry	[$ZnBr_2$]/[BMMA]	yield[a] (%)	DP (M_w/M_n)[b]
1	0	>99[c]	55 (3.1)
2	0.1	90	110 (3.2)[c]
3	0.2	85	67 (2.7)
4	0.5	88	95 (2.6)
5[d]	1.5	87	82 (3.2)
6	2.5	>99	82 (2.4)
7	3.5	>99	78 (2.1)

[a] MeOH insoluble part. [b] Determined by SEC (polystyrene standard). [c] Hexane insoluble part. [d] Reference 5.

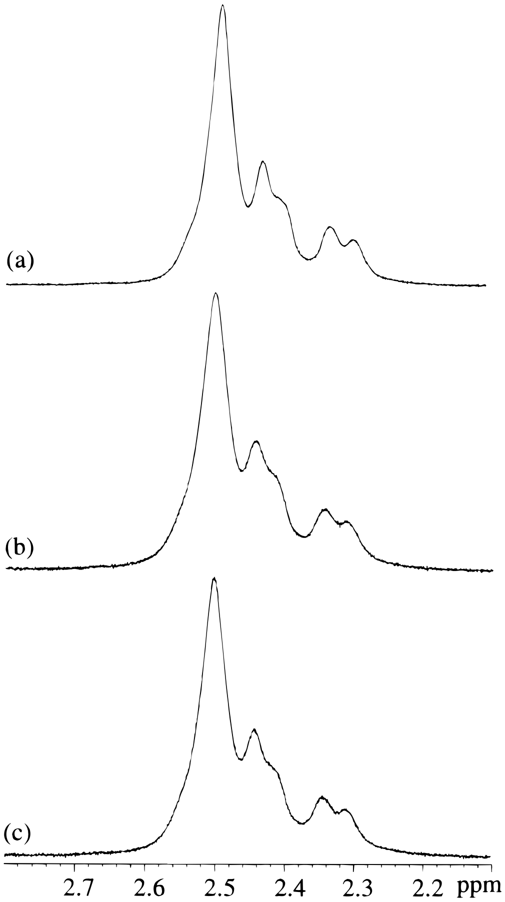

Figure 3. The 400 MHz ^{1}H NMR spectra of the main chain methylene protons in poly(BMMA) obtained with $ZnBr_2$ (0.1 equiv) (entry 2, Table 3) (a), with $ZnBr_2$ (0.5 equiv) (entry 4, Table 3) (b), and with $ZnBr_2$ (2.5 equiv) (entry 6, Table 3) (c) (nitrobenzene-d_5, 110 °C).

(Figure 1b). $ZnBr_2$ seems to control the stereochemistry more effectively than $ZnCl_2$ judging from the spectral pattern. These results indicate that a halogen, as well as a metal, in the salt is important for the stereocontrol in this system.

Table 2 shows the results for investigation of the effects of solvent and polymerization temperature on the radical polymerization of BMMA using $ZnBr_2$ as an additive. As shown in Figure 2, in addition to the polymerization in toluene and halogenated solvents, bulk polymerization also proceeded in the stereocontrolled manner (Table 2, entry 1) (Figure 2a), whose selectivity appears lower than that of the polymerization in CH_2Cl_2 (Table 2, entry 4) (Figure 2b),[5] while a polar solvent, THF, greatly reduced the effect of the stereocontrol by $ZnBr_2$ (Table 2, entry 6) (Figure 2d). The polymerization with 2,2′-azobis(isobutyronitrile) (AIBN) at 60 °C in the presence of zinc salt also resulted in a low stereoselectivity (Table 2, entry 3) (Figure 2c). These results suggest that the coordination of the zinc salts to the growing polymer and the monomer plays an important role in this system.

The effect on the ratio of $ZnBr_2$ to the monomer for the radical polymerization in toluene was examined (Table 3). It is noteworthy that 0.1 equiv of zinc salt (Table 3, entry 2) is enough to control the stereochemistry as shown in Figure 3a, whose spectral pattern is almost identical with that of the polymer prepared using $ZnBr_2$ (0.5 and 2.5 equiv) (Table 3, entries 4 and 6) (Figure 3b,c), while an excess amount of zinc salt did not demonstrate any improvements in the stereoselectivity. Therefore, the stereospecific radical polymerization of BMMA is affected by a catalytic amount of zinc salt, suggesting that the coordination of the zinc salt to the ω-end of the propagating polymer and the monomer is of importance, and the polymerization should exclusively proceed through the coordinated species.

Table 4. Radical Copolymerization of BMMA and MMA in the Presence of $ZnBr_2$ in Toluene at 30 °C[a]

entry	additive[b]	time (h)	yield[c] (%)	BMMA:MMA[d]	DP (M_w/M_n)[e]
1		10	35	43:57	7.6 × 10^4 (3.6)
2	$ZnBr_2$	4	33	48:52	2.9 × 10^4 (3.1)
3	$ZnBr_2$	10	64	48:52	2.9 × 10^4 (3.1)
4	$ZnBr_2$	30	86	48:52	2.9 × 10^4 (3.3)

[a] [BMMA]/[MMA] = 1, [monomers]/[(i-$PrOCO_2$)$_2$] = 56, polymerization was carried out with stirring. [b] [$ZnBr_2$]/[monomers] = 0.1. [c] MeOH insoluble part. [d] Determined by ^{1}H NMR analysis. [e] Determined by SEC (polystyrene standard).

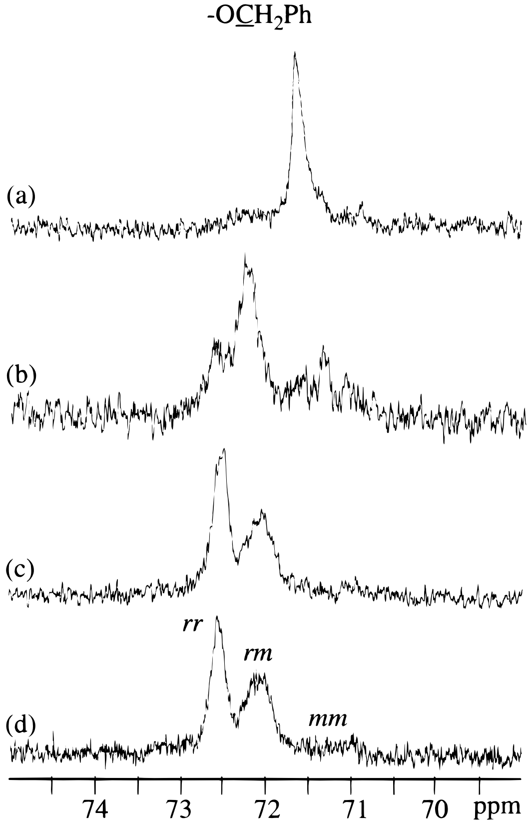

Figure 4. The 125 MHz ^{13}C NMR spectra of the methylene carbon in the ester groups of poly(BMMA) obtained with n-BuLi in toluene[4] (a), by radical method in CH_2Cl_2[5] (b), with $ZnBr_2$ (1.5 equiv) (entry 4, Table 2) (c), and with $ZnBr_2$ (0.1 equiv) (entry 2, Table 3) (d) ($CDCl_3$, 60 °C).

Table 5. Anionic and Radical Polymerization of α-(Alkoxymethyl)acrylates in Toluene[a]

entry	monomer	initiator	additive	yield[b] (%)	DP (M_w/M_n)[c]
1	BEMA	n-BuLi		98	88 (9.1)
2		$(i\text{-PrOCO}_2)_2$		84[d]	68 (2.7)
3		$(i\text{-PrOCO}_2)_2$	$ZnCl_2$	95	64 (2.8)
4		$(i\text{-PrOCO}_2)_2$	$ZnBr_2$	97	56 (2.6)
5	EEMA	n-BuLi		49[e]	94 (4.4)
6		$(i\text{-PrOCO}_2)_2$[f]		78[e]	310 (6.2)
7		$(i\text{-PrOCO}_2)_2$	$ZnBr_2$	81[e]	110 (2.3)

[a] Anionic polymerization: [monomer]/[n-BuLi] = 20, [monomer] = 1 M, temp = −78 °C, time = 48 h. Radical polymerization: [monomer]/[$(i\text{-PrOCO}_2)_2$] = 30, [additive]/[monomer] = 1, temp = 30 °C, time = 24 h. [b] MeOH insoluble part. [c] Determined by SEC (polystyrene standard). [d] Hexane insoluble part. [e] MeOH/H_2O (4/1) insoluble part. [f] Bulk, temp = 40 °C, time = 24 h, [monomer]/[$(i\text{-PrOCO}_2)_2$] = 50.

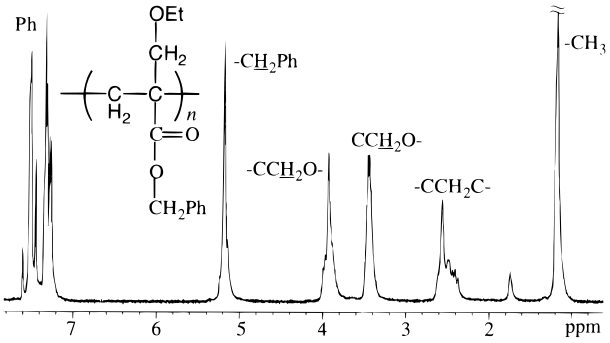

Figure 5. The 400 MHz ^{1}H NMR spectra of poly(BEMA) obtained with $ZnBr_2$ (entry 4, Table 5) (nitrobenzene-d_5, 150 °C).

As previously reported, no change was observed in the stereoregularity of the poly(benzyl methacrylate) radically obtained in the presence of $ZnBr_2$ as an additive. The radical polymerization of MMA with the zinc halides was also carried out using the same procedure as that for the polymerization of BMMA. The polymer was obtained using $ZnBr_2$ (1.5 equiv) in CH_2Cl_2 [initiator: $(i\text{-PrOCO}_2)_2$, 30 °C, 48 h] in 57% yield (DP = 160, $M_w/M_n = 1.4$) with a triad tacticity, mm:mr:rr = 3:30:67, while poly(MMA)s prepared in its absence (56% yield, DP = 180, $M_w/M_n = 1.5$) and in the presence of ZnF_2 (1.5 equiv) in CH_2Cl_2 (53% yield, DP = 330, $M_w/M_n = 1.6$) showed a tacticity, 3:31:66 and 3:29:68, respectively. These results support the fact that $ZnBr_2$ characteristically affects the stereoregularity of the α-(alkoxymethyl)acrylates during the radical polymerization, and a polar α-substituent on an acrylate is important for the stereocontrol of this system.

Radical copolymerization[7] of BMMA and MMA (1:1) with a catalytic amount of $ZnBr_2$ (0.1 equiv to the monomers) in toluene at 30 °C was accomplished (Table 4). The addition of $ZnBr_2$ accelerated the polymerization rate[8] or increased the radical concentration. After 10 h, the copolymerization with zinc salt proceeded in 64% yield (Table 4, entry 3), while the copolymer was obtained in 35% yield without $ZnBr_2$ (Table 4, entry 1). In addition, the ratio of the BMMA unit in the copolymers prepared in the presence of $ZnBr_2$ resulted in 48%, and the copolymers obtained in the absence of $ZnBr_2$ had a composition, BMMA:MMA = 43:57. Therefore, BMMA must be more activated by zinc halide than MMA in this system, and the polymerization preferably proceeds through the coordinated species.

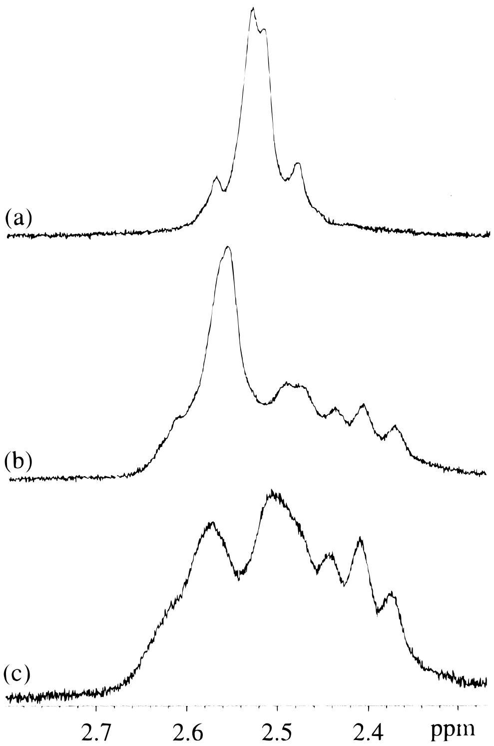

Figure 6. The 400 MHz ^{1}H NMR spectra of the main chain methylene protons in poly(BEMA) obtained with n-BuLi (entry 1, Table 5) (a), with radical method in the presence of $ZnBr_2$ (entry 4, Table 5) (b), and without $ZnBr_2$ (entry 2, Table 5) (c) (nitrobenzene-d_5, 150 °C).

In a previous paper,[5] the diad tacticity of poly(BMMA) was estimated from the ^{1}H NMR spectrum of the main chain methylene measured in nitrobenzene-d_5 under the supposition that the peaks from 2.3 to 2.4 ppm are ascribed to one of the protons of the *meso*-diad, although the higher order (tetrad) tacticity should be considered in the spectral pattern. Further investigation on the tacticity of poly(BMMA) was carried out. Figure 4 shows the ^{13}C NMR spectra of the methylene carbon in the ester group of the *isotactic*-poly(BMMA) prepared by an anionic method[4] (a) and polymers obtained by the radical method (b−d). The spectral pattern seems to exhibit splitting due to the triad sequences, and the peaks may be assigned to mm, mr, and rr from the high magnetic field as shown in the figure. The triad tacticities (rr:rm:mm) were estimated as 49:39:12 (r:m = 68.5:31.5) (Table 2, entry 4), 51:40:9 (71:29) (Table 3, entry 2), and 44:42:14 (65:35) (Table 1, entry 8) for the polymers obtained in the presence of zinc halides, while the polymer prepared without a zinc salt had a tacticity, 22:48:30 (46:54). These values are in good agreement with those evaluated from the ^{1}H NMR spectra of the main chain methylene.[5] The radical polymerization of BMMA in the presence of zinc salts should produce a polymer rich in syndiotacticity (up to r = 71%), while the polymer prepared by the normal radical method is nearly atactic.

The stereospecific radical polymerization in the presence of zinc halides was performed using other α-(alkoxymethyl)acrylates, BEMA and EEMA. These results are listed in Table 5, together with the data on the anionic and normal radical polymerizations in toluene. Figure 5 depicts the ^{1}H NMR spectrum of poly(BEMA) obtained with $ZnBr_2$ (Table 5, entry 4).[9] Each peak is assigned as shown in the figure. The spectral pattern of the main chain methylene protons around 2.5 ppm seems to

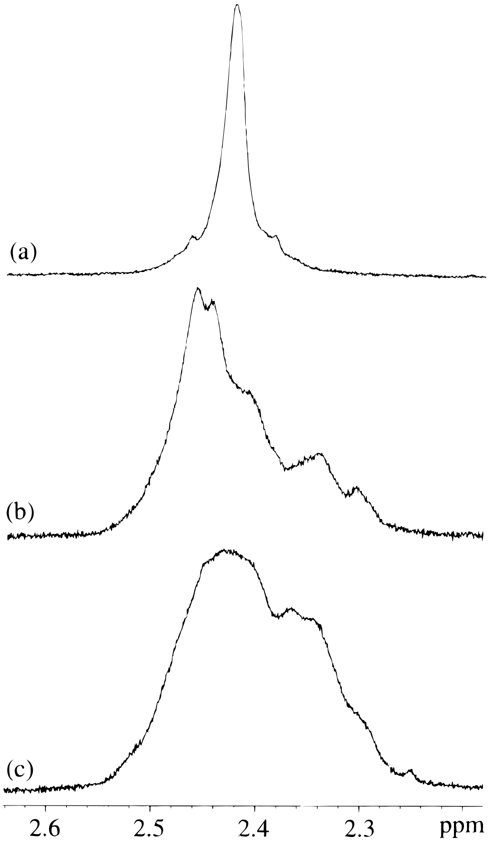

Figure 7. The 400 MHz ^{1}H NMR spectra of the main chain methylene protons in poly(EEMA) obtained with *n*-BuLi (entry 5, Table 5) (a), with radical method in the presence of $ZnBr_2$ (entry 7, Table 5) (b), and without $ZnBr_2$ (entry 6, Table 5) (c) (nitrobenzene-d_5, 150 °C).

exhibit splitting due to the stereoregularity similar to that of poly(BMMA).

Figures 6b and 7b show the expanded ^{1}H NMR spectra of the main chain methylene protons of poly(BEMA) and poly(EEMA) (Table 5, entry 7),[10] respectively, together with those of the polymers prepared without $ZnBr_2$ and with *n*-BuLi in toluene at −78 °C. The spectral pattern of the polymers anionically prepared shows a typical AB quartet (Figures 6a and 7a), indicating that these polymers are highly isotactic.[4] The pattern of the polymers obtained in the presence of $ZnBr_2$ are again quite different from those prepared without a salt, as well as those anionically prepared, indicating that some stereocontrol, probably similar to that in the polymerization of BMMA, takes place during the radical polymerization with $ZnBr_2$, although ^{13}C NMR analysis of the methylene carbon in the ester group of poly(BEMA) was unsuccessful. Zinc halides effectively change the stereochemistry in the radical polymerization of the α-(alkoxymethyl)acrylates.

In conclusion, the stereospecific radical polymerization of α-(alkoxymethyl)acrylates with a catalytic amount of zinc halides ($ZnCl_2$ and $ZnBr_2$) was realized, and the obtained polymers had very different tacticities rich in syndiotacticity compared with that prepared in the absence of a metal salt. The coordination of the zinc salts to the polar α-substituents on the ω-end of the propagating polymer and the monomer must play an important part in this system. This suggests the possibility that the stereochemistry during the radical polymerization of several vinyl monomers could be controlled by an analogous method.

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