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Monomer [1-(Isobutoxy)ethyl Methacrylate] That Can Undergo Anionic Polymerization and Can Also Be an Initiator for the Cationic Polymerization of Vinyl Ethers. Preparation of Comblike Polymers

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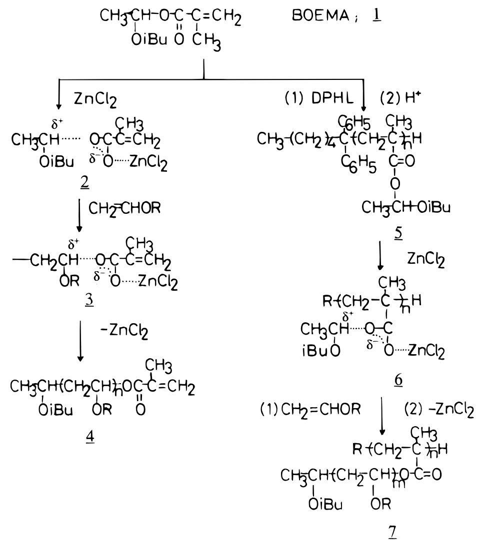
ABSTRACT: 1-(Isobutoxy)ethyl methacrylate (BOEMA) was prepared by the reaction between isobutyl vinyl ether and methacrylic acid. It can be used both as an initiator for the cationic polymerization of vinyl ether and as a monomer that can undergo anionic polymerization. Using zinc chloride as activator, BOEMA can induce the cationic polymerization of isobutyl vinyl ether or ethyl vinyl ether in toluene at 0 °C to generate an end-functional polymer. On the other hand, BOEMA can be polymerized itself by using (1,1-diphenylhexyl)lithium as an initiator, in tetrahydrofuran, at −60 °C, in the presence or absence of lithium chloride. The poly(BOEMA) obtained possesses a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.04−1.09). It can also be employed as a macroinitiator for the cationic polymerization of isobutyl vinyl ether or ethyl vinyl ether, by using zinc chloride as activator in toluene at 0 °C. Thus a graft copolymer consisting of polymethacrylate as the main chain and poly(isobutyl vinyl ether) or poly(ethyl vinyl ether) as side chains can be prepared.

Introduction

The molecular design of polymers that possess well-defined structures, selected molecular compositions, and particular properties is becoming an increasingly important route to high performance materials.[1−4] However, the number of monomers suitable for a certain kind of polymerization is limited. For instance, an alkyl methacrylate can be polymerized by radical or anionic polymerization but not by cationic polymerization. Similarly, vinyl ethers can undergo cationic polymerization but not radical or anionic polymerization. It is, therefore, necessary to combine two polymerization methods to prepare block or graft copolymers of the above two kinds of monomer.

Major progress was achieved recently in the living cationic polymerization of vinyl monomers.[5−8] Higashimura and his co-workers[9,10] discovered numerous initiator systems which induced the living cationic polymerization of vinyl ethers. For instance, they employed a series of acetic acid derivatives (RCOOH, where R can be CF_3, CCl_3, $CHCl_2$, CH_2Cl or CH_3), which, combined with zinc chloride, generated suitable nucleophilic counteranions which, by stabilizing the growing carbocation, allowed the isobutyl vinyl ether (IBVE) to undergo controlled cationic polymerization.[11] These substituted acetic acids react with IBVE to form esters. For instance, the addition reaction between IBVE and acetic acid generates an adduct, 1-isobutoxyethyl acetate (BOEA). BOEA cannot, by itself, induce the polymerization of IBVE,[12] but its ester linkage can be activated with zinc chloride to generate a partly dissociated carbocation, which can initiate the polymerization of a vinyl ether. The growing carbocation is stabilized by the nucleophilic counteranion ($^{-}OCOCH_3\cdots ZnCl_2$).

Scheme 1



In the present paper, a similar initiator, 1-(isobutoxy)ethyl methacrylate (BOEMA, **1** in Scheme 1), which is an adduct of IBVE with methacrylic acid (MAA) is prepared. Because its molecular structure is similar to that of BOEA, BOEMA is expected to be an initiator for the cationic polymerization of vinyl ether in the presence of the activator $ZnCl_2$ (Scheme 1, left). On the other hand, because of the presence of the electron-deficient C═C double bond in the methacrylate group, BOEMA is also an anionically polymerizable monomer, which can be also polymerized using an anionic initiator like (1,1-diphenylhexyl)lithium (DPHL). Every side chain of the poly(BOEMA) (**5**, Scheme 1) has a molecular structure similar to that of BOEA. Consequently, poly(BOEMA) constitutes a dormant macroinitiator for the cationic polymerization of any vinyl ether, which can be activated with $ZnCl_2$ to generate **6** in Scheme 1. The cationic polymerization of IBVE or ethyl vinyl ether (EVE) leads to a graft copolymer (**7**, Scheme 1) consisting of polymethacrylate as the main chain and poly(IBVE) or poly(EVE) as side chains.

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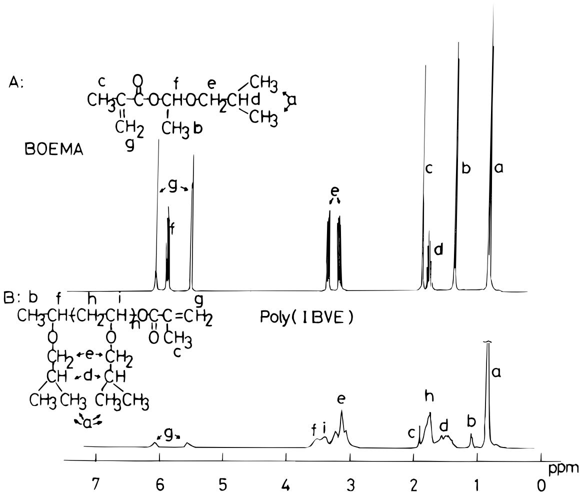

Figure 1. ^{1}H NMR spectra of BOEMA (A) and poly(IBVE) (B; no. 2 in Table 1).

Experimental Section

Materials. Tetrahydrofuran (THF, solvent for the anionic polymerization of BOEMA) was stirred with CaH_2 under reflux for more than 24 h, distilled, purified in the presence of naphthalene sodium, and finally distilled from a solution of DPHL just before use.[13] Toluene, which is used as solvent for the cationic polymerization and for the grafting of poly(IBVE) or poly(EVE) on poly(BOEMA) via cationic polymerization, was washed with concentrated sulfuric acid and then with water, dried over $MgSO_4$, and distilled twice over calcium hydride before use. Et_2O was dried over CaH_2 and distilled in the presence of $LiAlH_4$. Hexane was first dried and distilled over CaH_2 and then distilled from a solution of *n*-BuLi. IBVE or EVE (Aldrich, 99%; bp 82 and 33 °C, respectively) was washed with 10% aqueous sodium hydroxide solution and then water, dried overnight over potassium hydroxide, and distilled twice over CaH_2 prior to polymerization.[11,12] 1,1-Diphenylethylene (DPE, Aldrich, 97%) was doubly distilled from CaH_2 and then distilled in the presence of triphenylmethyllithium under reduced pressure (bp 75 °C/1.0 Torr).[14] Lithium chloride (Aldrich, 99.99%) was dried at 120 °C for 24 h and dissolved in THF.[15] $ZnCl_2$ (Aldrich, 1.0 M solution in diethyl ether) and *n*-BuLi (Aldrich, 1.6 M solution in hexane) were diluted with purified Et_2O and hexane, respectively.

Synthesis of 1-(Isobutoxy)ethyl Methacrylate (BOEMA). BOEMA was prepared by the reaction of IBVE with methacrylic acid (MAA).[11] MAA (66 mL, 0.77 mol) was dropwise added to IBVE (122 mL, 0.93 mol) with magnetic stirring at 55 °C and kept at this temperature for 8 h. The crude product was distilled twice from calcium hydride under reduced pressure (32 °C/0.2 Torr) and pure BOEMA was obtained as a sweet smelling, colorless oil, with an yield of 82% based on MAA. The purity (>99%) was determined by gas chromatography measurements. As shown in Figure 1, the chemical shifts and their intensities in the ^{1}H NMR spectrum of the prepared BOEMA are consistent with its molecular structure.

Polymerizations. Polymerization was carried out in a 100 mL round-bottom glass flask under an overpressure of nitrogen with magnetic stirring. The cationic polymerization of IBVE or EVE was initiated by adding, via a dry syringe, an Et_2O solution of $ZnCl_2$ to a toluene solution of the monomer and BOEMA at 0 °C. The polymerization was terminated with methanol (ca. 2 mL) containing a small amount of ammonia. The quenched reaction mixture was washed with 10% aqueous sodium thiosulfate solution and then with water, evaporated to dryness under reduced pressure, and vacuum dried (40 °C, 1.0 Torr) to obtain the product polymer.

The anionic polymerization of BOEMA was carried out in THF at −60 °C in the presence or absence of LiCl. After THF, DPE and a THF solution of LiCl were added with dry syringes, the flask was cooled to −60 °C and *n*-BuLi (in hexane) was added. The deep red color of DPHL appeared immediately, and the reaction between *n*-BuLi and DPE was allowed to continue for about 15 min. The polymerization reaction was induced by the addition of a prechilled THF solution of BOEMA to the above DPHL solution. After a certain time (40 or 60 min), the reaction was quenched with a small amount of methanol and the solution was poured into a cooled mixture of ethanol and water (−20 °C) to precipitate the polymer. The polymer was reprecipitated from its THF solution with the above mixture and dried in vacuum (40 °C, 1.0 Torr) overnight.

Table 1. Cationic Polymerization of IBVE or EVE with BOEMA as Initiator[a]

no.	$[BOEMA]_o$ (mM)	$[M]_o$ (M)	$[ZnCl_2]$ (mM)	$\bar{M}_n$ calcd	$\bar{M}_n$ GPC[b]	$\bar{M}_n$ NMR[c]	$\bar{M}_w/\bar{M}_n$[b]
1	110	IBVE, 1.08	20.0	1190	1760	1200	2.70
2	53.6	IBVE, 1.12	10.4	2280	3180	2430	2.81
3	13.6	IBVE, 1.14	5.27	8530	8670		2.60
4	16.7	EVE, 1.54	13.8	3580	5860		2.96

[a] The polymerization was carried out in toluene at 0 °C; for nos. 1, 2 and 3, the polymerization time was 6 h and the monomer conversion = 100%; for no. 4, the polymerization time was 3 h and the monomer conversion = 51%. [b] Determined from the GPC measurements. [c] Calculated from the ^{1}H NMR spectra of poly(IBVE).

Graft copolymerization was carried out under conditions similar to those for cationic polymerization described above. Poly(BOEMA) was freeze-dried from its benzene solution for 8 h, then vacuum dried (50 °C, 1.0 Torr) for more than 10 h. The purified toluene and monomer (IBVE or EVE) were introduced into the flask that contained the dried poly(BOEMA). After the polymer was completely dissolved and cooled to 0 °C, $ZnCl_2$ (in Et_2O) was added to induce the graft copolymerization reaction. The termination of the reaction and the purification of the obtained copolymer were carried out as described for the cationic polymerization.

Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$ on a VXR-400 spectrometer. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the polymer were determined by gel permeation chromatography (GPC) on the basis of a polystyrene calibration curve. The GPC measurements were carried out with THF as solvent, at 30 °C, using two polystyrene gel columns (Waters, Linear, 7.8 × 300 mm, Part No. 10681) connected to a Waters 515 precision pump.

Results and Discussion

1. Cationic Polymerization of IBVE or EVE.

Aoshima and co-workers[16] prepared a poly(vinyl ether) macromer having a methacrylate group at one end. The adduct $[CH_2{=}C(CH_3)COOCH_2CH_2OCHICH_3]$ obtained via the reaction of 2-(vinyloxy)ethyl methacrylate with hydrogen iodide was employed as initiator to induce the living cationic polymerization of EVE in the presence of a small amount of iodine. Obviously, the methacrylate group is located at the initial end of the polymer. In contrast, in the present paper, the methacrylate group constitutes a counteranion which is moving to the terminus of the polymer as the chain propagating reaction proceeds (Scheme 1, left).

The cationic polymerization of IBVE or EVE was carried out in toluene at 0 °C. When $ZnCl_2$ was added to the mixture of toluene, monomer, and BOEMA, the polymerization system became either transparent (no. 3, Table 1), or yellow (no. 2) or red (no. 1), depending on the initial concentrations of BOEMA and $ZnCl_2$. The monomer conversion can reach 100% in 6 h for IBVE, and the number average molecular weight, determined either by GPC or ^{1}H NMR, increased as the ratio $[M]_o/[BOEMA]_o$ became larger. However, the molecular weight distribution of the polymer obtained is broad ($\bar{M}_w/\bar{M}_n = 2.60-2.96$) for both monomers. This may be

Table 2. Anionic Polymerization of BOEMA[a]

no.	$[n\text{-BuLi}]_o$ (mM)	[DPE] (mM)	[LiCl] (mM)	$[M]_o$ (M)	$\bar{M}_n$ calcd	$\bar{M}_n$ GPC[b]	$\bar{M}_n$ NMR[c]	$\bar{M}_w/\bar{M}_n$[b]
5	50.4	60.5	0	0.61	2500	2800		1.17
6	152	182	64	0.56	920	900	930	1.13
7	69.4	83.3	117	0.51	1600	1800	1590	1.07
8	50.4	60.5	101	0.61	2490	2630	2650	1.04
9	42.9	57.1	150	0.63	2970	3200		1.05
10	20.8	25.0	42.0	0.61	5690	7900		1.09
11	12.3	14.8	25.0	0.61	8050	13200		1.07

[a] The polymerization was carried out in THF at −60 °C for 40 (nos. 5−9) and 60 (nos. 10 and 11) min. The monomer conversion was 100%. [b] See Table 1. [c] Calculated from the ^{1}H NMR spectra of poly(BOEMA)s.

a result of the strong nucleophilicity of the counteranion $[CH_2{=}C(CH_3)COO^-]$[11].

Figure 1 depicts the ^{1}H NMR spectra of BOEMA and poly(IBVE). After the polymerization of IBVE, some of the peaks of the moiety originating from BOEMA can be still observed. The peaks b and f are shifted, the peaks c and g did not change, and the other peaks are overlapped with those due to poly(IBVE). In addition, the molecular weight calculated from the ^{1}H NMR spectra is close to the theoretical value calculated assuming that one polymer chain is generated by each BOEMA molecule present.

2. Anionic Polymerization of BOEMA. Teyssie and co-workers[15,17,18] suggested that the addition of a ligand, such as LiCl, can be effective in the living anionic polymerization of *tert*-butyl acrylate and methyl methacrylate because a μ-type complex[19] is formed between LiCl and the growing site, which impedes side reactions from occurring at the propagating site, thus leading to monodisperse polymers. In this paper, we employ this polymerization technique for the anionic polymerization of BOEMA, to prepare nearly monodisperse poly(BOEMA).

The initiator, DPHL, was synthesized by the reaction of *n*-BuLi with DPE at a ratio $[\text{DPE}]/[n\text{-BuLi}]_o = 1.2$ (Table 2). The anionic polymerization was carried out in THF at −60 °C for $[\text{LiCl}]/[n\text{-BuLi}]_o$ ratios of 0, 0.5, 1.5, 2.0, and 3.0 (no. 5 to no. 9, Table 2). As shown in Table 2, poly(BOEMA) can be obtained, regardless if LiCl is added or not. However, the molecular weight distribution of the obtained polymer is narrower for larger $[\text{LiCl}]/[n\text{-BuLi}]_o$ ratios, and nearly monodisperse poly(BOEMA) can be obtained when $[\text{LiCl}]/[n\text{-BuLi}]_o > 2$ (no. 8 and no. 9, Table 2). Polymerizations no. 5 and no. 8 of Table 2 differ only in the values of the ratio $[\text{LiCl}]/[n\text{-BuLi}]_o$. As shown in Figure 2, the GPC curve B of poly(BOEMA) prepared in the presence of LiCl ($[\text{LiCl}]/[n\text{-BuLi}]_o = 2$, no. 8) is much narrower than that for no. 5 obtained in the absence of LiCl (curve A) and as narrow as that of the polystyrene standard (C).

The calculated number-average molecular weight of poly(BOEMA) is comparable to those determined by GPC or ^{1}H NMR when the molecular weight is small (nos. 6−9). When the concentration of *n*-BuLi is low (nos. 10 and 11), the difference between the calculated and determined values is large. The initiator efficiency decreases to 72 and 61% for no. 10 and no. 11, respectively, but the molecular weight distribution remains narrow ($\bar{M}_w/\bar{M}_n = 1.09$ and 1.07). These results indicate that the initiator is involved in an undetermined side reaction during the initiation stage. Alkyl acrylates or methacrylates can generally be purified prior to polymerization with a strong Lewis acid, like trialkylaluminum. BOEMA cannot be, however, purified with this reagent, because the presence of a strong Lewis acid results in its decomposition. The search for a suitable reagent for the purification of BOEMA is ongoing.

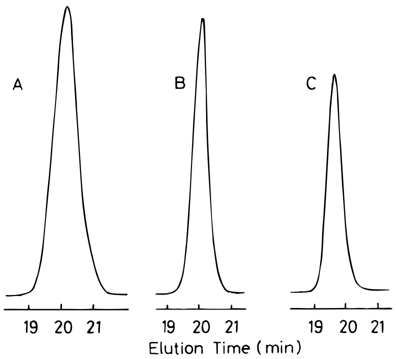

Figure 2. GPC traces of poly(BOEMA)s prepared in the absence (A; no. 5 in Table 2) or presence (B; no. 8 in Table 2) of LiCl and standard polystyrene (C; Pressure Chemical Company, $\bar{M}_n = 4000$, $\bar{M}_w/\bar{M}_n = 1.06$, Lot No. 61110).

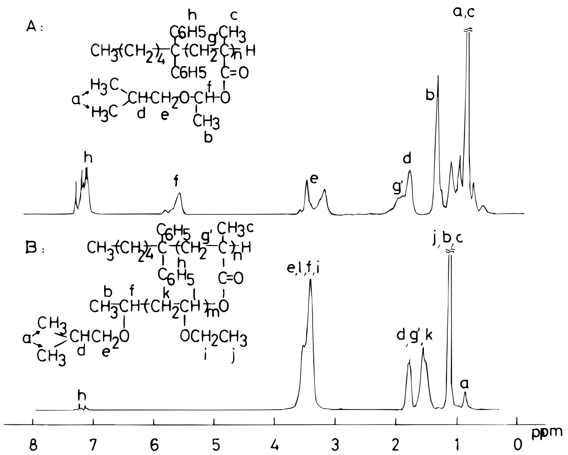

Figure 3. ^{1}H NMR spectra of poly(BOEMA) (A; no. 7 in Table 2) and poly(BOEMA-*g*-EVE) (B; for the preparation conditions, see Figure 4B and the text).

The ^{1}H NMR spectrum of poly(BOEMA) (no. 7, Table 2) is depicted in Figure 3A. Compared to the spectrum of BOEMA (Figure 1A), the absorptions (g) of the C=C double bond have disappeared, the peak (c) corresponding to the α-methyl group is shifted from 1.89 ppm to between 0.68 and 1.21 ppm. New peaks, (g′ and h), originating from the methylene group of the main chain and the phenyl group of DPHL emerge. In contrast, the absorptions (a, b, d, e, f) of the ester group did not change after polymerization. The chemical shift and the intensity of the peaks are consistent with the molecular structure of poly(BOEMA), and the number-average molecular weight calculated from the ^{1}H NMR spectrum is in good agreement with the theoretical value, calculated assuming that one polymer chain is formed from each DPHL molecule present (Table 2).

3. Grafting of Poly(IBVE) or Poly(EVE) to Poly(BOEMA). The grafting of poly(IBVE) or poly(EVE) to poly(BOEMA) was carried out in toluene at 0 °C. When the prechilled monomer was added to the toluene solution of poly(BOEMA) in the absence of $ZnCl_2$, no reaction took place and the poly(BOEMA) could be recovered without any change, indicating that poly(BOEMA) is in its stable dormant state and cannot alone induce the cationic polymerization of vinyl ether. In contrast, when $ZnCl_2$ was added to the toluene solution of poly(BOEMA) and monomer (IBVE or EVE), the graft copolymerization could proceed. Two examples

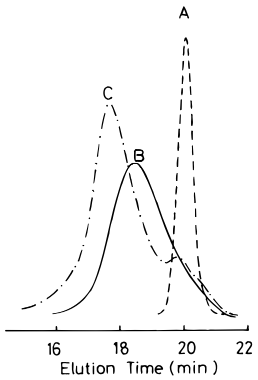

Figure 4. GPC traces: (A) poly(BOEMA) (no. 8 in Table 2, $\bar{M}_n = 2630$, $\bar{M}_w/\bar{M}_n = 1.04$); (B) poly(BOEMA-*g*-EVE) prepared by the cationic polymerization of EVE in toluene at 0 °C from poly(BOEMA) (no. 8, 0.50 g) in the presence of $ZnCl_2$ (concentration of the repeating units of poly(BOEMA) $[BOEMA]_o = 60$ mM, $[ZnCl_2] = 30$ mM, $[EVE]_o = 1.59$ M; polymerization time, 4 h; monomer conversion = 100%); (C) poly(BOEMA-*g*-EVE) prepared under the same conditions as B, except $[ZnCl_2] = 15$ mM.

are presented in Figure 4. The freeze-dried poly(BOEMA) (no. 8 in Table 2, 0.5 g) was dissolved in 34 mL of toluene and after EVE (4.0 g) was added, the system was cooled to 0 °C. When $ZnCl_2$ (1.20 mL, 1.0 M in Et_2O) was introduced, the system acquired a yellow color which changed gradually to red. The polymerization reaction lasted 4 h. As shown in Figure 4, the peak (A) of poly(BOEMA) used as macroinitiator disappeared completely and a broad peak (B) corresponding to the graft copolymer emerged. This result indicates that all of the poly(BOEMA) was consumed to initiate the graft polymerization of EVE. The molecular weight determined by GPC on the basis of a polystyrene calibration curve is 1.9×10^4, which is smaller than the theoretical value (2.3×10^4). The molecular weight distribution is broad because the nucleophilicity of the large anion is strong, and as a result, the rate of initiation is small compared to that of propagation. When the amount of $ZnCl_2$ was reduced to 0.60 mL (1.0 M, in Et_2O) while the other conditions were not changed, no yellow or red color appeared in the system and a small amount of poly(BOEMA) remained unreacted (Figure 4, peak C).

The ^{1}H NMR spectrum of the graft copolymer is presented in Figure 3B. After graft copolymerization of EVE, the peak (f) in the spectrum of poly(BOEMA) disappeared. However, the absorption (a) of the methyls of the ester groups remained unchanged and can be observed at 0.85 ppm. The other peaks overlapped with those of poly(EVE) of the side chains. Both the GPC and ^{1}H NMR measurements indicate that a pure graft copolymer can be obtained by the method of Scheme 1.

Conclusion

1-Isobutoxyethyl methacrylate (BOEMA) can be used as both an initiator for the cationic polymerizations of vinyl ethers and a monomer that can undergo anionic polymerization. In the presence of an activator, $ZnCl_2$, in toluene at 0 °C, BOEMA can induce the cationic polymerization of isobutyl vinyl ether or ethyl vinyl ether to generate an end-functional polymer, which possesses a methacrylate group at one end. On the other hand, BOEMA itself can be polymerized with the anionic initiator (1,1-diphenylhexyl)lithium. When the polymerization was carried out in the presence of LiCl, in THF, at −60 °C, the poly(BOEMA) obtained had a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.04-1.09$). Further, the poly(BOEMA) was used in the presence of $ZnCl_2$ as a macroinitiator for the cationic graft copolymerization of isobutyl vinyl ether or ethyl vinyl ether.

References and Notes

(1) Lubnin, A. V.; Kennedy, J. P. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *31*, 1943.
(2) Zaschke, B.; Kennedy, J. P. *Macromolecules* **1995**, *28*, 4426.
(3) Faust, R. Makromol. Chem., *Macromol. Symp.* **1994**, *85*, 295.
(4) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 6414.
(5) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111.
(6) Majoros, I.; Nagy, A.; Kennedy, J. P. *Adv. Polym. Sci.* **1994**, *112*, 1.
(7) Gyor, M.; Wang, H. C.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29*, 639.
(8) Fodor, Zs.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32*, 575.
(9) Higashimura, T.; Aoshima, S.; Sawamoto, M. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 457.
(10) Sawamoto, M.; Higashimura, T. *Makromol. Chem., Macromol, Symp.* **1990**, *31*, 131.
(11) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 3988.
(12) Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, *22*, 1009.
(13) Fujimoto, T.; Zhang, H. M.; Kazama, T.; Isono, Y.; Hasegawa, H.; Hashimoto, T. *Polymer* **1992**, *33*, 2208.
(14) Zhang, H. M.; Ishikawa, H.; Ohata, M.; Kazama, T.; Isono, Y.; Fujimoto, T. *Polymer* **1992**, *33*, 828.
(15) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1990**, *23*, 2618.
(16) Aoshima, S.; Ebara, K.; Higashimura, T. *Polym. Bull.* **1985**, *14*, 425.
(17) Fayt, R.; Forte, R.; Jacobs, C.; Jerome, R.; Ouhadi, T.; Teyssie, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442.
(18) Varshney, S. K.; Jerome, R.; Bayard, P.; Jacobs, C.; Fayt, R.; Teyssie, Ph. *Macromolecules*, **1992**, *25*, 4457.
(19) Kunkel, D.; Muller, A. H. E.; Janata, M.; Lochmann, L. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 315.

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