

Atom Transfer Radical Polymerization of Poly(vinyl ether) Macromonomers

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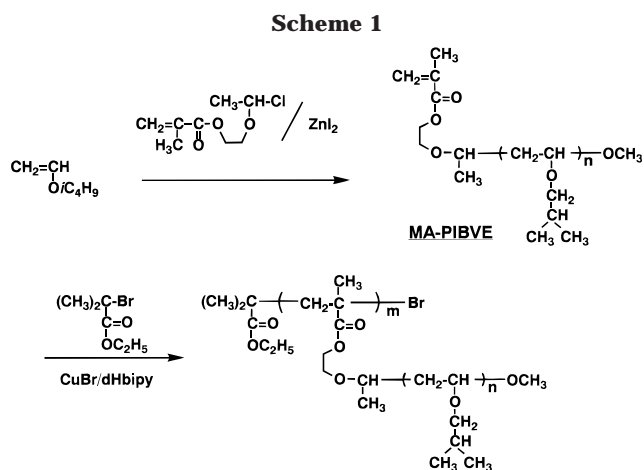
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ABSTRACT: The present paper focuses on the atom transfer radical polymerization (ATRP) of vinyl ether (VE) based macromonomers with a methacryloyl group at the chain end. Living cationic polymerization of isobutyl VE (IBVE) initiated with the HCl adduct of a VE carrying a pendant methacryloyl group in conjunction with ZnI_2 yielded the macromonomer (MA-PIBVE) with a narrow molecular weight distribution (MWD) ($\bar{M}_w/\bar{M}_n < 1.1$). The ATRP of MA-PIBVE was carried out using a halide initiator and the CuBr/4,4'-di-*n*-heptyl-2,2'-bipyridine catalytic system. The number-average molecular weight of the polymacromonomer increased in proportion to the monomer conversion, while the MWDs stayed fairly narrow ($\bar{M}_w/\bar{M}_n \sim 1.2$). Thus a novel type of polymacromonomers with controlled chain lengths for both the backbone and the side chain have been synthesized through a combination of living cationic polymerization and ATRP techniques.

Introduction

There have been a number of studies concerning the synthesis and application of macromonomers in the literature.¹ In the past, macromonomers were used mainly for the synthesis of graft copolymers by their copolymerization with conventional monomers. However, there has been increasing interest in polymacromonomers, which are prepared by the homopolymerization of macromonomers.^{2–8} They are regular multi-branched macromolecules characterized by an extremely high branch density along the backbone. They can have unique molecular morphologies ranging from star-shaped spheres to rodlike cylinders, depending on the degrees of polymerization (DP) of the backbone and branch chains.³ For instance, polymacromonomers with a sufficiently large DP and long branches have been reported to exhibit a lyotropic phase, which originates from the steric overcrowding of side chains forcing the macromolecule to take a rodlike conformation.⁴ It has been difficult, however, to synthesize polymacromonomers with a high DP because of the inherently low concentration of polymerizable groups and the steric hindrance of side chains. Indeed, it was not until recently that the radical homopolymerization of a macromonomer in a highly concentrated medium yielded polymacromonomers with a high DP.² It has also been reported that the poly(ethylene oxide) macromonomers organized into a micellar structure in an aqueous medium undergo radical polymerization at an unusually high rate.⁵ Other polymerization techniques such as anionic,⁹ cationic,¹⁰ and group transfer polymerizations¹¹ have been reported to give only oligomacromonomers. Still more difficult has been the living polymerization of macromonomers in a controlled manner.^{9–13}

On the other hand, the recent development in the controlled/"living" radical polymerizations¹⁴ based on the use of reversibly blocking agents, such as sulfur compounds,¹⁵ stable nitroxyls,^{16,17} organometal complexes,¹⁸



and halogens,^{19–22} has provided possibilities for the synthesis of not only well-defined polymers with low polydispersities but also those with novel and complex architectures. Among them is the transition metal-catalyzed atom transfer radical polymerization (ATRP),^{19–22} which is proving to provide a versatile route for the synthesis of polymers with well-controlled structures from a variety of radically polymerizable monomers. Herein, we report on the ATRP of isobutyl vinyl ether (IBVE) based macromonomers with the methacryloyl group at the initiating end (MA-PIBVE). This macromonomer is synthesized by living cationic polymerization. The combined use of living cationic polymerization and ATRP has led to a new type of well-defined polymacromonomer that is controlled with respect to both backbone and side chain lengths and length distributions (Scheme 1).

Results and Discussion

1. Macromonomer Synthesis by Living Cationic Polymerization. The IBVE-based macromonomer carrying a methacryloyl group at the α -initiating end was synthesized by living cationic polymerization.^{23,24} The living cationic polymerization of IBVE was conducted

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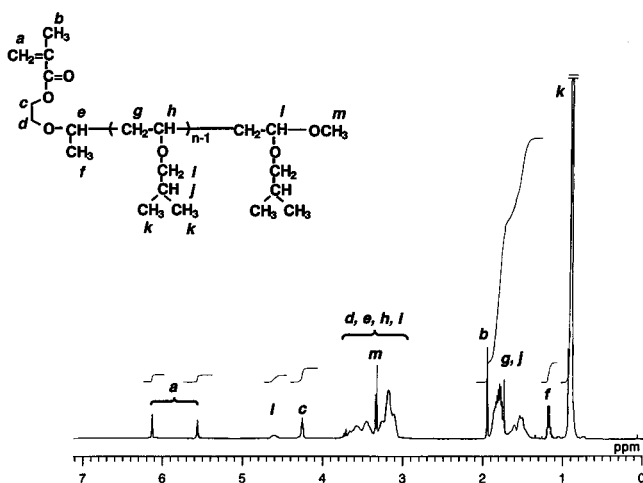


Figure 1. ^1H NMR spectrum of MA-PIBVE (**M1**) in CDCl_3 at room temperature.

Table 1. Synthesis of PIBVE Macromonomers^a

code	$\overline{\text{DP}}_n$		\bar{M}_n^d	\bar{M}_w/\bar{M}_n^d	\bar{F}_n^e
	calcd ^b	obsd ^c			
M1	10	11	1600	1.07	1.03
M2	20	21	3000	1.04	0.97
M3	40	39	5300	1.04	0.98

^a Reaction conditions: with VEM-HCl/ZnI₂ in toluene at -40 °C. $[\text{IBVE}]_0 = 0.5$ M, $[\text{VEM-HCl}]_0 = 50$ mM, $[\text{ZnI}_2]_0 = 1.0$ mM (**M1**); $[\text{IBVE}]_0 = 0.5$ M, $[\text{VEM-HCl}]_0 = 25$ mM, $[\text{ZnI}_2]_0 = 1.5$ mM (**M2**); $[\text{IBVE}]_0 = 1.0$ M, $[\text{VEM-HCl}]_0 = 25$ mM, $[\text{ZnI}_2]_0 = 2.0$ mM (**M3**). Conversion $\sim 100\%$. ^b $\overline{\text{DP}}_n$ (calcd) = $[\text{IBVE}]_0/[\text{VEM-HCl}]_0$.

^c Determined by the ^1H NMR peak intensity ratio; $\overline{\text{DP}}_n$ (obsd) = $k/3a$ (see Figure 1 and text). ^d Estimated by polystyrene-calibrated GPC. ^e Determined by the ^1H NMR peak intensity ratio; $\bar{F}_n = a/2l$ (see Figure 1 and text).

by the HCl adduct of 2-(vinyl)oxyethyl methacrylate (VEM-HCl)²⁵ as the initiator in conjunction with zinc iodide (ZnI₂) in toluene at -40 °C (Scheme 1). In a typical run with $[\text{IBVE}]_0 = 0.5$ M, $[\text{VEM-HCl}]_0 = 50$ mM, and $[\text{ZnI}_2]_0 = 1.0$ mM, the polymerization quantitatively proceeded to yield a macromonomer (**M1**) with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.07$). Figure 1 shows the ^1H NMR spectrum of **M1**. The spectrum exhibits all the key signals arising from IBVE repeating unit ($g-k$), methacryloyl group at the initiating end ($a-f$), and the terminal acetal groups (l and m). The number-average end functionality (\bar{F}_n) was derived from the peak intensity ratio of the vinyl protons in the methacryloyl group a to the one at the ω -end group l ($a/2l$). The estimated \bar{F}_n was close to unity, indicating that the macromonomer has one methacryloyl group at the initiating end. The number-average degree of polymerization ($\overline{\text{DP}}_n$) of MA-PIBVE was also determined from the ^1H NMR peak intensity ratio of the methyl protons in the isobutyl groups k to the vinyl protons in the methacryloyl group a ($k/3a$). The evaluated $\overline{\text{DP}}_n$ s were in good agreement with the IBVE/initiator (VEM-HCl) feed molar ratios. Table 1 summarizes the synthesis of a series of MA-PIBVEs with various $\overline{\text{DP}}_n$ s of PIBVE by regulating the IBVE/initiator ratio. Apparently, all the macromonomers have a narrow molecular weight distribution (MWD) and controlled $\overline{\text{DP}}_n$.

2. ATRP of Macromonomers. As with ATRP for low molecular weight monomers, the polymerization of MA-PIBVE by ATRP was conducted under a homogeneous

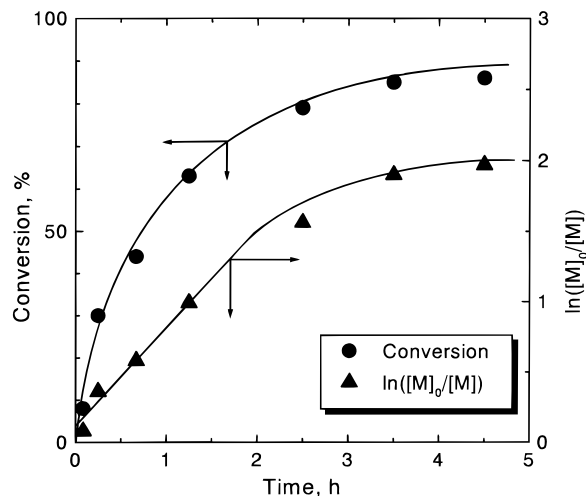


Figure 2. Plots of conversion and $\ln[M]_0/[M]$ vs time for the polymerization of **M1** in diphenyl ether (50 wt %) at 50 °C: $[\text{M1}]_0/[\text{initiator}]_0/[\text{CuBr}]_0/[\text{dHbipy}]_0 = 30/1/1/2$ (molar ratio). Ethyl 2-bromoisobutyrate was used as the initiator.

condition using 4,4'-di-*n*-heptyl-2,2'-bipyridine (dHbipy) as the ligand, which coordinates copper(I) to solubilize the resulting complexes in the polymerization medium.^{20c} The polymerization was carried out using ethyl 2-bromoisobutyrate as the initiator in conjunction with copper(I) bromide (CuBr) in diphenyl ether solution (50 wt %) at 50 °C. Figure 2 shows the time-conversion curves for the polymerization of **M1** with a molar ratio $[\text{M1}]_0/[\text{I}]_0/[\text{CuBr}]_0/[\text{dHbipy}]_0 = 30/1/1/2$. The polymerization smoothly occurred without an induction period, and the conversion reached ca. 90% in 5 h. Moreover, the plot of $\ln[M]_0/[M]$ vs time was linear up to about 70% conversion, indicating that the number of growing radicals remained constant. Deviations from the linear line were observed at higher conversions. This might be attributed to the increasingly high viscosity of the polymerization medium rather than to irreversible termination reactions such as recombination of growing radicals. It has been suggested for the ATRP of 4-acetoxystyrene,²⁶ the radical polymerization of bulky monodendritic monomers,²⁷ and the homopolymerization of macromonomers² that as the polymerization proceeds and the viscosity of the medium increases, the propagation mechanism can change from a chemically controlled to a diffusion controlled process. Even though direct evidence is lacking, we believe that such a mechanistic change in the propagation step of macromonomer polymerization is likely to occur.

As shown in Figure 3, the number-average molecular weights (\bar{M}_n) of the obtained polymacromonomers increased linearly with the conversion, while the MWDs stayed fairly narrow with $\bar{M}_w/\bar{M}_n < 1.2$ (slightly increasing with conversion). These \bar{M}_n and \bar{M}_w/\bar{M}_n values were estimated by polystyrene-calibrated GPC, and hence they are apparent values. Static light scattering measurements were made for one of the polymacromonomers (entry 1 in Table 2). The weight-average molecular weight (\bar{M}_w) determined by light scattering was 5.0×10^4 . This value is much larger than the GPC value ($\bar{M}_w = 2.4 \times 10^4$) but reasonably well agrees with the theoretical value of 4.2×10^4 calculated from $\bar{M}_w = \bar{M}_{n,\text{calcd}} \times (\bar{M}_w/\bar{M}_n)_{\text{GPC}}$, where $\bar{M}_{n,\text{calcd}}$ is the \bar{M}_n value calculated with the initiator to (converted) monomer ($\bar{M}_{n,\text{calcd}} = 1260$) ratio, and $(\bar{M}_w/\bar{M}_n)_{\text{GPC}}$ is the GPC polydispersity index. All these results support the

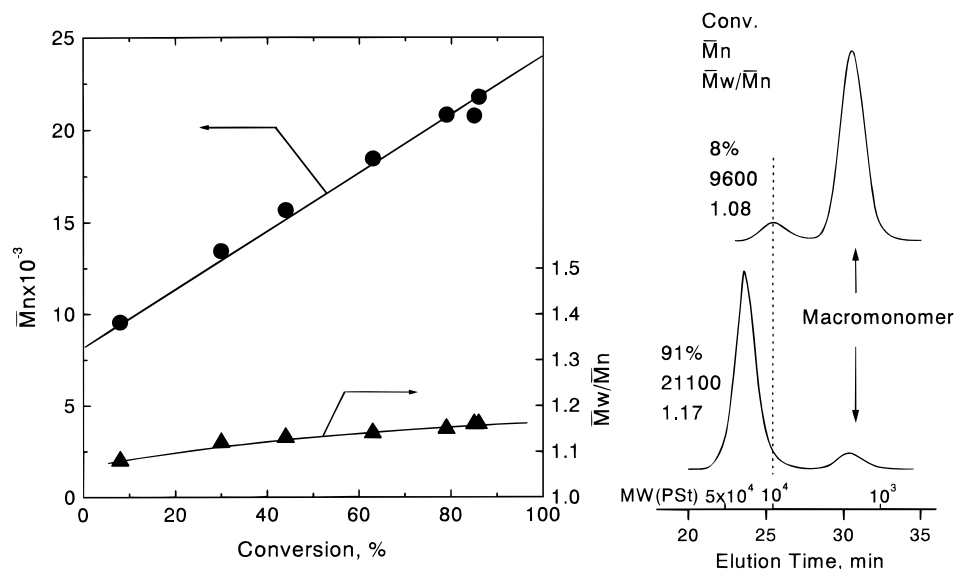


Figure 3. \bar{M}_n , \bar{M}_w/\bar{M}_n , and MWD curves of polymacromonomers obtained by the ATRP of **M1**. See Figure 2 for reaction conditions.

Table 2. ATRP of MA-PIBVEs

entry	MA-PIBVE	$[M]_0/[I]_0/[C]_0^a$	time, h	conversion, %	\bar{M}_n^b	\bar{M}_w/\bar{M}_n^b
1	M1	30/1/1	25	93	19 800	1.20
2		60/1/2	21	91	30 400	1.27
3		100/1/3.3	25	91	45 400	1.25
4		200/1/4.8	110	87	99 200	1.19
5	M2	30/1/2	19.5	79	40 000	1.24
6		100/1/4.6	96	72	62 200	1.10
7	M3	30/1/10	22	26	46 000	1.12

^a Key: M, MA-PIBVE; I, initiator; C, CuBr. $[M] = 50$ wt % for all cases. ^b Determined by polystyrene-calibrated GPC.

“living” nature of the ATRP of MA-PIBVE. The small value of \bar{M}_w (or \bar{M}_n) estimated by GPC suggests the multibranch structure of the polymacromonomer that is more compact in hydrodynamic volume than the linear analogue with a similar molecular weight.

Experiments were also carried out with higher $[M]_0/[I]_0$ ratios and higher molecular weight macromonomers (Table 2). Preliminary experiments using **M1** with the molar ratios of $[M]_0/[I]_0/[CuBr]_0 = 60/1/1$ and $100/1/1$ showed that the polymerization proceeded too slowly or did not occur at all. We then attempted polymerization with an increased $[CuBr]_0/[I]_0$ ratio to promote polymerizability (entries 2–4 in Table 2). In all cases up to the ratio of $[M]_0/[I]_0 \sim 200$, the polymerization proceeded in a controlled manner to give polymacromonomers with a narrow MWD. The ATRP of the higher molecular weight macromonomers (**M2** and **M3**, entries 5–7 in Table 2) were also accomplished and gave polymacromonomers with low polydispersities. In the case of **M3**, however, the conversion was rather low despite a high concentration of CuBr. This is due to the low molar concentration of the polymerizable methacryloyl groups in **M3**. A much longer reaction time would be required to achieve high conversions with this macromonomer.

In conclusion, we have synthesized IBVE-based macromonomers carrying a methacryloyl group at the α -initiating end by living cationic polymerization. The ATRP of these macromonomers yielded a new type of well-defined polymacromonomers, i.e., those with a low-polydispersity backbone as well as low-polydispersity side chains.

Experimental Section

Materials. 2-(Vinylxy)ethyl methacrylate (VEM)²⁸ and its HCl adduct²⁵ were prepared as already reported. Commercial IBVE (Tokyo Kasei) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight over potassium hydroxide (pellets), and distilled twice over calcium hydride before use. Toluene (polymerization solvent) and carbon tetrachloride (internal standard for gas chromatography) were purified by the usual methods and distilled twice over calcium hydride prior to use. ZnI_2 (Aldrich; purity > 99.99%) was used as received. Diethyl ether (Dojin, anhydrous) for the ZnI_2 solvent was distilled over calcium hydride before use. Diphenyl ether was dried over molecular sieves. Ethyl 2-bromoisobutyrate and CuBr were used without further purification. 4,4'-Di-*n*-heptyl-2,2'-bipyridine (dHbipy) was prepared as already reported.^{20c}

Cationic Polymerization. Cationic polymerization was carried out under dry nitrogen in a 50-mL baked flask equipped with a three-way stopcock with magnetic stirring at -40 °C. The reaction was initiated by the sequential addition of chilled solutions of the initiator (VEM-HCl adduct in toluene; 1.50 mL) and of ZnI_2 (in diethyl ether; 1.50 mL) into the monomer solution (in toluene; 17.0 mL) under dry nitrogen and terminated by the addition of chilled ammoniacal methanol (10 mL). The quenched reaction mixture was washed with a 10% aqueous sodium thiosulfate solution and then with water to remove the initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to yield the macromonomers, MA-PIBVE.

ATRP of Macromonomers. Into a glass tube were weighed CuBr and dHbipy, and the mixture of the macromonomer and initiator in diphenyl ether was added in predetermined ratios. The concentration of macromonomer was kept constant at 50 wt %. The mixture was immediately degassed several times by freeze-pump-thaw cycles. The tube was then sealed under vacuum and placed in an oil bath at 50 °C. After a prescribed time, the reaction mixture was cooled to room temperature, dissolved in THF, and subjected to GPC measurement. Conversion of the macromonomer was determined by comparing the GPC peak area of the resulting polymacromonomer with that of the macromonomer.

Measurements. ¹H NMR spectra were obtained using a JEOL AL-400 spectrometer operating at 400 MHz. The GPC measurements were carried out in THF at 40 °C using a TOSOH HLC-8020 high-speed liquid chromatograph equipped with polystyrene gel columns (TOSOH G2500H, G3000H, and G4000H) and a refractive index detector. The number-average molecular weight (\bar{M}_n) and polydispersity ratio (\bar{M}_w/\bar{M}_n) were estimated on the basis of a polystyrene calibration. Static light

scattering measurements were performed in ethyl acetate at 25 °C with a DLS-7000 photometer (Otsuka Electronics, Japan), which was calibrated with benzene. The refractive index increment (dn/dc) in ethyl acetate at 25 °C was determined to be 9.05×10^{-2} mL/g by a DRM-1030 differential refractometer (Otsuka Electronics).

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References and Notes

- (1) For reviews, see: (a) Rempp, P. F.; Franta, E. *Adv. Polym. Sci.* **1984**, *58*, 1. (b) Yamashita, Y., Ed.; *Chemistry and Industry of Macromonomers*; Hüthig & Wepf: Basel, Switzerland, 1993.
- (2) (a) Tsukahara, Y.; Mizuno, K.; Segawa, A.; Yamashita, Y. *Macromolecules* **1989**, *22*, 1546. (b) Tsukahara, Y.; Tsutsumi, K.; Yamashita, Y.; Shimada, S. *Macromolecules* **1990**, *23*, 5201.
- (3) (a) Wintermantel, M.; Schmidt, M.; Tsukahara, Y.; Kajiwara, K.; Kohjiya, S. *Makromol. Rapid Commun.* **1994**, *15*, 279. (b) Wintermantel, M.; Gerle, M.; Fisher, K.; Schmidt, M.; Wataoka, I.; Urakawa, H.; Kajiwara, K.; Tsukahara, Y. *Macromolecules* **1996**, *29*, 978. (c) Sheiko, S. S.; Gerle, M.; Fischer, K.; Schmidt, M.; Möller, M. *Langmuir* **1997**, *13*, 5368. (d) Dziezok, P.; Sheiko, S. S.; Fischer, K.; Schmidt, M.; Möller, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2812.
- (4) (a) Wintermantel, M.; Fischer, K.; Gerle, M.; Ries, R.; Schmidt, M.; Kajiwara, K.; Urakawa, H.; Wataoka, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1472. (b) Tsukahara, Y.; Ohta, Y.; Senoo, K. *Polymer* **1995**, *36*, 3413.
- (5) (a) Ito, K.; Tanaka, K.; Tanaka, H.; Imai, G.; Kawaguchi, S.; Itsuno, S. *Macromolecules* **1991**, *24*, 2348. (b) Nomura, E.; Ito, K.; Kajiwara, A.; Kamachi, M. *Macromolecules* **1997**, *30*, 2811.
- (6) (a) Hatada, K.; Kitayama, T.; Masuda, E.; Kamachi, M. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 101. (b) Masuda, E.; Kishiro, S.; Kitayama, T.; Hatada, K. *Polym. J.* **1991**, *23*, 847.
- (7) Grassl, B.; Rempp, S.; Galin, J. C. *Macromol. Chem. Phys.* **1998**, *199*, 239.
- (8) (a) Ishizu, K.; Yukishima, S.; Saito, R. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 3073. (b) Ishizu, K.; Tsubaki, K.; Ono, T. *Polymer* **1997**, *39*, 2935.
- (9) Rempp, P.; Lutz, P.; Masson, P.; Chaumont, P.; Franta, E. *Makromol. Chem., Suppl.* **1985**, *13*, 47.
- (10) Kanaoka, S.; Sueoka, M.; Sawamoto, M.; Higashimura, T. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2513.
- (11) Asami, R.; Takaki, M.; Moriyama, Y. *Polym. Bull.* **1986**, *16*, 125.
- (12) Feast, W. J.; Gibson, V. C.; Johnson, A. F.; Khosravi, E.; Mohsin, M. A. *Polymer* **1994**, *35*, 3542.
- (13) (a) Breunig, S.; Heroguez, V.; Gnanou, Y.; Fontanille, M. *Macromol. Symp.* **1995**, *95*, 151. (b) Heroguez, V.; Gnanou, Y.; Fontanille, M. *Macromolecules* **1997**, *30*, 4791.
- (14) For reviews, see: (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamaer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (b) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Pergamon: Oxford, U.K., 1995; p 335. (c) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365. (d) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371. (e) Hawker, C. J. *Acc. Chem. Res.* **1997**, *40*, 373. (f) Matyjaszewski, K., Ed.; *Controlled Radical Polymerization*; ACS Symposium Series No. 685; American Chemical Society: Washington, DC, 1998.
- (15) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127.
- (16) (a) Solomon, D. H.; Rizzardo, E.; Cacioli, P. Eur. Pat. Appl. 135280, 1985. (b) Rizzardo, E. *Chem. Aust.* **1987**, *54*, 32.
- (17) (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamaer, G. K. *Macromolecules* **1993**, *26*, 2987. (b) Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1997**, *30*, 2232. (c) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185. (d) Catala, J. M.; Bubel, F.; Hammouch, S. O. *Macromolecules* **1995**, *28*, 8441. (e) Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T.; Shimizu, Y. *Macromolecules* **1996**, *29*, 3050. (f) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. *Macromolecules* **1996**, *29*, 6393. (g) Greszta, D.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 7661.
- (18) (a) Wayland, B. B.; Pozmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943. (b) Wayland, B. B.; Basicckes, L.; Mukerjee, S.; Wei, M.; Fryd, M. *Macromolecules* **1997**, *30*, 8109.
- (19) (a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (b) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070. (c) Ando, T.; Kamigaito, M.; Sawamoto, M. *Tetrahedron* **1997**, *53*, 15445.
- (20) (a) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (b) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901. (c) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.
- (21) (a) Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 8576. (b) Lecomte, Ph.; Drapier, I.; Dubois, Ph.; Teyssié, Ph.; Jérôme, R. *Macromolecules* **1997**, *30*, 7631.
- (22) (a) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970. (b) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.
- (23) For reviews, see (a) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111. (b) Kennedy, J. P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*, Hanser, Munich, Germany, 1992. (c) Sawamoto, M.; Kamigaito, M. In *New Methods of Polymer Synthesis*; Ebdon, J. R., Eastmond, G. C., Eds.; Blackie: Glasgow, U.K., 1995; Vol. 2, p 37.
- (24) Aoshima, S.; Ebara, K.; Higashimura, T. *Polym. Bull.* **1985**, *14*, 425.
- (25) Miyashita, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1994**, *27*, 1093.
- (26) Gao, B.; Chen, X.; Ivan, B.; Kops, J.; Batsberg, W. *Makromol. Rapid Commun.* **1997**, *18*, 1095.
- (27) Percec, V.; Ahn, C.-H.; Barboiu, B. *J. Am. Chem. Soc.* **1997**, *119*, 12978.
- (28) (a) Kato, M.; Ichijo, T.; Ishii, K.; Hasegawa, M. *J. Polym. Sci., Part A-1* **1971**, *9*, 2109. (b) Aoshima, S.; Hasegawa, O.; Higashimura, T. *Polym. Bull.* **1985**, *13*, 229.

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