Macromolecules

Volume 30, Number 18 September 8, 1997

Block Copolymer Preparation Using Sequential Normal/Living Radical Polymerization Techniques

I. Q. Li and B. A. Howell*

Center for Applications in Polymer Science, Central Michigan University, Mount Pleasant, Michigan 48859

M. T. Dineen, P. E. Kastl, J. W. Lyons, D. M. Meunier, and P. B. Smith

Dow Analytical Sciences, 1897 Building, Midland, Michigan 48667

D. B. Priddy

Dow Polystyrene R&D, 438 bldg, Midland, MI 48667

Received January 30, 1997; Revised Manuscript Received June 13, 1997[⊗]

ABSTRACT: Anionic and nitroxide-mediated (NM) radical polymerization works well for styrene but not for acrylates. We have overcome this problem and successfully prepared styrene-*b*-*n*-butyl acrylate (S-BA), styrene-*b*-methyl methacrylate (S-MMA), styrene-*b*-isoprene (S-IP), and styrene-*alt*-acrylonitrile-*b*-isoprene (SAN-IP) polymers using a sequential normal/living radical polymerization scheme. Clear (S-IP and SAN-IP) to translucent (S-BA and S-MMA) films were obtained having microphase-separated polymer morphology. GPC studies and chemical digestion of the IP segments of S-IP and SAN-IP block copolymers confirmed their block structure. The sequential normal/living radical polymerization approach provides a new route to synthesize block polymers that have previously proven very difficult to make.

Introduction

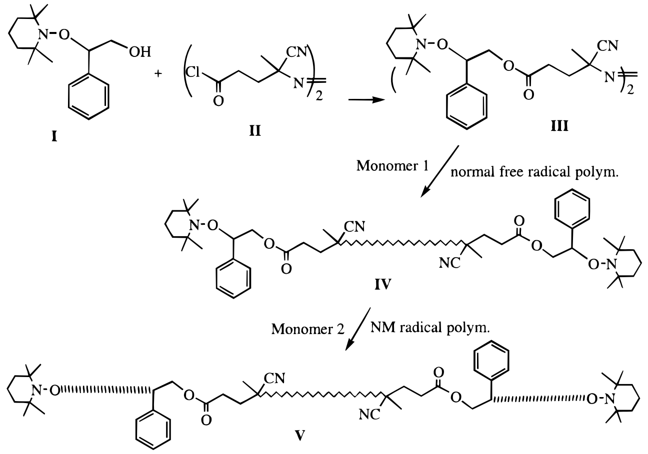
Normal free radical polymerization is very limited in its utility for making polymers of controlled architecture because the initiation, propagation, and termination steps are simultaneous, which leads to very broad polydispersity.[1] Also, termination occurs by a variety of processes including radical coupling, disproportionation, primary radical coupling, and chain transfer to monomer, to solvent, and even to polymer resulting in the formation of polymer chains having a variety of end-group structures.[2] The use of nitroxides to mediate styrene polymerization appears to greatly reduce the termination processes and has found limited utility for the preparation of narrow polydispersity polystyrene (PS) and styrene-*stat*-acrylonitrile (SAN) and styrene-*stat*-methyl methacrylate (SMMA) copolymers.[3−14] The chemistry has also been found to yield certain block copolymers[1,8,14−28] but has not been found to work well for making copolymers containing non-S containing (e.g., acrylate) blocks. Recently, Steenbock *et al.*[29] reported marginal success in the preparation of S-*b*-MMA copolymers. They attempted to initiate living radical polymerization of MMA using PS having a 2,2,6,6-tetramethylpipridinyloxy (TEMPO) end-group as a macroinitiator. Under neutral conditions they were unsuccessful in initiating living radical polymerization of the MMA block. However, by the addition of camphorsulfonic acid (CSA) they were able to obtain evidence of S-*b*-MMA copolymer formation. However, analytical studies revealed that the material they produced was contaminated by high levels of homo-PS. They concluded that “quantitative block copolymer formation in the TEMPO mediated radical polymerization is not possible”. A review of block polymer synthesis using radical polymerization techniques has recently appeared.[30]

The chemistry that is generally used to make block copolymers is anionic polymerization because of the control of the termination step that it offers. However, anionic polymerization chemistry is very limited in the block copolymers that can be produced. In general, acrylates, methacrylates, and AN are not compatible with anionic polymerization unless prepared at very low temperatures.[31] Besides S-*b*-acrylate, another block polymer system that has proven difficult to make is block polymers containing SAN segments.[32]

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

S0024-9297(97)00130-7 CCC: $14.00

Scheme 1. Synthetic Approach to Block Copolymers Using Sequential Normal/Living Radical Polymerization



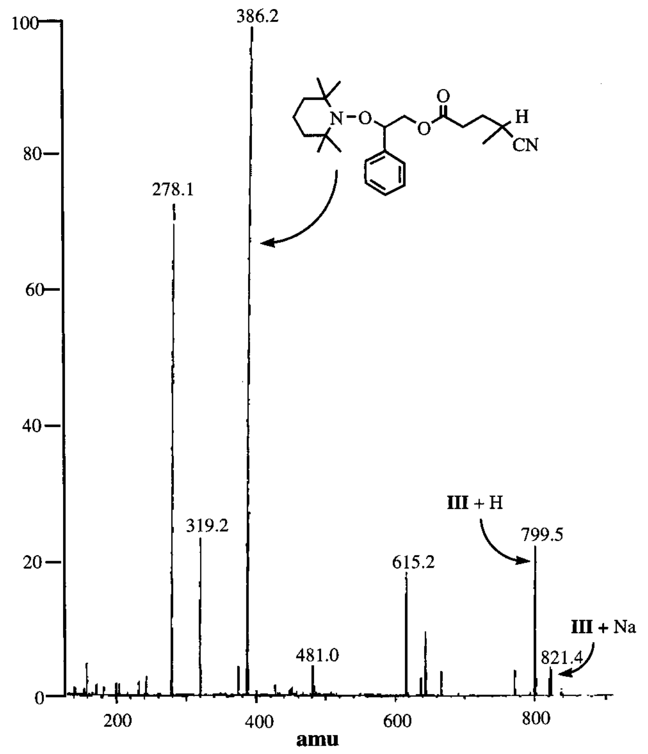


Figure 1. Mass spectrum of **III**.

In an effort to overcome the incompatibilities of anionic and living radical polymerization chemistries with acrylates and acrylonitrile, we investigated a sequential polymerization scheme using first normal free radical polymerization to make one block followed by preparation of the S or SAN block using nitroxide-mediated (NM) radical polymerization.

Results and Discussion

The synthetic approach we pursued is depicted in Scheme 1. The nitroxide-functional azo-initiator 4,4′-azobis[2-phenyl-2-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethyl 4-cyanopentanoate] (**III**) was prepared by condensing the acid chloride of azobis(cyanovaleric acid) (**II**) (prepared using the method of Onen)[33] with the hydroxy functional benzyloxyamine **I** (prepared following the method of Hawker).[16] The structure of **III** was confirmed using mass spectroscopy (Figure 1), ^{1}H-NMR (Figure 2), and ^{13}C-NMR (Figure 3).

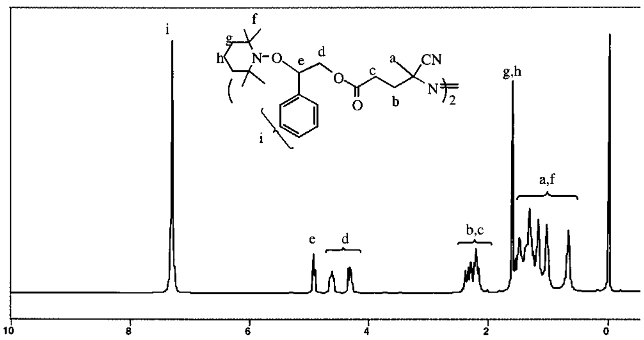


Figure 2. ^{1}H-NMR spectrum of **III** in $CDCl_3$.

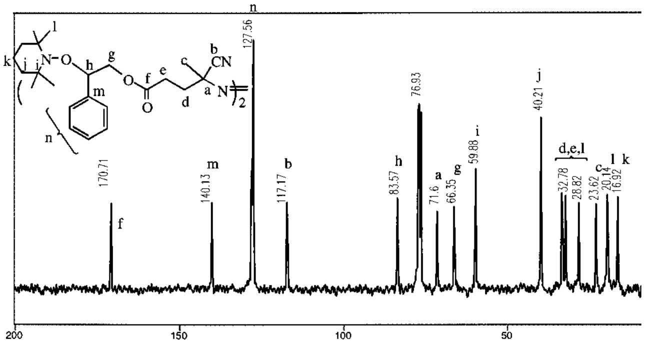


Figure 3. ^{13}C-NMR spectrum of **III** in $CDCl_3$.

Table 1. Normal Radical Polymerization of BA, MMA, and IP Using AIBN and III

monomer	initiator/ conc (mmol)	temp (°C)	time (h)	solids (% w/w)	M_w/ 1000	M_n/ 1000	polymer
BA	AIBN/4.3	100	0.33	84.7	97.8	42.1	PBA-1
BA	**III**/4.3	100	0.33	82.1	114.5	47.2	PBA-2
MMA	AIBN/4.5	90	0.67	27.1	135.1	76.9	PMMA-1
MMA	**III**/4.5	90	0.67	24.5	115.6	65.2	PMMA-2
IP	AIBN/3	80	27	6.3	67.4	23.5	PIP-1
IP	**III**/3	80	27	5.4	39.3	24.1	PIP-2
IP	AIBN/4.2	90	5	3.4	42.5	17.3	PIP-3
IP	**III**/4.2	90	5	5.8	28.8	17.1	PIP-4

Table 2. Spontaneous Polymerization of S or SAN at 140 °C in the Presence of 5% w/w of the Polymers Described in Table 1

polymer	monomer	time (min)	solids (% w/w)	M_w/ 1000	M_n/ 1000	M_w/ M_n	film clarity
PBA-1	styrene	15	11	299.4	112	2.7	opaque
PBA-2	styrene	15	10.3	185	82.1	2.3	transluc
PMMA-1	styrene	20	15.6	243	116.6	2.1	opaque
PMMA-2	styrene	20	9.8	151.7	79	1.9	transluc
PIP-1	styrene	25	17.2	245.6	82.8	3.0	opaque
PIP-2	styrene	25	18.8	83.4	50.6	1.6	clear
PIP-3	SAN(75:25)	15	11.2	205.3	42.4	4.8	opaque
PIP-4	SAN(75:25)	15	14.7	55.1	35.8	1.5	clear

The nitroxy-functional azo initiator **III** was used to carry out normal free radical polymerization of the first monomer to make a nitroxide-functional polymer (**IV**) (Table 1). The nitroxide-functional polymer was isolated and then dissolved in either S or a mixture (azeotropic copolymerization monomer ratio = 75:25 w/w S:AN) of S and AN and polymerized in evacuated glass ampules at 140 °C to form the S or SAN block under living radical polymerization conditions (Table 2). Each polymerization experiment was accompanied by an appropriate control that was run in exactly the same way except that the non-nitroxy-functional azo initiator azobis(isobutyronitrile) (AIBN) was used in place of **III**. Since termination reactions that take place during the normal free radical polymerization are manifold (but primarily by radical coupling), we anticipate that both mono- and

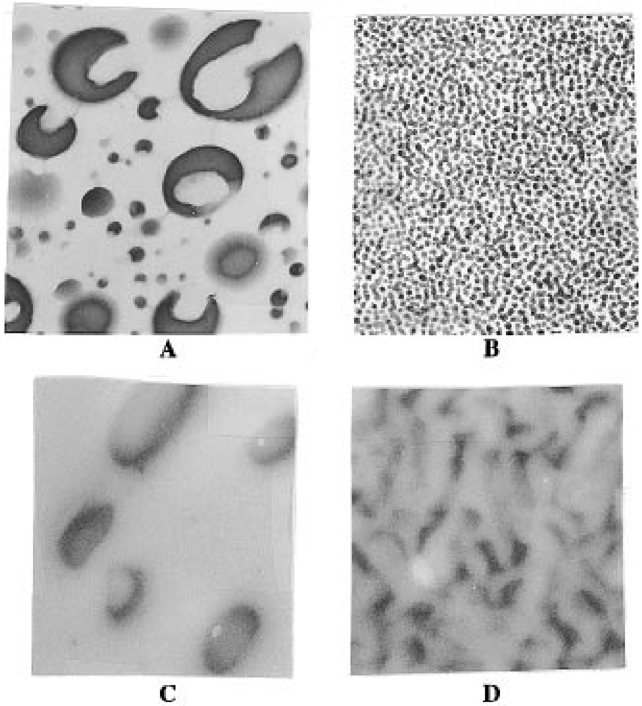


Figure 4. TEMs (30000×) of S spontaneously polymerized at 140 °C in the presence of (A) PIP-1, (B) PIP-2, (C) PBA-1, and (D) PBA-2. Figure reduced to 93% for publication.

dinitroxide-functionalized (telechelic) polymer chains were produced during formation of the first segment using **III** (with the telechlic polymer predominating). Thus the block polymers that we prepared were likely A–B–A triblock polymers contaminated by some A–B diblock material. This novel approach allowed us to prepare clear to translucent microphase separated block copolymers.

The normal free radical control polymerizations of BA, MMA, and IP were carried out using AIBN in evacuated glass ampules (using the freeze–thaw technique) and polymerized under identical conditions as when using **III**. The PBA, PMMA, and PIP were isolated (by evaporation of the unchanged monomer in a vacuum oven) and dissolved and subsequently polymerized in either styrene or a mixture of S and AN exactly as described for **III**. All of the polymers were analyzed using gel permeation chromatography (GPC). The GPC data consistently revealed that the AIBN initiated control polymers (PBA-1, PMMA-1, PIP-1, and PIP-3) produced broader polydispersity polymers than their **III**-initiated counterparts (PBA-2, PMMA-2, PIP-2, and PIP-4) (Table 2). All of the solvent-cast polymer films isolated from the control runs were opaque and extremely brittle, while the solvent-cast films of the polymers initiated using **III** were translucent and flexible. Side by side comparison of the transmission electron micrographs (TEMs) of the polymers (Figure 4) clearly show significant differences in morphology.

To confirm that we had indeed formed block polymers using the sequential approach, all of the polymers were analyzed using GPC equipped with differential refractive index detection. The control polymers produced by polymerizing S or S and AN in the presence of PBA-1, PMMA-1, PIP-1, and PIP-3 appear to be mixtures (i.e., bimodal GPC curve) of polymers, while the polymers produced using **III** as the initiator appear to be homogeneous (Figure 5).

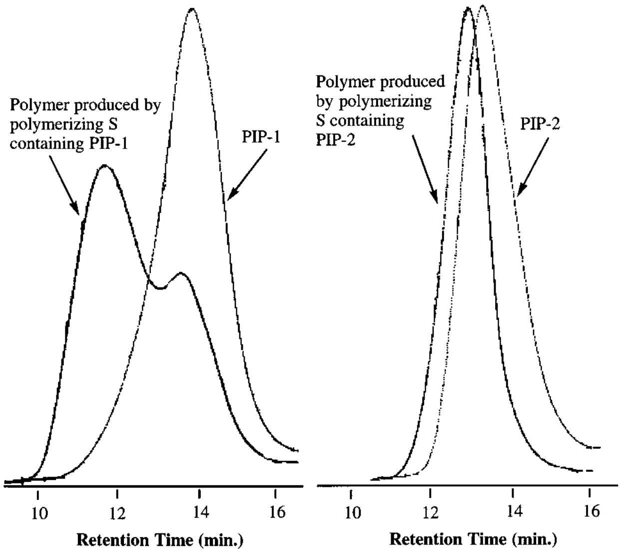


Figure 5. Overlay of the GPC curves (RI detector) of PIP-1 and PIP-2 with their respective polymers produced by polymerizing S containing them.

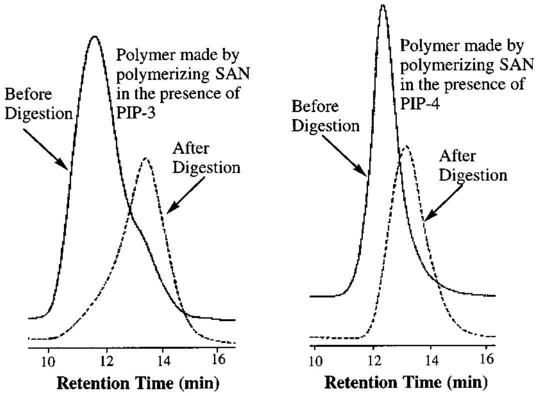
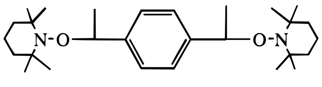


Figure 6. Comparison of the GPC chromatograms before and after chemical digestion (OsO_4) of resins obtained by spontaneous polymerization of SAN in the presence of PIP-1 and PIP-2 at 140 °C.

To further confirm that we had indeed formed block polymers using the sequential approach, the polymers obtained by polymerizing a mixture of S and AN in the presence of PIP-3 and PIP-4 were chemically digested using osmium tetroxide to totally degrade the PIP segments.[34] GPC analysis of the polymers before and after osmium tetroxide digestion are shown in Figure 6. The solid lines are the GPC curves of the polymers before osmium tetroxide digestion. The polymer formed by polymerizing SAN in the presence of PIP-3 shows a low molecular weight shoulder. After osmium tetroxide digestion, all that remains is a polymer having the same peak retention time as the shoulder indicating, that the low molecular weight shoulder is SAN. Thus the polymer was a mixture of PIP and PSAN. However, the resin obtained by polymerizing SAN in the presence of PIP-4 shows a complete shift of the GPC curve to lower molecular weight polymer upon osmium tetroxide digestion. This is consistent with loss of the PIP segment of a SAN-*b*-IP copolymer.

The preparation of block copolymers using nitroxide-functionalized polymers as macroinitiators for NM radical polymerization of S and SAN at 140 °C may seem surprising due to the fast rate of spontaneous or autopolymerization at that temperature. However, the polymerization times were very short and the monomer conversions less than 10%. Typically, camphorsulfonic acid (CSA) is added to NM radical polymerization of S to inhibit autopolymerization,[3,13,35–39] but no CSA was added in our experiments. In an earlier study we successfully prepared telechelic polystyrene having nitroxide end-functionality close to 2.0 by initiating NM radical polymerization of styrene using the dinitroxide adduct of 1,4-diethylbenzene (**VI**)[40] under similar conditions without the addition of CSA.[41]



VI

Conclusions

The approach of normal/living radical polymerization yields clear to translucent films having microphase-separated polymer morphology indicative of block copolymers with incompatible segments. GPC and chemical digestion (using osmium tetroxide) studies confirmed that block copolymers had been produced. Control polymer blends prepared by polymerizing styrene in the presence of another dissolved polymer yielded brittle and opaque films generally having morphologies showing large domains of one polymer dispersed in the other and no sign of microphase separation. The sequential normal/living radical polymerization approach provides a new route to synthesize block polymers (e.g., SAN-*g*-PIP) that were previously very difficult to make.

Experimental Section

Chemicals. All reagents and solvents were purchased from Aldrich Chemical Co. and used as received.

Preparation of 4,4′-Azobis[2-phenyl-2-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethyl 4-cyanopentanoate] (III). A 100 mL, round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet was charged with 3.4 g (12 mmol) of **I** (prepared by the method of Hawker),[16] 20 mL of methylene chloride, and 0.74 g (10 mmol) of pyridine. A solution of 1.58 g (5 mmol) of **II** (prepared by the method of Onen)[33] in 10 mL of methylene chloride was added followed by stirring at room temperature for 0.5 h. The reaction mixture was washed with water followed by drying over anhydrous sodium sulfate. The solution was concentrated using rotary evaporation yielding a light yellow oil that was purified by flash chromatography on silica gel (80:20 hexane/ethyl ether followed by 60:40 hexane/ether). The product is a white crystalline solid (mp = 111 °C, decomposes) (yield = 1.1 g, 28%). MS: m/z (relative intensity) 799.5 (M + H, 22%), 615.2 (19%), 481 (7%), 386.2 (100%), 319.2 (26%), 278.1 (77%). ^{1}H-NMR ($CDCl_3$): δ 1.2 (m, 30H), 1.8 (s, 8H), 2.15 (m, 8H), 4.3 (m, 4H), 5.0 (t, 2H), and 7.5 (m, 10H). ^{13}C-NMR ($CDCl_3$): δ 16.92, 20.14, 23.62, 28.82, 32.17, 40.21, 59.88, 66.35, 71.60, 76.93, 83.57, 117.17, 127.56, 140.13, 170.71.

Preparation of Nitroxide-Terminated PBA (PBA-2). A solution of **III** in BA (4.3 mmol) was diluted with an equal weight of toluene (to eliminate the gel effect) and sealed in evacuated glass ampules (3 mm i.d. × 30 cm) using the freeze−thaw technique. The ampules were heated in an oil bath at 100 °C for 20 min. The contents of the ampules was poured into a shallow dish and devolatilized in a vacuum (<5 mmHg) oven at 50 °C for 2 h. The weight of the remaining polymer vs the weight of the amount of syrup added to the dish was used to calculate percent solids. The molecular weight was determined using GPC. The data are shown in Table 1.

The PBA-1 control was prepared by polymerizing BA under identical conditions using AIBN (4.3 mmol) instead of **III** as the initiator.

Preparation of Nitroxy-Terminated PMMA (PMMA-2). A solution of **III** in MMA (4.5 mmol) was diluted with an equal weight of benzene (to eliminate the gel effect) and sealed in evacuated glass ampules (3 mm i.d. × 30 cm) using the freeze−thaw technique. The ampules were heated in an oil bath at 90 °C for 40 min. The contents of the ampules was poured into a shallow dish and devolatilized in a vacuum (<5 mmHg) oven at 50 °C for 2 h. The weight of the remaining polymer vs the weight of the amount of syrup added to the dish was used to calculate percent solids. The molecular weight was determined using GPC. The data are shown in Table 1.

The PMMA-1 control was prepared by polymerizing MMA under identical conditions using AIBN (4.5 mmol) instead of **III** as the initiator.

Preparation of Nitroxide-Terminated PIP (PIP-2 and PIP-4). Two solutions of **III** (3 and 4.2 mmol) in IP were prepared and sealed under vacuum (<5 mmHg) in glass ampules (3 mm i.d. × 30 cm) using the freeze−thaw technique. The ampules containing 3 and 4.2 mmol of **III** were heated in an oil bath at 80 °C for 27 h and 90 °C for 5 h, respectively. The ampules were removed and cooled to room temperature. The ampule contents were poured into a shallow dish and placed in a vacuum oven at 50 °C/<5 mmHg for 2 h. The weight of the remaining polymer vs the weight of the amount of syrup added to the dish was used to calculate percent solids. The molecular weight was determined using GPC. The data are shown in Table 1.

The PIP-1 and PIP-3 controls were prepared by polymerizing IP under conditions identical to those of their PIP-2 and PIP-4 counterparts using AIBN instead of **III** as the initiator at the same respective molar concentrations.

Polymerization of Styrene and SAN in the Presence of PBA, PMMA, and PIP. PBA, PMMA, or PIP (0.148 g) was dissolved in styrene (2.96 g) or a mixture of styrene and acrylonitrile (75:25 w/w) (2.96 g), and the solutions were sealed under vacuum in glass ampules (3 mm i.d. × 30 cm) using the freeze−thaw technique. The ampules were placed in an oil bath at the desired temperature and time. The ampule contents were dried in a vacuum oven at 230 °C at <10 mmHg for 20 min.

Transmission Electron Microscopy (TEM). Samples containing PIP were stained to increase the contrast in the TEM by immersion in a 2% aqueous solution of OsO4 for 24 h at room temperature.[42] The samples were then rinsed with water and thin sectioned on a Reichert-Jung Ultracut E Ultramicrotome with a diamond knife. Thin sections of 90 ± 10 nm were collected on carbon-coated, copper TEM grids and were examined in a Hitachi H-600 TEM at 100 kV. Samples that did not contain a phase that could be stained (e.g., S-*b*-BA) were irradiated with a controlled, high electron beam dose, resulting in a preferential phase mass loss and increasing contrast between the phases.[43]

GPC Analyses. Columns: Two Polymer Labs 5 micron Mixed-C calibrated using PS standards. Solvent: HPLC grade tetrahydrofuran sparged with helium. Sample concentration: 0.25% w/w. Pump/flow rate: Waters M-6000/1 mL/min. Detector: Waters 410 DRI. Data system: Polymer Laboratories Caliber GPC/SEC, version 5.20.

References and Notes

(1) Webster, O. W. *Science* **1991**, *251*, 887.
(2) Priddy, D. B. *Adv. Polym. Sci.* **1994**, *111*, 67.
(3) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 4161.
(4) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 3346.
(5) Barclay, G. G.; Orellana, A.; Hawker, C. J.; Elce, E.; Dao, J. *Polym. Mater. Sci. Eng.* **1996**, *74*,, 311.
(6) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 2746.
(7) Mueller, A. H. E.; Litvinenko, G.; Yan, D. *Macromolecules* **1996**, *29*, 2346.
(8) Fryd, M.; Wayland, B. B.; Poszmick, G.; Mukerjee, S. L. Living radical polymerization of vinyl monomers (du Pont de Nemours, E. I., and Co.). Int. Patent Appl. WO 9525765 A2, 1995.
(9) Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 4391.
(10) Kazmaier, P. M.; Moffat, K. A.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K. *Macromolecules* **1995**, *28*, 1841.
(11) Saban, M. D.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 7032.

(12) Keoshkerian, B.; Georges, M. K.; Boils-Boissier. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1994**, *35*, 675.
(13) Georges, M. K.; Kee, R. A.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *J. Phys. Org. Chem.* **1995**, *8*, 301.
(14) Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D. *Macromolecules* **1995**, *28*, 6381.
(15) Roha, M.; Wang, H.-T.; Harwood, H. J.; Sebenik, A. *Macromol. Symp.* **1995**, *91*, 81.
(16) Hawker, C. J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993.
(17) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185.
(18) Zheng, Q.; Sun, Y.; Lin, P.; Zhang, W. *Huadong Huagong Xueyuan Xuebao* **1989**, *15*, 348.
(19) Lee, M.; Morigami, T.; Minoura, Y. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1738.
(20) Li, I.; Howell, B. A.; Priddy, D. B.; Smith, P. B. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1996**, *37*, 612.
(21) Leduc, M. R.; Hawker, C. J.; Dao, J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1996**, *118*, 11111.
(22) Schmidt-Naake, G.; Butz, S. *Macromol. Rapid Commun.* **1996**, *17*, 661.
(23) Krstina, J.; Moad, G.; Rizzardo, E.; Winzor, C. L.; Berge, C. T.; Fryd, M. *Macromolecules* **1995**, *28*, 5381.
(24) Georges, M. K.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *Macromol. Symp.* **1994**, *88*, 89.
(25) Haque, S. A. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 827.
(26) Turner, S. R.; Blevins, R. W. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1988**, *29*, 6.
(27) Kamachi, M. *Kobunshi* **1984**, *33*, 870.
(28) Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T.; Shimizu, Y. *Macromolecules* **1996**, *29*, 3050.
(29) Steenbock, M.; Klapper, M.; Mullen, K.; Pinhal, N.; Hubrick, M. *Acta Polym.* **1996**, *47*, 276.
(30) Ameduri, B.; Boutevin, B.; Gramain, P. *Adv. Polym. Sci.* **1997**, *127*, 87.
(31) Vlcek, P.; Otoupalova, J.; Sikora, A.; Kriz, J. *Macromolecules* **1995**, *28*, 7262.
(32) Kroeze, E.; ten Brinke, G.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 6650.
(33) Onen, A.; Yagci, Y. *J. Macromol. Sci., Chem.* **1990**, *A27*, 743.
(34) Kranz, D.; Dinges, K.; Wendling, P. *Angew. Makromol. Chem.* **1976**, 51, 25.
(35) Buzanowski, W. C.; Graham, J. D.; Priddy, D. B.; Shero, E. *Polymer* **1992**, *33*, 3055.
(36) Baldovi, M. V.; Mohtat, N.; Scaiano, J. C. *Macromolecules* **1996**, *29*, 5497.
(37) Georges, M. K.; Saban, M.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1994**, *35*, 737.
(38) Li, I.; Howell, B. A.; Matyjaszewski, K.; Shigemoto, T.; Smith, P. B.; Priddy, D. B. *Macromolecules* **1995**, *28*, 6692.
(39) Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Brousmiche, D.; Georges, M. K. *Macromolecules* **1995**, *28*, 8453.
(40) Howell, B. A.; Priddy, D. B.; Li, I. Q.; Smith, P. B.; Kastl, P. E. *Polym. Bull.* **1996**, *37*, 451.
(41) Li, I. Q.; Howell, B. A.; Koster, R.; Priddy, D. B. *Macromolecules* **1996**, *29*, 8554.
(42) Frisch, H. L.; Xue, Y. *Polym. J. (Tokyo)* **1994**, *26*, 828.
(43) Sawyer, L. C.; Grubb, D. T. *Polymer Microscopy*; Chapman and Hall: New York, 1987; pp 62−69.

MA9701301