Copolymerization and Addition of Styrene and *N*-Phenylmaleimide in the Presence of Nitroxide

J. LOKAJ, P. HOLLER, J. KŘÍŽ

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

ABSTRACT: The copolymerization and addition reaction of styrene (S) with *N*-phenyl-maleimide (PMI), either neat or in xylene, have been found to proceed at 125°C in the presence of 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) radicals. TEMPO-terminated alternating S-PMI copolymers and comonomer adducts were obtained. The amounts of the low molecular weight compounds increased with the increasing content of PMI in the initial mixture. The reaction suggests formation of monofunctional unimolecular initiators. In the autopolymerization of neat comonomers, a mediating role of TEMPO was observed. The synthesized copolymers containing TEMPO end groups were used as macroinitiators to initiate polymerization of styrene. The molecular weight distributions of resulting poly(styrene-*alt-N*-phenylmaleimide)-*block*-polystyrene copolymers indicated the presence of both low molecular weight termination products and some copolymer precursor. The copolymers and comonomer adducts were characterized using the nitrogen analysis, size-exclusion chromatography (SEC), and NMR spectroscopy. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1093–1099, 2000

Key words: styrene–*N*-phenylmaleimide copolymers; comonomer adducts; TEMPO end groups; block copolymers

INTRODUCTION

The free radical polymerization in the presence of stable nitroxyl radicals, such as 2,2,6,6-tetra-methylpiperidin-1-yloxy (TEMPO), ranks among modern and attractive methods in the field of polymer synthesis.[1–24] Using this technique, a variety of high molecular weight products with controlled structures and properties can be prepared. Bimolecular, irreversible termination reactions, typical of a conventional free radical polymerization, are substantially reduced by decreasing the number of growing radical chains. The nitroxyl radicals can capture the propagating polymer chains by forming thermally unstable alkoxy-amines. At temperatures above 100°C, the C—ON bond of the alkoxyamine undergoes dissociation to regenerate both the nitroxyl and polymer radicals. The polymer radical can add more monomer units and be trapped again by the nitroxyl. Due to the reversible trapping reactions, the growth of the polymer chains proceeds in a controlled manner.

Initially, two-component systems consisting of a thermal radical initiator, as a rule dibenzoyl peroxide, in combination with nitroxyl radicals were used in the initiation of controlled radical polymerizations.[1] Recently, unimolecular initiators based on an alkoxyamine structure were developed.[25–27] They contain both a latent initiating group and nitroxide in the 1 : 1 stoichiometry. The success of the controlled radical polymerization process depends on the strength of the C—ON bond in the initiators. For styrene-based monomers and comonomer mixtures, the relatively

high temperatures, at which the nitroxide-mediated polymerizations are conducted, may result in additional radicals being formed by autopolymerization. These radicals may be captured with added nitroxides to give *in situ* unimolecular initiators.[28–31] Thus, the nitroxide-mediated polymerization in the absence of added initiating systems, i.e., the controlled autopolymerization, can be performed.

In our recent work,[32] we have synthesized styrene–*N*-butylmaleimide copolymers by the autopolymerization in the presence of TEMPO. The autopolymerization proceeded in a pseudoliving manner and yielded copolymers of a fairly narrow molecular weight distribution ($\approx$1.3). The obtained TEMPO-terminated styrene–*N*-butylmaleimide copolymers readily initiated the polymerization of styrene. In this way, the poly-(styrene-*alt*-*N*-butylmaleimide)-*block*-polystyrene copolymers with various polystyrene chain lengths and a narrow molecular weight distribution have been prepared. The aim of this study was to synthesize analogous nitroxide-terminated copolymer precursors and block copolymers by substituting for *N*-butylmaleimide a more available maleimide derivative with a rigid aromatic group, *N*-phenylmaleimide. The autopolymerization and solution copolymerization of styrene–*N*-phenylmaleimide–TEMPO mixtures as well as the block copolymer synthesis using the prepared copolymers with TEMPO end groups as macroinitiators were carried out, and the resulting products were characterized. The participation of the comonomers in an addition reaction proceeding in parallel to the copolymerization was also observed.

EXPERIMENTAL

Materials

Styrene (S) (Kaučuk Group Co., Kralupy, Czech Republic) (b.p. 36°C/1.56 kPa) was distilled under reduced pressure prior to use. *N*-Phenylmaleimide (PMI) (m.p. 89–90°C) and 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) radical (m.p. 36–39°C) were commercial products of Fluka. Dibenzoyl peroxide (BP) (Fluka) (m.p. 104°C) was reprecipitated from chloroform solutions with methanol. The solvents used were of analytical grade.

Synthesis of TEMPO-Terminated Styrene–*N*-Phenylmaleimide Copolymers

Mixtures of styrene, *N*-phenylmaleimide, and TEMPO were heated in sealed glass ampoules in nitrogen atmosphere at 125°C. The total amount of comonomers was 2×10^{-2} or 4×10^{-2} mol, that of TEMPO 0.5×10^{-4}, 1.5×10^{-4}, or 3×10^{-4} mol. The molar fractions of PMI (F_{PMI}) varied within 0.1–0.7. After 30 or 45 min, the mixtures were cooled, diluted with CHCl$_3$, and the resulting products were precipitated with ethanol. The products were twice reprecipitated with methanol from chloroform solutions and dried in vacuum at room temperature. The total yields, composition, molecular weights, and molecular weight distributions of copolymers are given in Table I. The TEMPO-terminated styrene–*N*-phenylmaleimide copolymers were also prepared in xylene as a solvent. In this case, both the uninitiated copolymerization and that initiated with dibenzoyl peroxide (1×10^{-4} mol) in the presence of TEMPO (1.5×10^{-4} mol) were carried out (Table II). For comparison, copolymerizations of styrene and *N*-phenylmaleimide at $F_{PMI} = 0.4$ in the absence of TEMPO were conducted (Tables I and II).

Low Molecular Weight Compounds

Table III summarizes the results on the addition reaction of comonomers proceeding along with their copolymerization. The adducts of comonomers were obtained by evaporation of solvents after the second reprecipitation of products formed in the autopolymerization of neat comonomers.

Polymerization of Styrene Initiated with TEMPO-Terminated Styrene–*N*-Phenylmaleimide Copolymers

A solution containing the copolymer C3, C9, or C10 (Tables I and II) (0.2 g), 5 mL of styrene, and 0.1 mL of *N*,*N*-dimethylformamide (DMF) was heated in sealed glass ampoules in nitrogen atmosphere at 125°C for 20 or 60 min. A small amount of DMF was added to homogenize the reaction mixture. The resulting viscous reaction mixture was diluted with chloroform and poured into a 10-fold excess of ethanol. The obtained polymer products were reprecipitated with ethanol from chloroform solutions and dried in vacuum at room temperature. A 24-h extraction with cyclohexane followed to remove polystyrene formed by a spontaneous thermal homopolymer-

Table I   Spontaneous Thermal Copolymerization of Styrene (S) and *N*-Phenylmaleimide (PMI) at 125°C in the Presence of TEMPO[a]

Copolymer	F_{PMI}	f_{PMI}	Total Yield (%)	$M_n \times 10^{-3}$ [b]	M_w/M_n
C0[c]	0.4	0.46	78.8	49.5	4.43
C1	0.1	0.35	25.7	9.6	1.49
C1[d]	0.1	0.38	6.8	2.9	1.18
C2	0.2	0.42	37.3	12.3	1.60
C2[d]	0.2	0.41	30.5	4.6	1.33
C3	0.3	0.49	58.0	13.5	1.60
C3[e]	0.3	0.48	36.4	5.7	1.40
C4	0.4	0.50	72.7	14.8	1.65
C4[e]	0.4	0.48	52.4	5.6	1.42
C5	0.5	0.51	86.6	18.3	1.67
C5[e]	0.5	0.50	64.5	6.1	1.42
C6	0.6	0.54	68.4	14.6	1.70
C7	0.7	0.65	50.2	13.1	1.65

F_{PMI} and f_{PMI} are molar fractions of PMI in the feed and in the copolymer, respectively.
[a] 2×10^{-2} mol of comonomers, 0.5×10^{-4} mol of TEMPO, 45 min.
[b] The polystyrene-equivalent molecular weight of the copolymer determined by SEC.
[c] Without TEMPO; the mixture solidified after 3 min.
[d] 4×10^{-2} mol of comonomers, 3×10^{-4} mol of TEMPO, 30 min.
[e] 2×10^{-2} mol of comonomers, 1.5×10^{-4} mol of TEMPO, 30 min.

ization of styrene.[33] The characteristics of the products before and after the extraction are in Table IV.

Measurements

The yields of products were determined gravimetrically, the contents of both copolymers and low molecular weight compounds in samples after the first reprecipitation were evaluated using size-exclusion chromatography (SEC). The compositions of the S–PMI copolymers, low molecular weight adducts, and block copolymers were found

from nitrogen analysis. The structure of the adducts was studied using NMR spectroscopy.

SEC Measurements

The measurements were carried out on a PSS 10000 column (8 × 500 mm, Polymer Standard

Table II   Copolymerization of Styrene (S) and *N*-Phenylmaleimide (PMI) at 125°C in Xylene[a]

Copolymer	Total Yield (%)	$M_n \times 10^{-3}$ [b]	M_w/M_n
C8	80.5;0[c]	40.2	2.30
C9[d]	23.9	5.8	1.61
C10[e]	22.8	7.7	1.57

[a] 2×10^{-2} mol of comonomers (molar fraction of PMI in the feed = 0.4), 10 mL of xylene, 1 h.
[b] The polystyrene-equivalent molecular weight of the copolymer determined by SEC.
[c] 1.5×10^{-4} mol of TEMPO.
[d] 1.0×10^{-4} mol of dibenzoyl peroxide, 1.5×10^{-4} mol of TEMPO.
[e] 0.5×10^{-4} mol of TEMPO, 5 mL of xylene, 45 min.

Table III   Formation of Low Molecular Weight Compounds L1–L7 in the Spontaneous Thermal Copolymerization of Styrene (S) with *N*-Phenylmaleimide (PMI) at 125°C in the Presence of TEMPO (cf. Table I)[a]

Compound	F_{PMI}	A_1 [b] (%)	PMI/S[c]
L1	0.1	15.2	—
L2	0.2	19.1	—
L3	0.3	36.7; 24.1[d]	1.9
L4	0.4	41.7	2.0
L5	0.5	45.8	—
L6	0.6	55.7	2.0
L7	0.7	60.1	2.1

F_{PMI} and PMI/S are the molar fraction of PMI in the feed and the molar ratio of comonomer units in the low molecular weight compounds, respectively.
[a] 2×10^{-2} mol of comonomers, 0.5×10^{-4} mol of TEMPO, 45 min.
[b] The low molecular weight fraction determined by SEC; $M_n < 500$.
[c] From nitrogen analysis.
[d] 1.5×10^{-4} mol of TEMPO, 30 min.

Table IV Polymerization of Styrene Initiated with TEMPO-Terminated Styrene (S)–N-Phenylmaleimide (PMI) Copolymer Precursors[a]

Block Copolymer	Precursor[b]	Time (min)	Yield (g)	$M_n \times 10^{-4}$ [c]	M_w/M_n	[d]	[e]
						Nitrogen Content (%)	
BC1	C3	20	0.32	2.89	1.90	4.94	2.19
							2.21[f]
BC2	C9	60	0.70	3.94	1.55	4.79	1.24
							1.54[f]
BC3	C10	60	0.72	3.60	1.77	4.75	1.20
							1.41[f]

[a] 0.2 g of the precursor, 5 mL of styrene, 0.1 mL of *N,N*-dimethylformamide, 125°C.
[b] See Tables I and II.
[c] The polystyrene-equivalent molecular weight of the copolymer determined by SEC.
[d] In precursor.
[e] In block copolymer.
[f] After extraction with cyclohexane.

Service, Germany), filled with 5 μm sorbent particles. Tetrahydrofuran (Fluka), distilled and dried over molecular sieves (4 Å), was used as a mobile phase. The chromatographic data from refractometric and UV (254 nm) detectors in a series connection were evaluated using the Data-Monitor system (Watrex, Czech Republic). For the determination of molecular weights, a universal calibration equation calculated from the data on polystyrene standards (Merck, Germany) was used.

NMR Measurements

^{1}H- and ^{13}C-NMR spectra of a 10% w/w sample in CDCl$_3$ were measured at 300.13 and 75.45 MHz, respectively, with a Bruker Avance DPX 300 spectrometer using 32 kpoints and quadrature detection. ^{13}C APT, DEPT, and SSLR INEPT spectra were measured with the same number of points and with the evolution delays 7.35, 3.86, and 25 ms, respectively.

RESULTS AND DISCUSSION

TEMPO-Terminated Styrene–N-Phenylmaleimide Copolymers

On heating a mixture of styrene and *N*-phenylmaleimide in the presence of TEMPO radicals, a fast autopolymerization takes place (Table I). The total yield of isolated products reaches its maximum at $F_{PMI} = 0.5$, and decreases with increasing content of PMI in the feed. SEC revealed that the products consist of both copolymers and low molecular weight comonomer adducts. A typical eluogram is given in Figure 1. The adducts can be removed by a repeated reprecipitation of the products. Contrary to the uncontrolled autopolymerization without any added nitroxide giving the copolymer C0 with a high molecular weight (4.95×10^4) and a broad molecular weight distribution (4.43), TEMPO radicals distinctly moderate the reaction process. As a result, copolymers of markedly lower molecular weights and narrower distributions
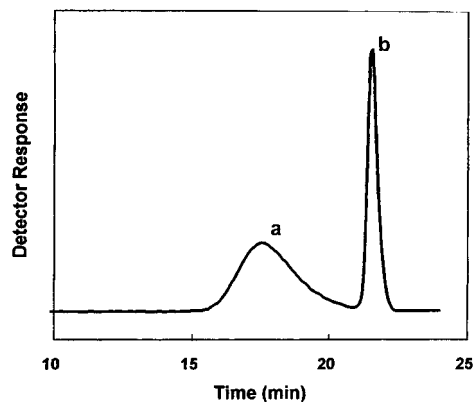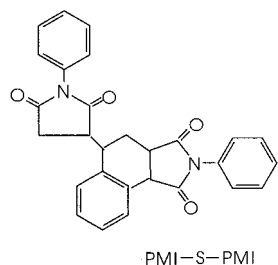

Figure 1 SEC curve of C5 (Table I) (a), and L5 (Table III) (b).
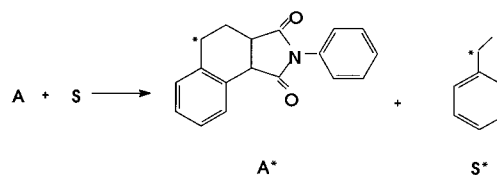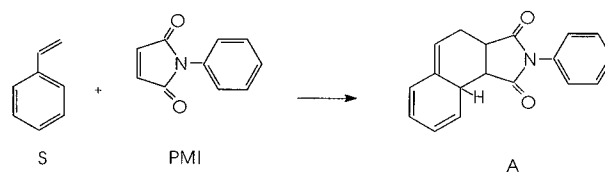
PMI−S−PMI

Scheme 1

Scheme 2

are formed. Their compositions suggest an alternating nature of the copolymerization. Both the molecular weights and molecular weight distributions were found to be reduced in autopolymerization at higher contents of TEMPO and at shorter reaction times. However, the analogous TEMPO-terminated styrene–N-butylmaleimide copolymers, which were prepared earlier under similar reaction conditions, showed better molecular weight distributions (about 1.3).[32] This indicates that in copolymerizations of styrene and N-phenylmaleimide, irreversible termination reactions occur to a larger extent.

The fast uncontrolled autopolymerization of styrene–N-phenylmaleimide mixtures proceeded also in xylene (copolymer C8, Table II). Due to the dilution of comonomers, the molecular weight and distribution of C8 (4.08×10^4 and 2.30, respectively) were lower than those of C0. Using 2 $\times 10^{-2}$ mol of comonomers, 1.5×10^{-4} mol of TEMPO, and 10 mL of xylene, no autopolymerization was observed, while at 0.5×10^{-4} mol of TEMPO and 5 mL of xylene, copolymer C10 ($M_n = 5.8 \times 10^3$, $M_w/M_n = 1.61$) was obtained. A copolymer (C9) of similar characteristics ($M_n = 7.7 \times 10^3$, $M_w/M_n = 1.57$) as C10 was prepared by the styrene–N-phenylmaleimide copolymerization in xylene initiated with the dibenzoyl peroxide (1×10^{-4} mol)–TEMPO (1.5×10^{-4} mol) system.

Comonomer Adducts

As mentioned above, the autopolymerization of styrene and N-phenylmaleimide is accompanied by a parallel addition reaction of the comonomers (Table III). The SEC measurements showed that the amounts of comonomer adducts increased with the increasing content of PMI in the initial reaction mixture. At $F_{PMI} = 0.6$ or 0.7, the low molecular weight compounds even predominated over copolymers. Their formation was a little reduced using a higher amount of TEMPO and a

shorter reaction time (cf. L3). According to the nitrogen analysis and NMR measurements, all the isolated compounds L3, L4, L6, and L7 corresponded to a trimer PMI-S-PMI. A detailed NMR study on the trimer showed[34] that it has constitution of N-phenyl-4-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-1,2,3,4-tetrahydronaphtalene-1,2-dicarboximide (Scheme 1).

Similar to the thermal autopolymerization of styrene,[35] an initial Diels-Alder reaction of styrene and N-phenylmaleimide giving the nonaromatized adduct, A, can be assumed (Scheme 2). The reaction of A with another molecule of styrene leads to radicals A* and S*. In the presence of TEMPO, the radicals can be captured to give the thermally unstable alkoxyamines A-TEMPO and S-TEMPO (Scheme 3). An addition of PMI to A-TEMPO followed by the reaction of a generated

A-TEMPO

S−TEMPO

Scheme 3

A—TE MPO + PMI ⇌ TE MPO

A-PMI—TE MPO
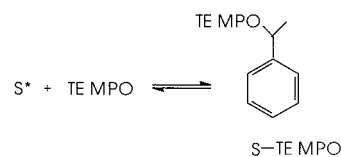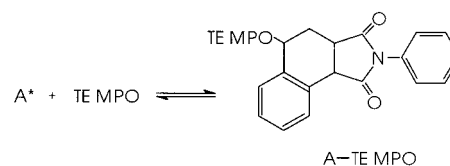
A—PMI—TE MPO + A ⇌ + A—TE MPO
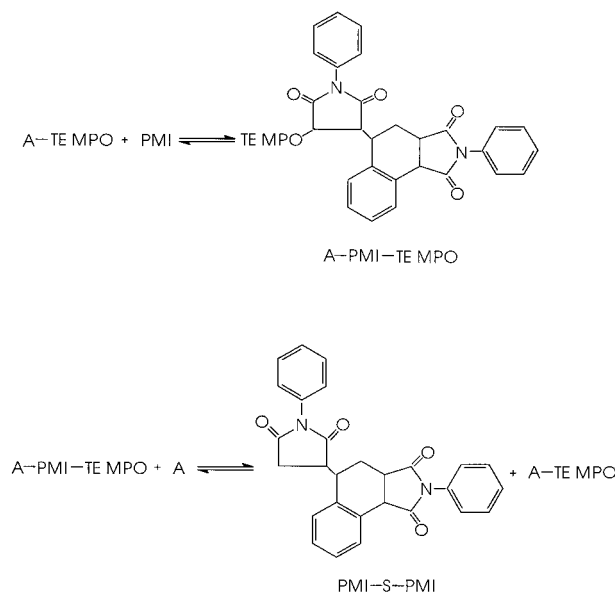
PMI—S—PMI

Scheme 4

alkoxyamine, A-PMI-TEMPO, with A may result in the formation of trimer PMI-S-PMI (Scheme 4).

Poly(styrene-*alt-N*-phenylmaleimide)-*block*-Polystyrene Copolymers

The polymerization of styrene at 125°C in the presence of TEMPO-terminated copolymers C3 (Table I), C9, or C10 (Table II) yielded polymer products of higher molecular weights and lower nitrogen contents than those of the initial precursors (Table IV). Evidently, poly(styrene-*alt-N*-phenylmaleimide)-*block*-polystyrene block copolymers (BC1–BC3) were obtained.

In a SEC curve of BC1, almost identical with that after its extraction with cyclohexane, a low molecular weight tail was observed (Fig. 2). A similar tailing also appeared for BC2 and BC3. A slightly increased nitrogen content in the extracted BC2 and BC3 copolymers rather than hardly detectable changes in the corresponding SEC curves indicated that some polystyrene was removed. Irreversible termination reactions of growing chains obviously take place in the block copolymer syntheses. Besides, the precursor chains containing TEMPO groups bound to terminal *N*-phenylmaleimide units are probably less efficient the broadening of the molecular weight distribution being associated with their presence in the resulting block copolymers.

Using C9 and C10 precursors, block copolymers of similar characteristics were prepared. Under the well-founded assumption that all C9

chains bear one benzoyloxy and one TEMPO end group from the initiation and termination reaction, respectively,[3] both C9 and C10 (the latter being synthesized by autopolymerization) can be regarded as monofunctional macroinitiators. This conclusion is in agreement with the proposed formation of alkoxyamines in the autopolymerization process (Scheme 3). They contain latent monofunctional initiating centers, and, consequently, diblock copolymers are generated under given conditions.

CONCLUSIONS

Styrene (S) and *N*-phenylmaleimide (PMI) undergo copolymerization accompanied by an addition reaction at 125°C in the presence of TEMPO. The molecular weight distributions of the virtually alternating TEMPO-terminated S–PMI copolymers ($\approx$1.65) were markedly lower than those of the copolymers prepared in the absence of TEMPO (4.43 or 2.30). A higher TEMPO concentration and a shorter reaction time led to a decrease in molecular weights and their distributions. The amounts of comonomer adducts increased with the increasing content of PMI in the feed. At $F_{PMI} \geq 0.6$, the addition reaction even predominated over copolymerization. A Diels-Alder adduct of the comonomers and monofunctional unimolecular initiators are assumed to take part in the reaction. Using the S-PMI copolymers containing TEMPO end groups for initiation of polymerization of styrene, poly(styrene-*alt-N*-phenylmaleimide)-*block*-polystyrene copol-
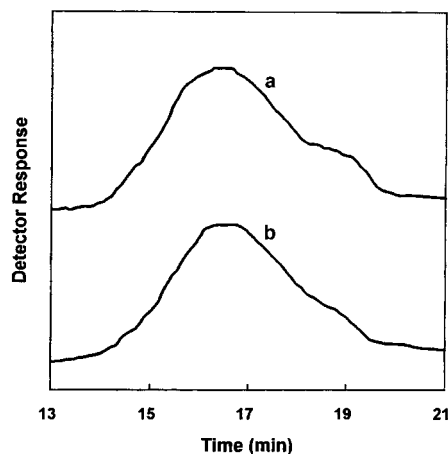

Figure 2 SEC curves of BC1 (Table IV) before (a), and after extraction with cyclohexane (b).

ymers were prepared. Both low molecular weight termination products and some precursor chains broaden molecular weight distributions of the synthesized block copolymers.

REFERENCES

1. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 2987.
2. Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K.; Macromolecules 1993, 26, 5316.
3. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Trends Polym Sci 1994, 2, 66.
4. Greszta, D.; Mardare, D.; Matyjaszewski, K. Macromolecules 1994, 27, 638.
5. Gaynor, S.; Greszta, D.; Mardare, D.; Teodorescu, M.; Matyjaszewski, K.; J Macromol Sci Pure Appl Chem 1994, 31, 1561.
6. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. Macromolecules 1994, 27, 7228.
7. Hawker, C. J.; Hedrick, J. L. Macromolecules 1995, 28, 2993.
8. Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. Macromolecules 1995, 28, 4391.
9. Keoskerian, B.; Georges, M. K.; Boies-Boissier, D. Macromolecules 1995, 28, 6381.
10. Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Brousmiche, D.; Georges, M. K. Macromolecules 1995, 28, 8453.
11. Hawker, C. J.; Elce, E.; Dao, J.; Volksen, W.; Russell, T. P.; Barclay, G. G. Macromolecules 1996, 29, 2686.
12. Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. Macromolecules 1996, 29, 2746.
13. Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. Macromolecules 1996, 29, 4161.
14. Kazmaier, P. M.; Daimon, K.; Georges, M. K.; Hamer, G. K.; Veregin, R. P. N. Macromolecules 1997, 30, 2228.
15. Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Georges, M. K. Macromolecules 1997, 30, 2232.
16. Goto, A.; Fukuda, T. Macromolecules 1997, 30, 4272.
17. Goto, A.; Fukuda T. Macromolecules 1997, 30, 5183.
18. Lokaj, J.; Vlček, P.; Kříž, J. Macromolecules 1997, 30, 7644.
19. Ohno, K.; Ejaz, M.; Fukuda, T.; Miyamoto, T.; Shimizu, Y. Macromol Chem Phys 1998, 199, 291.
20. Ohno, K.; Tsujii, Y.; Miyamoto, T.; Fukuda, T.; Goto, M.; Kobayashi, K.; Akaike, T. Macromolecules 1998, 31, 1064.
21. Wendler, U.; Bohrisch, J.; Jaeger, W.; Rother, G.; Dautzenberg, H. Macromol Rapid Commun 1998, 19, 185.
22. Georges, M. K.; Hamer, G. K.; Listigovers, N. A. Macromolecules 1998, 31, 9087.
23. Malmström, E. E.;Hawker, C. J. Macromol Chem Phys 1998, 199, 923.
24. Ide; N.; Fukuda, T. Macromolecules 1999, 32, 95.
25. Hawker, C. J. J Am Chem Soc 1994, 116, 11185.
26. Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. Macromolecules 1996, 29, 5245.
27. Wang, D.; Wu, Z. Macromolecules 1998, 31, 6727.
28. Georges, M. K.; Kee, R. K.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. J Phys Org Chem 1995, 8, 301.
29. Greszta, D.; Matyjaszewski, K. Macromolecules 1996, 29, 7661.
30. Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T.; Shimizu, Y. Macromolecules 1996, 29, 3050.
31. Devonport, W.; Michalak, L.; Malmström, E.; Mate, M.; Kurdi, B.; Hawker, C. J.; Barclay, G. G.; Sinta, R. Macromolecules 1997, 30, 1929.
32. Lokaj, J.; Vlček, P.; Kříž, J. J Appl Polym Sci 1999, 74, 2378.
33. Lokaj, J.; Bouchal, K.; Konečný, D.; J Appl Polym Sci 1996, 62, 1129.
34. Kříž, J.; Lokaj, J.; Kurková, D.; Holler, P. Macromolecules, submitted.
35. Mayo, F. R. J Am Chem Soc 1968, 90, 1289.