Synthesis of Well-Defined Alternating Copolymers Poly(methyl methacrylate-*alt*-styrene) by RAFT Polymerization in the Presence of Lewis Acid

Betül Kırcı, Jean-François Lutz, and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University,
4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received November 13, 2001

Introduction. Controlled/“living” radical polymerizations allow complex macromolecular architectures to be synthesized. Numerous examples of star, block, graft, comb, and brush copolymers made by atom transfer radical polymerization (ATRP), reversible addition−fragmentation transfer polymerization (RAFT), or nitroxide-mediated polymerization (NMP) have been reported.[1,2]

However, only a few studies describe the synthesis of copolymers possessing controlled sequences (gradient or alternating copolymers) by controlled/“living” radical polymerization, even though such structures could open a new avenue for the production of novel materials. Several gradient copolymers have been synthesized by ATRP.[3] Only a few alternating copolymers from comonomers that have a spontaneous tendency for alternation have been synthesized by ATRP,[4−6] RAFT,[7] or NMP.[8] However, the synthesis of alternating copolymers by controlled/“living” radical polymerization from monomers without this tendency has not yet been reported.

During the 1960s and 1970s, several studies reported the synthesis of alternating copolymers.[9] Acrylic monomers and styrene, which usually copolymerize randomly, may be copolymerized in an alternating fashion in the presence of Lewis acids.[10,11] Although the precise mechanism of this copolymerization is not yet fully understood, it seems that the alternating behavior is due to the formation of a complex between the acrylic monomer and the Lewis acids which is unable to self-propagate and strongly enhances the cross-propagation. However, no control of molecular weight and polydispersity was possible in these systems.

This communication describes the synthesis of controlled/“living” alternating copolymers of methyl methacrylate (M) with styrene (S) in the presence of diethylaluminum chloride by RAFT.[12] (The RAFT technique was chosen, since it provides smaller interference with Lewis acids than ATRP or NMP.) This new system controls the molecular weight, polydispersity, and the comonomer sequences. To show the superior control of this system, the kinetic behavior and the microstructure of the synthesized polymer have been compared to those obtained in a RAFT copolymerization without Et_2AlCl and in a conventional radical copolymerization in the presence of Et_2AlCl.

Experimental Part. a. Polymerization Conditions in the Presence of Lewis Acid. In a glovebox, dried methyl methacrylate (1.86 g, 18.6 mmol) and diethylaluminum chloride (0.89 g, 7.4 mmol) were added to a Schlenk flask. The mixture was stirred for 4 h in order to preform the complex between both reagents. Then, a degassed solution of 2,2′-azobis(isobutyronitrile) (AIBN) (1.63 mg, 0.0099 mmol) and optionally added cumyl dithiobenzoate (CDB) (27 mg, 0.099 mmol) dissolved in dried styrene (1.93 g, 18.6 mmol) was introduced via a degassed syringe. The mixture was thermostated at 60 °C, and samples were withdrawn through a degassed syringe at timed intervals. Monomer conversion was determined by gravimetry analysis on crude samples. Average molecular weight and polydispersities were measured by size exclusion chromatography calibrated with poly(methyl methacrylate) standards.

b. Polymerization Conditions in the Absence of Lewis Acid. Methyl methacrylate (1.86 g, 18.6 mmol), styrene (1,93 g, 18.6 mmol), 2,2′-azobis(isobutyronitrile) (1.6 mg, 0.0099 mmol), and cumyl dithiobenzoate (27 mg, 0.099 mmol) were added to a dry Schlenk flask. The mixture was thoroughly purged by nitrogen flushing and then heated at 60 °C. Analysis conditions were the same as described above.

Results and Discussion. Three polymerization systems were compared in this study: RAFT polymerization (system A), conventional radical polymerization in the presence of Et_2AlCl (system B), and RAFT polymerization in the presence of Et_2AlCl (system C). Table 1 (entries 1−5) shows the molar ratios between the compounds used in the polymerizations. In the following discussion, the kinetic behavior of these three polymerization systems will be first analyzed. Then, the ^1H NMR analysis of the microstructure of the synthesized copolymers will be compared.

All the reactions were stopped when the copolymerization mixture became glassy. Table 1 (entries 6−10) shows the overall final monomer conversion, final average molecular weights, and polydispersities for the three studied systems. The final molecular weights of both RAFT systems A and C are close to the expected theoretical values and polydispersity indexes are less than 1.5, indicating controlled/“living” behavior. On the other hand, for system B, as expected for a conventional radical process, very high molecular weights and high polydispersity ($M_w/M_n > 2$) were observed. These results indicate that only systems A and C allow one to synthesize P(M-*co*-S) copolymers with predetermined molecular weights and low polydispersities.

Figure 1a compares the plots of molecular weights M_n and polydispersities M_w/M_n vs conversion for systems A and C. In both cases, the molecular weight increases linearly with conversion, and the experimental values are close to the theoretical ones, assuming quantitative initiation. This behavior shows that the RAFT copolymerization of methyl methacrylate and styrene is controlled in both the absence and presence of Et_2AlCl. However, the polydispersity index is higher for system C than system A. In the presence of Et_2AlCl, cumyl dithiobenzoate end groups may also be complexed with the Lewis acid, as evidenced by the formation of an intense orange color. This complexation, due to steric and electronic effects, could reduce the rate of the exchange process, which may partially explain the increased polydispersity.

---

* Corresponding author. Fax 412 268 6897; e-mail km3b@andrew.cmu.edu.

10.1021/ma011986f CCC: $22.00 © 2002 American Chemical Society
Published on Web 02/22/2002

Table 1. Initial Molar Ratios of All Reagents and Final Experimental Results

		system A (RAFT)	system B (Lewis acid)	system C (RAFT/Lewis acid)
1	methyl methacrylate	190	190	190
2	diethylaluminum chloride	–	75	75
3	styrene	190	190	190
4	2,2′-azobis(isobutyronitrile)	0.1	0.1	0.1
5	cumyl dithiobenzoate	1		1
6	time (h)	73	0.8	1.6
7	final overall monomer conversion (%)	63	60	62.5
8	M_n experimental (g mol^{-1})	21600	112000	20000
9	M_w/M_n	1.14	2.70	1.38
10	M_n theoretical[a] (g mol^{-1})	20300	–	20200
11	F_x	0.499	0.272	0.259
12	F_y	0.404	0.478	0.497
13	F_z	0.096	0.249	0.244
14	σ	0.43	0.52	0.53
15	F_{SMS} (%)	52	92	87
16	F_{MMS} (%)	17	2	6
17	F_{MMM} (%)	14	4	1

[a] M_n theoretical = $([M]_0 + [S]_0)(conv)(104.15 + 100)/(2(2[AIBN]_0 + [CDB]_0))$.

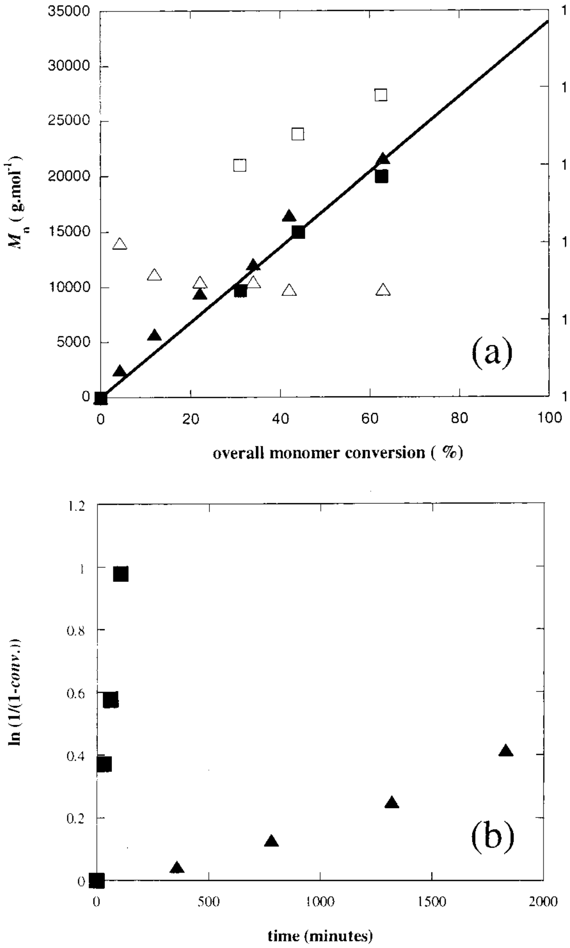

Figure 1. (a) Number-average molecular weight M_n (black symbols) and polydispersity index M_w/M_n (white symbols) as a function of overall monomer conversion (conv) **(b)** ln(1/(1 − conv)) vs time for the bulk copolymerization of methyl methacrylate and styrene at 60 °C: $[S]_0 = 3.67$ mol L^{-1}; $[M]_0 = 3.67$ mol L^{-1}; $[AIBN]_0 = 1.96 \times 10^{-3}$ mol L^{-1}; $[CDB]_0 = 1.96 \times 10^{-2}$ mol L^{-1}; $[Et_2AlCl] = 0$ mol L^{-1} (▲, △) (system A), 1.47 mol L^{-1} (■, □) (system C). Theoretical $M_n = ([M]_0 + [S]_0)(conv)(104.15 + 100)/(2(2[AIBN]_0 + [CDB]_0))$.

Semilogarithmic curves of conversion with time are plotted for systems A and C (Figure 1b). Comparison of the slopes of the curves indicates that the rate of polymerization of system C is about 40 times higher than that of system A. This is because the values of the cross-propagation rate constants in the presence of Et_2AlCl are markedly higher than in the absence of Et_2AlCl. Sigwalt et al.[13] have shown that the addition rate constant of the complex methyl methacrylate/Lewis acid onto the styryl radical ($k_{S-MC} = 2600$ L mol^{-1} s^{-1}) at 20 °C is about 40 times higher than that of methyl methacrylate ($k_{S-M} = 70$ L mol^{-1} s^{-1}). The rate constant of addition of styrene to the complexed methacrylic radical (k_{MC-S}) has not been precisely determined but could also be higher than the rate constant of addition of styrene to methacrylic radicals (k_{M-S}). Consequently, the ratio of the rate constant of propagation to that of exchange is higher for system C than system A, which may additionally explain the enhancement of polydispersity observed for system C.[14] However, although the kinetic behavior of systems A and C is different, both copolymerizations of methyl methacrylate and styrene are controlled.

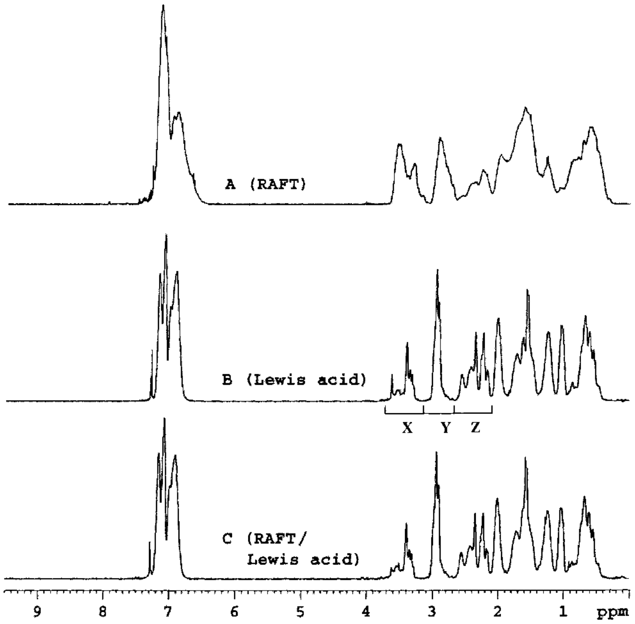

Figure 2. 600 MHz ^{1}H NMR spectra of copolymers P(M-*co*-S) in $CDCl_3$ at 28 °C.

Figure 2 compares the ^{1}H NMR spectra of the copolymers P(M-*co*-S) synthesized via systems A, B, and C. According to the literature,[15−17] the region from 3.7 to 2.1 ppm is due to the poly(methyl methacrylate) methoxy protons. This range can be subdivided into three subregions 3.7−3.2 ppm (X), 3.2−2.7 ppm (Y), and 2.7−2.1 ppm (Z), which are respectively representative of the M-centered triads with none, one, and two meso MS diads.[15,16] The fractions of the various M-centered triads (MMM (homopolymer), MMS/SMM (random), SMS (alternating)) may be correlated to the fractions of the areas X, Y, and Z of the methoxy resonance of the copolymer (eqs 1−3).[18]

$$F_x = F_{MMM} + 2(1 - \sigma)F_{MMS} + (1 - \sigma)^2 F_{SMS} \quad (1)$$

$$F_y = 2\sigma F_{MMS} + 2\sigma(1 - \sigma)F_{SMS} \quad (2)$$

$$F_z = \sigma^2 F_{SMS} \quad (3)$$

Here σ represents the probability of alternating M and S units having the same "coisotactic" configurations, with the assumption that σ is constant regardless of the sequence of addition (i.e., $\sigma = \sigma_{MS} = \sigma_{SM}$). San Román et al.[19] have shown that σ may be calculated from eq 4,

$$\sigma = (1 - F_x^{1/2})(1 + r_M)(F_M/F_S) \quad (4)$$

where r_M is the reactivity ratio of the methacrylic radical, F_M is the mole fraction of methyl methacrylate in the copolymer, and F_S is the mole fraction of styrene in the copolymer.

Table 1 (entries 11−14) shows the value of F_x, F_y, and F_z and σ for systems A, B, and C. The areas X and Y can be determined by direct integration of the NMR spectra with measurement errors less than 1%. Because of overlap with the methine region, area Z cannot be measured by integration. O'Driscoll et al.[20] have shown that the area Z can be calculated by using eq 5.

$$\text{area Z} = (3/8)(F_M)(\text{total area of the spectra}) - \text{area X} - \text{area Y} \quad (5)$$

The monomer compositions of the copolymer F_M and F_S were determined by elemental analysis and were both equal to 0.5 in all cases. The reactivity ratio r_M is equal to 0.08 in the presence of Et_2AlCl[21] and 0.47 in its absence.[22]

The values of F_x, F_y, and F_z and σ were used to calculate the fractions of the M-centered triads (Table 1, entries 15−17) from eqs 1−3. For system A, the proportion of random triads MMS/SMM ($2F_{MMS}$) is equal to 34%. This behavior indicates that in the absence of Lewis acid the synthesized copolymer has a low tendency to alternate. On the other hand, the predominant structure of systems B and C is the alternating triad SMS, with values of 92% and 87%, respectively. The copolymers synthesized in the presence of Et_2AlCl are predominantly alternating. In the presence of Lewis acid, system C produces alternating copolymers P(M-*alt*-S) nearly as efficiently as the conventional radical polymerization process (system B).

The microstructure of the copolymer can be qualitatively evaluated from the expanded region X.[16] Inside this region (Figure 3), it is possible to distinguish three signals: a signal from 3.25 to 3.44 ppm due to the alternate triad SMS, a signal from 3.44 to 3.58 ppm due to the random triad MMS, and a signal from 3.58 to 3.65 ppm due to the homopolymer triad MMM. The signals inside region X are broad for system A. This behavior indicates that in the absence of Lewis acid the copolymer contains all triads. On the other hand, for system B and C, inside the range 3.7−3.2 ppm, although it is possible to distinguish all three previously described peaks, the most intense peaks are due to the alternating triad SMS.

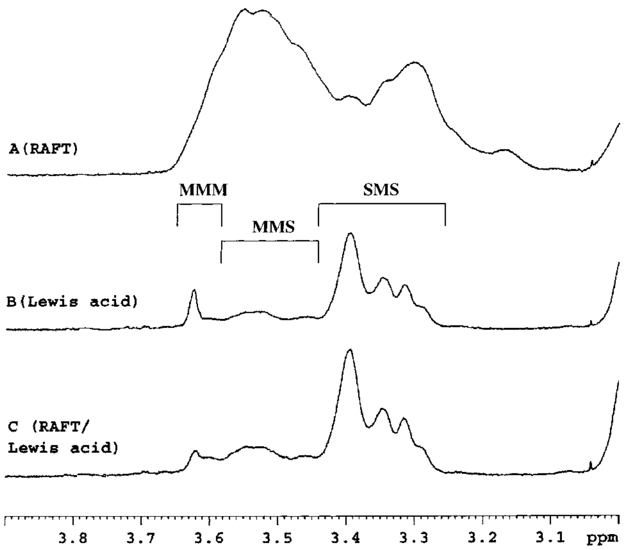

Figure 3. Expansion of the region X of the 600 MHz ^1H NMR spectra of copolymers P(M-*co*-S) in $CDCl_3$ at 28 °C.

In conclusion, RAFT copolymerization in the presence of a Lewis acid (system C) produces well-defined alternating copolymers P(M-*alt*-S), whereas RAFT copolymerization alone (system A) only controls the chain length and polydispersity, and standard radical copolymerization in the presence of Lewis acids (system B) only controls the comonomer sequences. System C can be applied to other Lewis acids and to various monomers. These results will be reported in more details in a forthcoming paper.

Acknowledgment. The authors thank the National Science Foundation (DMR-0090409) and the members of the CRP Consortium at Carnegie Mellon University for financial support and Virgil Simplaceanu for the NMR measurements.

References and Notes

(1) Matyjaszewski, K., Ed.; *Controlled Radical Polymerization*; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998.
(2) Matyjaszewski, K., Ed.; *Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT*; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000.
(3) Matyjaszewski, K.; Ziegler, M. J.; Arehart, S. V.; Greszta, D.; Pakula, T. *J. Phys. Org. Chem.* **2000**, *13*, 775−786.
(4) Coca, S.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37*, 573−574.
(5) Gaynor, S. G.; Matyjaszewski, K. *ACS Symp. Ser.* **1998**, *685*, 396.
(6) Chen, G.-Q.; Wu, Z.-Q.; Wu, J.-R.; Li, Z.-C.; Li, F.-M. *Macromolecules* **2000**, *33*, 232−234.
(7) De Brouwer, H.; Schellekens, M. A. J.; Klumperman, B.; Monteiro, M. J.; German, A. L. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3596−3603.
(8) Benoit, D.; Hawker, C. J.; Huang, E. E.; Lin, Z.; Russell, T. P. *Macromolecules* **2000**, *33*, 1505−1507.
(9) Cowie, J. M. G., Ed.; *Alternating Copolymers*; 1985.
(10) Hirai, H. *J. Polym. Sci., Macromol. Rev.* **1976**, *11*, 47−91.
(11) Afchar-Momtaz, J.; Polton, A.; Tardi, M.; Sigwalt, P. *Eur. Polym. J.* **1985**, *21*, 583−589.
(12) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C.

L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.
(13) Afchar-Momtaz, J.; Polton, A.; Tardi, M.; Sigwalt, P. *Eur. Polym. J.* **1985**, *21*, 1067−1073.
(14) Goto, A.; Sato, K.; Tsujii, Y.; Fukuda, T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2001**, *34*, 402−408.
(15) Ito, K.; Yamashita, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 625−630.
(16) Hirai, H.; Tanabe, T.; Koinuma, H. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 843−857.
(17) Aerdts, A. M.; de Haan, J. W.; German, A. L. *Macromolecules* **1993**, *26*, 1965−1971.
(18) Ito, K.; Iwase, S.; Umehara, K.; Yamashita, Y. *J. Macromol. Sci., Part A* **1967**, *1*, 891−908.
(19) San Roman, J.; Madruga, E. L.; Del Puerto, M. A. *Angew. Makromol. Chem.* **1979**, *78*, 129−143.
(20) Kale, L. T.; O'Driscoll, K. F.; Dinan, F. J.; Uebel, J. J. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 3145−3149.
(21) Rogueda, C.; Tardi, M.; Polton, A.; Sigwalt, P. *Eur. Polym. J.* **1989**, *25*, 885−889.
(22) Brandrup, J., Immergut, E. H., Eds.; *Polymer Handbook*, 4th ed.; 1998.

MA011986F