Synthesis of Alternating Copolymers of N-Substituted Maleimides with Styrene via Atom Transfer Radical Polymerization

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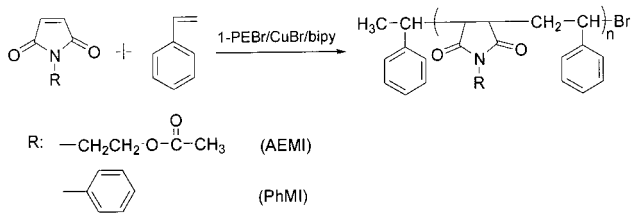
Introduction. As a novel precision polymerization, atom transfer radical polymerization (ATRP) has received rapidly increased interest recently, since it furnishes control over the resulting polymers, which possess narrower molecular weight distributions.[1,2] The merit of the ATRP system is that it can be performed by an ordinary radical polymerization procedure. A general ATRP catalyst is composed of a simple alkyl halide as an initiator and a copper(I)−bipyridine complex as a catalyst. The mechanism of ATRP is shown to be a reversible homolytic cleavage of a carbon−halogen bond catalyzed by a transition metal in the form of a complex. Many vinyl monomers were successfully demonstrated by ATRP to be usable for the preparation of traditional homopolymers, random copolymers, block/graft copolymers, and gradient copolymers. In addition, ATRP also shows its potential in the synthesis of a variety of new well-defined macromolecular architectures such as comb,[3] star, and dendritic macromolecules.[4] However, reports on the synthesis of well-defined alternating copolymers via ATRP are scarce.[5]

It is well-known that an alternating copolymer can be easily obtained by the copolymerization of an electron-rich monomer and an electron-deficient monomer through the formation of charge transfer complexes (CTCs). One of the extensively studied systems is maleic anhydride (MAn) and styrene (St). The polymerization can be initiated by radical initiators such as AIBN or by UV light irradiation, but the polymerization process is uncontrollable.[6,7] Therefore, whether a controllable alternating copolymerization of CTCs forming a monomer pair takes place by ATRP is of concern. Matyjaszewski et al. reported on the copolymerization of donor monomers such as isobutene and vinyl isobutyl ether with acceptor monomers such as butyl acrylate via ATRP, showing that the polymerization was controllable.[8] In this article, the copolymerization of styrene (St) with N-substituted maleimides, i.e., *N*-(2-acetoxyethyl) maleimide (AEMI) and *N*-phenylmaleimide (PhMI), by ATRP have been reported aiming to evaluate whether the CTCs forming a monomer pair takes place by controllable/"living" copolymerization and whether the resulting copolymers possess the predominantly alternating structure.

Experimental Section. Materials. *N*-(2-Acetoxyethyl)maleimide (AEMI), mp 77−78 °C (lit. mp 79 °C)[9], *N*-phenylmaleimide (PhMI), mp 88.5−89.5 °C (lit. mp 89−89.8 °C),[10] and 1-phenylethyl bromide (1-PEBr), n_D^{20} = 1.5614 (lit. n_D^{20} 1.5600)[11] were prepared according to the literature. Styrene (St; AR; Beijing Chemicals Co.) was distilled under reduced pressure. Maleic anhydride (MAn; AR; Lushun Chemicals Co.) was recrystallized from benzene. CuBr (CP; Beijing Chemicals Co.) was purified by subsequently washing with acetic acid and ethanol and then dried in vacuo. 2,2′-Bipyridine (bipy; AR; Beijing Chemicals Co.) and other reagents were used as received.

Scheme 1



Atom Transfer Radical Polymerization. The bulk polymerization was conducted in a sealed glass tube. A representative feed was AEMI (or PhMI):St:1-PEBr:CuBr:bipy = 50:50:1:1:2 (in molar ratio). After the mixture was degassed three times, the tube was sealed under vacuum and then was kept in an oil bath at 80 °C to conduct the polymerization. After an interval of time, $CHCl_3$ was added to stop the polymerization. The polymer was obtained by precipitation from methanol. The crude products were dissolved in $CHCl_3$ again; the $CHCl_3$ solution was passed through a silica column to remove the catalyst. The polymer was recovered by precipitating it from a large excess of methanol and then dried under vacuum at 60 °C. The polymers obtained were white fine powders.

Thermal Polymerization. The bulk polymerization was conducted at 80 °C in a sealed glass tube. The monomer feed was AEMI (or PhMI):St = 1:1 (in molar ratio). The entire procedure is similar to that of ATRP.

Characterization. The polymerization kinetics was pursued gravimetrically. The molecular weight and molecular weight distribution were measured on a Waters 150-C gel permeation chromatography equipped with three Ultrastyragel columns (1×10^4, 1×10^3, and 500 Å pore sizes) at room temperature. THF was used as an eluent and polystyrene standards were used as calibrations.

The copolymer composition was determined by analyzing the nitrogen content.

Results and Discussion. MAn and St are one of the extensively studied monomer pairs for the exploration of alternating copolymerization.[6] It was recognized that a CTC was formed between MAn and St; when it was initiated with radical initiators such as AIBN or BPO, a copolymer with predominantly alternating structure can be obtained even though the feed molar ratios of monomer pairs are not in equimolar.

We tried the copolymerization of MAn and St by the general procedure of ATRP, but the polymerization did not take place. This maybe ascribed to the reaction of MAn with a component of the ATRP catalyst such as Cu(I) or/and 2,2′-pyridine. Instead of MAn, N-substituted maleimides, e.g. AEMI and PhMI, are not as likely to react with the components of the ATRP catalytic system under the polymerization conditions. The structures are illustrated in Scheme 1.

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Table 1. Molecular Weight, Molecular Weight Distribution, and Composition of AEMI−St and PhMI−St Copolymers Obtained by ATRP[a]

copolymer	time (h)	yield (%)	M_n(theory)	M_n[b](found)	M_w/M_n[b]	nitrogen content (%)	AEMI or PhMI in copolymer (mol %)[d]
AEMI−St-1	0.33	32.1	4600	6600	1.18	4.61	47.2
AEMI−St-2	1.0	70.2	10000	12500	1.25	4.73	48.5
AEMI−St-3[c]	0.5	93.5		gel	gel	4.82	49.4
PhMI−St-1	3.0	23.1	3200	3500	1.26	4.75	47.0
PhMI−St-2	10	61.4	8500	7400	1.16	4.95	49.0
PhMI−St-3[c]	2.5	96.0		1.0×10^7	2.10	5.01	49.6

[a] $[monomers]_0:[1\text{-PEBr}]:[CuBr]:[bipy] = 100:1:1:2$; 80 °C. [b] Via GPC in THF at room temperature. [c] Thermal polymerization; the monomer feed is 1:1(molar ratio), at 80 °C. [d] Calculated based on the nitrogen content from the elemental analysis.

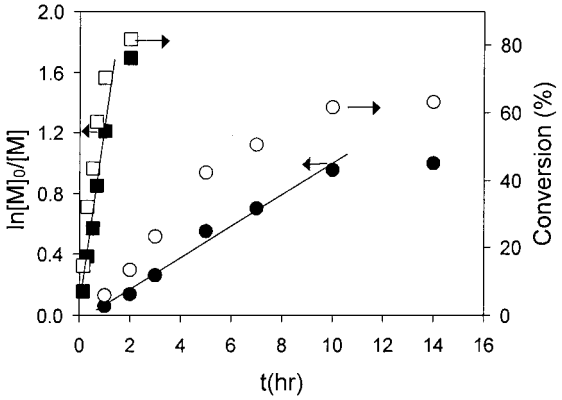

Figure 1. Kinetics of the copolymerization of AEMI and PhMI with St by ATRP$[AEMI]_0$ or $[PhMI]_0:[St]_0:[1\text{-PEBr}]:[CuBr]:[bipy] = 50:50:1:1:2$, at 80 °C (■ and □, AEMI; ● and ○, PhMI).

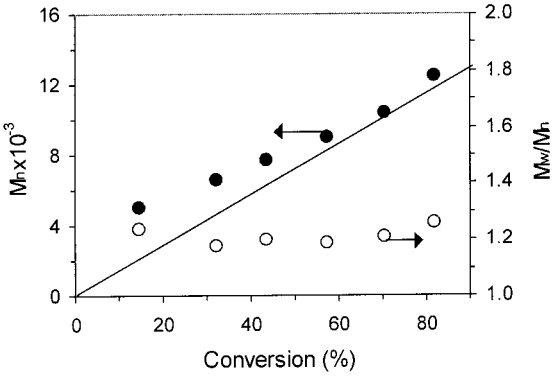

Figure 2. M_n and M_w/M_n vs polymerization conversion plot for the copolymerization of AEMI with St by ATRP$[AEMI]_0:[St]_0:[1\text{-PEBr}]:[CuBr]:[bipy] = 50:50:1:1:2$, 80 °C.

Both AEMI and PhMI dissolve well in St at 80 °C in equimolar amounts. The complex of Cu(I) and bipy also dissolves in the polymerization system at 80 °C with a dark brown color and a red brown color for AEMI and PhMI, respectively, but a trace of CuBr always remained as a residue in the polymerization system.

The copolymerization of AEMI with St took place smoothly by ATRP. The plot shown in Figure 1 is the relationship between the polymerization conversion and time for the copolymerization of St with AEMI and PhMI initiated by the PEBr−Cu^IBr−bipy catalytic system. A linear relationship between $\ln([M]_0/[M])$ and polymerization time is preserved until a higher polymerization conversion of 60−70% is reached, which indicates that the polymerization kinetics is of first-order nature. This means that the numbers of active species keep constant during the copolymerization of St with AEMI or PhMI via ATRP. From Figure 1, it can also be seen that the copolymerization rate of AEMI with St is faster than that of PhMI with St. This may be attributed to the fact that the solubility of Cu(I)−bipy complex in the AEMI−St system is higher than that in the PhMI−St system.

Figure 2 shows the plots of number-average molecular weight (M_n) or molecular weight distribution (M_w/M_n) vs polymerization conversion for the copolymerization of St with AEMI. For ATRP of PhMI and St, similar plots have been obtained. It is seen that the plot of M_n determined by GPC against the polymerization conversion is nearly a linear relationship and matches the theoretical calculated M_n. This indicates that the anticipated average molecular weight of P(AEMI-*co*-St) or P(PhMI-*co*-St) can be controlled by terminating the polymerization on an appropriate polymerization conversion. It is seen that the M_n vs polymerization conversion plot deviates from linearity, especially at lower polymerization conversion, which maybe due to low initiator efficiency or the gel effect caused by the rapidly increased viscosity of the polymerization system at higher conversions.[12] It is also seen that P(AEMI-*co*-St) possesses a narrow molecular weight distribution (M_w/M_n) in the range 1.16−1.36. The observation of the copolymerization kinetics together with the linear evolution of molecular weight vs polymerization conversion suggests that the contribution of chain breaking and transfer as well as termination reactions during the copolymerization can be neglected until higher polymerization conversion. This result supports the conclusion that the copolymerization process of AEMI and PhMI with St initiated by ATRP catalyst is controllable and of a "living" polymerization nature.

In comparison, the thermal copolymerization of AEMI and PhMI with St at 80 °C in the absence of the PEBr−Cu(I)−bipy catalytic system was also demonstrated. Table 1 summarized the related results. It can be seen that the copolymer PhMI−St-3, obtained by ordinary thermal radical initiation, possesses a higher molecular weight up to 1.0×10^7 with a broader M_w/M_n of 2.1, whereas the M_w/M_n of PhMI−St-1 and PhMI−St-2 copolymers obtained by ATRP was as narrower as 1.3. As regards to the sample of AEMI−St-3 obtained by a thermal polymerization, it was not soluble in THF or chloroform at room temperature, which implies that the copolymer is a cross-linked one. This was attributed to a chain transfer reaction occurring on the methyl group of acetyl moiety of AEMI monomer. The fact that no obvious gelation was observed for ATRP of AEMI and St may be attributed to the low conversion of the monomers and low molecular weights of the resulting copolymers. This result might also imply that the ATRP polymerization of AEMI and St can be controlled at least better than the thermal polymerization.

It can be seen from Table 1 that the compositions of the copolymers obtained via ATRP are always close to 1:1 in equimolar comonomer feed at different polymer-

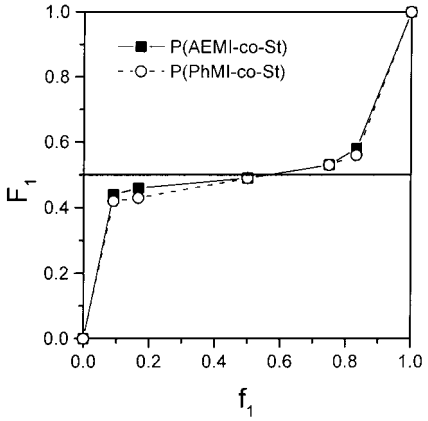

Figure 3. Relationship between the comonomer feed and the composition of AEMI−St and PhMI−St copolymers for polymerization via ATRP, $[\text{monomers}]_0$:[1-PEBr]:[CuBr]:[bipy] = 100:1:1:2, at 80 °C.

ization conversions. To further clarify that the AEMI−St and PhMI−St copolymers possess an alternating structure, the copolymerization of AEMI and PhMI with St at different comonomer feeds was undertaken. Figure 3 shows the relationship between the monomer feed and the composition of the copolymers obtained at lower conversion. The result shows that the copolymers possess a predominantly alternating structure in a large range of the monomer feeds. Thus, the copolymers obtained by ATRP at different molar ratios of comonomer feeds possess an alternating structure.

In conclusion, controlled/"living" ATRP of AEMI and PhMI with St has been successfully carried out using a PEBr/Cu^{I}Br/bipy catalytic system. The copolymers obtained possess a designed molecular weight with narrow molecular weight distribution. The copolymers are predominantly alternating in structure clarified by classical method. The transition-metal-mediated copolymerization of other CTC-forming monomer pairs is underway.

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References and Notes

(1) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(2) Matyjaszewski, K.; Wang, J. S. *Macromolecules* **1995**, *28*, 7901.
(3) Husseman, M.; Malmström, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424.
(4) Hedrich, J. L.; Trollsås, M.; Hawker, C. J.; Atthoff, B.; Claesson, H.; Heise, A.; Miller, R. D.; Mecerreges, D.; Jéröme, R.; Dubois, Ph. *Macromolecules* **1998**, *31*, 8691.
(5) (a) Gaynor, S. G.; Matyjaszewski, K. In *Controlled Radical Polymerization*, ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998; pp 258, 396. (b) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, 10, 901. (c) Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Jo, S. M.; Nakagawa, Y. US Patent No. 5,789,487, 1998.
(6) Hirai, H.; Gotoh, Y. Alternating Radical Copolymerization. In *Polymeric materials Encyclopedia*; CRC Press: Boca Raton, FL, 1996.
(7) Cowei, J. M. G. *Alternating Copolymers*; Plenum Press: New York, 1985.
(8) Coca, S.; Matyjaszewski, K. *Polym. Prepr.* **1996**, *37* (1), 573.
(9) Yamada, M.; Takase, I.; Tatsuo, T.; Hayashi, K.; et al. *Kobunshi Kagaku*, **1969** *22* (2), 166; *Chem. Abstr. 63*, 490a.
(10) Cava, M. P.; Deana, A. A.; Muth, K.; Michell, M. J. *Org. Synth., Collect. Vol. 5*, 944.
(11) Ladini, D.; Rolla, F. *J. Org. Chem.* **1980**, *45*, 3527.
(12) Matyjaszewski, K. *Polym. Prepr.* **1997**, *38* (2), 383.

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