6142 *Macromolecules* **2002,** *35,* 6142−6148

Synthesis of Styrene−Acrylonitrile Copolymers and Related Block Copolymers by Atom Transfer Radical Polymerization

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Received April 8, 2002; Revised Manuscript Received May 28, 2002

ABSTRACT: Atom transfer radical polymerization (ATRP) was successfully applied to the synthesis of styrene−acrylonitrile (SAN) copolymers of predetermined molecular weights and low polydispersities. The monomers were copolymerized under azeotropic conditions (ca. 63 mol % styrene and 37 mol % acrylonitrile) in bulk using mono- and difunctional alkyl halide initiators such as 2-bromopropionitrile, 1-phenylethyl bromide, methyl 2-bromopropionate, poly(ethylene oxide) monomethyl ether 2-bromopropionate, and the bis(2-bromopropionate) esters derived from poly(ethylene oxide), poly(propylene oxide), or poly(ϵ-caprolactone) diols of various molecular weights in combination with two catalytic systems: CuBr/2,2′-bipyridine (bpy) and CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA). The synthesized copolymers had high chain end-functionalities, as proven by further chain extension with styrene, *n*-butyl, *tert*-butyl, or glycidyl acrylate, and methyl methacrylate. In the last case, the reaction in the presence of CuBr/bpy led to a block copolymer of high polydispersity, which was decreased to $M_w/M_n = 1.5$ using halogen exchange (i.e., CuCl/bpy as the catalytic system). All other block copolymers (including di-, tri-, and pentablock copolymers) had narrow molecular weight distributions ($M_w/M_n = 1.1-1.4$).

Introduction

Copolymers of styrene and acrylonitrile (SAN copolymers) are thermoplastics that have found a wide range of applications due to their chemical and thermal stability, mechanical (e.g., rigidity, dimensional stability, stress resistance, and craze resistance) and optical properties, and their easy processability.[1] Typically, SAN copolymers are prepared by radical polymerization. The kinetics of SAN copolymerization in bulk,[2−4] solution,[5] or heterogeneous systems such as aqueous emulsions[6,7] or microemulsions[8,9] has been extensively studied. Although the values of the reactivity ratios of the two monomers reported in the literature vary to some extent,[3,4,10,11] and there are some indications about their dependency on reaction temperature[12] and nature of the solvent,[5] the behavior of the couple is relatively well-known. Copolymerization of styrene (Sty) and acrylonitrile (AN) can be described by the penultimate model and shows a significant penultimate effect for both monomers.[4] In a radical copolymerization, the reactivity ratios of Sty and AN differ, and therefore the composition of the copolymer deviates from the composition of the monomer feed. However, both ratios are lower than unity, and an azeotropic feed composition exists, at which no compositional drift is observed throughout the copolymerization.

The major drawback of conventional radical polymerization is that it leads to materials of poorly controlled molecular weight distribution and chain-end functionalities. It is very important to control the molecular weight of the SAN copolymers since their ease of fabrication depends on this parameter.[1] In the early literature,[13] some degree of control over the molecular weights was achieved by regulating the temperature of the polymerizing mixture. The control over the molecular weight distribution was far from satisfactory, and the control over the end-functionalities still remained a challenge. The introduction of the various controlled radical polymerization techniques opened new possibilities for the preparation of well-defined polymeric materials with different compositions, macromolecular architecture, and end-functional groups.[14,15] Among these methods, atom transfer radical polymerization (ATRP)[16−21] has a great potential due to its applicability to a variety of monomers, the possibility for synthesis of end-functionalized polymeric materials, and its tolerance to many solvents, additives, and impurities often encountered in industrial systems.[22,23] A plethora of monomers with different polarities and functional groups have been polymerized in controlled fashion using ATRP, including both Sty[16,24] and AN.[25−27]

Nitroxide-mediated radical polymerization has already been applied for the preparation of SAN copolymers.[28,29] The reactions in the presence of TEMPO are relatively slow and require elevated temperatures. It has been noted[29] that molecular weights increase linearly during the reaction but only up to ca. 60% conversion and then they level off, which is accompanied by a broadening of the molecular weight distribution (M_w/M_n or polydispersity index (PDI) is in the range 1.2−1.5 depending on reaction conditions). However, it has been reported[30] that, using other nitroxides, SAN copolymers with low polydispersity could be synthesized. Nevertheless, the controlled polymerization of Sty and AN up to high monomer consumption still needs to be addressed.

Chain extension reactions of end-functional SAN copolymers leading to block copolymers have not been reported. Such reactions are of a great interest, since in many applications, polymers are used as blends, because synergetic effects lead to improved chemical and physical properties. There are numerous reports about the properties and application of blends of SAN copolymers with other polymeric materials including polyure-

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10.1021/ma020560d CCC: $22.00

thanes,[31−34] poly(meth)acrylates,[35−40] etc. A significant problem in some of the cases is the poor miscibility of the components of the blends (see, for example, refs 41 and 42). Polymer blends often phase separate because of the poor miscibility of the components. One of the widely used concepts for avoiding macroscopic phase separation and improving compatibility is the synthesis of block copolymers. ATRP allows the easy preparation of such materials, and from this point of view it is a very promising technique for making polyurethanes and polyamides with blocky structure in addition to the block copolymers with a variety of vinyl monomers.

In the present work we have studied the copolymerization of Sty and AN by copper-mediated ATRP, using both low-molecular-weight and polymeric initiators. Feed composition close to the azeotropic monomer ratio was used in all experiments. The end-functionality of the copolymers was estimated from chain extension reactions with Sty, *n*-butyl, *tert*-butyl, or glycidyl acrylate (*n*-BA, *t*-BA, or GA), and methyl methacrylate (MMA).

Experimental Section

Materials. Inhibitor was removed by passing the neat monomers through a column filled with neutral alumina. Prior to use, the monomers were purged with nitrogen for at least 30 min. *N*,*N*,*N′*,*N″*,*N″*-Pentamethyldiethylenetriamine (PMDETA) was distilled under reduced pressure. CuBr and CuCl were purified by a modified procedure of Keller and Wycoff:[43] washing with glacial acetic acid followed by 2-propanol. All other reagents were used as received.

Synthetic Procedures. *Synthesis of Polymeric 2-Bromoesters as Macroinitiators for ATRP.* Poly(ethylene oxide)-based macroinitiators have been previously synthesized from the polymeric alcohol and α-haloacyl bromide in the presence of a base such as triethylamine.[44,45] This procedure typically gives high yields but requires thorough drying of all reagents and uses the malodorous acyl bromides, which are known lacrimators. Therefore, an alternative synthetic method was employed, namely, the esterification of a polymeric alcohol (mono- and dihydroxypoly(ethylene oxide), poly(propylene oxide), and poly(ϵ-caprolactone) of various molecular weights) with an α-haloacid (2-bromopropionic or 2-bromoisobutyric) in the presence of dicyclohexylcarbodiimide (DCC) and catalytic amounts of 4-(*N*,*N*-dimethylamino)pyridine (4-DMAP) in methylene chloride.[46,47] The yields exceeded 90%, and the purification of the polymeric esters was very easy. A typical esterification procedure is given below.

40.0 g (2×10^{-2} mol) of dihydroxypoly(ϵ-caprolactone) of M_n = 2000 g/mol was mixed with 3.62 mL (4×10^{-2} mol) of 2-bromopropionic acid in 100 mL of methylene chloride. The solution was cooled in an ice−water bath, and 8.261 g (4×10^{-2} mol) of DCC dissolved in 100 mL of methylene chloride was added followed by 0.8 g of 4-DMAP. The mixture was stirred in the cooling bath for 5 min and then at room temperature for 25 h. Precipitated dicyclohexylurea (DCHU) was filtered off and washed with 60 mL of methylene chloride on the filter. The solvent was removed from the combined solution by rotary evaporation. The macroinitiator was purified by dissolving it in 150 mL of THF, filtering the solution (to remove the white insoluble impurities), and evaporating the solvent. The obtained viscous oil solidified on standing at room temperature. The yield, determined by gravimetry, was 96%. All other solid macroinitiators were purified in the same way. The liquid polymeric esters can be conveniently purified by cooling them to −20 °C. At this temperature the impurities crystallize. After warming to room temperature, the oils are filtered. (Several cooling and warming cycles may be necessary before no further crystal formation is observed.)

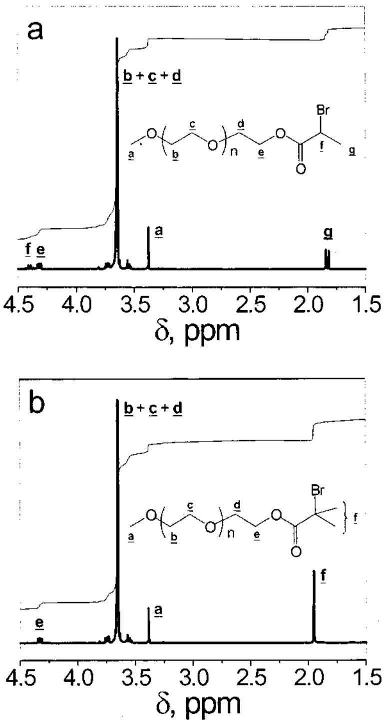

Figure 1. ^{1}H NMR spectra of macroinitiators MePEO(BP)-560 (a) and MePEO(BiB)-640 (b).

The ^{1}H NMR spectra of macroinitiators derived from 2-bromopropionic or 2-bromoisobutyric acid and poly(ethylene oxide) monomethyl ether are shown in Figure 1. The analysis of the spectra was based on comparison of the integrals of the ether methyl group (3.38 ppm) and the methyl group(s) from the acid moiety (1.83 ppm in the case of the 2-bromopropionate and 1.92 ppm in the case of the 2-bromoisobutyrate) and indicates that the esterification reaction is very efficient; i.e., no significant amount of nonfunctionalized polymeric alcohol remained in the case of these two esters.

In this text, abbreviations such as PEO(BP)$_2$-1300 are used to designate the macroinitiators; PEO, PPO, and PCL stand for poly(ethylene oxide), poly(propylene oxide), and poly(ϵ-caprolactone), respectively, BP and BiB are used for 2-bromopropionate and 2-bromo-2-methylpropionate (2-bromoisobutyrate), respectively, and the number at the end denotes the molecular weight (determined by SEC, as described below).

Copolymerization of Styrene and Acrylonitrile Using Low-Molecular-Weight Initiators. In a typical experiment, a dry Schlenk flask was charged with 2,2′-bipyridine (bpy) (0.26 g, 1.66×10^{-3} mol) and was then cycled three times between vacuum and nitrogen to remove oxygen. Deoxygenated monomers (4 mL, 3.636 g, 35.6×10^{-3} mol of Sty, and 1.52 mL, 1.23 g, 23.2×10^{-3} mol of AN) and 0.5 mL of anisole (internal standard for the determination of conversion by gas chromatography (GC)) were added using degassed syringes. After three freeze−pump−thaw cycles and addition of CuBr (0.119 g, 0.83×10^{-3} mol) the mixture was stirred at room temperature until it was homogeneous. Then, 185 μL (0.277 g, 1.66×10^{-3} mol) of methyl 2-bromopropionate was added, and the flask was placed in an oil bath thermostated at the desired temperature. After complex formation (judged by the development of brown color), an initial sample was removed. Samples were periodically withdrawn from the reaction mixture in order to follow conversions and evolution of molecular weights.

Copolymerization of Styrene and Acrylonitrile Using Macroinitiators. The difunctional macroinitiator (5×10^{-4} mol), 0.3 mL of diphenyl ether (internal standard for GC), 0.98 mL (0.78 g, 1.49×10^{-2} mol) of AN, and 2.90 mL (2.64 g, 2.53×10^{-2} mol) of Sty were mixed together in a Schlenk flask. The resulting clear solution was degassed by four freeze−pump−thaw cycles, the flask was filled with nitrogen, and while the mixture was immersed in liquid nitrogen, 0.072 g (5×10^{-4} mol) of CuBr and 0.156 g (1×10^{-3} mol) of bpy were added. The flask was then sealed with a glass stopper, evacuated, and back-filled with nitrogen four times. After melting the

Table 1. SAN Copolymers Prepared by ATRP in Bulk at 90 °C (Reaction Time 5 h)

entry	initiator[a] (mol × 10^3)	monomers ([Sty]/[AN]) (mol × 10^3)	CuBr/CuBr$_2$ (mol × 10^3)	bpy (mol × 10^3)	overall conversion (%)	M_n[b] (g/mol)	M_w/M_n[b]
1	BPN; 1	32/19	0.33/0.017	0.54	65	3640	1.14
2	BPN; 1	32/19	0.33/−	0.5	71	3600	1.14
3	PEB; 0.5	25.3/14.9	0.5/−	1.0	92	5530	1.15
4	PEB; 0.5	25.3/14.9	0.45/0.05	1.0	90	5770	1.14
5	MBP; 1.66	34.9/23.2	0.83/−	1.66	91	3000	1.18

[a] BPN = 2-bromopropionitrile, MBP = methyl 2-bromopropionate, PEB = 1-phenylethyl bromide. [b] Determined by SEC using polystyrene standards.

mixture, a brown solution containing a small amount of solid catalyst was formed. The polymerizations were carried out at temperatures in the range 80−90 °C.

When CuBr/PMDETA was used as the catalyst, the polymerization procedure was similar, but the deoxygenated ligand was introduced with a syringe after all other reagents were charged and freeze−pump−thaw cycles had been performed.

In some cases (typically, in the fast reactions employing the more active catalyst, CuBr/PMDETA), a small amount (5−10 mol %) of CuBr$_2$ was added as an additional deactivator. Its role was to enhance the deactivation step of the ATRP equilibrium, decrease the radical concentration, reduce the termination reactions, and consequently decrease the polydispersity of the polymers.

To isolate sufficient amounts of the copolymers, the reactions were scaled up. In those cases, the final reaction mixtures were diluted with THF, the solutions were filtered through a column filled with basic alumina, and the copolymers were precipitated in excess of hexane. Solvents such as alcohols and water can also be used but were generally avoided because of their nucleophilicity, which would lead to a loss of the bromine end groups.

Chain Extension of Poly(SAN). Bromine-terminated poly(SAN) of $M_n = 3000$ g/mol (0.553 g, 1.84×10^{-4} mol), CuBr (0.0132 g, 0.92×10^{-4} mol), and anisole (0.2 mL as an internal standard for GC) were added to a 10 mL Schlenk flask containing a stir bar. The flask was sealed with a rubber septum, cooled, and then evacuated and back-filled with nitrogen three times. Deoxygenated Sty was added (1.26 mL, 1.1×10^{-2} mol) via a syringe purged with nitrogen, and the polymer was dissolved. Then the reaction mixture was frozen using liquid nitrogen, and three more freeze−pump−thaw cycles were performed. 2,2′-Bipyridine (0.029 g, 1.84×10^{-4} mol) was added, and the mixture was stirred. An initial sample was removed for GC analysis and the flask was heated to 90 °C in a thermostated oil bath. After 16 h the reaction was stopped by exposing it to air and diluting with THF. GC analysis of a sample dissolved in THF showed that the monomer conversion was 58%. The polymer had $M_n = 11\,300$ g/mol and $M_w/M_n = 1.10$.

A similar procedure was followed when other monomers, such as *n*-BA, *t*-BA, GA, or MMA were used in the chain extension reactions. In the last case, as will be discussed later, CuCl/bpy had to be used as the catalyst in order to prepare block copolymers of narrow molecular weight distribution.

ABA difunctional triblock copolymers with middle block being PEO, PPO, or PCL, and SAN end blocks were used as macroinitiators for the preparation of symmetrical pentablock copolymers after chain extension with *n*-BA.

Analysis and Measurements. Conversions were determined on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector and using a capillary column (CEC-Wax, 30 m × 0.53 mm × 1.0 μm, Chrom Expert Co.). Because of the volatility of AN, the kinetic samples were injected immediately into the GC (after dilution with THF). Diphenyl ether or anisole which had been added initially to the mixture was used as internal standards for these measurements. The samples were then filtered through a short column filled with alumina followed by a 0.4 μm PTFE filter, and the solutions were used for determination of molecular weights. Size exclusion chromatography (SEC) measurements were conducted using THF as the eluent (flow rate 1 mL/min, 30 °C), with a series of three Styrogel columns (10^5, 10^3, 100 Å; Polymer Standard Services) and a Waters 2410 differential refractometer. Diphenyl ether was used as the internal standard. Calibration based on polystyrene standards was applied for the determination of molecular weights of all polymers including the macroinitiators. The ^{1}H NMR spectra in CDCl$_3$ were taken on a Bruker spectrometer operating at 300 MHz, using TMS as a reference compound.

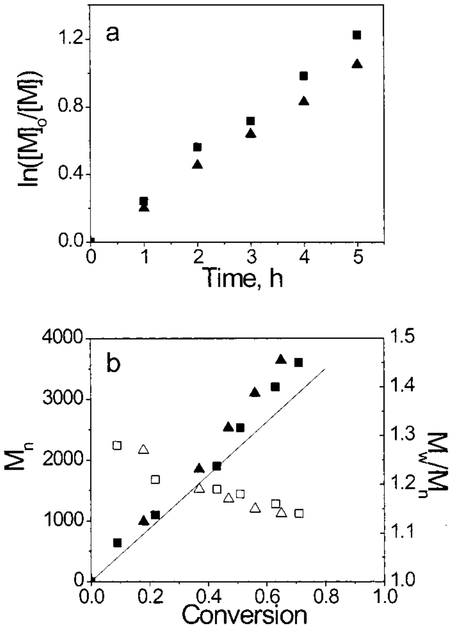

Figure 2. Semilogarithmic kinetic plots (a) and dependence of molecular weights (closed symbols) and molecular weight distributions (open symbols) (b) for ATRP of Sty and AN at 90 °C in bulk: [Sty]:[AN]:[BPN]:[CuBr]:[bpy]:[CuBr$_2$ (bpy)$_2$] = 30:20:1:0.33:0.5:0.017 (▲, △); [Sty]:[AN]:[BPN]:[CuBr]:[bpy] = 30:20:1:0.33:0.5 (■, □).

Results and Discussion

In all experiments an azeotropic feed composition of Sty and AN was used (ca. 63 mol % Sty). The copolymerization was studied using both low-molecular-weight and polymeric initiators. The experimental data for the copolymerization of the two monomers using low-molecular-weight initiators in the presence of CuBr/bpy as the catalytic system are presented in Table 1.

The first initiators used in the preparation of SAN copolymers were 2-bromopropionitrile (BPN) and 1-phenylethyl bromide (PEB), which have structures resembling closely those of the polymer chain end with AN or Sty terminal monomer unit, respectively.

The results for BPN are presented in Figure 2. The semilogarithmic kinetic plots were linear, indicating a constant number of active propagating chains throughout the reaction—one of the criteria used to assess the “living” character of the polymerization. The addition of small amounts of CuBr$_2$ as a supplementary deactivator led to a decrease of the reaction rate. The

Table 2. SAN Block Copolymers Prepared by ATRP

entry	macroinitiator[a] (M_w/M_n) (mol × 10^4)	monomers ([Sty]/[AN]) (mol × 10^3)	CuBr/CuBr$_2$ (mol × 10^4)	ligand (mol × 10^4)	T (°C)	time (h)	overall conversion (%)	M_n[b] (g/mol)	M_w/M_n[b]
1	MePEO(BP)−560 (1.22); 10	25.3/14.9	5/−	bpy; 10	80	5.5	87	4870	1.20
2	MePEO(BiB)−2640 (1.11); 5	25.3/14.9	5/−	bpy; 10	80	7.5	49	9040	1.12
3	PEO(BP)$_2$−1300 (1.05); 1.56	7.48/4.05	1.56/0.08	PMDETA; 1.56	85	5	84	7300	1.26
4	PEO(BP)$_2$−1500 (1.05); 1.50	8.9/5.9	1.48/0.07	bpy; 3.1	90	5	47	5100	1.13
5	PEO(BP)$_2$−1500 (1.05); 0.74	8.9/5.9	0.74/0.037	bpy; 1.55	90	5	38	6900	1.17
6	PEO(BP)$_2$−1500 (1.05); 0.74	22.2/14.8	0.74/0.037	bpy; 1.55	90	7	21	8700	1.16
7	PEO(BP)$_2$−5600 (1.07); 1.56	7.48/4.05	1.56/0.08	PMDETA; 1.56	80	4	81	13100	1.15
8	PPO(BP)$_2$−710 (1.07); 5	25.3/14.9	5/−	bpy; 10	80	5.5	93	8050	1.17
9	PPO(BP)$_2$−1470 (1.06); 5	25.3/14.9	5/−	bpy; 10	80	6.5	83	7310	1.18
10	PPO(BP)$_2$−2520 (1.15); 5	25.3/14.9	5/−	bpy; 10	80	6.75	85	8640	1.20
11	PPO(BP)$_2$−6780 (1.21[c]); 25	126.6/74.5	25/−	bpy; 50	80	8	79	7450	1.43[c]
12	PCL(BP)$_2$−3360 (1.71); 25	126.6/74.5	25/−	bpy; 50	80	6.5	89	11040	1.17

[a] For the notation, see the Experimental Section; molecular weights and PDI (the number in the parentheses) are determined by SEC in THF vs polystyrene standards. [b] Determined by SEC using polystyrene standards. [c] Bimodal SEC trace.

polydispersities of the polymers in the presence of additional deactivator were slightly lower throughout the polymerization (at least, up to 60% conversion; see Figure 2b), but the final products isolated at conversion of 70% or higher had the same values of M_w/M_n (Table 1, entries 1 and 2). Up to moderate conversions, the extra deactivator gives better control over the polymerization, but as the polymerization proceeds, the amount of Cu(II) accumulated in the system where no deactivator had been initially added becomes sufficient and polymers of low polydispersity are produced in this case as well. Because of the limited solubility of the CuBr$_2$/bpy complex, one may safely assume that, after reaching moderate conversions, in both studied cases the deactivator concentration reaches the values of the saturated solution, and this is why the degree of control over the polymerizations becomes virtually the same.

Similar behavior was observed when PEB was used as the initiator (entries 3 and 4 in Table 1).

The macroinitiators used in this study were (with one exception) esters of 2-bromopropionic acid. Before using these polymeric initiators, it was important to test the control over the polymerization when a simpler, low-molecular-weight ester of the same acid, namely methyl 2-bromopropionate (MBP), was employed as the initiator. Since the results obtained with the two other low-molecular-weight initiators had shown that addition of CuBr$_2$ was not necessary to achieve a well-controlled polymerization, in this case the reaction was run in the presence of activator only (CuBr/bpy). As seen from Table 1, entry 5, the control over the polymerization was good with the 2-bromopropionate initiator.

Typically, AB or ABA block copolymers are synthesized using mono- or difunctional macroinitiators. Some materials of interest include such combining hydrophilic−hydrophobic or flexible−rigid structures.[48] Thus, we used polyethers (materials with low T_g, due to a high chain flexibility) such as PEO and PPO to prepare 2-bromopropionate or 2-bromoisobutyrate macroinitiators. PCL-based macroinitiators were also used to form block copolymers comprising polyester sequences, which could be hydrolytically degraded for further applications. The macroinitiators discussed herein included both mono- and difunctional ones (i.e., mono- and bis(2-bromopropionate) esters) of varying molecular weights. The targeted molecular weights of the SAN blocks were kept in the range 3000−4000 g/mol.

The experimental data for the copolymerization of Sty and AN using the various macroinitiators studied are summarized in Table 2.

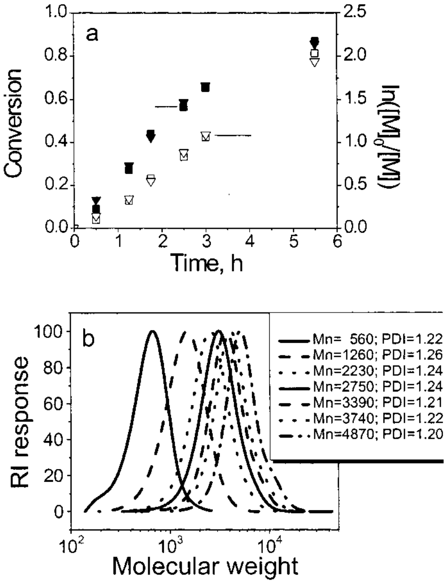

Figure 3. Kinetic plots (a) and evolution of the SEC traces (b) for ATRP of Sty (■, □) and AN (▼, ▽) at 80 °C. [Sty]:[AN]:[MePEO(BP)-560]:[CuBr]:[bpy] = 25.3:14.9:1:0.5:1.

First, the monofunctional initiators PEO monomethyl ether 2-bromopropionate (MePEO(BP)-560) or 2-bromoisobutyrate (MePEO(BiB)-2640) were used. The results obtained with the 2-bromopropionate ester are shown in Figure 3.

Both monomers were consumed at the same rate. The semilogarithmic plots did not significantly deviate from the straight lines expected for reactions with a constant radical concentration, and a clean shift of the entire molecular weight distribution to the higher molecular weight region was observed. The values of M_w/M_n remained below 1.3 throughout the polymerization. The corresponding 2-bromoisobutyrate ester of PEO monomethyl ether was also used as initiator, but in this case the initiation efficiency was low (compare entries 1 and 2 in Table 2; note that the targeted molecular weight was 2 times higher in the case of the 2-bromoisobutyrate). In all other reactions, 2-bromopropionate esters were preferred as initiators.

As mentioned in the Experimental Section, two different catalytic systems were used in this study, namely CuBr/PMDETA and CuBr/bpy. The polymerizations in the former case were faster, as expected: the Cu(I) complexes of PMDETA are known to be significantly more active than those of bpy.[49,50] This higher activity

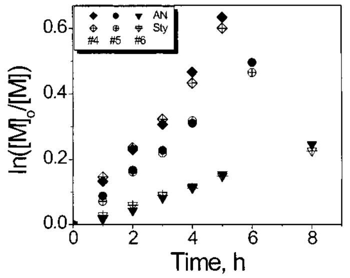

Figure 4. Semilogarithmic kinetic plots for copolymerization of Sty and AN using PEO-based macroinitiators for different targeted degrees of polymerization (entries 4−6, Table 2).

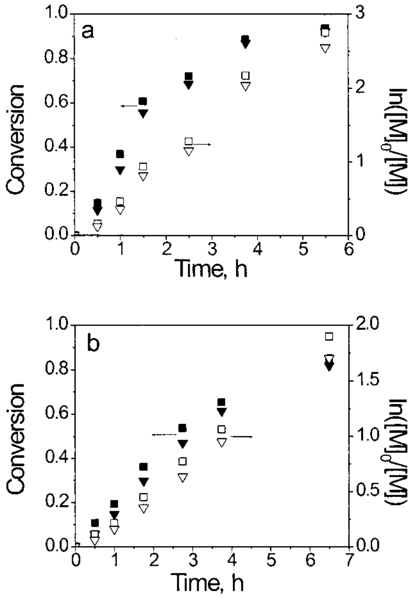

Figure 5. Kinetic plots for copolymerization of Sty (▼, ▽) and AN (■, □) using (a) PPO-based macroinitiator (entry 8, Table 2) and (b) PCL-based macroinitiator (entry 12, Table 2).

(expressed as higher ATRP equilibrium constant) may be accompanied by a lower initiation efficiency (due to high initial concentration of radicals and therefore higher termination rate). To suppress the initial termination reactions, it was necessary to use a catalyst containing small amounts of $CuBr_2$ as additional deactivator. In this case, the control was improved, and all subsequent SAN copolymerizations with PMDETA were performed in the presence of $CuBr_2$. The higher activity of the PMDETA-based catalyst allows one to perform the reactions at either lower temperature or over shorter reaction times without significant loss of control, provided that deactivator is present in the reaction mixture from the beginning. The two catalytic systems studied are compared in Table 2 (see, for example, entries 3 and 4), and overall they both gave satisfactory results.

The kinetics of polymerization initiated by the various bis(2-bromopropionates) of polymeric diols (PEO-, PPO-, and PCL-based) were similar: linear semilogarithmic plots were observed (Figures 4 and 5). A decrease in initiator and catalyst concentration led to a decrease of the reaction rate, as presented in Figure 4.

As expected for an azeotropic feed composition, both monomers were consumed at the same rate (within the bounds of experimental error associated with the GC measurements) rate. The molecular weights increased linearly with conversion, and the values of M_w/M_n remained low and generally decreased during the reactions (Figure 6).

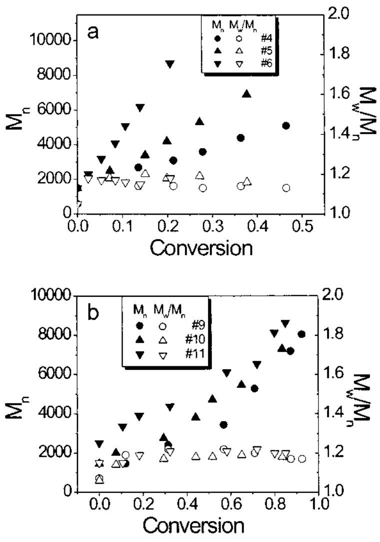

Figure 6. Dependence of molecular weights (closed symbols) and molecular weight distributions (open symbols) upon conversion for Sty and AN copolymerization using (a) PEO-based macroinitiators (entries 4−6 in Table 2) for different targeted degrees of polymerization and (b) PPO-based macroinitiators (entries 8−10 in Table 2).

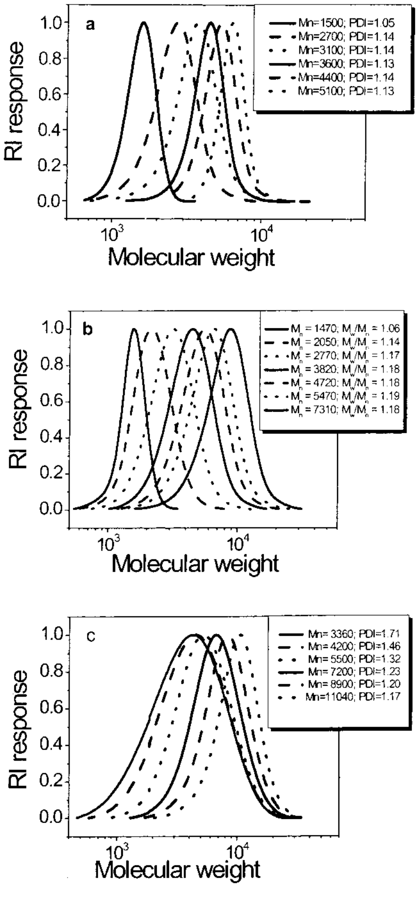

Figure 7. Evolution of SEC traces for SAN triblock copolymers with (a) PEO (entry 4 in Table 2), (b) PPO (entry 9 in Table 2), and (c) PCL (entry 12 in Table 2).

It was observed (Figure 7) that in all cases the SEC traces of the polymers remained monomodal and symmetrical, indicating negligible amount of dead chains and insignificant termination.

In the case of poly(caprolactone) bis(2-bromopropionate) macroinitiator, the polydispersities at the initial stages of the reaction were relatively high, as shown in

Table 3. Chain Extension Experiments

entry	SAN macroinitiator (M_n, M_w/M_n) (mol × 10^4)	monomer (mol × 10^2)	CuBr/CuBr$_2$ (mol × 10^4)	ligand (mol × 10^4)	solvent (mL)	T (°C)	time (h)	conv (%)	M_n (g/mol)	M_w/M_n
1	(SAN)-Br (3000, 1.18); 1.8	Sty; 1.1	0.9/–	bpy; 1.8		90	16	58	11 300	1.10
2	(SAN)-Br (2400, 1.19); 2.1	*n*-BA; 4.2	1.0/0.05	PMDETA; 1	acetone; 2	60	10	50	13 900	1.10
3	(SAN)-Br (2400, 1.19); 2.1	*t*-BA; 2.0	1.0/0.05	PMDETA; 1	acetone; 1	60	10	76	11 400	1.14
4	(SAN)-Br (2400, 1.19); 2.1	GA; 4.4	1.0/0.05	bpy; 1.5	anisole; 6	90	2	35	12 000	1.35
5	(SAN)-Br (3050, 1.16); 1.4	MMA; 2.8	1.4/–	bpy; 2.8	butanone; 1	80	4	45	12 390	1.68
6	(SAN)-Br (3050, 1.16); 1.4	MMA; 2.8	1.4 (CuCl)/–	bpy; 2.8	butanone; 1	80	4	39	11 960	1.48
7	Br(SAN-*b*-PCL-*b*-SAN)Br (10840, 1.21); 0.7	*n*-BA; 2.8	0.7/–	PMDETA; 0.7	butanone; 2	70	21	40	21 600	1.22
8	Br(SAN-*b*-PPO-*b*-SAN)Br (10650, 1.16); 0.7	*n*-BA; 2.8	0.7/–	PMDETA; 0.7	butanone; 2	70	21	43	24 220	1.22
9	Br(SAN-*b*-PEO-*b*-SAN)Br (7300, 1.26); 0.7	*n*-BA; 2.8	1.4/0.07	PMDETA; 1.5	toluene; 2	70	12	15	14 900	1.24

Figure 7c. This was due to the broad molecular weight distribution of the macroinitiators prepared from commercially available polymeric alcohols. However, since the fraction of the PCL in the copolymers decreased as the polymerization proceeded, and the molecular weight distribution of the poly(SAN) blocks was narrow, the polydispersity of the polymers significantly decreased (from 1.71 to 1.17) with conversion.

The molecular weights from the SEC analyses can deviate from the precise values due to differences of the hydrodynamic volume of the copolymers and the polystyrene standards used for calibration. Therefore, the molecular weights of three of the block copolymers (with PEO, PPO, and PCL middle blocks; entries 7, 10, and 12 in Table 2, respectively) were determined by NMR. For all three cases, the molecular weights determined by NMR were in good agreement with the theoretically predicted from the ratio Δ[monomer]/[initiator]$_0$. Thus, the M_n value for entry 7 in Table 2 (PEO middle block) determined by NMR was 10 900 g/mol (theory: 10 600 g/mol; SEC: 13 100 g/mol) and this for entry 10 (PPO middle block) was 7700 g/mol (theory: 8000 g/mol; SEC: 8640 g/mol). A somewhat larger deviation between the theoretical and experimental (NMR analysis) molecular weights was observed for the copolymer with PCL middle block (entry 12 in Table 2): the M_n determined by NMR was 9000 g/mol (theory: 7800 g/mol; SEC: 11 040 g/mol).

For the successful synthesis of block copolymers, both a high efficiency of initiation and high end-functionality of the macroinitiators are crucial to avoid the presence of homopolymer (from the unreacted macroinitiator) in the final product. The high end-functionality of the synthesized SAN copolymers was verified by conducting chain extension reactions with a variety of monomers, which are summarized in Table 3.

Very clean shifts of the entire molecular weight distributions were observed, as illustrated in Figure 8a for the case of chain extension with Sty in bulk.

In the chain-extension reactions with Sty or acrylate monomers, well-defined polymeric materials of narrow molecular weight distributions were obtained. However, as seen from Table 3, entry 5, when MMA was used as the monomer for chain extension, a block copolymer of relatively high polydispersity was obtained. Such behavior is often observed when acrylate- or styrene-based macroinitiators are chain-extended with the more reactive methacrylates, unless the technique of halogen switch (CuCl- instead of CuBr-based ATRP catalyst) is been used.[51,52] To prove this, an experiment was run with CuCl/bpy as the catalyst (entry 6 in Table 3). Although the polydispersities remained relatively high (compared to the chain extension reactions with Sty or acrylates), they were lower when compared to the chain extension with MMA in the presence of CuBr/bpy.

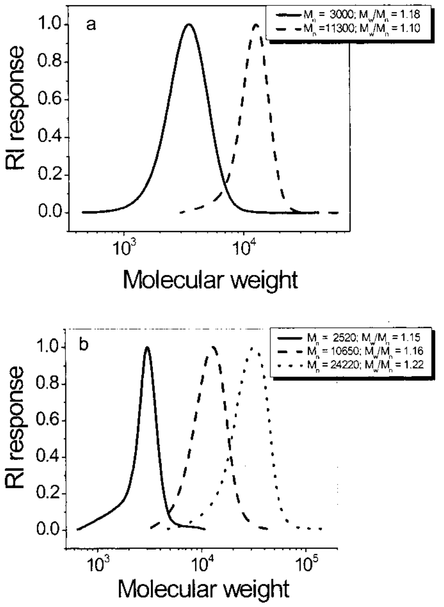

Figure 8. SEC traces for chain extension reactions of (a) monofunctional SAN-based macroinitiator with Sty (entry 1 in Table 3) and (b) the difunctional triblock copolymer poly(SAN-*b*-PPO-*b*-SAN) with *n*-BA (entry 8 in Table 3); the SEC trace of the starting macroinitiator PPO(BP)$_2$-2520 is also included.

Chain extension reactions were carried out using different monomers (*n*-BA, *t*-BA, GA, and MMA) and both mono- and difunctional SAN-based macroinitiators. For example, two ABCBA pentablock copolymers with PPO and PCL middle blocks were successfully prepared. The SEC traces of a PPO-based difunctional macroinitiator and the poly(SAN-*b*-PPO-*b*-SAN) triblock copolymer and poly(BA-*b*-SAN-*b*-PPO-*b*-SAN-*b*-BA) pentablock copolymer prepared from it are shown in Figure 8b.

Two of the prepared pentablock copolymers (with PCL and PPO middle blocks; entries 7 and 8 in Table 3) were also analyzed by NMR in order to determine their molecular weights and compare them to the ones obtained from SEC. The composition of the pentablock copolymer with PCL middle block (entry 7 in Table 3) was $(BA)_{42}(SAN)_{45}(PCL)_{17}(SAN)_{45}(BA)_{42}$, corresponding to M_n = 20 700 g/mol (M_n from SEC: 21 600 g/mol). The pentablock copolymer with PPO middle block (entry 8 in Table 3) had the composition $(BA)_{73}(SAN)_{37}(PPO)_{34}$-$(SAN)_{37}(BA)_{73}$, corresponding to M_n = 27 100 g/mol (M_n from SEC: 24 220 g/mol).

Conclusions

Well-defined SAN copolymers have been synthesized by ATRP using two different catalytic systems CuBr/bpy or CuBr/PMDETA. To better control the reactions performed using the latter catalytic system and to reduce the amount of terminated chains and increase the control over the polymerization, extra deactivator ($CuBr_2$) was added initially. Various bromine-containing low-molecular-weight initiators as well as macroinitiators derived from PEO, PPO, or PCL of different molecular weights were successfully used. Reactions were conducted in bulk using the azeotropic composition of the monomers. Similar to conventional radical polymerization, the two monomers were consumed at the same rate, indicating that the reactivity ratios in ATRP match those observed in the conventional systems. The polymers had high chain-end functionality, as shown by chain extension reactions with styrene, *n*-butyl, *tert*-butyl, or glycidyl acrylate, and methyl methacrylate.

The highly end-functionalized polymers reported here are promising materials not only for the synthesis of block copolymers, illustrated in the present paper, but also of polymers with a variety of end groups, such as amine, thiol, etc. The latter can be further used for preparing other step growth polymers comprising SAN segments in the main chain.

Acknowledgment. The authors gratefully acknowledge the financial support by the National Science Foundation (DMR00-90409) and the members of the ATRP/CRP Consortia at Carnegie Mellon University. The contributions of Lars G. Hahn at the initial stages of this project are also acknowledged.

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MA020560D