Block Copolymerizations of Vinyl Acetate by Combination of Conventional and Atom Transfer Radical Polymerization

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ABSTRACT: Four different methods of block copolymerization, combining atom transfer radical polymerization (ATRP) and conventional radical polymerization, were studied. The first two methods employed azo compounds containing activated halogen atoms. 2,2′-Azobis[2-methyl-*N*-(2-(4-chloromethylbenzoyloxy)-ethyl)propionamide] (AMCBP) was used to initiate the polymerization of vinyl acetate (VAc) at 90 °C. The resulting pVAc with a Cl terminal group (M_n = 47 900; M_w/M_n = 2.21) was subsequently used as a macroinitiator for styrene (St) to yield pVAc-*b*-pSt (M_n = 91 600; M_w/M_n = 1.80). In the second method, 2,2′-azobis[2-methyl-*N*-(2-(2-bromoisobutyryloxy)ethyl)propionamide] (AMBEP) was first used to polymerize *n*-butyl acrylate (BA) at 30 °C in the presence of CuBr/tris[2-(dimethylamino)ethyl]amine (Me_6-TREN). The pBA (M_n = 7500; M_w/M_n = 1.15) with the preserved central azo unit was dissolved in VAc and extended to a block copolymer (M_n = 41 800; M_w/M_n = 3.56). Alternatively, ATRP has been combined with a redox initiated system. VAc was polymerized in the presence of CCl_4/Fe(OAc)$_2$/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) to yield pVAc with trichloromethyl end groups (M_n = 3600; M_w/M_n = 1.81). The polymer obtained was dissolved in styrene and block copolymerized by ATRP to form pVAc-*b*-pSt (M_n = 24 300; M_w/M_n = 1.42). In the last method, pBA with a bromine end group (M_n = 2460; M_w/M_n = 1.32) as prepared by ATRP was dissolved in VAc together with CuBr/1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4-cyclam) to initiate VAc polymerization. A block copolymer with M_n = 4450 and M_w/M_n = 2.58 was prepared. In the presence of 20 mol % of $CuBr_2$, the polydispersity was further reduced to 1.73.

Introduction

Controlled radical polymerization (CRP) enables the preparation of many novel polymeric materials that could not be previously obtained via conventional radical processes.[1,2] These materials include well-defined polymers such as linear homo- and copolymers with controlled end functionalities and compositions.

Radical polymerization has several advantages over other polymerization methods, including a tolerance to a wide range of monomers with various functional groups, facile copolymerization, and undemanding reaction conditions.[3] Particularly, the diversity of monomers that can be polymerized enables the preparation of new materials since various combinations of monomers produce copolymers with novel properties. In this respect, CRPs are currently limited because not all of the radically polymerizable monomers in conventional processes can be applied to CRPs. For example, styrenic derivatives can be polymerized in a well-controlled fashion by nitroxide-based polymerization. Acrylates have also been polymerized with nitroxides[4,5] but have not shown the level of control observed in styrene polymerization until the recent development of new nitroxides.[6,7] The polymerization of methacrylates still cannot be controlled by nitroxide-mediated polymerization. Degenerative transfer processes, especially the radical addition−fragmentation chain transfer (RAFT) process, expands significantly the range of polymerizable monomers by CRPs.[8,9]

Although the atom transfer radical polymerization (ATRP)[10−12] can polymerize a relatively broad range of monomers such as styrenes,[13,14] acrylates,[15] methacrylates,[16] and acrylonitrile,[17] etc., not all alkenes can be successfully polymerized by ATRP. ATRP has not yet been successful in polymerizing vinyl acetate, olefins, etc., presumably due to either relatively strong carbon−halogen bonds or low radical reactivities. Several efforts to overcome this limitation have been made. First, CRPs were combined with different polymerization methods to prepare novel block copolymers, i.e., with cationic polymerization,[18−22] ROMP,[23] condensation,[24,25] and anionic polymerization.[26−29] Another approach is to combine CRP with conventional radical polymerization. Priddy et al. reported a method to prepare copolymers by combining conventional radical polymerization and TEMPO-based CRP.[30] Recently, Destarac and Boutevin reported a similar approach, the use of difunctional initiator using conventional radical polymerization and ATRP for the formation of block copolymers of styrene with *n*-butyl acrylate.[31]

In this paper, we report four different methods for the synthesis of block copolymers using ATRP and conventional radical polymerization. They can be grouped in two different classes: using a difunctional (azo−alkyl halide) initiator and redox initiation of a halogen-terminated (macro)initiator. In the first class, using a difunctional initiator containing an ATRP initiator and a decomposable azo functionality, block copolymerization was performed by applying first either ATRP or conventional radical polymerization and then followed by the other method. In the second category, vinyl acetate was polymerized by redox initiation using a (macro)initiator either before or after ATRP.

Experimental Section

Materials. All monomers were distilled from CaH_2 and stored under argon or nitrogen at −30 °C. 4,4′-Di(5-nonyl)-

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2,2′-bipyridyl [dNbpy] was prepared by the procedure described previously.[13] $Cu^{I}Br$ was purified according to the literature procedure.[32] 2,2′-Azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] was provided by WAKO Chemicals. Tris[2-(dimethylamino)ethyl]amine (Me_6-TREN) was prepared according to a previously reported procedure.[33] Other chemicals were used as received.

Preparation of 2,2′-Azobis[2-methyl-*N*-(2-(2-bromoisobutyryloxy)ethyl) propionamide] (AMBEP). Under argon, 2-bromoisobutyryl bromide (5.63 mL, 43.4 mmol) was added dropwise to a stirring mixture of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (5.00 g, 17.3 mmol) and triethylamine (6.02 mL, 43.4 mmol) in 150 mL of $CHCl_3$ in an ice bath for 1 h. After complete addition of the acid bromide, the reaction was stirred at room temperature for 3 h. The reaction mixture was washed with water (3 × 150 mL) and then dried over $MgSO_4$. After filtration, evaporation of $CHCl_3$ gave a white product. This solid was recrystallized from diethyl ether/ethyl acetate (3.35 g, yield 44.1%). ^{1}H NMR ($CDCl_3$) δ: 7.18 (s, 2H), 4.32 (t, 4H), 3.67 (q, 4H), 1.90 (s, 12H), 1.35 (s, 12H). ESI MS ($M + Na^+$): calculated, 609.3; found, 608.8.

Preparation of 2,2′-Azobis[2-methyl-*N*-(2-(4-chloromethylbenzoyloxy)ethyl) propionamide] (AMCBP). Prepared by a similar procedure as for AMBEP. ^{1}H NMR ($CDCl_3$) δ: 7.97 (d, 2 H), 7.43 (d, 4H), 7.23 (s, 2H), 4.58 (s, 4H), 4.45 (t, 4H), 3.74 (q, 4H), 1.26 (s, 12H). ESI MS ($M + Na^+$): calculated, 616.5; found, 614.9.

Typical Procedure for Polymerization. All of the polymerizations were performed according to the following procedure, unless otherwise noted. To a glass tube, all of the solid chemicals were weighed under ambient atmosphere. Deaerated monomer (with macroinitiator dissolved, for copolymerizations) was added via a syringe under argon or nitrogen atmosphere followed by the addition of ligand and initiator (if liquid). After three freeze−pump−thaw cycles, the glass tube was sealed under vacuum, and the reaction mixture was heated in an oil bath with a temperature controller. After the desired amount of time, the tube was removed from the bath, and the reaction mixture was dissolved in tetrahydrofuran (THF) for further characterization and purification. All the SEC samples were prepared by dissolving products in THF and passing through an alumina column (if necessary) before precipitation. pSt and pSt-*b*-pBA (method 1) were precipitated from THF into MeOH. pVAc (method 1) was purified using dialysis in MeOH to remove AMCBP with regenerated cellulose dialysis membranes (MW limit 2000 Da) from Spectrum Laboratory. Other polymers were isolated by dissolving in THF and passing through alumina (if transition metal contained) and then isolated by either precipitation into cold hexane or evaporation of monomer.

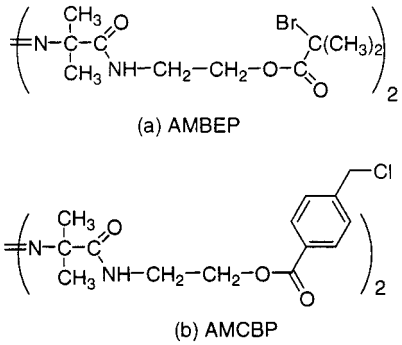


Figure 1. Difunctional initiators.

Characterization. Size exclusion chromatography (SEC) was performed using a Waters 712 WISP autosampler, 510 HPLC pump, 410 differential detector, and the following PSS columns: guard, 10^5, 10^3, and 10^2 Å. All samples were run in THF at 35 °C at rate of 1 mL/min. Linear polystyrene standards were used for calibration. ^{1}H NMR spectra were recorded using a Bruker AM 300. Electrospray ionization mass spectroscopy (ESI MS) was conducted using a Finnegan LCQ, equipped with an octupole and an ion trap mass analyzer.

Results and Discussion

Method 1. Use of Difunctional Initiator for Conventional Radical Polymerization Followed by ATRP. The difunctional initiators (Figure 1) were prepared by esterification of the hydroxyl−azo compound with the acid halides. Both difunctional initiators are derived from the commercially available hydroxyl−azo initiator that has an 8 h half-life time at 90 °C in water.[34] The structures of the difunctional initiators were confirmed by ^{1}H NMR and electrospray ionization mass spectroscopy (ESI MS). They were first used to initiate radical polymerization of the vinyl acetate through the thermal decomposition of the azo group (Scheme 1). As the fragments from the decomposition of the initiator initiate polymerization, each polymer chain can have one or two ATRP initiator groups (benzyl chloride or 2-bromoisobutyryloxy), depending on the

Scheme 1

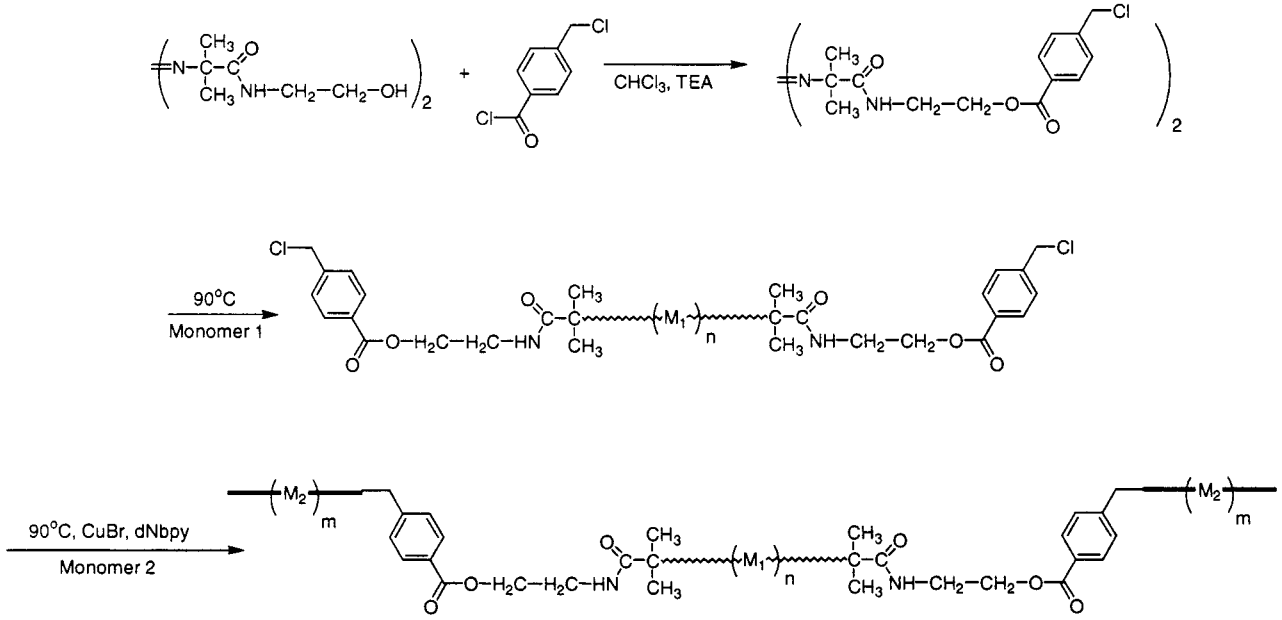


Table 1. Block Copolymerization Using Difunctional Initiator[a]

no.	monomer	initiator	time [h]	conv [%]	M_n [10^3]	M_w/M_n
1	VAc[b]	AMBEP (1 mol %)	36	1.7	6.0	2.50
2	VAc[b]	AMBEP (0.1 mol %)	36	3.3	20.0	2.37
3	St[c]	AMBEP (2 mol %)	10	96.2	39.4	2.48
4	BA[c]	pSt-Br/CuBr/dNbpy[d]	1	19.6	86.4	1.53
5	BA[c]	pSt-Br/CuBr/dNbpy[d]	4	49.3	127.0	1.49
6	VAc[b]	AMBCP (1.5 mol %)	8	60.5	47.9	2.21
7	St[c]	pVAc−Cl/CuCl/dNbpy[e]	4	7.7	67.8	1.80
8	St[c]	pVAc−Cl/CuCl/dNbpy[e]	10	17.7	91.6	1.80

[a] Temp = 90 °C. [b] 50 vol % benzene solution. [c] Bulk. [d] $[\text{pSt-Br}]_0 = 3.36 \times 10^{-3}$ M, $[\text{CuBr}]_0 = [\text{dNbpy}]_0/2 = 6.98 \times 10^{-2}$ M. [e] $[\text{pVAc-Cl}]_0 = 2.08 \times 10^{-3}$ M, $[\text{CuCl}]_0 = [\text{dNbpy}]_0/2 = 6.98 \times 10^{-2}$ M.

mode of termination. If termination occurs predominantly by coupling, then an ATRP macroinitiator would have two initiating groups at both chain ends (Scheme 1), and if by disproportionation, a macroinitiator with one initiating group would be obtained. The macroinitiator was isolated and subsequently used to initiate ATRP of the second monomer in the presence of a copper catalyst.

AMBEP has a 2-bromoisobutyryloxy group, an analogue of methyl 2-bromoisobutyrate. AMBEP was first used for the polymerization of vinyl acetate, since previous studies in our group have shown that methyl 2-bromoisobutyrate efficiently initiates a wide range of monomers including styrene and (meth)acrylates by ATRP. However, the preparation of poly(vinyl acetate) (pVAc) using AMBEP was not successful. The polymerization reached only low conversions and yielded low molecular weight oligomers (entries 1 and 2 in Table 1). In contrast, the polymerization of styrene using AMBEP successfully produced a polystyrene macroinitiator (entry 3 in Table 1). This different behavior was attributed to transfer of the bromine in the AMBEP to the propagating vinyl acetate radical, followed by slow cross-propagation.[3] Since the styryl radical has lower reactivity than vinyl acetate radical,[3] such a behavior was not observed for styrene. The polystyrene macroinitiator (pSt) was chain-extended by the ATRP of *n*-butyl acrylate (BA) (entries 4 and 5 in Table 1), which showed then typical features of CRP; i.e., molecular weights increased and polydispersities decreased with conversion (Figure 2). A similar approach was reported before but for the reverse block sequence.[31]

When the molecular weight of the pBA block exceeded $M_n > 100\,000$, an increase in polydispersities was noticed, possibly due to transfer to polymer.[35] The ^{1}H NMR spectrum confirmed the progressive incorporation of *n*-butyl acrylate into the product with reaction time (Figure 3).

This successful preparation of pSt-*b*-pBA confirmed the feasibility of the difunctional initiator approach. However, to incorporate vinyl acetate into a block copolymer, a different difunctional initiator, AMCBP, was prepared and used for the polymerization of vinyl acetate (Figure 1b). AMCBP has a benzyl chloride moiety to initiate the ATRP process. The vinyl acetate radical was expected to undergo less transfer to the benzyl chloride than to the 2-bromoisobutylic group. Using AMCBP, the preparation of the pVAc macroinitiator was successful (entry 6 in Table 1). The pVAc macroinitiator was purified by dialysis in methanol since precipitation could not remove residual difunctional initiator. The ATRP of styrene using the pVAc macroinitiator (entries 7 and 8 in Table 1) resulted in an increase in molecular weight and a decrease in polydispersity (Figure 4). The SEC and ^{1}H NMR data (Figure 5) support the formation of the block copolymer.

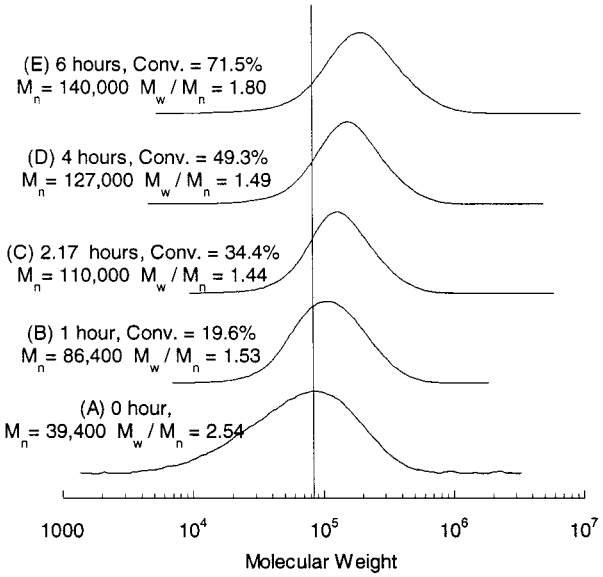


Figure 2. SEC chromatograms of pSt macroinitiator and pSt-*b*-pBA copolymers. Conditions: $[\text{BA}]_0 = 6.98$ M, $[\text{pSt-Br}]_0 = 3.36 \times 10^{-3}$ M, $[\text{CuBr}]_0 = [\text{dNbpy}]_0/2 = 6.98 \times 10^{-2}$ M, bulk, $T = 90$ °C.

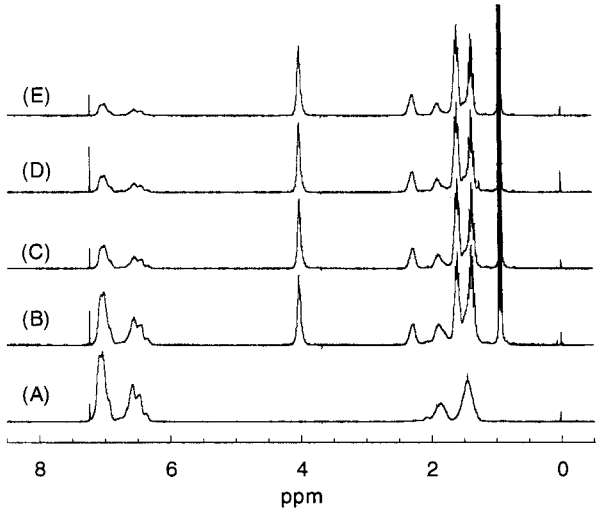


Figure 3. ^{1}H NMR spectrum of pSt macroinitiator and pSt-*b*-pBA copolymers. Content of *n*-butyl acrylate in mol %: (A) 0, (B) 44.4, (C) 64.8, (D) 71.2, (E) 78.4. See Figure 2 for detailed conditions.

Method 2. Use of Difunctional Initiator in ATRP Followed by Conventional Radical Polymerization. The combination of conventional radical polymerization with ATRP using a difunctional initiator can be achieved in an alternative way to that described in method 1. Since acrylates can be polymerized in a controlled manner by ATRP at relatively low temperatures (e.g., 20 °C) with the catalyst, CuBr/tris[2-(dimethylamino)ethyl]amine (Me_6-TREN),[33] a well-defined azo macroinitiator, was prepared without significant loss of the azo functional group (Scheme 2). BA was polymerized with CuBr/Me_6TREN/AMBEP in 50 vol % ethyl acetate at 30 °C for 10 h. Under these conditions, the percentage of the decomposed difunctional initiator is expected to be below 0.5%.[34] The agreement of the

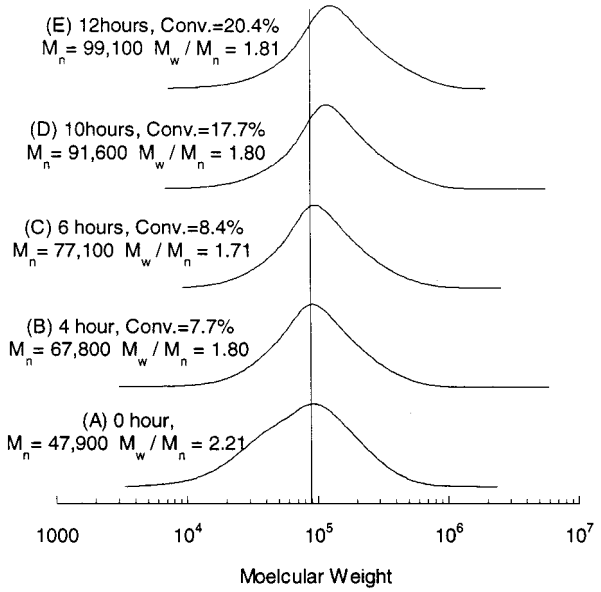


Figure 4. SEC chromatograms of pVAc macroinitiator and pVAc-*b*-pSt copolymers. Conditions: $[St]_0 = 8.73$ M, $[pVAc\text{-}Cl]_0 = 2.08 \times 10^{-3}$ M, $[CuCl]_0 = [dNbpy]_0/2 = 6.98 \times 10^{-2}$ M, bulk, $T = 90$ °C.

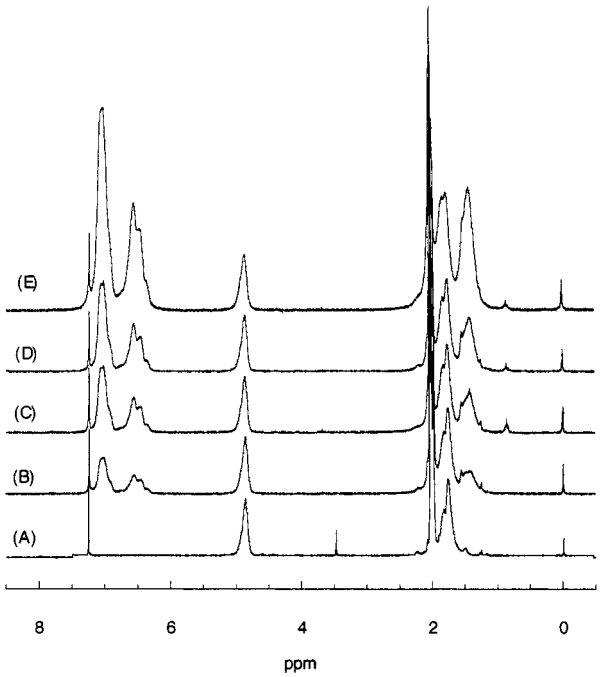


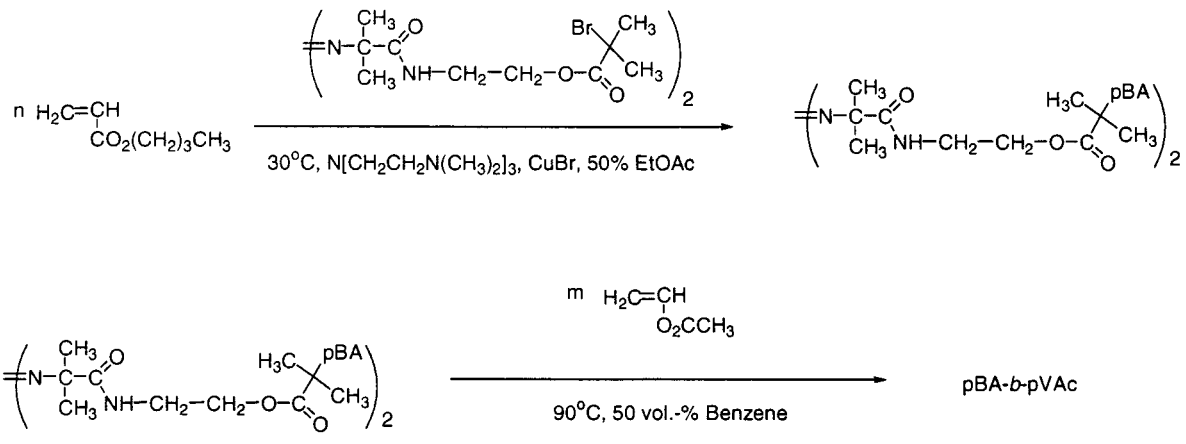
Figure 5. ^{1}H NMR spectrum of pVAc macroinitiator and pVAc-*b*-pSt copolymers. Content of styrene in mol %: (A) 0, (B) 25.3, (C) 37.6, (D) 54.9, (E) 63.1. See Figure 4 for detailed conditions.

experimental molecular weight ($M_{n,\,exp} = 7500$) with the predicted value ($M_{n,\,th} = 6900$) based on the conversion and the narrow molecular weight distribution (PDI = 1.15) of obtained polymer indicated successful ATRP and the preservation of the azo functionality.

The pBA macroinitiator containing the central azo linkage was used for the block copolymerization with vinyl acetate. The polymerization was carried out at 90 °C for 66 h, which is the time required for over 99% decomposition of the initiator. In the SEC traces (Figure 6), the block copolymer with high molecular weight appeared; however, a significant amount of the macroinitiator remained even after 66 h. The radicals formed by the thermal dissociation of the azo group in the pBA macroinitiator can be involved in three reactions: (a) in-cage termination by coupling, (b) in-cage termination by disproportionation, and (c) escape from the cage followed by the cross-propagation and the formation of the block copolymer with vinyl acetate (Scheme 3). All three products can be observed in the SEC chromatogram (Figures 6 and 7). In Figure 7, one can see that peak **a** decreased as the polymerization progressed and block copolymer (peak **c**) was formed. Also, a lower molecular weight peak is formed (peak **b**). At the end of the polymerization, all three peaks are clearly observed. We ascribed peak **a** to the coupling product of the macroinitiator radical in the solvent cage, peak **b** to the disproportionated product of initial macroradicals, and peak **c** to the pBA-*b*-pVAc block copolymer.

The efficiency of blocking, estimated from the SEC chromatogram, was about 50%. This value was calculated assuming similar refractive indexes for pBA and pVAc.[36] Presumably, due to the lower mobility of the macroradical, escape from the cage is less efficient than for a low molecular mass species, resulting in a large amount of termination between macroradicals. The progressive increase of peak **b** (Figure 7), corresponding to the half value of the molecular weight of the macroinitiator, suggests some contribution of disproportionation (about 10% in the final sample). This type of azo macroinitiator with narrow molecular weight distribution may be used to study in more detail the

Scheme 2



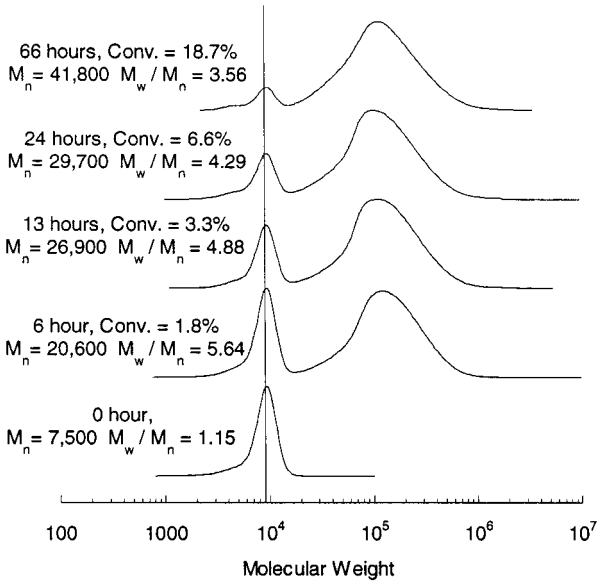


Figure 6. SEC chromatograms of pBA macroinitiator and pBA-*b*-pVAc copolymers. Conditions: $[VAc]_0 = 5.41$ M, $[pBA]_0 = 2.87 \times 10^{-3}$ M, 50 vol % benzene, $T = 90$ °C.

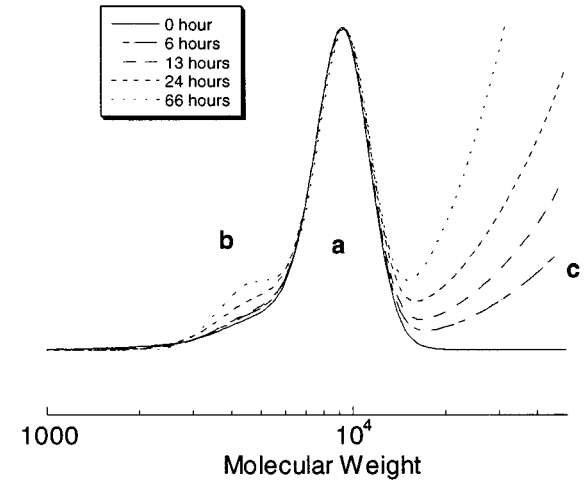


Figure 7. Expanded SEC chromatograms for decomposed pBA macrointiator with vinyl acetate. See Figure 6 for detailed conditions.

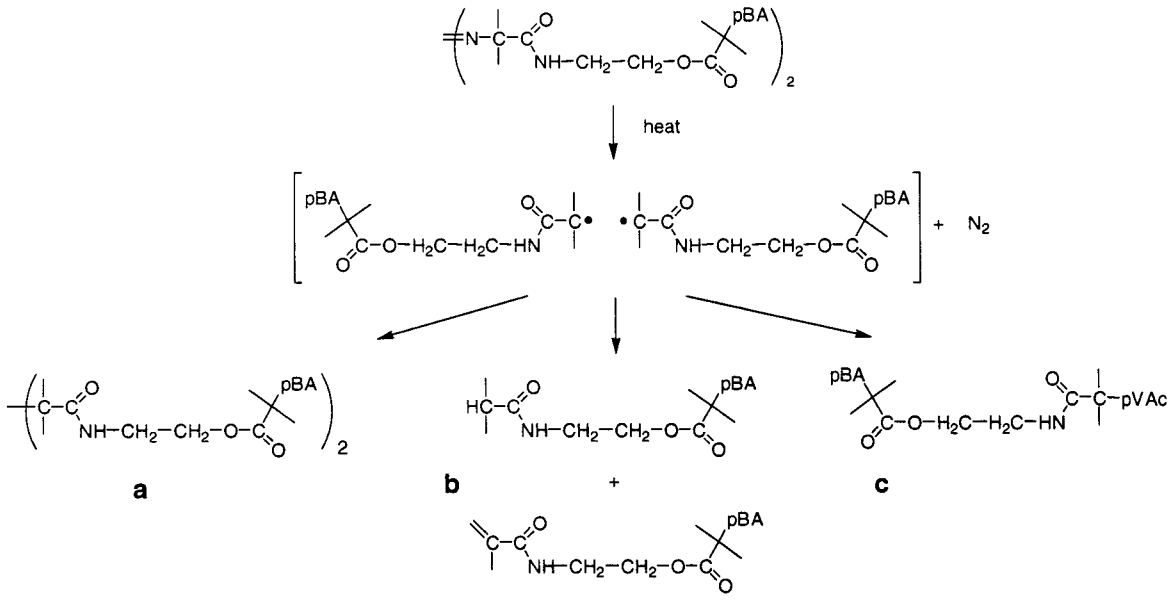
initiation mechanism of macroradicals; previously prepared azo macroinitiators[37] generally have broad molecular weight distributions that may mask any differences between the three peaks.

Method 3. Redox-Initiated Polymerization Followed by ATRP. Functional end groups capable of initiating ATRP can also be incorporated by redox-initiated polymerization and telomerization. The polymerization of vinyl acetate was initiated by CCl_4/$Fe(OAc)_2$/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA); the iron catalyst acts as a redox initiator and not as a catalyst for ATRP. The vinyl acetate polymerization is dominated by transfer to CCl_4, resulting in chains that contain trichloromethyl end groups.[38] There are several advantages of using CCl_4 in comparison with chloroform as a transfer agent, reported before.[39] First, CCl_4 acts as both initiator and transfer agent, meaning that there are no end groups originating from the conventional radical initiator (BPO or AIBN). Also, the transfer coefficient for CCl_4 in polymerization of VAc is very close to unity, providing polymers with much lower polydispersities at wider range of conversions, in contrast to chloroform (c_T = 0.01).[36] The resulting polymers with trichloromethyl chain ends can then be used to initiate ATRP (Scheme 4).

The existence of trichloromethyl groups was confirmed by ESI MS (Figure 8). The main series correspond to CCl_3-pVAc−Cl with a sodium cation [m = 118.5 + n (86) + 35.5 + 23; for n = 15, m = 1467]. The minor series match the molecular weight of polymer which is doubly charged with two sodium cations [m = (118.5 + n (86) + 35.5 + 23 + 23)/2; for n = 32, m = 1476; for n = 33, m = 1519]. In Figure 8b, the expanded spectrum showed a similar isotope pattern to a simulated isotope pattern (Figure 8c), supporting the existence of four chlorine atoms per polymer chain.

The ATRP of styrene using the pVAc macroinitiator yielded a pVAc-*b*-pSt diblock copolymer. The molecular weights increased with conversion, and the polydispersities decreased after styrene units were added, indicat-

Scheme 3



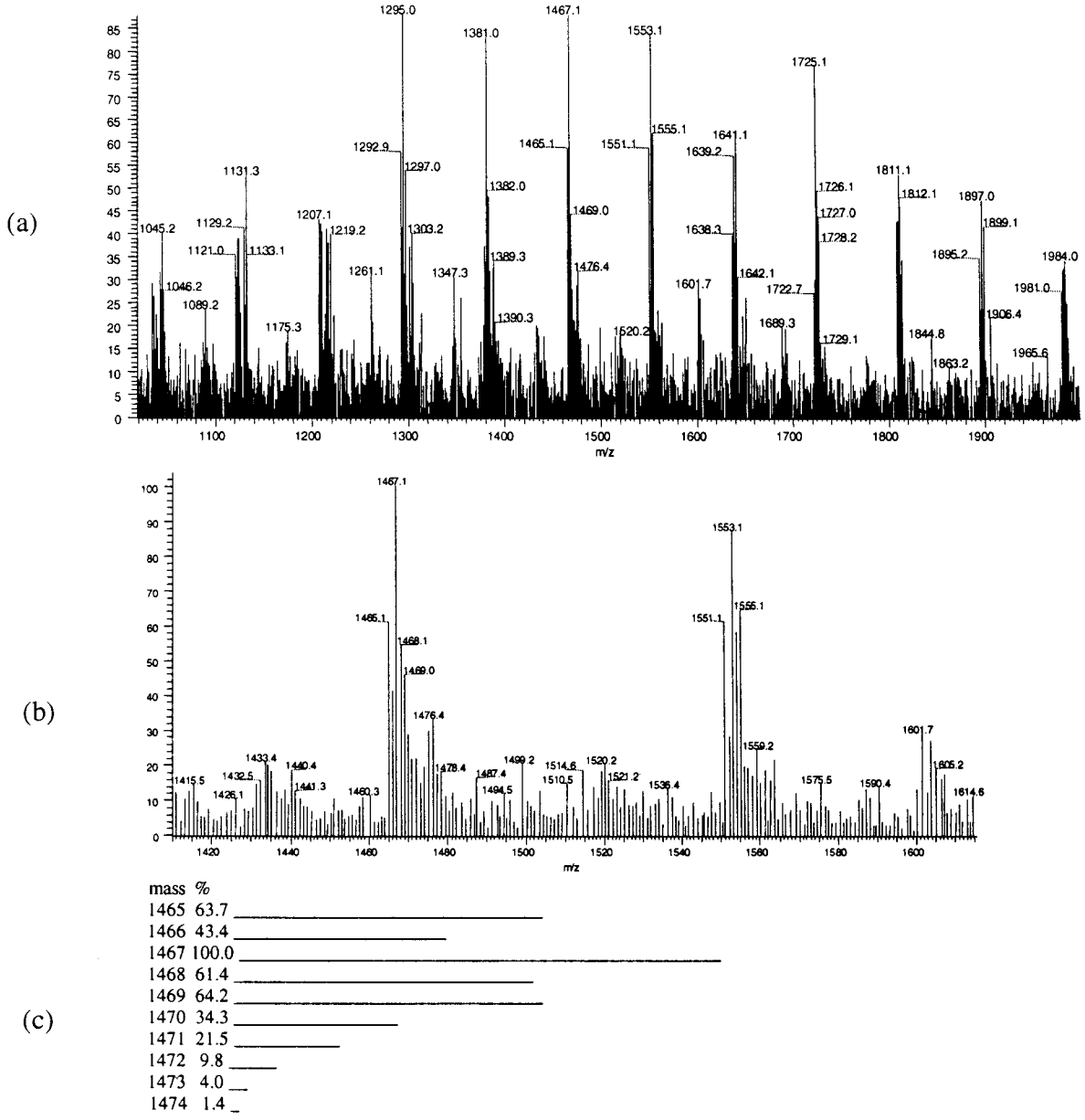
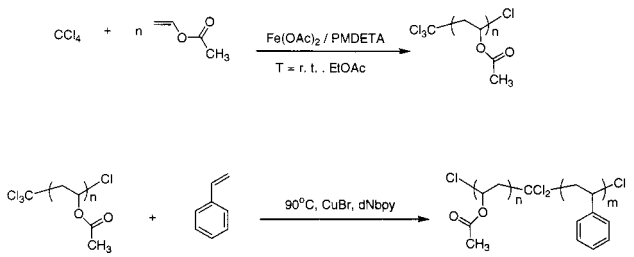


Figure 8. (a) ESI mass spectrum, (b) expanded ESI mass spectrum, and (c) simulated isotope pattern of pVA-Cl.

Scheme 4



ing that the polymerization was relatively well controlled (Figure 9). The ^{1}H NMR spectrum (Figure 10) showed the existence of pVAc and pSt block units and the increase in the amount of styrene in the polymer with reaction time.

Method 4. ATRP Followed by Redox-Initiated Polymerization. The last approach used to prepare block copolymers containing vinyl acetate was to use bromo-terminated pBA as a macroinitiator in the redox initiation of vinyl acetate. The chain end initiates the polymerization of vinyl acetate in the presence of CuBr/1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4-cyclam) in 50 vol % ethanol. It has been earlier observed in our group that the polymerization of BA using CuBr/Me_4-cyclam with methyl 2-bromopropionate as an initiating system led to relatively poorly controlled polymerization.[40] Presumably, the metal complex can abstract the halogen atom from the initiator to form a radical, but the deactivation rate (abstraction of the halogen from metal by the growing radical) is much slower than for the CuBr/bpy, CuBr/PMDETA, or CuBr/Me_6TREN catalyst system. Slow deactivation results in poor control and resembles a redox type initiation. On the basis of this observation, it was expected that this catalyst could activate the bromo-terminated pBA chain to form macroradicals which would then initiate the polymerization of vinyl acetate. The pBA macroinitiator was prepared using methyl 2-bromopropionate and CuBr/PMDETA in the presence of 20 mol % of $Cu^{II}Br_2$ with respect to CuBr. This combination of initiator and catalyst afforded well-

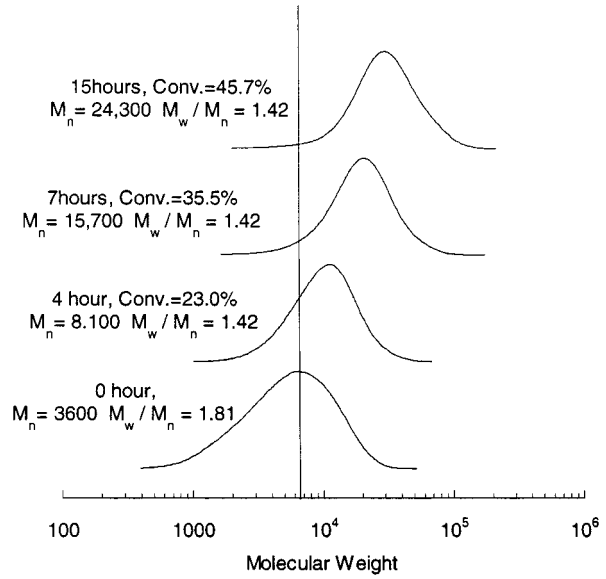


Figure 9. SEC chromatograms of pVAc macroinitiator and pVAc-*b*-pSt copolymers. Conditions: $[St]_0 = 8.73$ M, $[pVAc\text{-}Cl]_0 = 1.39 \times 10^{-2}$ M, $[CuBr]_0 = [dNbpy]_0/2 = 3.49 \times 10^{-2}$ M, bulk, $T = 90$ °C.

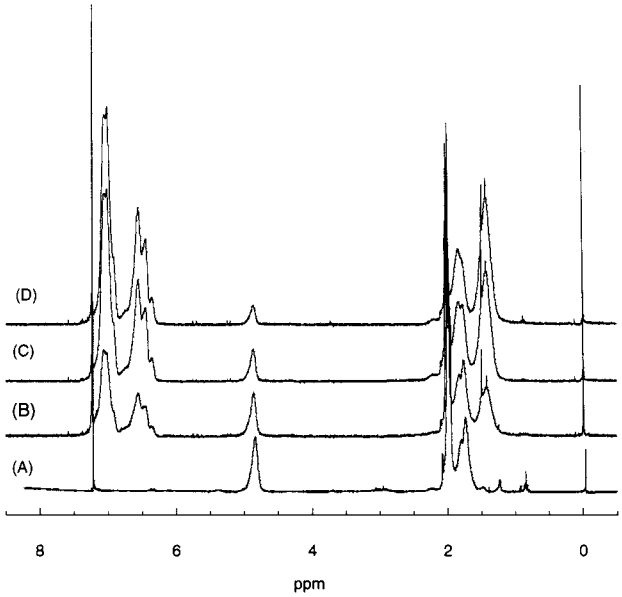
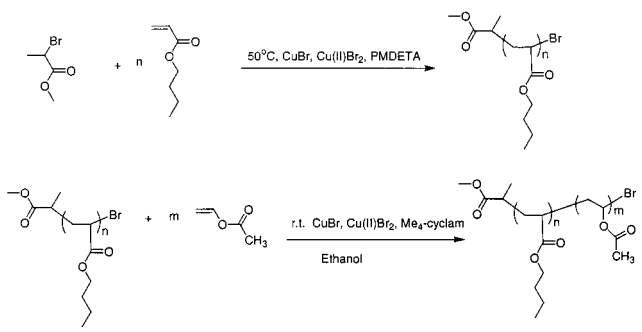


Figure 10. ^{1}H NMR spectrum of pVAc macroinitiator and pVAc-*b*-pSt. Content of styrene in mol %: (A) 0, (B) 55.4, (C) 77.0, (D) 87.1 See Figure 9 for detailed conditions.

Scheme 5



defined pBA with a terminal bromine end group (M_n = 2460, $M_w/M_n = 1.33$). The end functionality was confirmed using ESI MS and a chain extension experiment with methyl acrylate (Figures 11 and 12). Since the detection limit of used ES mass spectrometer was 2000 amu, the entire range of molecular weights could not be analyzed. However, the obtained spectrum indicated that there was no significant end group loss. The main series correspond to the bromo-terminated pBA with a sodium cation ($m = 87 + n$ (128) + 79/81 + 23; for n = 10, m = 1469/1471), and the minor series match the molecular weight of polymer which is doubly charged with two sodium cations [$m = (87 + n$ (128) + 79/81 + 23 + 23)/2; for $n = 21$, m = 1450/1451] (Figure 11). A chain extension experiment with methyl acrylate in the presence of PMDETA/CuBr/Cu(II)Br_2 also supports the high degree of end group functionality of pBA. From the SEC chromatogram, no detectable amount of remaining pBA was observed (Figure 12). These two results indicate the high functionality of the bromo end groups in pBA.

The pBA was block copolymerized with vinyl acetate using CuBr/Me_4-cyclam in the presence of 20 mol % of $Cu^{II}Br_2$ relative to CuBr in 50 vol % ethanol at room temperature. SEC chromatograms of the pBA macroinitiator and the obtained product after 24 h are shown in Figure 13. The polymerization without addition of $Cu^{II}Br_2$ yielded a product with a higher molecular weight shoulder (Figure 13C). The $Cu^{II}Br_2$ was added to deactivate the growing pVAc chain more rapidly and thus prevent transfer or termination by coupling. However, the rate of deactivation is still much lower than the rate of propagation, leading to an ill-defined polymer. The ^{1}H NMR spectrum (Figure 14) showed that the product has pVAc units. Unfortunately, it was not possible to quantify the blocking efficiency because of the similar solubilities of pVAc and pBA.

Comparison of Methods 1−4. Method 1 allowed for the preparation of pVAc first and then subsequent addition of styrene by ATRP by the use of difunctional azo initiator. It is possible to prepare a high molecular weight macroinitiator with reasonable functionalities from various radically polymerizable monomers by varying the initiator concentration or reaction temperature. Initiation by decomposition of the azo initiator can also avoid the problems associated with cross-propagation because the generated radical after decomposition of azo initiator can be chosen with the targeted monomers in mind. In addition, method 1 can also minimize contamination of the in-cage terminated products from the macroinitiator because they can be easily separated during purification.

A difficulty in method 1 is the presence of transfer reactions involving the activated halogens of the initiator. It appears that better initiators for ATRP also behave as better transfer agents. Therefore, the careful initiator selection is required to provide acceptable rates of the initiation for ATRP and minimal rates of transfer during conventional radical polymerization. Thus, using chlorine instead of bromine reduced transfer and allowed the preparation of pVAc-*b*-pSt. Also, it should be noted that the termination mode during the preparation of the macroinitiator determines the type of final product. Disproportionation or transfer results in a monofunctional macroinitiator and leads to the formation of a diblock copolymer, while termination by coupling produces a difunctional macroinitiator, resulting in a triblock copolymer.

Method 2, where a difunctional azo macroinitiator was prepared by ATRP and then used to initiate conventional radical polymerization, led to limited

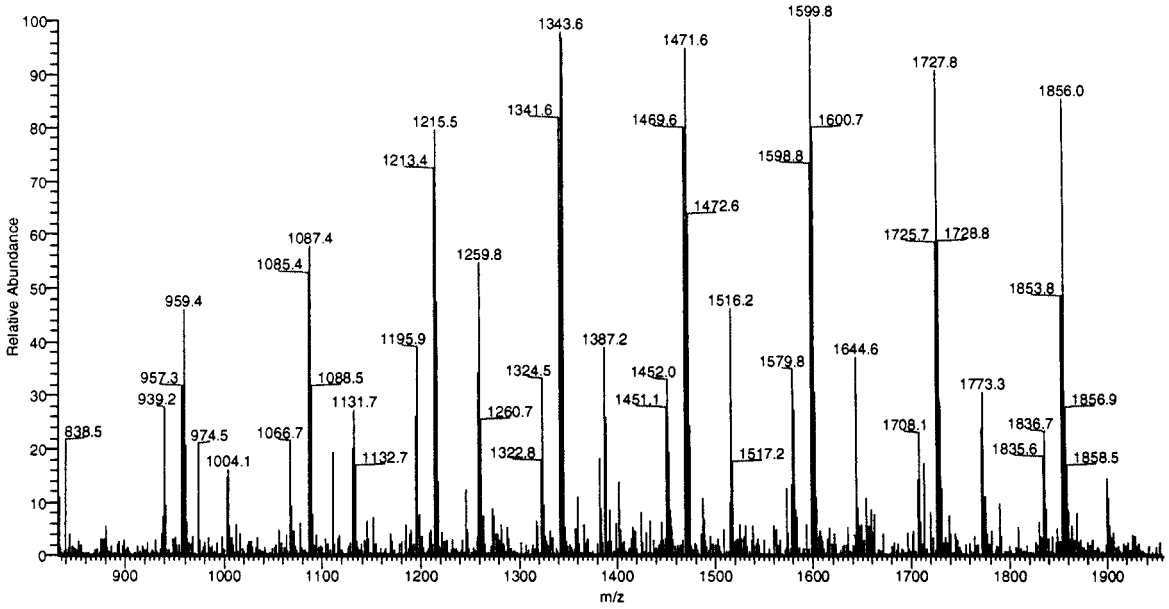


Figure 11. ESI mass spectrum of pBA-Br. Conditions for polymerization: $[BA]_0 = 6.98$ M [methyl 2-bromopropionate]$_0 = 2.98 \times 10^{-1}$ M, $[CuBr]_0 = 2.98 \times 10^{-2}$ M, $[Cu^{II}Br_2]_0 = 5.96 \times 10^{-3}$ M, $[PMDETA]_0 = 3.58 \times 10^{-2}$ M, bulk, $T = 50$ °C, 30 min.

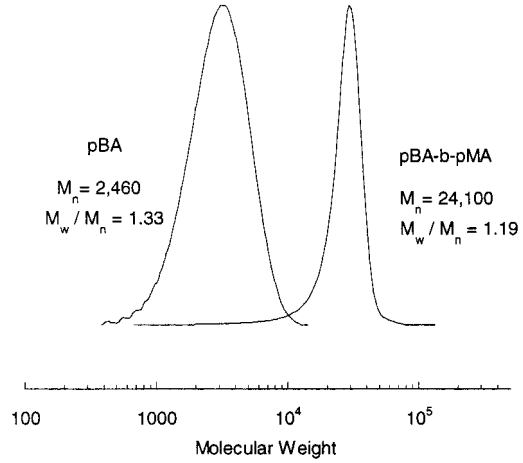


Figure 12. SEC chromatograms of pBA-Br macroinitiator and pBA-*b*-PMA block copolymer Conditions: $[MA]_0 = 11.1$ M, $[pBA\text{-}Br]_0 = 2.56 \times 10^{-2}$ M, $[CuBr]_0 = 1.11 \times 10^{-1}$ M, $[Cu^{II}Br_2]_0 = 2.22 \times 10^{-2}$ M, $[PMDETA]_0 = 1.33 \times 10^{-1}$ M, bulk, $T = 70$ °C, 4 h.

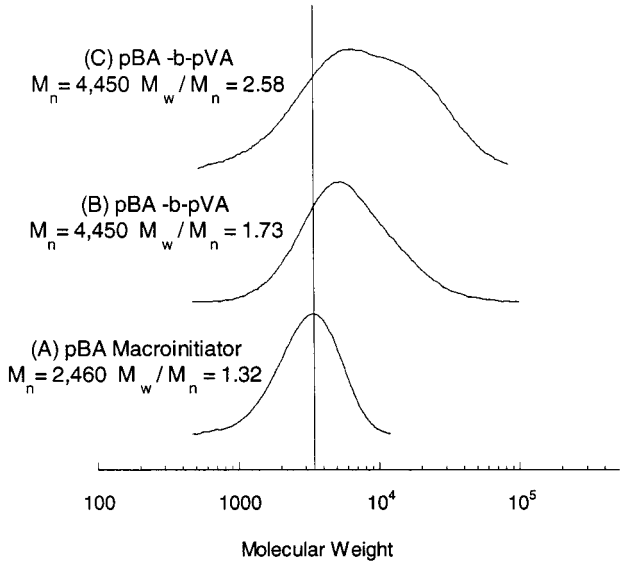


Figure 13. SEC chromatograms of pBA macroinitiator (A) and pBA-*b*-pVAc copolymers. Conditions: $[VAc]_0 = 5.42$ M, $[pBA\text{-}Br]_0 = 1.92 \times 10^{-2}$ M, $[CuBr]_0 = [Me_4\text{-cyclam}]_0 = 5.51 \times 10^{-2}$ M, in 50 vol % ethanol, $T = 25$ °C (B) with 20 mol % of $Cu^{II}Br_2/Me_4$-cyclam relative to CuBr/Me_4-cyclam (C) without Cu(II)Br_2, T = room temperature, 24 h.

blocking efficiency due to the low mobility of the macroradical in the solvent cage. As pointed out above, in method 1 the cage coupling and disproportionation products resulting from initiator decomposition can be removed during purification. However, the same products from the decomposition of the macroinitiator used in method 2 are difficult to separate from the desired block copolymer. Therefore, conventional radical polymerization followed by ATRP (method 1) can yield block copolymers with less contamination of homopolymer than in ATRP followed by conventional radical polymerization (method 2).

For redox-initiated polymerization followed by ATRP (method 3), various monomers can be used to prepare macroinitiators with good end functionalities. Therefore, high blocking efficiency can be attained, providing a high degree of functionality and appropriate reactivity of macroinitiators.

In method 4, the first block is prepared in a controlled manner and then used in the redox initiation of a second monomer. Macroinitiators with complex architecture (e.g., star) can also be introduced depending on the structure of the initiator for ATRP. A disadvantage of this method is that it may be difficult to add the second monomer to the first block because cross-propagation may be slow and incomplete. For example, a polystyrene macroinitiator may be difficult to extend with vinyl acetate using this method since the reactivity ratio of styryl radicals toward vinyl acetate is almost zero.[3]

Overall, the four methods presented provide access to block copolymers comprised of monomers that cannot yet be polymerized by controlled radical polymerization. It is worth noting that none of these methods require any end group transformation or other intermediates.

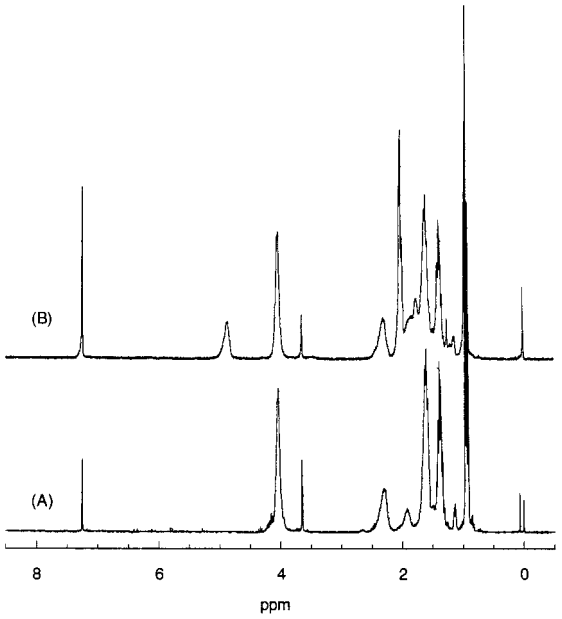


Figure 14. ^{1}H NMR spectrum of pBA macroinitiator (A) and pBA-*b*-pVAc (B). Conditions: $[VAc]_0 = 5.42$ M, $[pBA\text{-}Br]_0 = 1.92 \times 10^{-2}$ M, $[CuBr]_0 = [Me_4\text{-cyclam}]_0 = 5.51 \times 10^{-2}$ M, in 50 vol % ethanol, $T = 25$ °C with 20 mol % of $Cu^{II}Br_2/Me_4$-cyclam relative to $CuBr/Me_4$-cyclam.

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