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Preparation of Polyacrylonitrile-*block*-poly(*n*-butyl acrylate) Copolymers Using Atom Transfer Radical Polymerization and Nitroxide Mediated Polymerization Processes

Chuanbing Tang, Tomasz Kowalewski, and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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ABSTRACT: The preparation of block copolymers with acrylonitrile (AN) and *n*-butyl acrylate (*n*-BA) was examined using two controlled radical polymerization (CRP) processes: atom transfer radical polymerization (ATRP) and nitroxide mediated polymerization (NMP). When crossing from poly(*n*-butyl acrylate) (PBA) to polymerization of AN, the use of halogen exchange in an ATRP process improved control of polymerization. However, when switching from polyacrylonitrile (PAN) to *n*-BA, the cross-propagation was well controlled without halogen exchange. These differences in blocking efficiency can be explained by differences in the bond dissociation energy of the terminal carbon−halogen bond. In NMP, an efficient transition from a preformed PBA block to AN polymerization required the presence of excess of nitroxide. However, chain-extension from PAN to PBA, even under homogeneous conditions and with an excess nitroxide, was less efficient, and GPC traces showed bimodality.

Introduction

The use of controlled/living radical polymerization (CRP) allows the synthesis of well-defined polymers with predetermined molecular weight, narrow molecular weight distribution, and precisely controlled architectures.[1−3] Atom transfer radical polymerization (ATRP)[4−6] and nitroxide-mediated polymerization (NMP)[7] are two of the most widely used CRP methods, and both involve a fast dynamic equilibrium between dormant species and active radical species to provide control. The conditions of the polymerization are selected so that the equilibrium between dormant and active species is strongly shifted toward dormant species in order to establish a low concentration of propagating radicals and reduce proportion of unavoidable termination reactions.

The use of a controlled polymerization process allows one to synthesize block copolymers[8,9] that can combine two incompatible polymer segments. CRP has therefore been employed to prepare various types of block copolymers, some of which have been composed of the same class of monomers such as two different methacrylates and some of which have been prepared by using different classes of monomers such as an acrylate and a methacrylate; examples include poly(butyl acrylate)-*b*-poly(methyl methacrylate), poly(methyl methacrylate)-*b*-poly(butyl acrylate), poly(methyl methacrylate)-*b*-poly(butyl acrylate)-*b*-poly(methyl methacrylate), and polystyrene-*b*-poly(butyl acrylate)-*b*-poly(methyl acrylate).[10−14] In the preparation of block copolymers by CRP, blocking efficiency depends on the sequence of block synthesis. Sometimes, it is possible to chain extend from a specific "A" block to the desired "B" block, but it may be not possible to chain extend from a preformed "B" block to the same "A" block.[4] For example, a methacrylate macroinitiator can be chain extended with acrylate monomers with good control over the synthesis of the second block. However, in the reverse sequence of block formation, an acrylate-based macroinitiator usually chain extends with poor control when methacrylate monomers are used for the second block.[10] To attain high blocking efficiency, the rate of cross-propagation should be at least comparable to the rate of the subsequent propagation reaction. In ATRP, this can be achieved by introducing of a halogen exchange technique, which alters the equilibrium constant.[15] The rate of cross-propagation for a bromine-terminated acrylate is comparable to the propagation rate for chlorine-terminated methacrylate because the carbon−bromine (C−Br) bond has a lower bond dissociation energy than the carbon−chlorine (C−Cl) bond.[12] In the NMP process, it is difficult to alter these equilibrium constants because similar techniques cannot be introduced.

Only a few studies have been reported on the synthesis of block copolymers containing polyacrylonitrile (PAN) segments. Most of the prior work has been concerned with random copolymerization of acrylonitrile with styrene or butadiene followed by block copolymerization with other monomers: e.g., polystyrene-*b*-poly(styrene-*co*-acrylonitrile) and poly(styrene-*co*-acrylonitrile)-*b*-polybutadiene-*b*-poly(styrene-*co*-acrylonitrile).[16−19] The synthesis of block copolymers containing pure polyacrylonitrile segments in the backbone presented some obstacles to the preparation of well-defined block copolymers. First, polyacrylonitrile is difficult to dissolve in solvents typically used in CRP such as anisole, xylene, and toluene or in monomers such as acrylonitrile, acrylates, styrene and methacrylates. Second, blocking efficiency is also difficult to control.

Another reason for the previous lack of success in the preparation of well-defined block copolymers may be the incompatibility of the constituent segments in polyacrylonitrile−polyacrylate (or polymethacrylate) block copolymers which leads to strong microphase separation of the copolymers into various morphologies.[20] We have previously reported the synthesis of triblock copolymers of AN and *n*-BA forming a polyacrylonitrile-*b*-poly(*n*-

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* Corresponding author. E-mail: km3b@andrew.cmu.edu.

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butyl acrylate)-*b*-polyacrylonitrile with polydispersity $M_w/M_n > 1.5$.[21] However, better control of this block copolymerization was subsequently obtained.[22] The latter report was focused on the morphologies of the resulting block copolymers, and no details of the kinetics of the polymerization were provided.

The homopolymerization of acrylonitrile by ATRP has previously been reported yielding polymers with polydispersity as low as $M_w/M_n < 1.1$.[23−25] The Hawker group has also briefly reported the synthesis of polyacrylonitrile by NMP.[26] However, no kinetic studies or even evolution of molecular weight were described. On the other hand, poly(*n*-butyl acrylate) has been successfully synthesized by both methods.[26−30]

As mentioned above, the preparation of block copolymers of AN and *n*-BA is a worthwhile challenge because of the morphological and mechanical properties expected from these block copolymers. Desirable physical properties are partly realized through the combination of a well-phase-separated block copolymer with a hard, high T_g block (PAN segments) and a soft, low T_g block (PBA segments). Furthermore, these block copolymers are of interest since, after pyrolysis, they can result in well-organized nanostructured carbon materials.[22] In this paper, we present a comprehensive study of the block copolymerization of AN and *n*-BA using ATRP and NMP techniques. We explain the blocking efficiency of PAN and PBA using the kinetics, molecular weight evolution, and molecular weight distribution development for these two techniques and, as a result, can make a comparison on the suitability of the techniques for these specific block polymerizations.

Experimental Section

Analysis. Conversion of monomers was measured using a Shimadzu GC14-A gas chromatograph with a FID detector equipped with a J&W Scientific 30m DB WAX Megabore column. Injector and detector were kept at 250 °C. Molecular weights were measured on a GPC system consisting of a Waters 510 HPLC pump, three Waters Ultrastyragel columns (500, 10^3, and 10^5Å), and a Waters 410 DRI detector, with a DMF flow rate of 1.0 mL/min, and polystyrene was used as standard. The composition of block copolymers was characterized using elemental analysis by Midwest Microlab, LLC.

Materials. *n*-Butyl acrylate (*n*-BA) and acrylonitrile (AN) were obtained from Aldrich; the inhibitor was removed by passing through a column of alumina. Cu^IBr and Cu^ICl were obtained from Aldrich and purified according to published procedures.[31] *N-tert*-Butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN or SG1, 93%) was received from Atofina (France) and used without further purification. $CuCl_2$ was obtained from Aldrich and used without purification. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA), methyl 2-bromopropionate (MBP), 2-bromopropionitrile (BPN), tetrahydrofuran (THF), ethylene carbonate (EC), dimethylformamide (DMF), and 2,2′-bipyridine (bpy), anisole, and azobis(isobutyronitrile) (AIBN) were used as received (Aldrich).

Typical Polymerization Procedures. (1) ATRP Process: Preparation of Poly(*n*-butyl acrylate) (PBA) Macroinitiator by ATRP (Table 1**, Entry 16**). First, 10 mL of *n*-BA (6.98×10^{-2} mol), 1.47×10^{-1} mL of PMDETA (6.98×10^{-4} mol), 1.56×10^{-1} mL of MBP (1.40×10^{-3} mol), and 5.0×10^{-1} mL of anisole (GC standard for conversion measurement) were mixed in a 25 mL Schlenk flask equipped with a magnetic stirring bar. The flask was subjected to three freeze−pump−thaw (FPT) cycles. Then, 1.002×10^{-1} g of CuBr (6.98×10^{-4} mol) was added to the flask while the contents were at a solid state and deoxygenated by vacuum followed by back-filling with nitrogen three times. The flask was placed in an oil bath set at 70 °C for 48 min. The reaction was terminated by the addition of aerated THF and passing through a column of alumina to remove the catalyst followed by evaporation. The solid products were dried in a vacuum oven, providing the desired polymer.

Table 1. Block Copolymerization from PBA to AN with Halogen Exchange at 70 °C by ATRP (Bold entries describe macroinitiators PBA)

no.	polymer	[monomer]/ [initiator]/ [CuX]/[ligand]	time (h)	convn (%)	M_n(GPC)	M_w/M_n
1[a]	**PBA**	**500:1:0.5:0.5**	**26**	**92.06**	**47000**	**1.11**
2[b]	PBA-*b*-PAN	1400:1:1:2	22.5	26.54	59 000	1.15
3[a]	**PBA**	**300:1:0.5:0.5**	**17**	**80.86**	**30000**	**1.17**
4[b]	PBA-*b*-PAN	1000:1:1:2	9.5	33.35	54 000	1.25
5[b]	PBA-*b*-PAN	600:1:1:2	6.75	21.64	47 000	1.16
6[b]	PBA-*b*-PAN	800:1:1:2	5.7	19.15	46 000	1.18
7[b]	PBA-*b*-PAN	1200:1:1:2	12	35.22	55 000	1.34
8[a]	**PBA**	**300:1:0.5:0.5**	**6**	**74.78**	**26000**	**1.18**
9[b]	PBA-*b*-PAN	1000:1:1:2	4.33	16.35	46 000	1.30
10[b]	PBA-*b*-PAN	1000:1:1:2	3	12.73	38 000	1.25
11[b]	PBA-*b*-PAN	1000:1:1:2	1.5	6.03	32 000	1.18
12[a]	**PBA**	**200:1:0.5:0.5**	**4.33**	**77.31**	**18000**	**1.20**
13[b]	PBA-*b*-PAN	800:1:1:2	4.5	25.64	42 000	1.36
14[a]	**PBA**	**100:1:0.5:0.5**	**1.15**	**81.43**	**10000**	**1.22**
15[b]	PBA-*b*-PAN	600:1:1:2	3	29.36	30 000	1.36
16[a]	**PBA**	**50:1:0.5:0.5**	**0.8**	**82.13**	**5100**	**1.23**
17[b]	PBA-*b*-PAN	400:1:1:2	5.25	47.75	28 000	1.32

[a] PBA series, monomer = *n*-BA, initiator = MBP, CuX = CuBr and Ligand = PMDETA; for block copolymer. [b] PBA-*b*-PAN series, monomer = AN, initiator = PBA (each block copolymer uses the PBA listed immediately above the copolymer in the table as the macroinitiator), CuX = CuCl and Ligand = bpy.

Chain Extension to Prepare a PBA-*b*-PAN Block Copolymer by ATRP (Table 1, Entry 17). First, 1.00 g of the above PBA macroinitiator (1.96×10^{-4} mol; M_n (GPC) = 5100 and $M_w/M_n = 1.23$), 5.2 mL of AN (7.84×10^{-2} mol), 0.6 mL of DMF, and 5.2 mL of EC were mixed in a 25 mL Schlenk flask equipped with a magnetic stirring bar. The flask was subjected to three FPT cycles. Then, 0.0194 g of CuCl (1.96×10^{-4} mol) and 0.0612 g of bpy (3.92×10^{-4} mol) were added to the flask, as above, and purged by back-filling with nitrogen. The flask was then placed in an oil bath set at 70 °C for 5.25 h. At the end of this time, the reaction mixture was dissolved in DMF, and the polymer was precipitated by adding into 50% aqueous methanol solution. The solid products were dried in a vacuum, yielding the desired block copolymer.

Preparation of Polyacrylonitrile (PAN) Macroinitiator by ATRP (Table 2, Entry 1). First, 10 mL of AN (1.52×10^{-1} mol), 6.74×10^{-2} mL of 2-bromopropionitrile (BPN) (7.60×10^{-4} mol), 0.1778 g of bpy (1.14×10^{-3} mol), and 10 mL of ethylene carbonate were mixed in a 50 mL Schlenk flask. The mixture was subjected to three FPT cycles. Copper(I) bromide (5.45×10^{-2} g, 3.80×10^{-4} mol) was added, as above, to the mixture which was then placed in an oil bath at 55 °C for 1.8 h. The purification procedure was the same as that used for the above PBA-*b*-PAN block copolymer.

Chain Extension to Prepare PAN-*b*-PBA by ATRP (Table 2, Entry 2). First, 2 mL of *n*-BA (1.40×10^{-2} mol), 0.366 g of the above PAN macroinitiator (1.0×10^{-6} mol; M_n (GPC) = 37000 and $M_w/M_n = 1.06$), 7.80×10^{-3} g of bipyridine (4.0×10^{-6} mol), 4 mL of dimethylformamide, and 0.4 mL of anisole were mixed in a 25 mL Schlenk flask. The mixture was degassed by conducting three FPT cycles. Then, 3.0×10^{-3} g copper(I) bromide (2.0×10^{-6} mol) was added to the mixture, as above, which was placed in an oil bath at 70 °C for 70 h. The purification procedure was same as that employed for the above PBA-*b*-PAN block copolymer.

(2) NMP process: Preparation of Nitroxide-Terminated Poly(*n*-butyl acrylate) (PBA) (Table 3, Entry 1). First, 10 mL of *n*-BA (6.98×10^{-2} mol), 0.0191 g of AIBN (1.16×10^{-4} mol), 0.1372 g of SG1 (4.66×10^{-4} mol), and 0.5 mL of anisole were mixed together in a 25 mL Schlenk flask. The homogeneous solution was a red-yellow color and was degassed by three FPT cycles and kept under a nitrogen atmosphere. The solution was then placed in an oil bath at 120 °C for 23.25

Table 2. Block Polymerization from PAN to *n*-BA at 70 °C by ATRP (Bold entries describe macroinitiators PAN)

no.	polymer	ligand	[monomer]/[initiator]/[catalyst]/[ligand]	time (h)	convn (%)	M_n(GPC)	M_w/M_n
1[a]	**PAN**	**bpy**	**200:1:0.5:1.5**	**1.8**	**68.70**	**37000**	**1.06**
2[b]	PAN-*b*-PBA	bpy	1400:1:2:4	70	no	/	/
3[b]	PAN-*b*-PBA	PMDETA	200:1:2:2	4.83	75.35	39 000	1.84
4[a]	**PAN**	**bpy**	**30:1:0.5:1.5**	**0.75**	**80.12**	**9800**	**1.08**
5[b]	PAN-*b*-PBA	PMDETA	60:1:2:2	22	81.77	30 000	2.28
6[a]	**PAN**	**bpy**	**40:1:0.1:0.3**	**2**	**44.61**	**5600**	**1.08**
7[b]	PAN-*b*-PBA	PMDETA	40:1:2:2	20.75	39.24	14 000	2.86
8[b]	PAN-*b*-PBA	PMDETA	40:1:0.3:0.3	3.17	90.74	11 000	1.08
9[b]	PAN-*b*-PBA	PMDETA	40:1:0.3:0.3:0.03[c]	164	60.14	7300	1.11

[a] PAN series, monomer = AN, initiator = BPN and CuX = CuBr; for block copolymer. [b] PAN-*b*-PBA series, monomer = *n*-BA, initiator = PAN (each block copolymer uses the PAN listed immediately above the copolymer in the table as the macroinitiator) and CuX = CuBr. Entry 9 used 10%. [c] $CuCl_2$.

Table 3. Block Polymerization from PBA to AN at 70 °C by NMP (Bold entries describe macroinitiators PBA)

no.	polymer	[monomer]/[initiator]/[SG1]	time (h)	convn (%)	M_n	M_w/M_n
1[a]	**PBA**	**600:1:4**	**23.25**	**84.68**	**31000**	**1.20**
2[b]	PBA-*b*-PAN	1000:1:0	4.33	85.48	47 000	1.22
3[b]	PBA-*b*-PAN	700:1:0	2	64.39	41 000	1.23
4[b]	PBA-*b*-PAN	400:1:0	2.17	64.02	37 000	1.23
5[a]	**PBA**	**600:1:4**	**11**	**80.60**	**27000**	**1.29**
6[b]	PBA-*b*-PAN	1000:1:0.1	9	64.87	30 000	1.38
7[a]	**PBA**	**100:1:4**	**24.42**	**73.50**	**5300**	**1.18**
8[b]	PBA-*b*-PAN	400:1:0.1	5.5	53.84	12 000	1.12
9[b]	PBA-*b*-PAN	400:1:0	9.83	48.11	15 000	1.18

[a] PBA series, monomer = *n*-BA and initiator = AIBN; for block copolymer. [b] PBA-*b*-PAN series, monomer = AN, initiator = PBA (each block copolymer uses the PBA listed immediately above the copolymer in the table as the macroinitiator).

Table 4. Block Polymerization from PAN to *n*-BA at 70 °C by NMP (Bold entries describe macroinitiators PAN)

no.	polymer	temp (°C)	[monomer]/[initiator]/[SG1]	time (h)	convn (%)	M_n	M_w/M_n
1[a]	**PAN**	**120**	**400:1:4**	**20**	**89.15**	**15000**	**1.10**
2[b]	PAN-*b*-PBA	120	1000:1:0	3.5	87.55	15 000	1.56
3[b]	PAN-*b*-PBA	80	1000:1:0	49	no		
4[b]	PAN-*b*-PBA	120	300:1:0.1	7.75	82.23	46 000	3.72
5[a]	**PAN**	**90**	**280:1:4**	**29**	**no**		
6[a]	**PAN**	**120**	**800:1:4**	**26.34**	**77.01**	**26000**	**1.22**
7[a]	**PAN**	**120**	**60:1:4**	**20.22**	**75.00**	**6400**	**1.07**
8[b]	PAN-*b*-PBA	120	88:1:0.1	5.58	73.45	13 000	1.17
9[b]	PAN-*b*-PBA	120	88:1:0	2.0	93.9	15 000	1.67

[a] PAN series, monomer = AN and initiator = AIBN; for block copolymer. [b] PAN-*b*-PBA series, monomer = *n*-BA, initiator = PAN (each block copolymer uses the PAN listed immediately above the copolymer in the table as the macroinitiator).

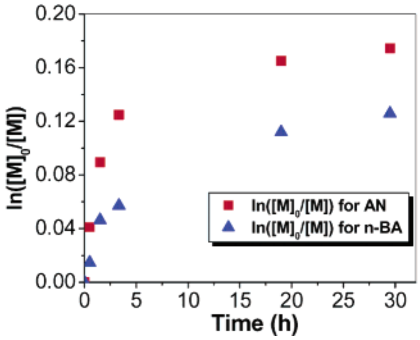

Figure 1. Simultaneous copolymerization: AN/*n*-BA = 30/70. First-order kinetic plots of monomer conversion as a function of reaction time for polymerization of *n*-BA and AN initiated by MBP in ethylene carbonate at 70 °C. [*n*-BA] = 2.76 M; [*n*-BA]/[AN]/[MBP]/[CuCl]/[bpy] = 70:30:0.5:0.5:1.

h. The purification procedure was same as that used above for PBA prepared by ATRP.

Chain Extension to Prepare Nitroxide-Terminated PBA-*b*-PAN (Table 3, Entry 2). First, 3.20 g of SG1-terminated PBA macroinitiator (1.04×10^{-4} mol; M_n (GPC) = 31000 and M_w/M_n = 1.20), 7 mL of AN ((1.04×10^{-1} mol), and 4 mL of ethylene carbonate were added to a 25 mL Schlenk flask, and the contents were degassed by three FPT cycles and placed under a nitrogen atmosphere. The solution was placed in an oil bath at 120 °C for 4.33 h. The purification procedure was the same as that used for the PBA-*b*-PAN block copolymer prepared by ATRP.

Preparation of Polyacrylonitrile (PAN) by NMP (Table 4, Entry 1). First, 5 mL of AN (7.60×10^{-2} mol), 0.0312 g of azobis(isobutyronitrile) (1.90×10^{-4} mol), 0.2234 g of SG1 (7.60×10^{-4} mol), and 5 mL of ethylene carbonate were mixed in a 25 mL Schlenk flask. The mixture was subjected to three FPT cycles and then placed in an oil bath at 120 °C for 20 h. The purification procedure was same as that used above for PAN prepared by ATRP.

Chain Extension to Prepare PAN-*b*-PBA by NMP (Table 4, Entry 2). First, 2 mL of *n*-BA (1.40×10^{-2} mol), 0.2044 g of the above PAN (1.42×10^{-5} mol; M_n (GPC) = 15000 and M_w/M_n = 1.10), 4 mL of dimethylformamide, and 0.4 mL of anisole were mixed in a 25 mL Schlenk flask. The mixture was subjected to three FPT cycles then placed in an oil bath at 120 °C for 3.5 h. The purification procedure was the same as that used for the PBA-*b*-PAN block copolymer prepared by ATRP.

Results and Discussion

1. Simultaneous Copolymerization of *n*-BA and AN by ATRP. These experiments were employed to investigate the relative reactivity ratios of AN and *n*-BA in random copolymerization. Mixtures of *n*-BA and AN with different molar ratios (*n*-BA/AN: 70/30 and 30/70) were employed for simultaneous copolymerization by ATRP. MBP was used as the initiator for 70/30 ratio and BPN was used for the 30/70 ratio. CuCl/bpy and EC were used as catalyst and solvent in both cases. As shown in Figures 1 and 2, the significant curvature of the kinetics plots indicates that the concentration of active species was not constant throughout the reaction. The rate of polymerization for AN was about 30−50% faster than that for *n*-BA. This may originate from different equilibrium constants for AN and *n*-BA systems.

On the basis of the above experiments, the reactivity ratios were calculated using the "sum-of square space" approach.[32] The obtained values of r_1(AN) = 1.72 ± 0.1 and r_2(*n*-BA) = 0.65 ± 0.1, were in acceptable agreement with the values measured by conventional radical copolymerization.[33,34] They indicated that an AN monomer had a higher reactivity for both AN and *n*-BA

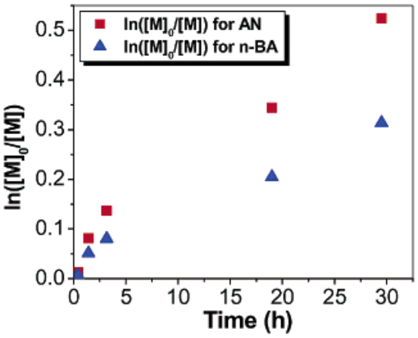

Figure 2. Simultaneous copolymerization: AN/*n*-BA = 70/30. First-order kinetic plots of monomer conversion as a function of reaction time for polymerization of *n*-BA and AN initiated by BPN in ethylene carbonate at 70 °C. [AN] = 3.68 M; [AN]/[*n*-BA]/[BPN]/[CuCl]/[bpy] = 70:30:0.5:0.5:1.

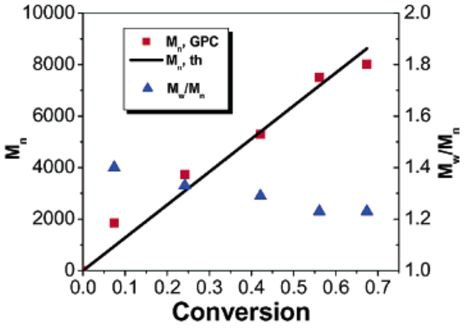

Figure 3. Number-average molecular weight and polydispersity as a function of conversion for bulk polymerization of *n*-BA initiated by BPN at 70 °C. [*n*-BA] = 6.58 M; [*n*-BA]/[BPN]/[CuBr]/[PMDETA] = 100:1:0.3:0.3.

radicals than an *n*-BA monomer. In ATRP systems, the homopolymerization of AN was faster than that of *n*-BA. This may be related to higher equilibrium constant in AN polymerization deduced from facile termination, which was supported by the following model studies.

2. ATRP. (1) ATRP Model Study. Model studies were conducted for polymerization of *n*-BA initiated by BPN (model of PAN−Br) and for polymerization of AN initiated by MBP (model of PBA−Br). The first-order plot for the polymerization of *n*-BA revealed a linear semilogarithmic relationship between monomer concentration and reaction time. The molecular weight increased linearly with conversion, which meant that the concentration of growing chains was essentially constant throughout the polymerization. The polydispersity decreased with conversion approaching the value of M_w/M_n = 1.23 at the end of polymerization (Figure 3). Together, all these factors indicated that the polymerization was well controlled. We can conclude from these model studies that a polyacrylonitrile macroinitiator should efficiently form a block copolymer with PBA.

The polymerization of acrylonitrile initiated by MBP was examined with and without halogen exchange. For both cases, the kinetics showed slight curvature at high conversion (Figure 4). The rate of polymerization without halogen exchange was faster than that with halogen exchange, which was attributed to slower activation of C−Cl bond in comparison to C−Br. The molecular weight also displayed a linear dependence on conversion (Figure 5). The values of molecular weight obtained by GPC were much higher than theoretical values due to the differences in hydrodynamic volumes of PAN and polystyrene standards.[35] The molecular weight and polydispersity for PAN prepared with halogen exchange were lower than those without halogen exchange. Moreover, the GPC traces for PAN with halogen exchange shifted more than the traces from polymers prepared without halogen exchange. Thus, for chain-extension from PBA to AN, introduction of halogen exchange technique should yield a more precise block copolymer than without halogen exchange.

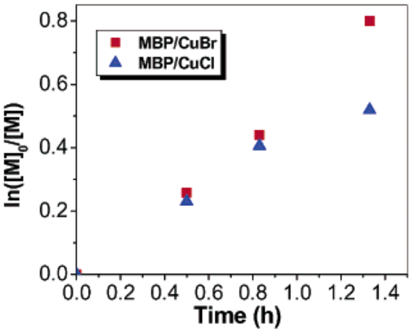

Figure 4. First-order kinetic plot of monomer conversion as a function of conversion for polymerization of AN initiated by MBP with or without halogen exchange in ethylene carbonate at 70 °C. [AN] = 7.21 M, [AN]/[MBP]/[CuX]/[bpy] = 200:1:1:2, and X = Br, Cl.

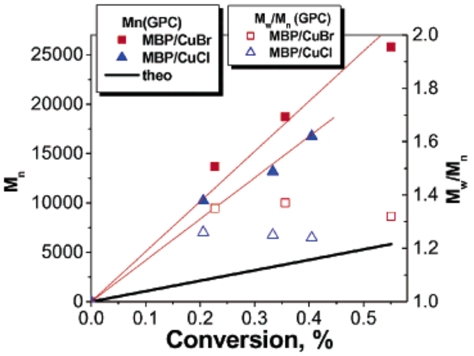

Figure 5. Number-average molecular weight and polydispersity as a function of conversion for polymerization of AN initiated by MBP with or without halogen exchange in ethylene carbonate at 70 °C. [AN] = 7.21 M, [AN]/[MBP]/[CuX]/[bpy] = 200:1:1:2, and X = Br, Cl.

(2) Block Polymerization from PBA to AN. I. Halogen Exchange. A series of PBA macroinitiators (Table 1, entries 1, 3, 8, 12, 14, and 16) and block copolymers (Table 1, entries 2, 4−7, 9−11, 13, 15, and 17) were synthesized. Reaction conditions and results for these series are shown in Table 1. All of these macroinitiators had well-defined functionality, predetermined molecular weight, and low polydispersity, ensuring that nearly all chains were functional and capable of initiating polymerization of a second block. The macroinitiators were subjected to chain extension with AN in ethylene carbonate at 70 °C leading to well-defined block copolymers. Kinetic studies (Figure 6) showed that the formation of the block copolymer obeyed first-order kinetics. An increase of the macroinitiator concentration (decrease of the molecular weight) resulted in an increase of the rate of polymerization. The molecular weight linearly increased with conversion while polydispersity remained low during the polymerization (Figure 7).

When a low molecular weight PBA was used as macroinitiator, the GPC traces shifted cleanly and completely. However, as the molecular weight of the macroinitiator increased, the GPC traces of the resulting block copolymers became slightly bimodal, especially

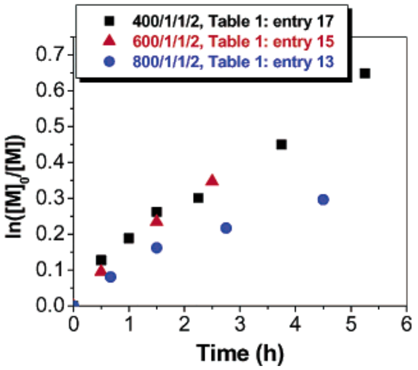

Figure 6. First-order kinetic plot of monomer conversion as a function of reaction time for block polymerization (Table 1: (■) entry 17; (▲) entry 15; (●) entry 13) of AN initiated by PBA with halogen exchange in ethylene carbonate at 70 °C with various [AN]/[PBA]/[CuCl]/[bpy] ratios and molecular weight of macroinitiator PBA (Table 1: (■) entry 16; (▲) entry 14; (●) entry 12). [AN] = 7.21 M.

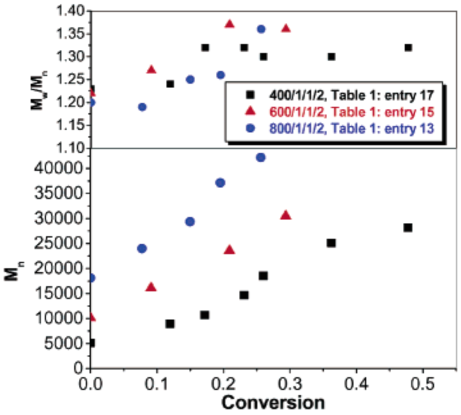

Figure 7. Number-average molecular weight and polydispersity as a function of conversion for block polymerization (Table 1: (■) entry 17; (▲) entry 15; (●) entry 13) of AN initiated by PBA with halogen exchange in ethylene carbonate at 70 °C with various [AN]/[PBA]/[CuCl]/[bpy] ratios and molecular weight of macroinitiator PBA (Table 1: (■) entry 16; (▲) entry 14; (●) entry 12). [AN] = 7.21 M.

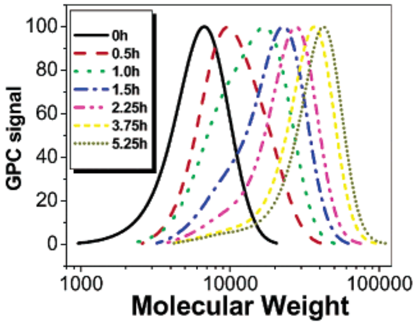

Figure 8. GPC traces for block polymerization (Table 1, entry 17) of AN initiated by PBA (Table 1, entry 16) with halogen exchange in ethylene carbonate at 70 °C. [AN] = 7.21 M; [PBA]/[CuCl]/[bpy] = 1:1:2.

when using a high molecular weight macroinitiator (Figures 8 and 9). This indicated that the blocking efficiency, or cross-propagation reaction, decreased when the molecular weight of macroinitiator increased.

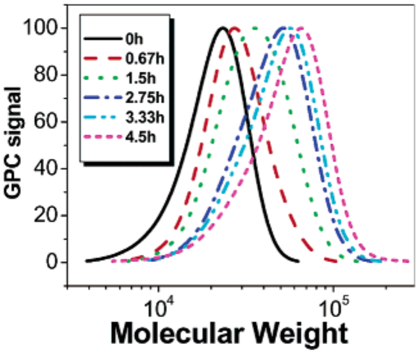

Figure 9. GPC traces for block polymerization (Table 1: entry 13) of AN initiated by PBA (Table 1, entry 12) with halogen exchange in ethylene carbonate at 70 °C. [AN] = 7.21 M; [PBA]/[CuCl]/[bpy] = 1:1:2.

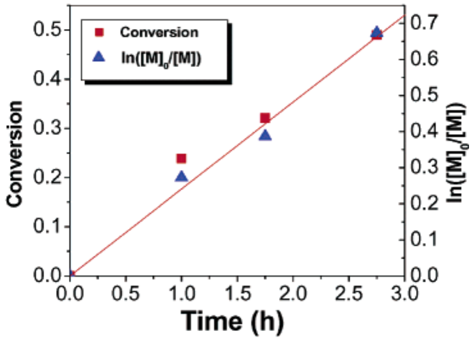

Figure 10. First-order kinetic plot of monomer conversion as a function of reaction time for block polymerization of AN initiated by PBA (Table 1, entry 16) without halogen exchange in ethylene carbonate at 70 °C. [AN] = 7.21 M; [AN]/[PBA]/[CuBr]/[bpy] = 400:1:1:2.

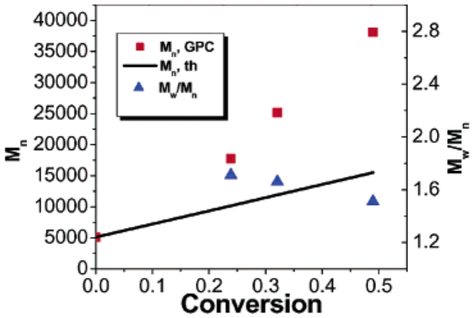

Figure 11. Number-average molecular weight and polydispersity as a function of conversion for block polymerization of AN initiated by PBA (Table 1, entry 16) without halogen exchange in ethylene carbonate at 70 °C. [AN] = 7.21 M; [AN]/[PBA]/[CuBr]/[bpy] = 400:1:1:2.

II. No Halogen Exchange. To examine the blocking efficiency without halogen exchange, a bromine-terminated PBA was used as the macroinitiator for polymerization of AN using CuBr as the catalyst instead of CuCl. All other experimental conditions were the same as for the synthesis with halogen exchange (Table 1, entry 17). The kinetic curve (Figure 10) indicated that the polymerization was also a first-order reaction. When compared with the synthesis using halogen exchange (Table 1, entry 17), the rate of polymerization without halogen exchange was faster. This was identical to the result obtained with model studies. The molecular weight increased linearly with conversion (Figure 11) while polydispersity decreased during the polymerization. However, the polydispersity index (PDI = 1.51) was significantly higher than when halogen exchange was used for the preparation of the second block. GPC traces showed that there was an initial bimodal distribution and a tail on the low molecular weight side remained discernible after the reaction ended, which meant that the initiation was not as fast as propagation. Thus, slow initiation resulted in lower blocking efficiency than that observed for the system employing halogen exchange. These results confirmed the results found in the model studies.

(3) Block Polymerization from PAN to *n*-BA. Since polyacrylonitrile was not soluble in *n*-BA, solvents (such as ethylene carbonate) had to be used. Since polyacrylonitrile easily lost chain end functionality, the preparation of block copolymers from a polyacrylonitrile macroinitiator was more challenging, although the model studies were successful.

A series of polyacrylonitrile macroinitiators (Table 2, entries 1, 4, and 6) were used for preparation of block copolymers (Table 2, entries 2, 3, 5, and 7−9). Reaction results and conditions used for homopolymerization to form the macroinitiators and for chain extension to prepare block copolymers are shown in Table 2.

In the first attempt, relatively higher molecular weight PAN was used as a macroinitiator (Table 2, entry 1). When bpy was used as a ligand, the rate of copolymerization of the second block was too low (Table 2, entry 2). High conversion and polymerization rate of *n*-BA could be achieved when bpy was replaced with PMDETA (Table 2, entry 3); however, the polydispersity of the product was high (PDI = 1.81). The bimodal molecular weight distribution of the attempted block copolymers could be attributed to the initial heterogeneity of this system due to poor solubility of high molecular weight PAN. Therefore, a lower molecular weight PAN (Table 2, entry 4) was also used as a macroinitiator. This PAN was soluble in a mixture of *n*-BA and ethylene carbonate. However, the GPC traces still showed a distinct bimodal distribution, with one peak obviously corresponding to the macroinitiator. This indicated that some macroinitiator chains were inactive. Indeed, NMR confirmed loss of chain end functionality: 61% of the bromine groups were lost (the methyl group originating from BPN at the end of the polymer chain absorbed at 1.3 ppm while the methine proton (−CH(CN)Br) of the *ω*-end group absorbed at 5.2 ppm. Integration of these signals provided information on chain end functionality and was a 3:1 ratio for 100% functionality), explaining the observed bimodal distribution.

It was reported earlier,[24] that in an ATRP homopolymerization of AN, chain end functionality can be significantly increased by decreasing the catalyst concentration. Following this result, polyacrylonitrile with high chain end-functionality was prepared by decreasing the molar ratio of the catalyst to the initiator from 0.5:1 (Table 2, entry 4) to 0.1:1 (Table 2, entry 6). The NMR spectrum of this polymer confirmed that most of the end groups were active. However, even when using this high functionality, low molecular weight PAN (Table 2, entry 6), block polymerization (Table 2, entry 7) was not successful. A well-defined copolymer with low polydispersity (PDI = 1.08) was obtained only when Cu(I): initiator ratio was decreased from 2:1 to 0.3:1 (Figure 12). This result confirmed that a high concentration of catalyst can cause the loss of chain end functionality not only in the homopolymerization of AN but also in the case when a PAN macroinitiator was used for block copolymerization. When the catalyst concentration was decreased, higher conversion of *n*-BA was attained and the rate of polymerization was even faster than in the polymerizations with higher catalyst concentration (Table 2, entries 7 and 8). The kinetics obeyed first order (Figure 13) and molecular weight correlated linearly with conversion (Figure 14). Introduction of 10% $CuCl_2$ vs CuBr (Table 2, entry 9), improved control but reduced the rate of polymerization. Halogen exchange was not necessary to attain good control in this chain-extension reaction.

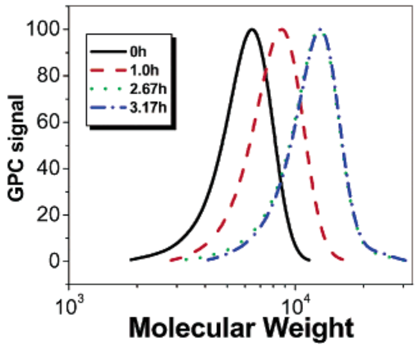

Figure 12. GPC traces for block polymerization (Table 2, entry 8) of *n*-BA initiated by PAN (Table 2, entry 6) in ethylene carbonate at 70 °C. [*n*-BA] = 2.22 M; [*n*-BA]/[PAN]/[CuBr]/[PMDETA] = 40:1:0.3:0.3.

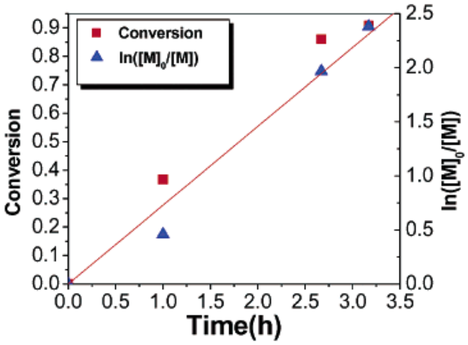

Figure 13. First-order kinetic plot of monomer conversion as a function of reaction time for block polymerization (Table 2, entry 8) of *n*-BA initiated by PAN (Table 2, entry 6) in ethylene carbonate at 70 °C. [*n*-BA] = 2.22 M; [*n*-BA]/[PAN]/[CuBr]/[PMDETA] = 40:1:0.3:0.3.

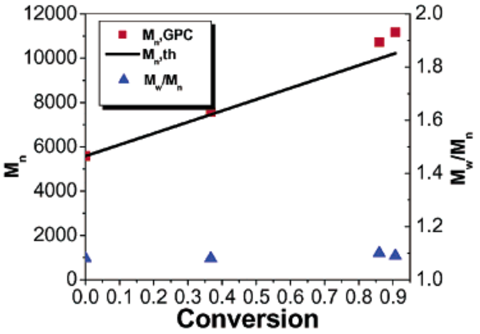

Figure 14. Number-average molecular weight and polydispersity as a function of conversion for block polymerization (Table 2, entry 8) of *n*-BA initiated by PAN (Table 2, entry 6) in ethylene carbonate at 70 °C. [*n*-BA] = 2.22 M; [*n*-BA]/[PAN]/[CuBr]/[PMDETA] = 40:1:0.3:0.3.

3. NMP. (1) Block Polymerization from PBA to AN. A series of nitroxide-terminated PBA homopolymers (Table 3, entries 1, 5, and 7) was prepared for block polymerization (Table 3, entries 2−4, 6, 8, and 9) studies. Polymerization of *n*-BA was carried out at AIBN:SG1 ratio of 1:4. SG1 was used in such excess in order to increase the rate of deactivation and thus improve the molecular weight distribution. Table 3 summarized the results for both the initial homopolym-

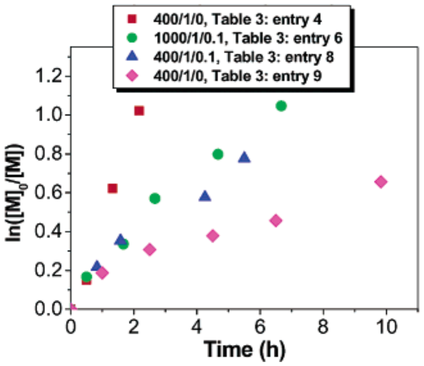

Figure 15. First-order kinetic plot of monomer conversion as a function of reaction time for block polymerization (Table 3: (■) entry 4; (●) entry 6; (▲) entry 8; (◆) entry 9) of AN initiated by PBA with/without SG1 at 120 °C under various [AN]/[PBA]/[SG1] ratios and molecular weight of macroinitiator PBA (Table 3: (■) entry 1; (●) entry 5; (▲, ◆) entry 7). [AN] = 9.23M.

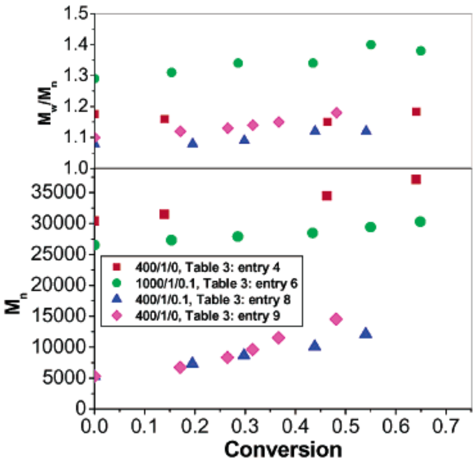

Figure 16. Number-average molecular weight and polydispersity as a function of conversion for block polymerization (Table 3: (■) entry 4; (●) entry 6; (▲) entry 8; (◆) entry 9) of AN initiated by PBA with/without SG1 at 120 °C under various [AN]/[PBA]/[SG1] ratios and molecular weight of macroinitiator PBA (Table 3: (■) entry 1; (●) entry 5; (▲, ◆) entry 7). [AN] = 9.23M.

erization step and subsequent block polymerization. In agreement with previous reports,[30,36] the *n*-BA polymerization showed linear kinetics, and molecular weight increased with conversion while polydispersity remained low.

The formation of block copolymers was investigated both with and without the presence of excess SG1 in the reaction medium. The semilogarithmic kinetic plots of ln($[M]_0$/[M]) vs time showed that in the absence of excess SG1, for both high and low molecular weight PBA macroinitiators, the conversion was proportional to the reaction time (Figure 15 and Table 3, entries 4 and 9). When an excess of SG1 was used, semilogarithmic kinetic plots for both high and low molecular weight PBA were also linear (Figure 15 and Table 3, entries 6 and 8), indicating that no detectable termination was occurring in these systems and that the radical concentration remained constant during the reaction. After the introduction of excess SG1, the rate of polymerization decreased since the excess SG1 increased the rate of deactivation. The evolution of molecular weight with conversion during the reaction is shown in Figure 16. A linear relationship between molecular weight and conversion was obtained, while polydispersity was maintained below 1.4. Moreover, the excess SG1 resulted in better control as indicated by the narrowing of the molecular weight distribution (Table 3, entry 8) and polydispersity as low as 1.12. The polydispersity of copolymer of entry 6 in Table 3 prepared with excess SG1 was a little higher because of the higher polydispersity of the corresponding macroinitiator PBA (Table 3, entry 5). In all experiments conducted without addition of excess SG1, the polydispersities were higher, which may be explained by the very low initial concentration of free nitroxide leading to a decrease in the initial rate of deactivation.

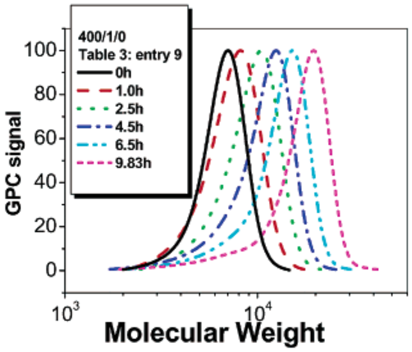

Figure 17. GPC traces for block polymerization (Table 3, entry 9) of AN initiated by PBA (Table 3, entry 7) without SG1 at 120 °C. [AN] = 9.23M; [AN]/[PBA] = 400:1.

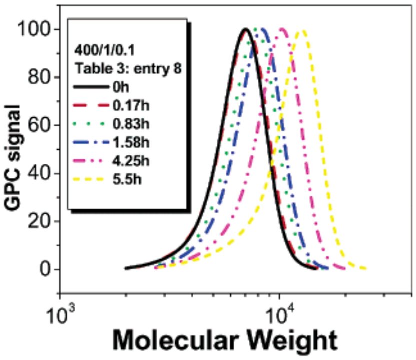

Figure 18. GPC traces for block polymerization (Table 3, entry 8) of AN initiated by PBA (Table 3, entry 7) with SG1 at 120 °C. [AN] = 9.23M; [AN]/[PBA]/[SG1] = 400:1:0.1.

GPC traces (Figures 17 and 18) also indicated that the presence of excess SG1 had a beneficial effect on narrowing the molecular weight distribution. Without added excess of SG1, the GPC traces of the resulting block copolymer showed a small shoulder on the low molecular weight side of molecular weight distribution, especially for those polymers prepared with high molecular weight PBA macroinitiator. Once SG1 was introduced, the GPC traces showed clean shift with monomodal distribution.

(2) Block Polymerization from PAN to *n*-BA. The homopolymerization of AN was investigated by using AIBN as an initiator and SG1 as a control agent. The results are shown in Table 4 (entries 1 and 5−7). At 90 °C, the rate of polymerization was either very slow or the reaction did not take place (Table 4, entry 5). When the temperature was increased to 120 °C, the rate of polymerization became much faster; this was similar to results previously reported.[26] The plot of ln($[M]_0$/[M]) vs reaction time was linear (Figure 19), indicating that the concentration of active radicals remained constant during the reaction. An NMR spectrum of the resulting

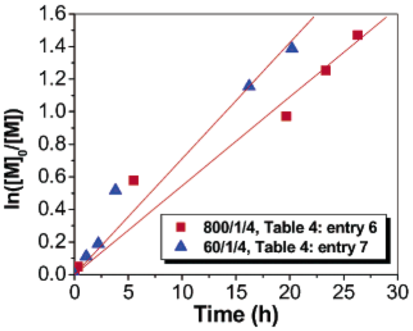

Figure 19. First-order kinetic plot of monomer conversion as a function of reaction time for homopolymerization (Table 4: (■) entry 6 and (▲) entry 7) of AN initiated by AIBN with SG1 at 120 °C under various [AN]/[AIBN]/[SG1] ratios. [AN] = 7.24 M.

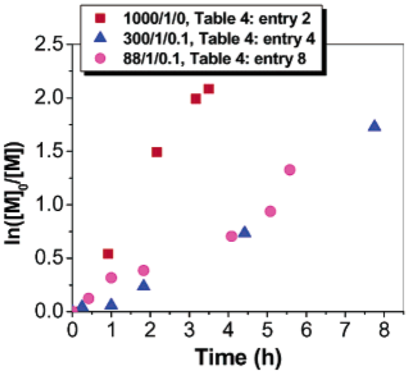

Figure 20. First-order kinetic plot of monomer conversion as a function of reaction time for block polymerization (Table 4: (■) entry 2; (▲) entry 4; (●) entry 8) of *n*-BA initiated by PAN with/without SG1 at 120 °C under various [AN]/[AIBN]/[SG1] ratios and molecular weight of macroinitiator PAN (Table 4: (■, ▲) entry 1; (●) entry 7). [*n*-BA] = 2.21 M.

polymer showed that most nitroxide functional groups remained at the end of the PAN polymer chain. This was in contrast to the results obtained with ATRP, and one can conclude that the end functional groups on PAN prepared by NMP were stable. The molecular weight increased linearly with conversion while polydispersity index remained below 1.10.

PAN-*b*-PBA block copolymers (Table 4, entries 2−4 and 8) were synthesized using PAN macroinitiators with and without addition of excess SG1. For this polymerization, the semilogarithmic plots of conversion vs reaction time (Figure 20) were in both cases linear. The initial polymerization experiment was conducted at 80 °C and no reaction occurred; therefore, all other experiments were run at 120 °C. When a higher molecular weight polyacrylonitrile (Table 4, entry 1) was used as the macroinitiator, without the addition of excess SG1, GPC traces of the resulting copolymer indicated that most of the macroinitiator remained unchanged. When excess SG1 was present, the GPC traces of the polymers shifted further into the higher molecular weight region in comparison with polymers prepared without excess SG1 (Figure 21), although the curves were still bimodal. This indicated that the addition of SG1 did improve blocking efficiency. High polydispersity of the resulting block copolymer might have been caused by the reaction medium heterogeneity due to insolubility of high molecular weight polyacrylonitrile in *n*-BA. If so, one would expect the improvement of the polydispersity when using the PAN macroinitiator with molecular weight low enough to ensure its solubility in *n*-BA. The successful preparation of a block copolymer of PAN-*b*-PBA from such lower molecular weight macroinitiator (Table 4, entry 8) confirmed this hypothesis. However, even though the polydispersity of the copolymer was low (PDI = 1.17) and its GPC traces were shifted to high molecular weight, a small shoulder was still discernible in the low molecular weight range (Figure 22). Compared to this experiment, entry 9 in Table 4 further confirmed that, with excess SG1, the control of molecular weight distribution was worse (PDI = 1.67). This indicated that the formation of a block copolymer through chain extension from PAN to *n*-BA was not as well controlled as when conducting chain extension from a PBA macroinitiator to AN.

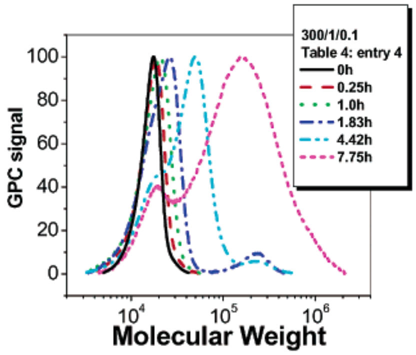

Figure 21. GPC traces for block polymerization (Table 4, entry 4) of *n*-BA initiated by PAN (Table 4, entry 1) with SG1 at 120 °C. [*n*-BA] = 2.21 M; [*n*-BA]/[PAN]/[SG1] = 300:1:0.1.

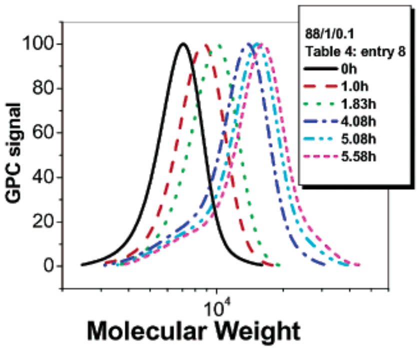

Figure 22. GPC traces for block polymerization (Table 4, entry 8) of *n*-BA initiated by PAN (Table 4, entry 7) with SG1 at 120 °C. [*n*-BA] = 2.21 M; [*n*-BA]/[PAN]/[SG1] = 88:1:0.1.

Conclusions

In conclusion, the formation of block copolymers of *n*-BA and AN was investigated using ATRP and NMP. The overall result was that a PAN macroinitiator (the first block) can more easily cross-propagate and polymerize *n*-BA (the second block) than the reverse block polymerization reaction from PBA to AN.

The use of ATRP allowed the synthesis of well controlled block copolymers from *n*-BA and AN employing either PAN or PBA as the macroinitiator. Actual block copolymerizations confirmed predictions from model studies. The studies indicated that polyacrylonitrile with high chain end-functionality can easily be prepared and the macroinitiators can be chain extended with *n*-BA in homogeneous systems forming a block copolymer. Blocking efficiency was high. In the preparation of block copolymers starting from a PBA macroinitiator, the use of the halogen exchange technique gave better control over the polymerization of AN than without halogen exchange. This observation can be explained by the inefficiency of chain-extension from a *n*-BA macroinitiator to AN in the absence of halogen exchange due to lower bond dissociation energy of C−X in 2-bromopropionitrile (or 2-chloropropionitrile) in comparison with C−X in 2-bromopropionate (or 2-chloropropionate) With halogen exchange, the C−Br bond in PBA can be rapidly converted to a C−Cl bond in PAN, making the rate of cross-propagation comparable to the subsequent rate of propagation. Therefore, block polymerization can be efficiently conducted. However, for the cross-propagation from PAN to *n*-BA, a well-defined block copolymer can be prepared without halogen exchange because C−Br in 2-bromopropionate has a higher bond dissociation energy than that in 2-bromopropionitrile. In NMP, the presence of excess SG1 played an important role in controlling the blocking efficiency. The excess SG1 increased the initial rate of deactivation and finally resulted in a decrease of polydispersities of block copolymers. The cross-propagation from PAN to *n*-BA was less efficient than that from PBA to AN.

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