Synthesis of Block Copoly(styrene-*b*-*p*-nitrophenyl methacrylate) and Its Derivatives by Atom Transfer Radical Polymerization

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ABSTRACT: The preparation of block poly(styrene-*b*-*p*-nitrophenyl methacrylate) (PSt-*b*-PNPMA) and its hydrolysis and amino substitution products, poly(styrene-*b*-methacrylic acid) (PSt-*b*-PMAA) and poly(styrene-b−N-butyl methacrylamide) (PSt-*b*-PBMAD), were described. Polystyrene macroinitiator (PSt-Br) with narrow molecular weight distribution (MWD; $M_w/M_n = 1.18$, $M_n = 14\,730$) was prepared by ATRP using ethyl 2-bromobutyrate (EBB) as initiator and CuBr/2,2′-bipyridine(bpy) as catalyst. Then, (PSt-*b*-PNPMA)s were synthesized by ATRP of NPMA using PSt-Br as initiator and CuBr/bpy as catalyst. GPC and NMR studies showed that the plot of $\ln([NPMA]_0/[NPMA])$ against polymerization time was linear, molecular weight (M_n) increased linearly with conversion, and the molecular weight distributions were narrow (1.26−1.38) and became narrower as M_n increased. PSt-*b*-PNPMA formed micelles in chloroform with PSt as shell and PNPMA as core but formed inverse micelles in dimethyl sulfoxide. PSt-*b*-PMAA and PSt-*b*-PBMAD were characterized by FTIR and NMR, but MWDs of PNPMA prepared by atom transfer radical polymerization were broad ($M_w/M_n = 1.57-2.45$). The difference between the copolymerization and homopolymerization of NPMA was discussed.

Introduction

Amphiphilic diblock copolymers, such as copoly(styrene-*b*-acrylic acid) and so on, in aqueous media generally yield colloidal micelles with hydrophobic blocks as the core and hydrophilic blocks as the shell.[1−3] The micelles have potential applications in, for example, controlled drug delivery.[4] For understanding of the structure−micelles morphology−properties relationships of the diblock copolymers, the preparation of the copolymers with well-defined structures, such as molecular weight (MW) and molecular weight distribution (MWD), composition, architecture and end group functionality, is very important, and this has been carried out by the following three methods:[5] (1) sequential monomer addition, (2) coupling reaction of "living" polymer chains, and (3) mechanism transformation. Among the amphiphilic diblock copolymers prepared, copoly(St-*b*-AA) and PSt-*b*-poly(*N*-alkyl acrylamide) (PSt-*b*-PNAAD) have not been prepared directly from the corresponding monomers. Because of the characters of monomers AA and NAAD, their polymerizations in the presence of anionic and cationic initiators are impossible. Thus, the second method, the first and the third methods involving ionic polymerization could not be used in the preparation of these diblock copolymers. Only controlled free radical polymerization is possible to prepare the diblock copolymers. Among the recent developed controlled/living radical polymerizations, stable free radical polymerization (SFRP),[6−8] atom transfer radical polymerization (ATRP),[9−15] and reversible addition−fragmentation chain transfer (RAFT),[16,17] only RAFT was used to prepare diblock copolymers, such aspoly(butyl acrylate)-*b*-poly(acrylic acid) (PBA-*b*-PAA) and poly(methyl methacrylate)-*b*-poly(*N*,*N*-dimethylacrylamide) (PMMA-*b*-PDMA), using sequential monomer addition.[17] However, all of the polymers and copolymers were yellow. Poly(methyl acrylate)-*b*-poly(*N*,*N*-dimethylacrylamide) prepared by ATRP was reported.[18] Until now, PSt-*b*-PAA was prepared by sequential anionic polymerization of St, followed by *tert*-butyl acrylate (tBA), and then hydrolysis of the diblock copolymer using *p*-toluenesulfonic acid as catalyst.[3] In comparison with tBA, p-nitrophenyl (meth)acrylate (NPMA) can more easily be hydrolyzed or substituted by amino group. PolyNPMA has been synthesized by normal radical polymerization. After being hydrolyzed or substituted by amino group, the corresponding derivatives have been found important applications in biological and medical fields.[19−22] So, it should be interesting to synthesize well-defined diblock copolymers from *p*-nitrophenyl (meth)acrylate and styrene. It has been proven that ATRP could be used to synthesize polymers with narrow molecular weight distribution (MWD),[10] well-defined block copolymers,[23,24] and star polymers.[25,26] In this paper, we reported the synthesis of well-defined block copoly(styrene-*b*-*p*-nitrophenyl methacrylate) (PSt-*b*-PNPMA) by ATRP and its derivatives, copoly(styrene-*b*-methacrylic acid) (PSt-*b*-PMAA) and copoly(styrene-*b*-*N*-butyl methacrylamide) (PSt-*b*-PBMAD), by hydrolysis and amino substitution respectively, as described in Scheme 1.

Experimental Section

Materials. Methacrylic chloride (Fluka) and *p*-nitrophenol (Shanghai Chemical Reagent Company) were used as received. *p*-Nitrophenyl methacrylate (NPMA) was synthesized[27] and purified by recrystallization from petroleum ether. Its melt point was 94−95 °C. Styrene (Shanghai Chemical Reagent Plant) was stirred over CaH_2 and was distilled prior to use. CuBr (Shanghai Chemical Reagent No. 1 Plant) was purified by stirring it in acetic acid, washing with methanol, and drying in a vacuum. Ethyl 2-bromobutyrate (EBB) (99% Aldrich) was distilled. 2,2′-Bipyridine (bpy) (Shanghai Chemical Reagent No. 1 Plant) was used as received. *n*-Butylamine (Shanghai Associate Chemical Plant) was distilled over KOH after refluxing for 6 h. All other solvents used were purified by standard procedures.

General Procedures of ATRP. In a dried glass tube with a magnetic bar, CuBr and bpy were mixed for about half an hour. Then, monomer and initiator were added successively.

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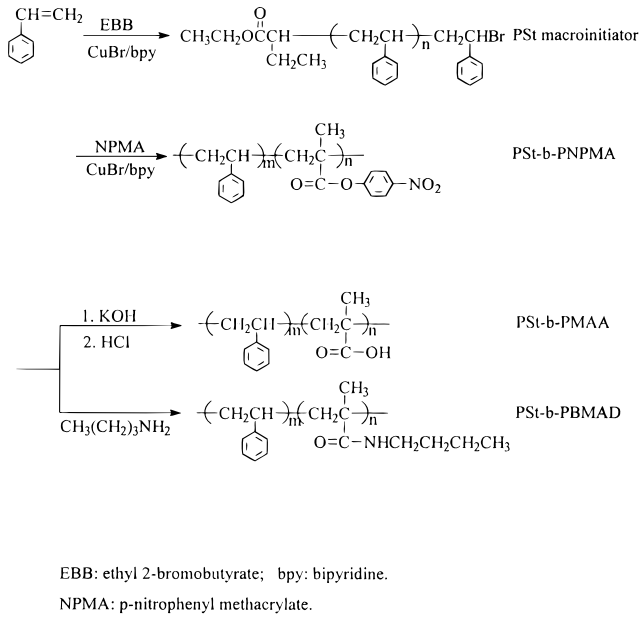
Scheme 1



EBB: ethyl 2-bromobutyrate; bpy: bipyridine.

NPMA: p-nitrophenyl methacrylate.

For homopolymerization of NPMA or St, EBB was used as initiator. The mixture of monomer, EBB, CuBr, and bpy was degassed three times before sealing under vacuum. The tube was then placed in an oil bath thermostated at 110 °C for a certain time. About 30 mg of the reaction mixture was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) for NMR measurements. On the basis of the intensities of the peak at 5.96 ppm ($I_{5.96}$) corresponding to vinyl protons in NPMA and the peak at 8.11−8.32 ppm representative of phenyl protons at positions ortho to a nitro group, conversion (conv) could be calculated according to eq 1:

$$\text{conv}(\%) = (I_{8.31} - 2I_{5.96})/I_{8.31} \times 100\% \qquad (1)$$

The remained reaction mixture was dissolved in THF and then passed through a column of neutral alumina for removing the metal salts. The polymer was precipitated from an excess of methanol, collected by filtration, and then dried under vacuum at 50 °C for 24 h. In block copolymerization of St with NPMA, PSt-Br prepared by ATRP was used as initiator. The polymerization procedure was the same as that of homopolymerization.

Hydrolysis of PSt-*b*-PNPMA. The copolymer (0.4 g), was dissolved in 4 mL of THF. The solution of potassium hydroxide in ethanol (1 M, KOH/NPMA = 4:1 in molar ratio) was added and refluxed for 24 h. Then, excess aqueous solution of hydrogen chloride was added. The precipitate was collected by filtration and dried under vacuum for 24 h at 50 °C.

Amino Substitution of PSt-*b*-PNPMA. The copolymer (0.4 g) was dissolved in 4 mL of THF. Then, *n*-butylamine (in 9:1 molar ratio to NPMA unit) was added and refluxed for 24 h. The product was obtained by precipitation in excess methanol and dried under vacuum for 24 h at 50 °C.

Characterization. ^{1}H NMR spectra were recorded on Bruker-500 spectrometer in DMSO-d_6 or $CDCl_3$. Gel permeation chromatography (GPC) analysis of the polymers was performed on a Water-150C GPC apparatus equipped with three columns (100, 10^3, and 10^5 Å) at 30 °C with a flow rate of 1.0 mL/min. DMF and THF were used as solvent for PNPMA and PSt-*b*-PNPMA, respectively. The calibrations were based on standard poly(methyl methacrylate) for PNPMA, and on standard PSt for PSt-*b*-PNPMA. FTIR spectra were recorded on a Bruker Vector-22 spectrometer. Dynamic laser light scattering was carried out at 25 °C using a modified commercial light-scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 digital time correlator and a solid-state laser (ADLAS DPY 425 II, output power ca. 400 mW at λ = 532 nm).

Table 1. Homopolymerization Results of NPMA by ATRP in Bulk at 110 °C[a]

#	NPMA/EBB[b] (molar ratio)	time (h)	conversion (%)	M_n (theo)[c]	M_n (GPC)	M_w/M_n
1	50	27	50	5 330	6 800	1.57
2	75	24	50	7 930	9 870	2.45
3	100	27	50	10 530	15 220	2.08
4	200	24	50	20 930	19 140	1.91

[a] Stoichiometry of [I]:[CuBr]:[bpy] = 1:1:2. [b] NPMA = *p*-nitrophenyl methacrylate; EBB = ethyl 2-bromobutyrate. [c] M_n (theo) = conversion × [NPMA]/[EBE] × 207 + 129.

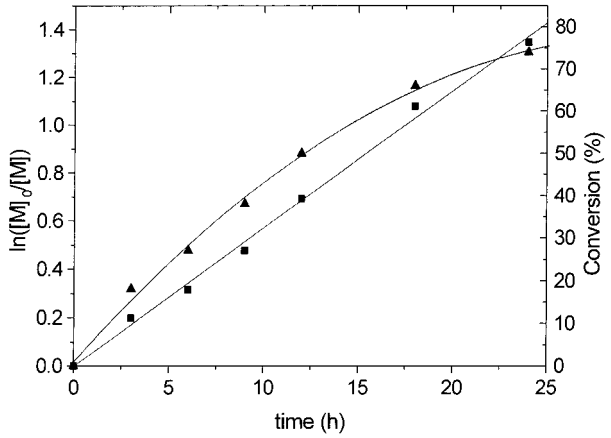


Figure 1. Plots of conversion and semilog of $[NPMA]_0/[NPMA]$ against polymerization time for the ATRP of NPMA using PSt-Br (prepared by ATRP, M_n = 14.730, M_w/M_n = 1.18) as initiator and CuBr/bpy as catalyst.

Results and Discussion

Homopolymerization of NPMA. ATRP of NPMA was performed at 110 °C in bulk. The results are listed in Table 1. Although the M_n's of the products could be controlled by feed ratio, MWD was broad. In addition, only about 50% conversion was obtained for all of the polymerizations, even when the reaction times were above 24 h. This result was not due to the impurities, because NPMA was purified by recrystallization from petroleum ether/ethanol mixture (6:1) three times, and no impurity was found in its NMR spectrum, although the same result was obtained. We could observe that as the polymerization proceeded, the color of the system changed to green (typical color for Cu^{II} species in the presence of Cu^{I})[28] gradually, indicating the accumulation of Cu^{II} in the polymerization system. Probably, this indicated the complexation of Cu^{II} with the forming polymer, resulted in the destruction of the fast reversible reactions between propagation chain radicals and $CuBr_2$. Therefore, low polymerization rate, low conversion, and broad MWD for ATRP of NPMA were observed.

Copolymerization of Styrene and NPMA. Because the ATRP of NPMA was poorly controlled, PSt-Br (M_n = 14 730, M_w/M_n = 1.18; GPC results), which was prepared by ATRP using EBB as initiator and CuBr/bpy as catalyst at 90 °C, was used as initiator for the preparation of block copolymers, PSt-*b*-PNPMA. The copolymerization was carried out in bulk using CuBr/bpy as catalyst. The color of the reaction mixtures remained brown throughout the whole polymerization process.

Figure 1 illustrates the curves of conversion and $\ln([M]_0/[M])$ against reaction time. The latter is linear. M_n of the block copolymer was measured by GPC and NMR.

Table 2. Copolymerization Results of NPMA and Styrene by ATRP in Bulk at 110 °C, Using Polystyrene Macroinitiator[a]

#	NPMA/St (mole)	time (h)	conv. (%)	M_n (theo)[b]	M_n (NMR)[c]	M_n (GPC)	M_w/M_n
5	1:1	3	18	20 007	20 940	12 680	1.38
6	1:1	6	27	22 646	24 280	12 400	1.38
7	1:1	9	38	25 871	25 890	13 160	1.35
8	1:1	12	50	29 389	30 200	13 020	1.33
9	1:1	18	66	33 963	35 540	12 610	1.32
10	1:1	24	74	36 426	37 470	23 440	1.29
11	3:2	24	71	45 954	44 640	25 200	1.26
12	1:2	24	71	25 138	28 270	19 210	1.36

[a] NPMA = *p*-nitrophenyl methacrylate. [I]:[CuBr]:[bpy] = 1:1:2 (molar ratio); PSt macroinitiator was prepared by ATRP of styrene using EBB as initiator and CuBr/bpy as catalyst at 90 °C; M_n = 14 730, M_w/M_n = 1.18. [b] M_n (theo) = conversion × [NPMA]/[I] × 207 + 14 730. [c] M_n (NMR) was calculated from eq 3.

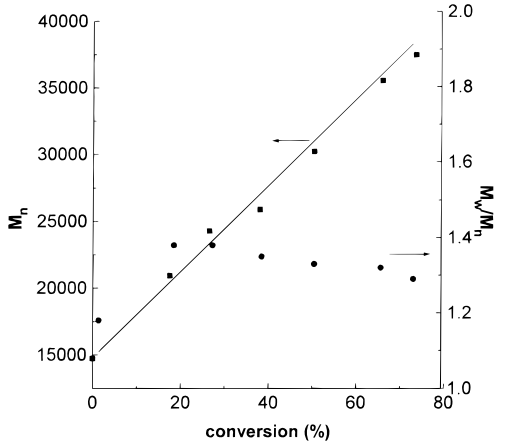


Figure 2. Dependence of molecular weight and molecular weight distribution on monomer conversion for ATRP of NPMA using PSt-Br as initiator (prepared by ATRP, M_n = 14730, M_w/M_n = 1.18) and CuBr/bpy as catalyst.

The block PSt-*b*-PNPMA could not be dissolved in $CHCl_3$ and DMSO at a molecular level. Therefore, the block PNPMA in the copolymer was transformed to poly(*N*-butyl methacrylamide) (PBMAD), which is completely dissolved in $CDCl_3$. Then, the molar ratios of St/NPMA and M_n of the copolymers were determined by their ^{1}H NMR spectra. The results are listed in Table 2. It can be seen that M_n (NMR) values determined by NMR are close to theoretical values, but M_n (theo) values are higher than M_n values measured by GPC. This may be attributed to different hydrodynamic volumes of the block copolymer PSt-*b*-PNPMA compared with standard polystyrene. Figure 2 shows the linear increase in M_n values (determined by NMR) with the conversion and that MWD got narrower as the polymerization proceeded. Meanwhile, as M_n values increased, MWD also became narrower, as illustrated in Figure 3. All of these facts demonstrated that the block copolymerization could be well-controlled. The constant brown color of the polymerization system indicated no change of fast reversible reaction between propagation chain radicals and $CuBr_2$ during the polymerization process. The probable reason is that NPMA is not a good solvent of PSt. The propagation occurred in the PSt chain coils. Thus, the reversible reaction between the propagation radical and $CuBr_2$ was mainly determined by the property of PSt.

When PSt-*b*-PNPMA was put into DMSO or $CHCl_3$, each afforded cloudy solution even after vigorous stirring. NMR spectra of sample 12 in Table 2 in DMSO-d_6 and $CDCl_3$ are shown in Figure 4. When the spectrum was measured in DMSO-d_6, the peaks of PSt block were significantly depressed, and in $CDCl_3$, the peaks of the PNPMA block almost disappeared. This illustrated that DMSO and $CHCl_3$ are good solvents for the PNPMA and PSt segment, respectively. Dynamic laser light scattering (DLS) measurement showed that micelles were formed in both DMSO and $CHCl_3$. For example, sample 10 in Table 2 formed micelles with average micelle diameters of 56 nm in DMSO and 30 nm in $CHCl_3$. The micelles with PSt as core and PNPMA as shell were formed in DMSO, and in $CHCl_3$, the micelles with PNPMA as core and PSt as shell were observed. The micelles formed in DMSO or $CHCl_3$ could be modified readily because the amino group could easily substitute the *p*-nitrophenyl unit in the micelles. This research is in progress.

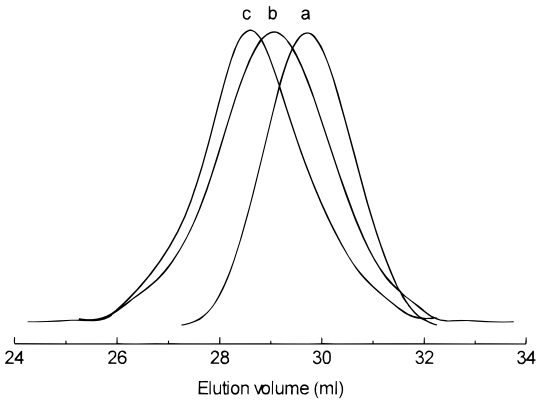
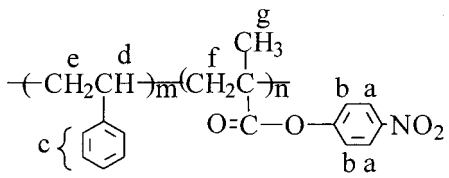
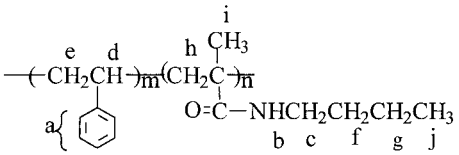


Figure 3. GPC traces of PSt-*b*-PNPMA and PSt macroinitiator: (a) polystyrene macroinitiator, (M_n (GPC) = 14 730, M_w/M_n = 1.18), (b) PSt-*b*-PNPMA (no. 12 in Table 2, M_n (GPC) = 19 210, M_w/M_n = 1.36), and (c) PSt-*b*-PNPMA (no. 10 in Table 2, M_n (GPC) = 23 440, M_w/M_n = 1.28).

Preparation of PSt-*b*-PMAA and PSt-*b*-PBMAD. Hydrolysis and amino substitution of block copolymer PSt-*b*-PNPMA could render the corresponding copolymers. Hydrolysis resulted in amphiphilic block copoly(styrene-*b*-methacrylic acid) (PSt-*b*-PMAA), which usually was prepared by anionic copolymerization of *tert*-butyl- or alkyl vinyl-protected methacrylic acid and St at low temperature and stringent conditions followed by hydrolysis.[29−33] The hydrolysis in this report was performed by adding 1 M KOH in ethanol to a THF solution of the block copolymers, refluxing for 24 h, and following by the addition of hydrogen chloride aqueous solution. Parts a and b of Figure 5 present the FTIR spectra of the block copolymer before and after hydrolysis, respectively. After the hydrolysis, the characteristic peaks of the ester group at 1755 cm^{-1} and of the *p*-nitrophenyl group at 1525, 1349, and 1205 cm^{-1} disappeared; meanwhile, the peaks of methacrylic acid at 1711 and 3428 cm^{-1} appeared.

When refluxing the solution of block copolymer and *n*-butylamine in THF for 24 h, the *p*-nitrophenyl group was substituted by *n*-butylamine, and the block copolymer PSt-*b*-PBMAD was obtained. FTIR spectrum of the product is presented in Figure 5c. The characteristic peaks of ester and *p*-nitrophenyl groups disappeared, and the peaks of amide at 1666 and 1715 cm^{-1} appeared. Figure 6 is the NMR spectrum of PSt-*b*-PBMAD. It can be seen that the peaks of aromatic protons of *p*-nitrophenyl group at 8.17 and 7.32 ppm disappeared,





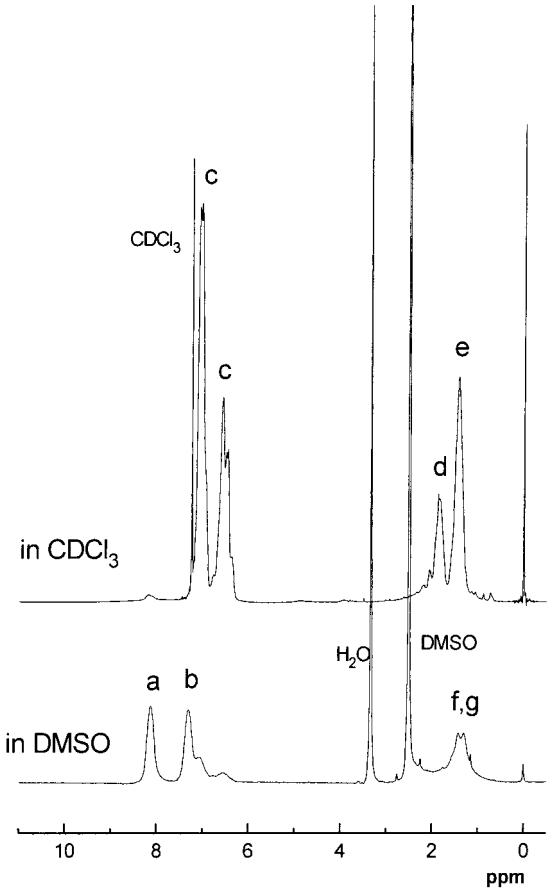


Figure 4. NMR spectra of PSt-*b*-PNPMA (no. 12 sample in Table 2) in $CDCl_3$ and DMSO-d_6, respectively.

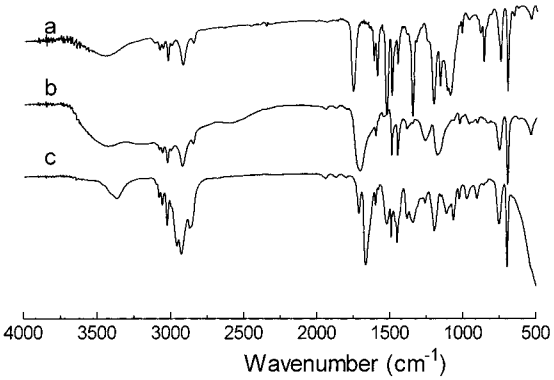


Figure 5. FT-IR spectra of (a) PSt-*b*-PNPMA (no. 10 in Table 2); (b) its hydrolysis product, PSt-*b*-PMAA; and (c) amino substitution product, PSt-*b*-PBMAD.

and the two peaks of methylene protons next to nitrogen atom appeared at 3.0−3.8 ppm and may be ascribed to their hydrogen bond and non-hydrogen bond. On the basis of the intensity of peaks at 3.0−3.8 ppm ($I_{3.0-3.8}$) and 0.8−2.2 ppm ($I_{0.8-2.2}$), the molar ratio of BMAD/St

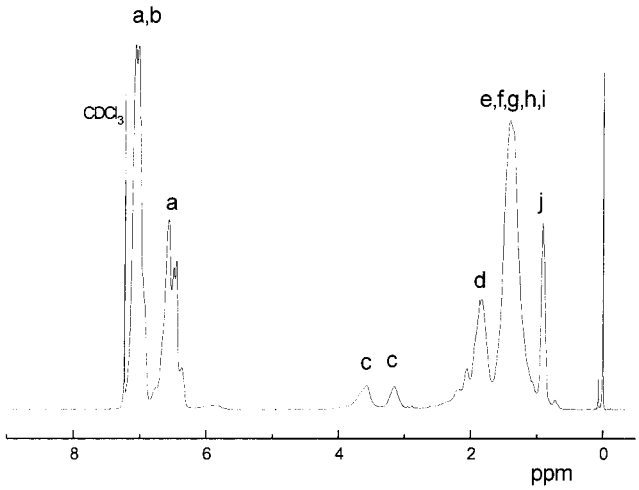


Figure 6. NMR spectrum of PSt-*b*-PBMAD obtained by *n*-butylamine substitution of PSt-*b*-PNPMA (no. 5 in Table 2).

could be calculated according to eq 2:

$$\text{BMAD/St} = [I_{3.0-3.8}/(I_{0.8-2.2} - 6I_{3.0-3.8})]1.5 \quad (2)$$

which is equal to the molar ratio of NPMA/St in PSt-*b*-PNPMA. Then, Mn(NMR) of PSt-*b*-PNPMA could be obtained as follows:

$$M_n\,(\text{NMR}) = 14\,730 + ([\text{NPMA}]/[\text{St}])(14\,730)(207/104) \quad (3)$$

The results are listed in Table 2. PBMAD was soluble in methanol, but polystyrene was not soluble in methanol. So, block copolymer PSt-*b*-PBMAD also was an amphiphilic block copolymer.

Conclusions

Homopolymerization of NPMA by ATRP was poorly controlled due to the complexation of copper with the forming polymer. However, block copolymerization of NPMA with St by ATRP using PSt-Br, which was also prepared by ATRP, as initiator was well-controlled and gave a linear molecular weight-conversion profile, predictable molecular weights from the ratio of monomer consumed to initiator, and a narrow MWD. When PSt-*b*-PNPMA was dissolved in $CHCl_3$, the micelles with PSt as shell and PNPMA as core were formed. In DMSO, the micelles formed consisted of PSt core and PNPMA shell. By hydrolysis or amino substitution in mild condition, PSt-*b*-PNPMA was converted to PSt-*b*-PMAA or PSt-*b*-PBMAD easily. This provides a new method to prepare amphiphilic block copolymers.

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