Preparation and Properties of Poly(WPSF-*co*-butyl acrylate) Copolymer Emulsion with Ultrasonic Radiation II. Monomer Conversion Rate and Characterization

Zhao Quan Ai, Hai Rong Zhang, Qing Liu, Ying Hu

Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, College of Chemistry and Chemical Engineering, Hubei University, WuHan 430062, China

ABSTRACT: A stable emulsion of poly(WPSF-*co*-butyl acrylate) based on butyl acrylate, waste polystyrene foam was synthesized through emulsion polymerization using sodium dodecyl sulfate and octyl phenyl polyoxyethylene ether as surfactant, ammonium persulfate and sodium hydrogen bisulfate as mixed redox initiator, under ultrasound irradiation in the absence of inert gas. The effects of various copolymerization conditions on the monomer conversion were reported. The copolymers were characterized by means of IR, ^{1}HNMR, and gel permeation chromatography. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3196–3201, 2009

Key words: emulsion polymerization; ultrasound; butyl acrylate; waste polystyrene foam

INTRODUCTION

Ultrasonic irradiation is an established technique in polymer synthesis. Since Lindstrom and Lamm[1] first used ultrasonic irradiation as an initiator for the polymerization of vinyl monomers in the early 1950s. In general, the conventional emulsion polymerization reactions are carried out at between 50 and 70°C to promote a rapid polymerization rate. When the bubbles collapsed in the solution, which results in temperatures as high as 5000 K and local pressures as high as 50.6 MPa (500 atm), heating and cooling rates greater than 10^9 K s^{-1}, and formation of very strong shock waves.[2] It is possible that by application of ultrasound to a polymerization at low temperature will be greatly accelerated by the polymerization rate. Researchers[3,4] successfully produced poly(methylmethacrylate) by ultrasonically irradiated bulk polymerization and proved that monomers could decompose to free radicals to initiate polymerization. In addition, Wang and co-workers[5,6] reported that the surfactant is responsible for initiation in the ultrasonically initiated miniemulsion polymerization of various monomers, including methylmethacrylate (MMA) and butyl acrylate (BA) being described as "one of the radical sources." Such conclusions were based on the comparison of conversion-time data both with and without added surfactant; in the absence of surfactant, little conversion was obtained, while with surfactant quite rapid conversion was observed. Chen et al.[7] studied the degradation behavior of polymers in the presence of a radical scavenger diphenyl picrylhydracyl proved that ultrasound can degrade polymer chains to macroradicals. The different macroradical can recombine into block/graft[7,8] copolymer.

All the previous works mentioned above showed that under ultrasonic irradiation radicals can be generated because of decomposition of monomer, solvent, water, or polymer to initiated further polymerization of monomer. However, in our work, although ultrasonic radiation could initiate the free-radical polymerization to some extent, the residual monomer is too high to reach the prime concern for many latex producers.

Many sonochemical researchers[5,9,10] reported that the presence of inert gas play an important role in the sonochemical reaction. Kruus et al.[11] reported that initiation of styrene polymerization occurs primarily through stable cavitation, which requires the presence of a gas flowing through the reaction solution. With no inert gas, the cavitation is transient, causing the formation of colored compounds similar to pyrolysis reaction products and depolymerization. However, in our work, no inert gas was introduced because the function of ultrasonic energy probably is to degrade polystyrene (pSt) and speed up the polymerization rate and the conversion.

pSt is a major type of thermoplastic used throughout the world, and the foam products of pSt can be applied in such applications as the packaging of electrical equipment, apparatus, instruments, and foods, thermal insulation materials for buildings and cold storage, and disposable dinner service. Unfortunately, waste polystyrene foam (WPSF), as well as other used plastic, is becoming a major environmental concern, because of its large production quantities and nonbiodegrade nature. In Western Europe alone, approximately 2.5 million tons of pSt are produced each year.[12] A solution of recycling WPSF that can bring higher value end products and increased potential of economic include mechanical[12] and chemical[13] methods. In previous work,[14] we examined prepared technology for copolymerization and the influence of various factors on coagulum ratio. In our work, the major influencing factors include polymer concentration, surfactant concentration, ultrasonic intensity, initiator concentration, and temperature on the monomer conversion were discussed. We examined the characterization by Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), and ^{1}HNMR spectroscopy of poly(WPSF-*co*-butyl acrylate) [p(WPSF-*co*-BA)] copolymers by using WPSF under ultrasonic radiation.

EXPERIMENTAL

Apparatus

The instrument used in this research was a 20–25 kHz ultrasonic generator (model YJ92-II, NingBo YinZhou YongJie Experimental apparatus Co., China) with a standard titanium horn 13 mm in diameter, the oscillator power was set at various points on a range from 20 to 90 (on a scale of 100), and cooling air was blown over the ultrasonic horn to prevent overheating. Ultrasonic irradiation of the monomer emulsion was conducted with the tip of the coupling horn immersed directly in the emulsion.

Reagents and materials

WPSF was selected from the package of household electric appliances, was washed with distilled water and dried at room temperature before use. BA (analytical grade) from Kermel (TianJing, China) was filtered through inhibitor removal columns, and the material was then refrigerated at 10°C before use. A mixture of ammonium persulfate (APS, analytical grade) and sodium hydrogen bisulfate (NaHSO$_3$, analytical grade) from Tianjin Reagent Manufacturer No. 6 (Tianjin, China) purified by crystallization was used as a redox initiator. Octyl phenyl polyoxyethylene ether (OP-10, analytical grade) and sodium dodecyl sulfate (SDS, analytical grade) were from Beijing Qiuxian Chemical Manufacturer (Beijing, China) was used as a surfactant, water was deionized.

Polymerization

The experimental schematic diagram of the apparatus used for the emulsion polymerization has been described previously.[14] In general, for all the polymerization reported here were carried out in a 150 mL, four-necked flask equipped with a reflux condenser, a stirrer, an ultrasonic horn, and a thermometer. The temperature was controlled with a thermostat water bath. Water was maintained a temperature of 45°C. After WPSF was dissolved in BA in the reactor, OP-10, AA, SDS, and water were fed into the reactor one by one. Mechanical stirring was done at room temperature for 30 min initially, then a certain amount of water-soluble initiator NaHSO$_3$ and APS with the ratio of 2 : 3 were added into the solution under stirring, and subjected to ultrasonic irradiation. The horn was always placed 4 cm from the bottom of the reaction vessel. When the blue fluorescence appeared, the ultrasound power was turned off, the emulsion was heated to 75°C for 2 h, cooled to room temperature, and discharged.

Measurement

Conversion data were obtained by gravimetry, with coagulum taken into account. To measure different factors on the monomer conversion rate, we only chosethe conversion rate was used at reaction time of 45 min.

The final latex solution was precipitated in methanol (v/v 1 : 2), and dried. The FTIR analyzes were performed on a Perkin-Elmer (Spectrum one) spectrophotometer in the frequency range of 450–4000 cm^{-1}. The solvent used was CHCl$_3$.

The molecular weight of polymer was measured by GPC using a chromatographic system (Waters 2965 Separations module) equipped with a Waters Model 2414 refractive index detector. *N,N*-Dimethylformamide (Fisher, Scharlau grade) was used as an eluting solvent, the flow rate was 1 mL/min, and the operation temperature was 35°C. Styragel packed columns, HR3, HT5, and HR4 were used. The column was calibrated using pSt standards.

The effluent of the first 17 min (elution time) from the GPC was collected and dried. The sample was dissolved in CDCl$_3$. The ^{1}H NMR spectra was obtained at 600 MHz using a Varian (INOVA 600) Fourier Transform NMR Spectrometer, with tetramethylsilane as an internal standard.
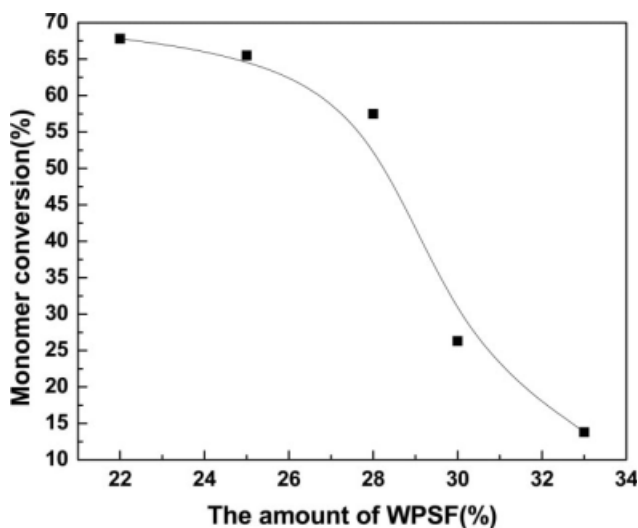
Figure 1 Effect of the amount of WPSF on the monomer conversion. Ultrasonic temperature = 45°C, surfactant concentration = 1.5%, ultrasonic intensity = 60%, initiator concentration = 0.1%, reaction time = 45 min.

RESULTS AND DISCUSSION

Effect of polymer concentration on the conversion of monomer

The effect of the amount of WPSF on the conversion of BA is shown in Figure 1. With an increase in the amount of WPSF, the conversion of monomer decreased significantly. This indicates that the conversion rate of monomer decreases with an increase in the amount of WPSF, with the conversion rate of monomer obtained at a concentration of 25% more than that obtained at a concentration of 33%. The viscosity of the emulsion increased with the amount of WPSF increasing, and the time for monomers to diffuse from monomer droplets to micelles and to be polymerized will be prolonged. Therefore, the conversion of BA decreases with increase in the amount of WPSF. Then, the effect of ultrasonic cavitation is weakened, and the amount of radicals produced by ultrasonic cavitation is reduced, thus the conversion is reduced. Furthermore, the rate of WPSF degradation decreases with an increase in the polymer concentration,[15] this may be attributed to the overlapping of polymer chains at higher concentrations, which reduces the efficiency of cavitation in a viscous solution.

Effect of surfactant concentration on the conversion of monomer

The effect of surfactant (SDS and OP-10) concentration on the conversion of monomer is shown in Figure 2. It is obvious that monomer conversion

increases with increasing surfactant concentration, which indicates that surfactant plays an important role in ultrasonically radiated emulsion polymerization. In the absence of surfactant, the coagulum ratio was greater than 50%,[12] the concentration of surfactant increases to 0.1%, and there is a rapid increase in the monomer conversion. A further increase in the surfactant concentration leads to a slight increase in the conversion rate. This result suggests that the monomer-swollen micelles are the main locus of polymerization, which is similar to a conventional emulsion polymerization. With increasing surfactant concentration, the number of free radicals and oligomers produced in the continuous phase generated increases, then the number of micelles increases, leading to more polymerization loci and better polymerization rates. Therefore, the higher surfactant concentration, higher is the system stability.

Wang et al.[6] and Chou and Stoffer[10] reported that the surfactant is served as both surfactant and initiator and is responsible for initiation in the ultrasonically initiated emulsion polymerization of various monomers, including MMA and BA being described as "one of the radical sources." In our work, when the emulsion, in the absence of the redox initiator, is subjected to ultrasonic irradiation, the polymerization rate is very low under these conditions. These results suggest that the role of the surfactant in the polymerization is purely in particle stabilization and not in free-radical chemistry.
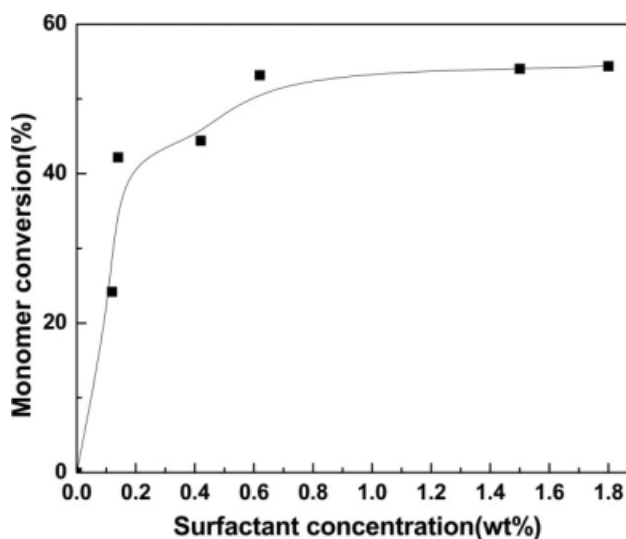

Figure 2 Effect of the surfactant concentration on the monomer conversion. Polymer concentration = 28%, ultrasonic temperature = 45°C, ultrasonic intensity = 60%, initiator concentration = 0.1%, SDS: OP-10 = 1 : 3 (w/w), reaction time = 45 min.
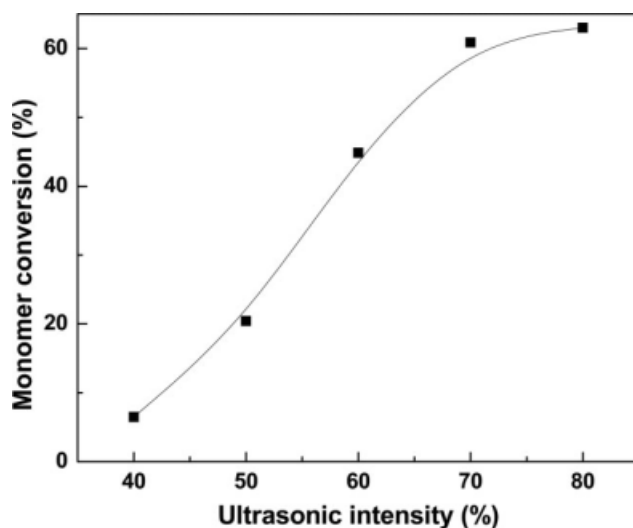
Figure 3 Effect of the ultrasonic intensity on the monomer conversion. Polymer concentration = 28%, ultrasonic temperature = 45°C, surfactant concentration = 1.5%, initiator concentration = 0.1%, reaction time = 45 min.

Effect of ultrasound intensity on the conversion of monomer

The effect of ultrasound intensity on the conversion of monomer is shown in Figure 3. It is obvious that monomer conversion increases with increasing ultrasound intensity. Ultrasonic intensity is the main parameter influencing the number of cavitation bubbles produced,[4] the number of cavitation bubbles would be proportional to the ultrasound intensity, which is an important affecting factor for the formation and stabilization of emulsion. Many authors[10] have found that as the ultrasound intensity increases, the rate of the reaction and monomer conversion increases to a maximum and then decreases with a continued increase in ultrasound intensity. In our work, we have not found this maximum, this is presumably because of the power limitation of the apparatus itself, the experiment cannot be carried out at much higher power conditions.

Effect of initiator concentration on the conversion of monomer

The effect of initiator concentration on the conversion of monomer is shown in Figure 4. With an increasing the amount of initiator, the conversion of monomer increased. Many researcher have reported the use of ultrasonic energy in emulsion polymerization produce free radicals as a result of a high local temperature and pressure produced when the bubbles collapses. The source of free radicals not only comes from the initiator but also may come from the monomers,[3,4] the polymer[7,8] and the surfactant.[5,6,10] In our work, we have found that monomer conversion is very low if a redox initiator is
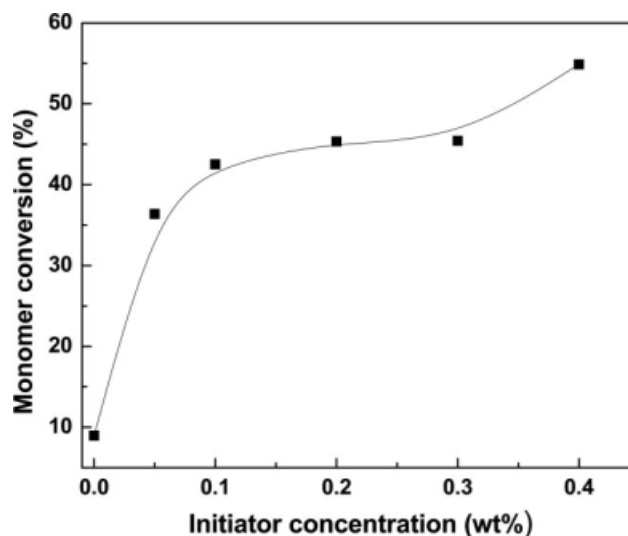

Figure 4 Effect of the initiator concentration on the monomer conversion. Polymer concentration = 28%, ultrasonic temperature = 45°C, surfactant concentration = 1.5%, ultrasonic intensity = 60%, reaction time = 45min.

not used, when add a few initiator, the monomer conversion sharply increase.

Effect of ultrasonic temperature on the conversion of monomer

The effect of the temperature on the conversion of monomer is shown in Figure 5. The monomer conversion increases as temperature increasing, this is opposite to the behavior of a conventional sonochemical reaction,[16] in which an increase in the ambient reaction temperature results in an overall decrease in the sonochemical effect. However, in this
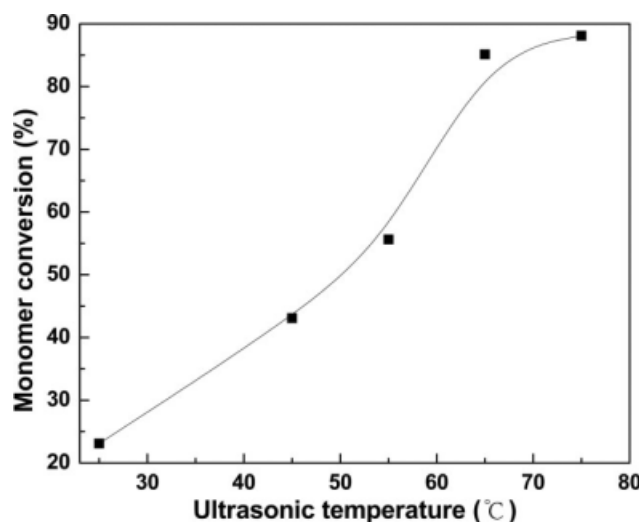

Figure 5 Effect of the ultrasonic temperature on the monomer conversion. Polymer concentration = 28%, surfactant concentration = 1.5%, ultrasonic intensity = 60%, initiator concentration = 0.1%, reaction time = 45 min.
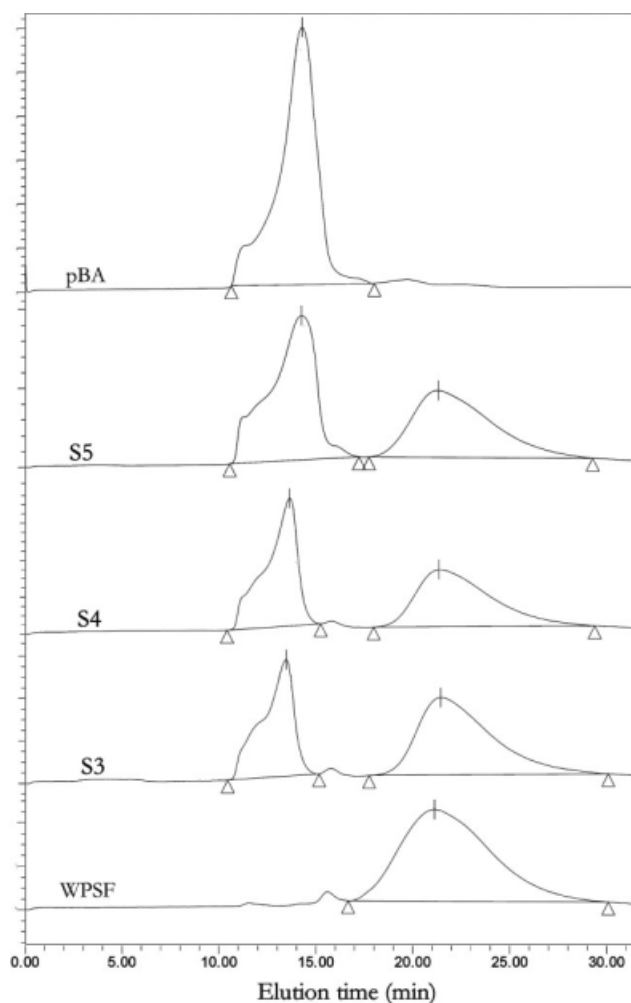
Figure 6 Gel permeation chromatograms of WPSF, pBA, and various p(WPSF-*co*-BA) copolymers (runs S3, S4, and S5 in Table I).

emulsion polymerization system, the monomer conversion increases with increasing temperature due to exist a redox initiator. Similar to a conventional emulsion polymerization, the propagation rate coefficient of monomers in the aqueous phase decreases with temperature decreasing. Furthermore, ultrasonic irradiation at a high temperature more easily generated free radical, and the decomposition rate of the initiator increased. Thus, the conversion of monomer increases with increasing bath temperature.

Characterization of the copolymer

The copolymers were characterized by means of GPC and FTIR spectroscopy. Figure 6 shows the gel permeation chromatograms of WPSF, pBA, and various p(WPSF-*co*-BA) copolymers. It can be seen from Table I, the copolymer molecular weight increases as the WPSF concentration increases. It can be noted that part of the unreacted WPSF is present in the co-

TABLE I
Variations of the p(WPSF-*co*-BA) Molecular Weight with Different WPSF Concentration

Run	WPSF (wt%)[a]	M_n[b] ($\times 10^5$)	M_w[c] ($\times 10^5$)	M_w/M_n
WPSF	100	1.2	2.3	1.92
S1	45	555.8	1104.2	1.99
S2	33	818.4	1285.1	1.57
S3	30	772.1	1252.9	1.62
S4	28	658.7	1119.8	1.70
S5	22	421.9	1098.4	2.60
pBA	0	383.1	1130.2	2.95

[a] The concentration of WPSF in the comonomer.
[b] Number-average molecular weight determined by GPC.
[c] Weight-average molecular weight determined by GPC.

polymer. On the other hand, we have attempted to purify the copolymer by extraction with different solvents have not been successful. The IR spectrum of the pBA, various copolymer and WPSF is shown in Figure 7. The characteristic bands in the range of 3150–3000 cm^{-1} in Figure 7 ascribe to the stretching vibration of arC—H, The characteristic peak at 1600–1585 cm^{-1} in Figure 7 belongs to the doublet stretching vibration of arC—C, and at 760–700 cm^{-1} corresponding to the doublet rocking out of plane vibration of arC—H.

The ^{1}H-NMR spectrum (Fig. 8) of the copolymer that before 17 minute(elution time) in the GPC exhibited peaks at $\delta = 0.9$ for protons of CH$_3$ of butyl ester, $\delta = 1.35$–1.6 for protons of CH$_2$ of butyl
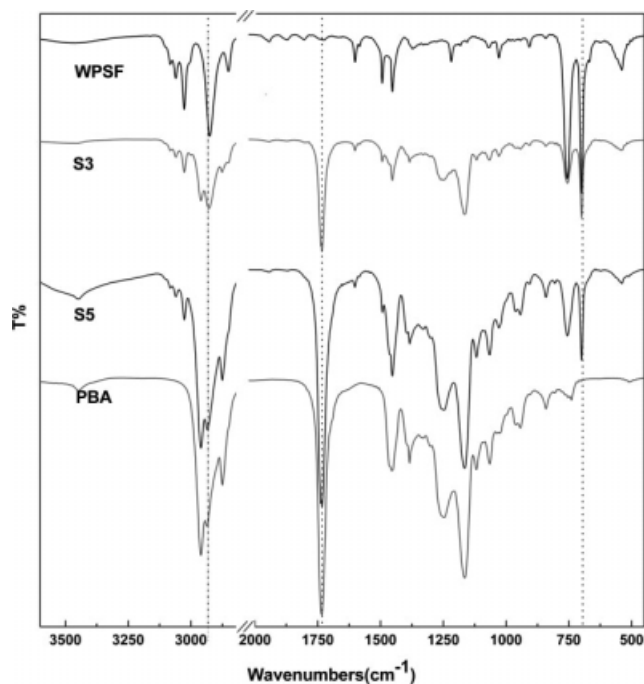

Figure 7 Infrared spectra of WPSF, pBA, and various p(WPSF-*co*-St) copolymers (runs S3 and S5 the Table I).
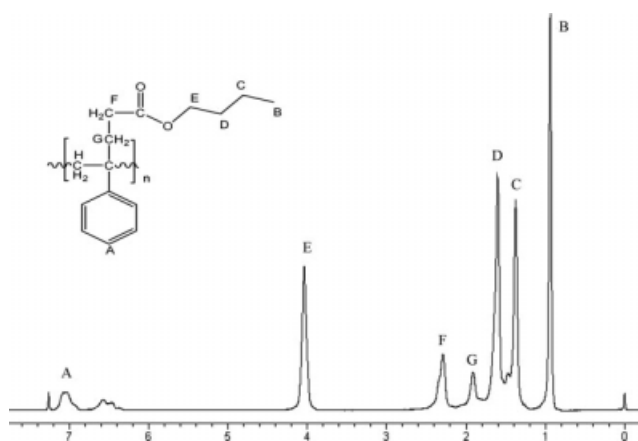
Figure 8 NMR spectra of p(WPSF-*co*-BA) copolymer collected at the first 17 min (elution time) from the GPC.

ester, $\delta = 1.87$ for protons of CH of pSt, $\delta = 1.89$ for protons of CH_2 groups in the acrylic groups, $\delta = 2.32$ for protons of CH groups in the acrylic groups, $\delta = 2.76$ for protons of CH_2 of pSt, $\delta = 4.08$ for protons of CH_2O groups in butoxy groups, and $\delta = 7.1$–7.3 for protons of phenyl groups of the pSt.

These two spectra demonstrate that the copolymer is indeed composed of pSt and pBA segments.

CONCLUSIONS

Redox-initiated emulsion copolymerization of BA and WPSF has been successfully carried out under ultrasound irradiation. The structures of copolymers were confirmed by GPC, FTIR, and NMR. Combining ultrasound and a redox initiator provides a good initiation system to produce a high polymer conversion. When the polymerization is not under ultrasound irradiation, the copolymer could not be prepared. WPSF and emulsifier concentrations have a significant effect on the emulsion polymerization. The monomer conversion increases with increase in the amount of SDS and monomer, ultrasonic intensity, or ultrasonic temperature.

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