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Text: PnBA-g-PS by Emulsion AGET ATRP and Miniemulsion Polymerization

Synthesis and Characterization of graft Copolymers P*n*BA-*g*-PS by Miniemulsion Polymerization

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ABSTRACT: In this paper, poly(*n*-butyl acrylate)–*g*–poly(styrene) graft copolymers were synthesized by macromonomer technique and miniemulsion copolymerization. The PS macromonomers were obtained by an activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) in emulsion system and subsequent allylation. Then the copolymerization of different PS macromonomers with *n*BA was carried out in miniemulsion system, obtaining graft copolymers with different molecular weight. The latex particles and distribution of emulsion AGET ATRP were characterized using laser light scattering. The molecular weight and polydispersity indices of macromonomers and graft copolymers were analyzed by gel permeation chromatography. In addition, the structural characteristics of macromonomer and graft copolymers were determined by infrared spectra and ¹H nuclear magnetic resonance spectroscopy. The thermal performance of copolymers were characterized by differential scanning calorimetry and thermogravimetric analysis as compared with macroinitiators.

Introduction

In recent years, graft copolymers have attracted much attention due to facilitating studying the materials with new and different properties from those of linear polymers. Aided by broad evolution of living/controlled polymerization such as anionic polymerization, ring-opening polymerization (ROP), atom transfer radical polymerization (ATRP), single electron transfer radical polymerization (SET-LRP), nitroxide-mediated polymerization (NMP), reversible addition-fragmentation transfer (RAFT), ring-opening metathesis polymerization (ROMP), there are many opportunities in the synthesis of well-defined graft polymers with flexibility, diversity and functionality. ¹⁻⁶ Especially, since the grafting density, the length of side chain and backbone and the number of junction points

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can be tuned by molecular design, graft copolymers have potential applications as compatibilizers, thermoplastic elastomers, impactresistant plastics, adhesive and renewable materials.⁷⁻⁹

According to the features of synthetic approaches, grafting-from, grafting-onto and graftingthrough techniques could be employed to synthesize well-defined graft copolymers. Graftingthrough or macromonomer technique is a simpler approach for the synthesis of graft copolymers that can control number of side chains. Since Milkovich¹⁰ developed the method of preparing copolymers with macromonomer technique, the synthesis of polystyrene (PS) and polymethyl methacrylate (PMMA) macromonomer and their copolymerization and homopolymerization have been studied extensively. Xie et al¹¹ synthesized PMMA macromonomer by radical polymerization with thioglycolic acid as a chain transfer agent, and followed by reaction with glycidyl methacrylate. And the graft copolymers as thermoplastic elastomer with good elastic properties were obtained by the copolymerization of PMMA macromonomers with n-butyl acrylate in benzene. Schulze¹² reported that PS macromonomers were prepared by ATRP in toluene. Moreover, a variety of macromonomers with topologies obtained by high vacuum anionic polymerization techniques have been studied by many researchers.^{8,13-16} But the preparation of macromonomers is carried out in solvent and the conditions for anionic polymerization are too demanding. And it is desirable to replace these hazardous organic solvents with water.^{17,18} Emulsion ATRP was initially attempted in 1998 by Krzysztof Matyjaszewski,¹⁹ whose work focused on successful preparation of well-defined polymers for *n*-butyl acrylate, methyl methacrylate, *n*-butyl methacrylate, and styrene as calculated by low PDIs and molecular weights in agreement with predicted values. Subsequently, AGET ATRP was successfully implemented in an ab initio emulsion system by Krzysztof Matyjaszewski,²⁰ which has overcome the inefficient transport of Cu-based catalysts across the aqueous phase to micelles or polymerizing particles.

In this paper, we describe the preparation of poly(n-butyl acrylate-g-styrene) graft copolymers with PnBA as the backbone and PS as side chains by macromonomer technique combining with emulsion ATRP and conventional emulsion copolymerization. The well-defined PS macromonomers were obtained via emulsion AGET ATRP (Scheme 1) and subsequently chain end modification. Then PnBA-g-PS graft copolymers having different molecular weight were prepared by eco-friendly miniemulsion copolymerization, initiated by azobis-(isobutyronitrile) (AIBN) (Scheme 2). Gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), FTIR and ¹H NMR were used to characterize the graft copolymers as compared with macroinitiators.

Experimental

Chemicals. Styrene (St) and *n*-butyl acrylate (*n*BA) were purchased from Tianjin Kermel Chemical Reagent Co.,Ltd and were purified by passing through a neutral alumina column to remove stabilizers. 2,2'-azobisisobutyronitrile (AIBN, Aldrich, 90%) was recrystallized in methanol before use. Copper (II) bromide, L-ascorbic acid, SDS, and titanium tetrachloride (all from Sinopharm Chemical Reagent Co.,Ltd), Brij98 (Acros), 4,4'-Dinonyl-2, 2'-bipyridyl (dNbpy, Alfa, \geq 97%), (1-bromoethyl) benzene (PhEtBr, Aldrich, \geq 99%), allyltrimethylsilane (ATMS, Aldrich, \geq 98%) were used as received without further purification. Dichloromethane was dried by refluxing over calcium hydride and was distilled under nitrogen atmosphere. Toluene, methanol, and tetrahudrofuran were used as received.

Synthesis of Macromonomers. Polystyrene with bromine chain end was synthesized by emulsion atom transfer radical polymerization (Schemel). The initiator was (1-bromoethyl) benzene (PhEtBr) and the catalyst was copper (II) bromide complexed with dNbpy. In a typical reaction, the Cu (II) complex was prepared by dissolving CuBr₂(12.9 mg, 0.057 mmol) and dNbpy (48.1 mg, 0.144 mmol) in St (4.56 g, 43.8 mmol) at room temperature. Then, the initiator, (1bromoethyl) benzene (PhEtBr, 0.4264 g, 2.189 mmol) was dissolved in above complex. The resulting solution was slowly added to an aqueous solution of polyoxyethylene (20) oleyl ether (Brij98, 14.11 ml) and sodium chloride (NaCl, 2 g/L) under stirring to form steady emulsion. After bubbling the emulsion with ultrahigh-purity nitrogen for 30 min, the flask was immersed in oil bath thermostated at 80°C. A predeoxygenated aqueous solution (1 ml) of L-ascorbic acid (5.0 mg) was injected into the emulsion to start the polymerization. The samples were withdrawn periodically to measure the monomer conversion gravimetrically. The resulting polymers were dissolved in THF, and the solution was purified by passing through a neutral alumina column. The polymers were precipitated into methanol. The precipitate was dissolved in tetrahydrofuran (THF) and then reprecipitated three times in methanol, and the final precipitate was dried in a vacuum oven at 40 $\,^\circ C$ for 24 h.

The halogen-terminated polymers (PS-Br) were dissolved in dichloromethane and it was

cooled to 0 $^{\circ}$ C under ultrahigh-purity dry nitrogen atmosphere. Then TiCl₄ was added to the stirred solutions and the reaction mixture was aged for 30 min before charging prechilled ATMS. About 1 h later the flask was opened and some methanol was added to deactivate TiCl₄. The resulting solutions was filtered off and subsequently dichloromethane and methanol were evaporated off. The resulting polymers were dissolved in dichloromethane and the solution was purified by passing through a neutral alumina column. The polymers were precipitated into methanol. The precipitate was dissolved in dichloromethane and then reprecipitated twice in methanol, and the final precipitate was dried in a vacuum oven at 50 $^{\circ}$ C for 24 h. The concentrations of reagents and other reaction conditions for synthesizing of PS macromonomers with different molecular weights are summarized in Table 1.

Synthesis of graft Copolymers. PnBA-g-PS graft copolymers were prepared by miniemulsion copolymerization (Scheme 2). In a typical copolymerization, the stable emulsions for copolymerization were obtained by adding organic solutions of toluene containing PS macromonomer, HD, AIBN and nBA dropwisely to aqueous solutions containing SDS and mixing simultaneously with magnetic stirring. The mixture was mixed under sonication in an ice bath for 10 min and then quickly transferred to a water bath at 60 °C for 24 h. The resulting products was obtained as a precipitate by adding the reaction mixture dropwisely to excess methanol to remove the surfactant. The final graft copolymers were purified by fractional precipitation to remove the unreacted macromonomer. The resulting graft copolymer was dried in a vacuum oven at 40 °C for 24 h.

Characterization

The molecular weights and polydispersity indices were measured at 35 °C by Gel Permeation Chromatography (GPC) equipped with a differential refractometer (Waters, 2414) and three waters styragel columns. A calibration curve was obtained with linear polySt standards (molecular weight range: $1.37 \times 10^3 - 2.58 \times 10^6$ g/mol) and Chromatographic grade tetrahydrofuran was used as the mobile phase at a rate of 1 mL/min. The particle size distributions of latex particle were measured at room temperature by Laser Light Scattering (LLS) with a Delsa TM Nano C from Beckman Coulter. Data acquisition and processing were carried out with Delsa Nano software. The measurement was done after the emulsion was diluted to a desired obscuration by deionized water according to the

DelsaTM Nano C catalog. The ¹HNMR spectra was obtained on a BRUKER AVANCE-600 spectrometer in CDCl₃ at room temperature, using TMS as a standard. Infrared spectra of macromonomer and graft copolymer were obtained at room temperature on a BRUKER TENSOR 27 FTIR spectrometer. The glass transition temperature and the heat of fusion were determined by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 823 instrucment by heating and cooling method with a heating and cooling rate of 10 °C/min from -80 °C to 150 °C under nitrogen. The polymer was heated and cooled at programmed rate of heating and then T_g was recorded in the second heating cycle. The thermal properties of polymers were characterized using TGA (TGA/DSC STARe apparatus, Mettler Toledo) with a heating rate of 10 °C/min from 25 °C to 700 °C under N₂.

Result and discussion Synthesis and characterization of macromonomer





Poly((*n*-butyl acrylate) -*g*- styrene) (P*n*BA-g-PS) multigraft copolymers were synthesized according to scheme 1. For synthesizing PS macromonomer, polystyrene macroinitiators (PS-Br) were prepared by emulsion AGET ATRP using the PhEtBr/CuBr₂/dNbpy initiating system. Then polystyrene macroinitiators were transformed to allyl-ended polystyrene macromonomers (PS-allyl) by quantitative carbocationic allylation with ATMS in the presence TiCl₄ Lewis acid.²¹ The preparation conditions and some characteristics of emulsion AGET ATRP are listed in Table 1. Table

1 shows that there was no coagulum with different reaction time in the process of emulsion AGET ATRP, and the final conversion was satisfactory. In addition, the size and distribution of latex particles from emulsion AGET ATRP are shown in Figure 1 and Table 1 indicates the mean diameter and C.V. value of each sample. As can be seen, the particles are homogeneous and the average diameters are from 114 to 126 nm with low C.V. value (14.4%~28.8%). Therefore, it is successful to proceed emulsion AGET ATRP and the emulsion latex was stable enough.

Table 1.5ynthesis conditions of macromitators by cindision ATKi											
sample	m_{St}/g	PhEtBr/g	CuBr ₂	t/min	^b Conversion/%	Coagulum/%	^c Latex	^d C.V./%			
							particles				
							size/nm				
PS(1849) 4.56	0.4264	0.0129	300	51.6	0	117	28.8			
PS(3970) 5.05	0.2361	0.0143	480	61.3	0	126	14.4			
PS(5048) 5.02	0.1878	0.0142	600	67.2	0	114	16.2			

Table 1.Synthesis conditions of macroinitiators by emulsion ATRP^a

^{*a*}All polymerizations were conducted with $CuBr_2$: dNbpy : ascorbic acid =1/2/0.5, 80°C. Brij 98 = 3 wt% vs monomer. Solid content = 12% (based on 100% conversion). ^{*b*}Conversion was determined by gravimetric analysis. ^{*c*,*d*}Latex particle size and distribution were measured by Laser Light Scattering.



Table 2.Synthesis Conditions of Allyl-terminated Polystyrene by Carbocationic Allylation

macromonomer	sample	$n_{\rm ATMS}$ (equiv)	$n_{\rm TiCl4}$ (equiv)	^a Mn (g/mol)	${}^{b}M_{w}/M_{n}$
1	PS(1849)	3	3	1849	1.17
2	PS(3970)	5	5	3970	1.36
3	PS(5048)	5	5	5048	1.29

^aMolecular weight and polydispersity indices were calculated before allylation. ^bMolecular weight

and polydispersity indices were calculated after allylation.

The GPC curve of three different PS macromonomers are shown in Figure 2, and the molecular weight and distribution are given in Table 2. From Figure 2 and Table 2, we can observe that the GPC curves of PS macromonomers with different molecular weight are unimodal and polydisersity indices are small (M_w/M_n =1.17~1.36), which were as expected when using emulsion AGET ATRP. The ¹H NMR spectrum of PS macromonomer 2 and PS(3970) is shown in Figure 3. The characteristic peak for vinyl protons from allyl chain end (CH₂=, δ =4.6-4.8 ppm; =CH-, δ =5.9-6.0 ppm)²² can be clearly seen in Figure 3 (b).Moreover, the characteristic peaks of phenyl protons can be also observed at 6.2~7.2 ppm⁸. ¹H NMR spectrum confirmed that PS macromonomer with different molecular weight was obtained successfully.



Figure 3. ¹HNMR spectra of PS(3970) and macromonomer 2 (a) PS(3970) (b) PS macromonomer 2



Scheme 2. Scheme for Synthesis of Graft Copolymers Poly(*n*-butyl acrylate)-g-polystyrene by Miniemulsion Polymerization Using PS Macromonomer

Miniemulsion polymerization of PS macromonomer and nBA was carried out in order to obtain graft copolymers, as shown in scheme 2. Table 3 is the recipes for miniemulsion polymerization in the presence of PS macromonomers. The high conversion of *n*-butyl acrylate determined by gravimetric analysis was expected. The conversion of PS macromonomer was evaluated by ¹H NMR later. The molecular weights and distributions of the graft copolymers before and after fractionation were characterized by GPC, and the chromatograms are shown in Figure 4. The GPC curves of PS macromonomer are also shown in Figure 4 for comparison. From the GPC curves in Figure 4, we can see that there are two peaks, which means that there was a small amount of residual PS macromonomer in the graft copolymers. Residual PS macromonomers reflects the longer polymer chains of such species have some influence on reactivity. As previous studies reported, Mays et al had synthesized PI-g-PS multigraft copolymers having regularly spaced trifunctional, tetrafunctional and hexafunctional branch points.²³⁻²⁵ However, the branch points of multigraft copolymers prepared by miniemulsion polymerization are considered to be random in our work. Because of PS macromonomer with high molecular weight, there is a big steric hindrance effect for copolymerization,²⁶ which makes its reactivity lower than styrene. Furthermore, the activity of allyl copolymerizing with acrylate monomers is low, and especially when the macromonomers were obtained by termination with ATMS, which means that the activity of macromonomers is lower than acrylate monomers in the process of radical copolymerization. These effects have been verified by our experimental data. As is implied in Table 4, graft copolymers with different characteristics were synthesized by adjusting the weight ratio of PS macromonomer to *n*-butyl acrylate.



Figure 4. GPC chromatograms for PS macromonomer and graft copolymers before and after fractionation

Table	3.	Miniemulsion	Radical	Copolymerization	of	nBA	in	the	presence	of	PS
Macromonomers for graft Copolymers											

samples	SDS/g	HD/g	DI	nBA/g	MacroPS/g	AIBN/g	$^{a}C_{nBA}$ /%
			water/g				
MG-3-1	0.0871	0.0605	20.01	2.0023	0.9012	0.0436	88.2
MG-3-2	0.1051	0.0730	20.31	2.0014	1.5012	0.0525	86.5
MG-3-3	0.0602	0.0418	20.15	1.5016	0.5041	0.0301	89.6

^aConversion of *n*BA was determined by gravimetric analysis.

Table 4. Molecular Characteristics of PnBA-g-PS

			0				
sample	M_n (g/mol)	$M_w(g/mol)$	M_w/M_n	PS ^a (wt%)	T_{5d}^{b} (°C)	$T_g^{c}(^{\circ}\mathbb{C})$	\mathbf{N}^{d}
MG-3-1	36179	106366	2.94	24.5	351	-10.1	4.8
MG-3-2	35266	120257	3.41	27.6	354	-6.7	5.3
MG-3-3	85542	311205	3.64	15.6	345	-35.4	3.4

^aThe mass ratio of PS in the graft copolymer was determined by ¹HNMR. ^bThe decomposition temperature of 5% weight loss (T_{5d}) was calculated by TGA. ^cDetermined by DSC analysis. ^dNumber of junction points per molecule ($N_{PnBA-g-PS}$) were measured according to the total M_n of multigraft copolymers and the mass ratio of PS and PnBA.



The FTIR spectra of PnBA-g-PS after purification are shown in Figure 5. In Figure 5, the peak at 1733 cm⁻¹ is assigned to the characteristic peak of carbonyl group (C=O) in *n*-butyl acrylate, and the absorption peak²⁷ of symmetric vibration of C-O-C from *n*-butyl acrylate is at 1160 cm⁻¹. Additionally, the characterization peaks of C-H in phenyl ring²⁷ are at 3065cm⁻¹, 3026 cm⁻¹ and 695 cm^{-1} , respectively. Thus, the structure of PnBA-g-PS graft copolymer can be clearly distinguished by FTIR spectra. In order to confirm the structure and composition of PnBA-g-PS graft copolymer, ¹H NMR spectra was shown in Figure 6. Figure 6 shows ¹H NMR spectra of MG-3-3 in CDCl₃. Signals at 0.9 - 0.95 ppm are assigned to *alfa*-methyl protons $(hH, iH)^{28}$. The peak at 1.36 - 1.41 ppm is ascribed to protons $(gH)^{28}$ of methylene in PnBA segments. The peaks at 1.58 - 1.61 are due to methylene protons (eH, fH) in PnBA and PS segments. The absorption at 1.89 and 2.28 ppm correspond to the methylene protons (dH) and methine proton (cH), respectively. In addition, the characteristic peaks for methylene ester protons (bH) from PnBA unit and phenyl protons (aH) from PS unit can be seen clearly at 4.0 ppm¹⁴ and 6.2-7.2 ppm¹⁴, respectively, which means, combined with GPC data, that copolymerization of PS macromonomer with nBA was successful. The molar ratio of PS to PnBA for final graft copolymer can be calculated from ¹H NMR according to eq 1 (S_b is the integration area of five protons of phenyl protons of PS side chains at 6.2 - 7.2 ppm, and S_a is the integration area of two protons of methylene ester protons of PnBA at 4.0 ppm). Then the weight composition of graft copolymers can be obtained as listed in Table 4.





Figure 6. Chain structure and ¹HNMR spectrum of MG-3-3 dissolved in CDCl₃



Figure 7. TGA curves for PnBA-g-PS graft copolymer



copolymers, and PS macromonomer

The thermal property is one of the most important factors to be considered for the application of graft copolymers. The thermal properties were evaluated using TGA and DSC. Figure 7 shows the TGA thermograms and the decomposition temperature of 5% mass loss (T_{5d}) for different samples are shown in Table 4. From Figure 7, it can be observed that the T_{5d} for all graft copolymers is 345~354 °C, which are much higher than that for PnBA (329°C), but little less than that for PS(356°C). Moreover, the thermal stability for graft copolymers was enhanced with increasing PS content. Glass transition temperature (T_g) is a significant physical parameter that has a great influence on the application performance of material, especially for thermoplastic elastomer. Figure 8 shows DSC heat flow curves for all samples, and DSC curves for PnBA homopolymer and PS macromonomer are also presented for comparison. The T_g for PnBA and PS is -51.2 °C and 86.2 °C, respectively. It can be clearly seen that all the glass transition temperature for graft copolymers shift towards larger values with increasing PS content, which is due to the fact that the rigid PS chains as physical crosslinking points hindered the mobility of the entire graft copolymers chains, leading to increasing T_{gs} . Besides, the DSC curves for graft copolymers displayed only one T_g which was between T_g of PnBA and PS macromonomer. The similar results has been reported by other literatures,^{14,29-30} and corresponding explanation can be as follows. On one hand, it may be ascribed to the relatively large PDIs in Table 4, which leads to a mass of PS short side chains dissolving in neighboring PnBA microdomains, thus showing only one T_g . On the other hand, the weight content of PS was far less than PnBA content in Table 4, hence the small amount of PS was embedded in substantial PnBA segments, making it difficult to detect another T_g .

Conclusion

In this paper, PnBA-g-PS graft copolymers were synthesized using macromonomer technique and miniemulsion copolymerization. The macromonomers were prepared by emulsion AGET ATRP and subsequent allylation, and copolymerization of different macromonomers with *n*BA was carried out in miniemulsion system, obtaining PnBA-g-PS graft copolymers successfully. The structure and PS content in PnBA-g-PS copolymers were determined by FTIR and ¹H NMR. The thermal performance was characterized by DSC and TGA. These graft copolymers may be promising for application as adhesive and thermoplastic elastomers. For the synthesis of macromonomers and preparation of graft copolymers, the whole process was carried out in emulsion system. Thus it is very environmental friendly to carry out reaction in an aqueous medium. Therefore, it appears that emulsion system is a promising low cost and environmental alternative to prepare thermoplastic elastomer. In future work, we will synthesize macromonmers having different structures and high activity for free radical polymerization so as to prepare graft copolymers with more complex structures, such as "centipede" and "barbwire" architectures.

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