Characterization and Properties of Amphiphilic Block Polymer Based on Poly(ethylene oxide) and Poly(butyl acrylate)

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ABSTRACT: PEO-b-PBA [PEO: poly(ethylene oxide); PBA: poly(butyl acrylate)], an amphiphilic block copolymer, prepared by redox radical polymerization, was characterized by infrared and ^{1}H nuclear magnetic resonance spectroscopy. The result revealed the existence of PEO and PBA segment in purified block copolymer. The thermal behavior of the block copolymer was determined by differential scanning calorimetry. With the introduction of PBA noncrystalline segment, the crystallinity of PEO was decreased. The emulsifying and water absorptive properties of PEO-b-PBA were also examined. It was found that the emulsifying volume and type were dependent on the amount of block copolymer and the PEO content in block copolymer. Under a certain range, the emulsifying volume increases with an increase of PEO content. The more the PEO content in block copolymer, the stronger the water absorptivity was. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3432–3436, 2003

Key words: amphiphilic block polymer; crystallinity; emulsifying volume; water absorptivity; PEO-b-PBA

INTRODUCTION

The characterization, properties, and applications of amiphiphilic block polymer containing poly(ethylene oxide) (PEG) segment have been the subject of recent investigation. This interest arises from the properties of hydrophilicity, crystallinity, and complexity with alkali metal ion of PEG segments. The PEO-containing amphiphilic block polymers can be used as emulsifiers, surface active agents, phase transfer catalysts, solid polymer electrolytes after complexing with alkali salts and antistatic agents, etc. Riess et al.[1] and Huynb-Ba-Gia et al.[2] studied the emulsifying properties of the amphiphilic block copolymer (ABP) of styrene (S) and ethylene oxide (EO). Lotz et al.[3] and Crystal et al.[4] investigated the crystalline properties and spherulite structures of block copolymers of PS–PEO. Kelly and coworkers[5] observed that the PS–PEO diblock copolymer could form a toluene-soluble complex with potassium phenolate, and used it as a phase transfer

catalyst in the Williamson reaction. Tao et al.[6] observed that the crystallinity and morphology of multiblock copolymers of PS–PEO were affected by the PEO content and type of casting solvent.

Poly(butyl acrylate) (PBA) has longer soft-side chains, a low glass-translation temperature, and quite a good elasticity. Blocking it with crystallinic PEG can improve its synthetical properties. For example, Chen[7] studied the mechanical properties of PEG–PPG synthesized by condensation polymerization, and pointed out that the PEG segment formed crystalline domains and played a role of physical crosslinkage, while the PPG segment containing soft chains acted as elasticity. Lang[8,9] synthesized the PEG-b-PBA by using the macromonomer poly(ethylene glycol) containing an azo group (pre-PEG) as initiator and studied the phase catalytic property. The results showed that the PEO-b-PBA can be used as phase transfer catalysts in the Williamson reaction and the conversion of potassium phenolate increases with the increase of the amount of PEO content. At the same time, PBA as a hydrophobic segment is well miscibilized with rubber and PEO is a hydrophilic polymer. So the combination of PEO and PBA can be used as a compatibilizer in the blend of water-absorbent resin and rubber to improve its compatibility. For example, Zhang et al.[10] utilized an amphiphilic PVA-g-PBA as compatibilizer in the blend of chlorohydrin rubber and crosslinked polyacrylate water-absorbent resin, and the results showed that the

mechanical properties and the water swelling ability could be improved.

We have previously synthesized an amphiphilic PEO-b-PBA by redox radical polymerization. This article deals with characterization and properties of this purified copolymer. In forthcoming studies, we will utilize it as compatibilizer in the blend of crosslinked polyacrylate water-absorbent resin and natural rubber to improve their miscibility and to prepare a water-swellable rubber with excellent elasticity and absorptivity. Compatibilization of PEO-b-PBA in the water-swellable rubber will be described in the next article.

EXPERIMENTAL

Sample preparation

The poly(ethylene oxide-b-butyl acrylate) (PEO-b-PBA) was synthesized by redox radical polymerization as described in our preciously study. Given amounts of PEG, BA, and water were placed in flasks and degassed by flushing with pure nitrogen. Appropriate amounts of ceric ammonium nitrate in $1M$ nitric acid solution were then added under nitrogen. Heterogeneous polymerization was conducted under N_2 with stirring in the dark. The polymer formed was dissolved in chloroform and precipitated from tenfold excess methanol. The precipitated polymer was filtered, washed, and then dried in vacuum to constant weight. The crude polymer was purified with solvent extractions.[8] PEG was extracted with water three times at room temperature and the homopolymer PBA was extracted with mixed solvent (cyclohexane/petroleum ether solution 4/6 v/v) three times at 10°C. The purified block copolymer was dried under a vacuum at room temperature.

Characterization of PEO-b-PBA

[1]H nuclear magnetic resonance (NMR) spectra were taken on a JEOL FX100 NMR spectrometer using CDCL$_3$ as solvent. Infrared spectra were taken on a Perkin-Elmer 177 grating spectrometer. Differential scanning calorimetry (DSC) experiments were run on a Perkin-Elmer DSC-7 differential scanning calorimeter and the traces were taken at a heating rate of 10°C min or −10°C. Crystallinity (X_c) of the PEG homopolymer was determined by a Rigaku 3015 wide-angle x-ray diffractor.

Properties of PEO-b-PBA

Measurement of the emulsifying volume

The emulsifying properties of the block copolymers were represented in term of the emulsifying volume, which was measured as follows. A certain amount of the block copolymers was dissolved in 30 mL of toluene; then 70 mL of water was added to it. The mixture was stirred thoroughly by a magnetic stirrer for 10 min, and then poured into a cylinder with a cover. Overnight, the system was separated into layers. The emulsifying volume was taken as the total volume of the toluene solution plus water minus the volume of the water or oil phase.

Measurement of the water absorptivity

The water absorptivity was measured as follows. Accurately weighed sample was dipped into 100 mL water. After keeping immersion for 48 h, the sample was gently blotted with tissue paper to remove the excess water on the surface and was weighed again. The water absorptivity S_w was given by

$$S_w = \frac{W_2 - W_1}{W_1} \times 100\% \qquad (1)$$

where W_1 is the weight of sample before immersion and W_2 is the weight of sample after immersion.

RESULTS AND DISCUSSION

Evidence of block copolymerization

Homopolymer PEG can be dissolved in water and mixed-solvent cyclohexane and petroleum ether in a proper proportion. The solvent can extract the PBA homopolymer but cannot extract the copolymer. So the crude product can be purified with solvent extraction. PEG was extracted with water three times at room temperature; then the homopolymer PBA was extracted with mixed solvent (cyclohexane/pretroleum ether solution 4/6 v/v) three times at 10°C. Finally, the undissolved solid was the block copolymer.

In contrast, PEG and PBA homopolymer were dissolved together in CHCl$_3$ solvent and when the solvent was removed, a solid blend was obtained. According to the above procedure, the blend was extracted with water and mixed solvent. As a result, the blend was completely dissolved and none of solid remained. Thus, it is clear that the undissolved solid is not derived from the blend of PEG and PBA, but from the block copolymer PEO-b-PBA. Because of chemical combination between PEO segment and PBA segment, PEO-b-PBA could not dissolve in water and mixed solvent.

PEO content in the block copolymer determined by ^{1}H-NMR

As shown in Figure 1, ^{1}H-NMR spectra of purified block copolymers demonstrated that they contained monomeric units of both EO and BA. The content of
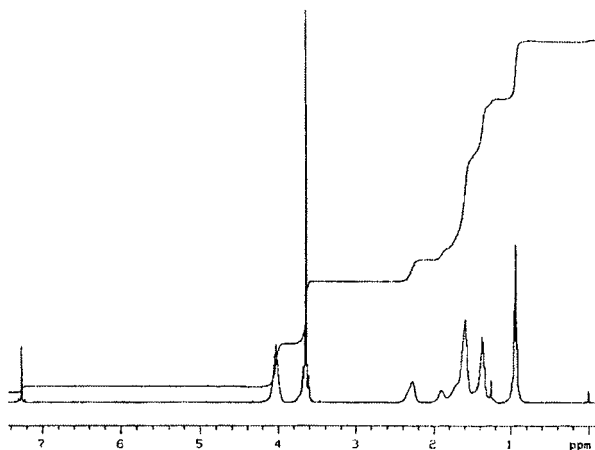
Figure 1 ^{1}H-NMR spectrum of PEO-b-PBA block copolymer.

PEO in the block copolymers is calculated according to the following equation:

$$PEO\% = \frac{A_e}{(2A_f + A_e)} \times 100\% \qquad (2)$$

where A_e is the area of the proton of δ_e (δ_e =3.6, for —CH$_2$CH$_2$—O—), A_f is the area of the proton of δ_f (δ_f =4.0, for —COOCH$_2$—) and the content is in mol percentage.

Thermal analysis of PEO-b-PBA

PEO-b-PBA shows a unique thermal behavior because it contains both the crystalline PEO segment and the noncrystalline PBA segment. The DSC curves of different samples are given in Figure 2. The right portion shows the melting behavior of samples, while the left part shows the crystallization behavior. The area of the endothermic peak in the DSC curves is proportional to the enthalpy of the fusion of PEO segment, so the crystallinity (X_c) of PEO in block copolymers is calculated as follows:

$$X_C = \Delta H_f / \Delta H \qquad (3)$$

where ΔH_f is the enthalpy of the fusion per mass unit of PEO segment in the block copolymers, and ΔH is the enthalpy of the fusion per mass unit perfectly crystallized PEO and its value is 221.7 J/g. The results are listed in Tables I and II.

Pure PEG has excellent crystallizability. But the introduction of PBA non-crystalline segment reduces its crystallinity, which shows mainly in three aspects.

First, as shown in Figure 2 and Table II, the crystalline temperature of PEG is 306 K, while that of PEO-b-PBA is 258 K , decreasing nearly 48 K. We all know that due to the hydrophilic and crystalline properties

of PEG homopolymer and the hydrophobic and soft chain properties of PBA homopolymer, they are not compatible in thermodynamics, and the film formed from the CHCl$_3$ solution of blend of PEG homopolymer and PBA homopolymer exhibits a macroscopic phase separation and each of them tends to aggregate respectively. Due to the chemical combination between the PEO segment and PBA segment, PEO-b-PBA is unable to form macroscopic phase separation, but is able to exist as a microphase separating structure. Guo[11] observed the microphase separation of the amphiphilic PB-b-PEO by transmission electron microscopy. When the content of PEO segment is much lower, it disperses in the form of domain in the PBA matrix. Thus, melted PEO segment crystallizes in domain and it can form a steady crystal under high supercooling. For the crystalline PEO-b-PBA, there exists both homogenous and heterogeneous nucleation, but a steady induction of the homogenous nucleation needs a much lower temperature.[9] In our experimental range, we found that only sample 1 exhibited double crystalline temperature. As shown in Figure 3(c′), the crystallization temperature locate at about 259 K is heterogeneously nucleated, and that at about 245 K is homogeneously nucleated.

Second, as shown in Table I, the melting temperature (T_m) of PEG is 336 K, while that of PEO-b-PBA is 321 K, which is about 15 K below the T_m of PEG. Low T_m of PEO-b-PBA is due to its low crystalline temperature. Crystal formed at a lower temperature is not perfect, and apt to be destroyed in low temperature, which leads to a fall in melting temperature.
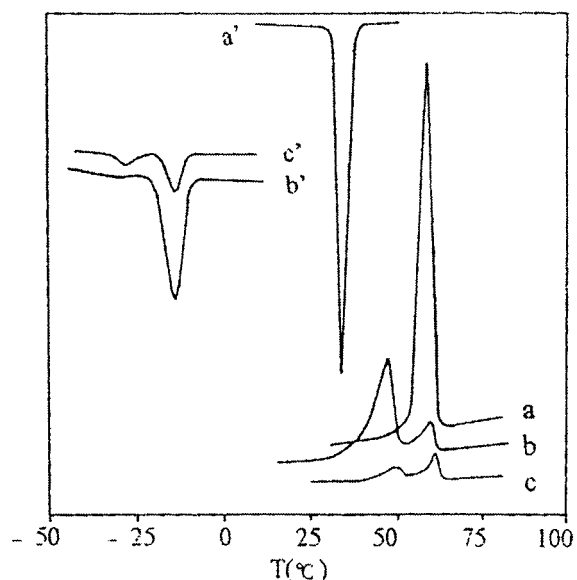

Figure 2 DSC thermograms. (a,b,c) Heating curve. (a′,b′,c′) Cooling samples. Sample: a,′a—PEG homopolymer; b,b′—PEG/PBA copolymer (PEO % = 35.2); c,c′—PEO/PBA copolymer (PEO % = 16.5).

TABLE I
DSC Experiment on Sample with Different PEO Content[a]

Sample	PEO content (mol %)	ΔH_f[b] (J/g)	Melt temperature (K)		Crystallinity (%)
1	16.5	4.3	322.2	334.2	1.9
2	19.6	12.6	321.4	333.8	5.7
3	26.4	15.9	321.7	333.5	7.2
4	35.2	14.4	320.3	333.0	6.5
5	42.3	30.1	320.5	332.7	13.6
6	100.0	182.2	335.6		82.3

[a] Heating speed 10°C/min.
[b] ΔH_f is the enthalpy of fusion per unit of block copolymer.

TABLE II
DSC Experiment on Sample with Different PEO Content[a]

Sample	PEO content (mol %)	ΔH_f (J/g)	Crystalline Temperature (K)		Crystallinity (%)
1	16.5	−3.0	245.0	259.2	1.4
2	19.6	−5.9	258.2		2.6
4	35.2	−9.5	259.1		4.3
5	42.3	−16.8	255.4		7.6

[a] Cooling speed 10°C/min.
[b] ΔH_f is the enthalpy of fusion per unit of block copolymer.

Third, under the same measure condition, crystallinity of PEO-b-PBA is lower than that of PEG and with the increase of the PBA noncrystalline segment, the crystallinity of PEO decreases (Tables I and II).

The crystalline and melting behaviors of the block copolymer are related to its thermal history. In the preparation process, all the PEO-b-PBA samples experienced twice thermal treatments respectively at 333 and 373 K as follows. After purification, the samples were dried at 333 K in vacuum for 2 h and cooled in a desiccator. After that, they were heated again at 373 K in vacuum for 0.5 h and cooled in a desiccator. Although the 373 K is a higher temperature, some of the crystalline segments readjust and the others still keep the states of the first thermal treatment as the heating time is shorter. Thus, in DSC curves, there emerges a double melting peak. On the DSC heating plate, the sample was treated by heating–cooling–heating, and we find that in the second heating, melting double peaks change to single peak.

Emulsifying property

As amphiphilic substance, an important application is that PEO-b-PBA can be used as the stability in the water–oil two-phase blend system. On condition that toluene acts as the oil phase and water to oil is 70 to 30 mL, emulsifying properties and types change with the amount of PEO-b-PBA and the content of PEO segment. Table III shows the changes of emulsifying volume and type with the increase of the amount of block polymer (PEO% in mol is 35.2%). When the amount is very small (0.0249 g), the emulsifying volume has reached 79 mL. It does not vary too much on increasing the amount of block copolymer in the confined range and the system remains an oil-in-water (O/W) type. But on continuing to increase the amount of block copolymer to 0.1682 g, the emulsifying volume decreases and the emulsion type transforms into water-in-oil (W/O).

As shown in Table IV, the higher the content of PEO in block copolymer, the larger the emulsifying volume

TABLE III
Relationship Between Emulsifying Property and Amount of Block Copolymer[a]

Block copolymer (g)	0.0249	0.0592	0.1253	0.1682	0.2712
Emulsifying volume (mL)	79	76	82	71	40
Emulsion type	O/W	O/W	O/W	W/O	W/O

[a] PEO content in block is 35.2%.

TABLE IV
Relationship Between Emulsifying Property and PEO Content in Block Copolymer[a]

PEO content (mol %)	19.6	26.4	35.2	42.3
Emulsifying Volume (mL)	17	35	71	80
Emulsion Type	W/O	W/O	W/O	O/W

[a] Weight of block copolymer is 0.1682 g.

TABLE V
Relationship Between Water Absorptivity and PEO Content in Block Copolymer

PEO content (mol %)	16.5	19.6	26.4	35.2	42.3
Absorptivity (%)	29.9	59.5	71.5	96.8	128.9

and the better the emulsifying ability. On increasing content of PEO to 42.3%, the emulsifying type changes from W/O to O/W. The transformation is probably because the increase of PEO content enhances the water absorptivity.

Water solvability and absorption

As shown in Table V, the water absorptivity is only 29.9% when the content of PEO equals 16.5%, and with the raising of the content of PEO, the water absorptivity increases markedly. As we know that although pure PEG-6000 is a crystalline polymer, it has excellent solvability not only in water, but also in some organic solvents (for example, chloroform). But PBA as hydrophobic polymer can only dissolve in organic solvents. When the content of PBA segment reaches a certain amount, PEO-b-PBA cannot dissolve in water any more. But because PEO segment can form a hydrogen bond with water and combine some amount of water, PEO-b-PBA can absorb some water. It is easily understood that the more the content of PEO segment in per mass PEO-b-PBA is, the more the amount of water is absorbed.

CONCLUSIONS

1. With the introduction of the PBA noncrystalline chain, the crystallizability of PEO decreases.

2. The emulsifying volume and type is affected by the amount of block and the PEO content in block copolymer. Under a certain range, the emulsifying volume increases with the increase of PEO contents.

3. The water absorptivity is related to the PEO content in block copolymer. The higher the PEO content in block, the stronger the water absorptivity is.

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