

# Poly(ethylene glycol)-*Block*-Poly(butyl acrylate). II. Characterization and Properties

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**ABSTRACT:** Poly(ethylene glycol)-*block*-poly(butyl acrylate) synthesized by radical polymerization in a one-step procedure were characterized by gel permeation chromatography, infrared, <sup>1</sup>H-NMR spectroscopy, and differential scanning calorimetry (DSC). The crystalline property, emulsifying property, and phase transfer catalytic effect in the Williamson reaction were studied. It was found that the crystallinity of the copolymer increased with an increase in both the content and molecular weight of poly(ethylene oxide) (PEO) sequences. DSC curves showed two distinct crystallization temperature due to the heterogeneous nucleation and homogeneous nucleation crystallization. The casting solvent significantly affected the morphology and crystallinity of the solvent cast films. Both the emulsifying volume and the phase transfer catalytic efficiency in the Williamson reaction increased with the amount and PEO content of the block copolymers used, but decreased with an increase in the molecular weight of PEO sequences. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1427–1436, 1998

**Key words:** amphiphilic block copolymers; emulsifying volume; crystallinity; phase transfer catalytic property; solvent cast film

## INTRODUCTION

The block copolymers of poly(ethylene oxide) (PEO) have been studied intensively both in preparation and in application. Recently, many synthetic methods have been developed, including anionic polymerization,<sup>1</sup> condensation polymerization,<sup>2–4</sup> and radical polymerization.<sup>5–8</sup> These block copolymers have many diversified applications because of the properties of hydrophilicity,

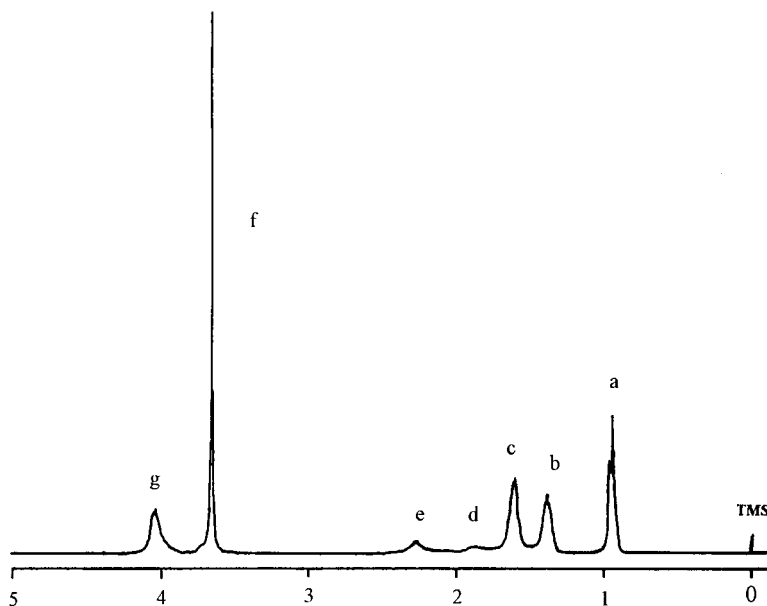
crystallinity, and complexity with alkali metal ion of PEO segments. For example, it was reported that such block copolymers have been used to improve the viscosity and detergent properties of the lubricating oils,<sup>9</sup> dyeability, and resistance to electrical charge build up.<sup>10</sup> Such block copolymers were also suggested as polymeric surfactants,<sup>11</sup> hydrogels,<sup>12</sup> and nonionic surface active reagent to emulsify the system of water–toluene.<sup>13</sup>

Huynb-Ba-Gia<sup>14</sup> studied the emulsifying characteristics of PS–PEO star block copolymers. Franta<sup>15</sup> and Gervais,<sup>16</sup> respectively, reported that block copolymers of PS–PEO and PB–PEO possessed a layer structure. Crystal et al.<sup>17</sup> found that solvent cast films of styrene–ethylene oxide block copolymers showed the spherulite. Hong-

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**Figure 1** The  $^1\text{H-NMR}$  spectrum of PEO-*b*-PBA.

quan Xie et al.<sup>18</sup> studied the emulsifying property, the phase transfer catalytic property, and the crystalline morphological structure of the star-shaped block copolymers of styrene and ethylene oxide and pointed out that the crystal regularity was higher when the melting copolymers were quenched at 20°C than that at 0°C. Tao Xuquan et al.<sup>19</sup> observed that the crystallinity and morphology of multiblock copolymers of PS-PEO were affected by the PEO content and the type of the casting solvent.

In a preceding article,<sup>20</sup> we have studied the synthesis of poly(ethylene glycol)-*b*-poly(butyl acrylate) (PEO-*b*-PBA) by radical polymerization in an one-step procedure. In this article, we will study the structure of PEO-*b*-PBA by infrared (IR),  $^1\text{H-NMR}$  spectroscopy differential scanning calorimetry (DSC), scanning electron microscopy (SEM), wide-angle X-ray diffraction (WAXD), and the properties of the emulsification and of the phase transfer catalysis.

## EXPERIMENTS

### Materials

Poly(ethylene oxide)-*block*-poly(butyl acrylate) was prepared as described in a preceding article.<sup>20</sup> Potassium phenylate was prepared by reacting potassium hydrate with an excess of phenyl hydroxide in water solution, and the residual phenyl

hydroxide was extracted by toluene. The purity was measured by the chlorhydric acid titration. Toluene was dried by anhydrous magnesium sulfate and distilled. All the other reagents were analytically pure and used as received.

### Handling of PEO-*b*-PBA (To Be Used to Observe the Spherulite)

A 5% solution of PEO-*b*-PBA was prepared in a different solvent and then cast on a flat glass. After the solvent evaporated at room temperature, the cast films were dried in the desiccator.

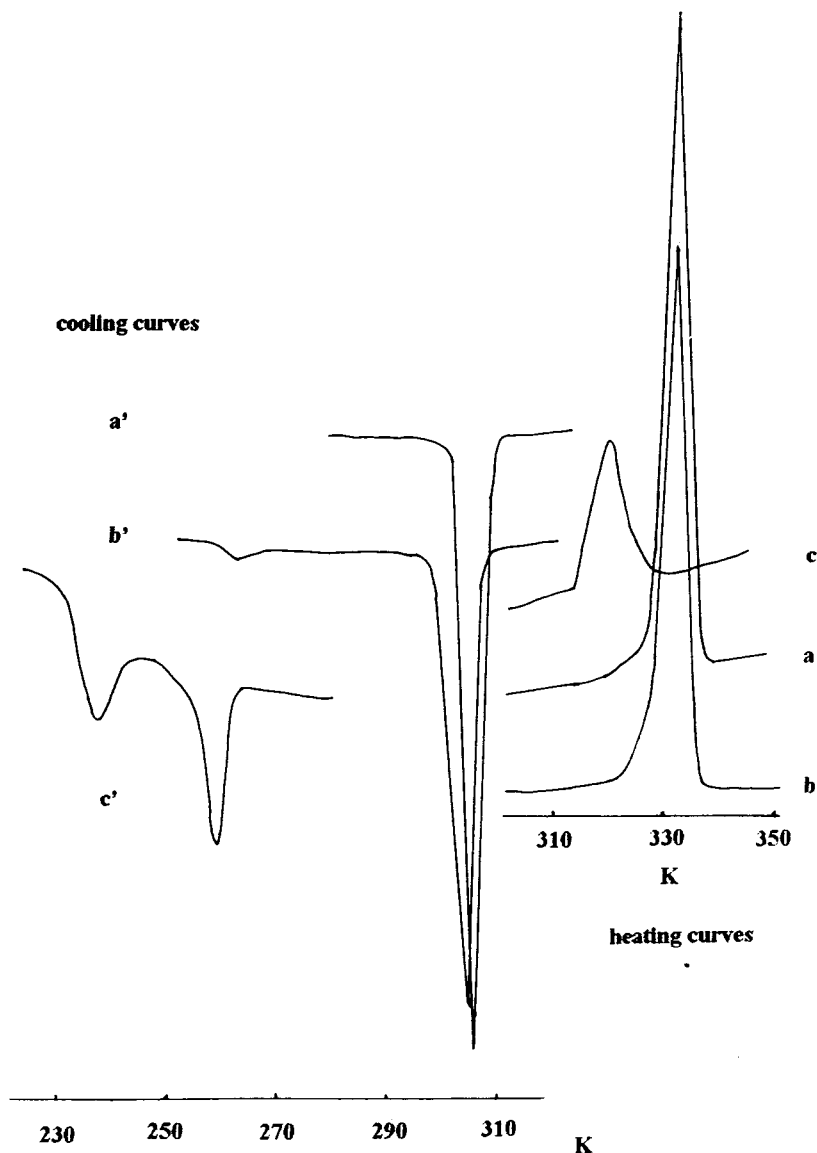
### Characterization of PEO-*b*-PBA

$^1\text{H-NMR}$  spectra were taken on a JEOL FX100 NMR spectrometer using  $\text{CDCl}_3$  as a solvent. 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 min. IR spectra were taken on a Perkin Elmer 177 grating spectrometer. Crystallinity ( $X_c$ ) of the poly(ethylene glycol) (PEG) homopolymer was determined by WAXD using a Rigaku 3015 apparatus. The crystalline morphology of the block copolymers were taken by a JEOL JXA-840 scanning microanalyzer.

### Properties of PEO-*b*-PBA

#### Measurement of the Emulsifying Volume

The emulsifying properties of the block copolymers were represented by the emulsifying volume



**Figure 2** DSC thermograms. (a–c) Heating curves. (a'–c') Cooling curves. (a–a') PEG homopolymer. (b–b') PEG–PBA blend. (c–c') PEO–PBA copolymer.

that 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. After keeping static for 48 h, the total volume and the volume of the water phase or oil phase were measured. The difference was recorded as the emulsifying volume.

#### **Measurement of the Phase Transfer Catalytic Efficiency in Williamson Reaction**

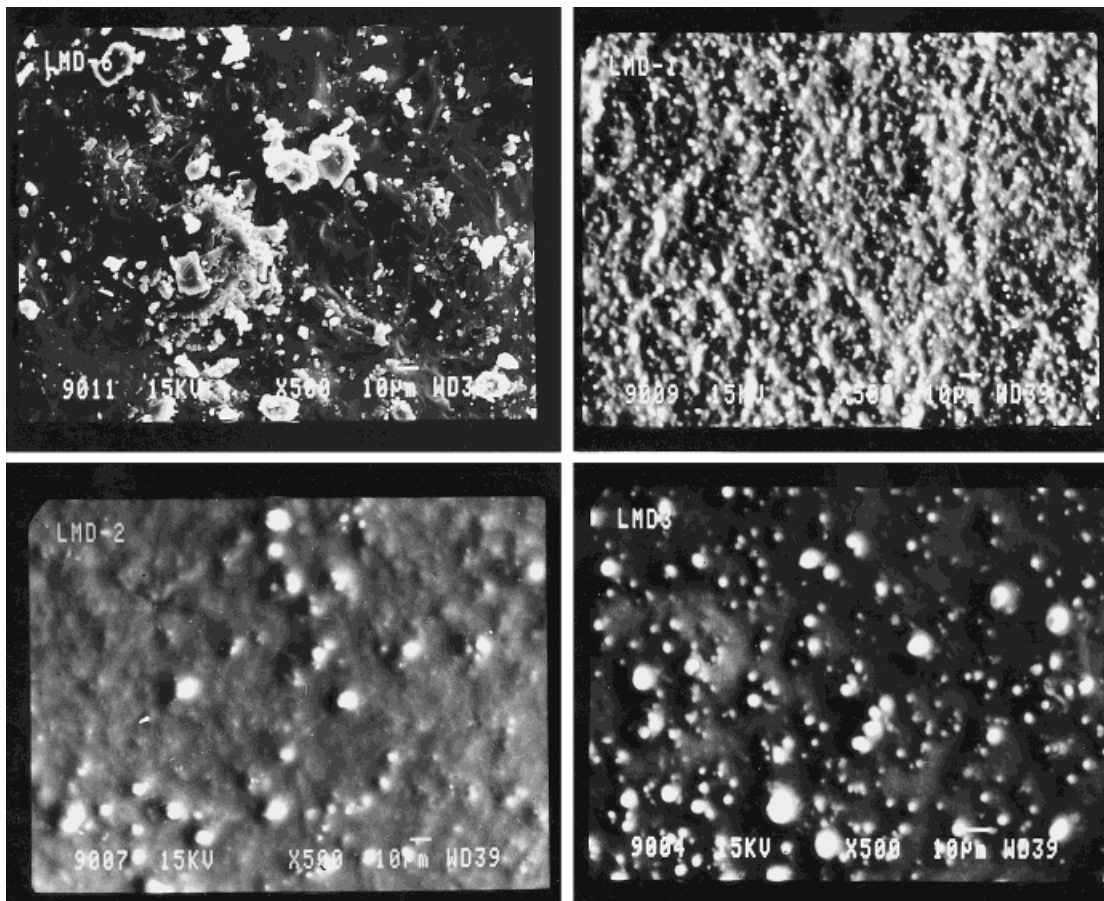
The phase transfer catalytic properties of PEO-*b*-PBA were measured as follows. 2.0 mL of butyl

bromide, 1.0 g of potassium phenylate, and a certain amount of the block copolymers was weighed accurately and dissolved in 40 mL of toluene, then stirred at 90°C for 4 h. The solution was kept statically to deposit the insoluble substance. The precipitates were dried at room temperature. The surplus potassium phenylate were measured by the chlorhydric acid titration using methyl red as an indicator. The conversion of potassium phenylate is given by

$$\text{conversion \%} = (W_a - W_b) \times 100/W_a \quad (1)$$

where  $W_a$  is the weight of potassium phenylate





**Figure 3** Scanning electron photomicrographs of PEG and PEO-PBA copolymer solvent casting films. Top left: PEG; the others, copolymers and their cast solvent: tetrahydrofuran (top right), toluene (bottom left), and chloroform (bottom right). Marker is 10  $\mu\text{m}$ .

Therefore, the PBA sequence makes  $T_m$  decrease only when it connects with PEO sequence to become the block copolymers.

A particular phenomenon observed was that there were two distinct crystallization temperatures ( $T_c$ ) of the block copolymer at about 21 K apart (Fig. 2, curve c'). The PEG homopolymer rapidly crystallizes at 306 K, about 30 K below than its  $T_m$  (Fig. 2, curve a'). The blend of PEG and PBA homopolymer mostly crystallizes at 301 K, at about 5 K below the  $T_c$  of the PEG homopolymer; and a little crystallizes at 264 K (Fig. 2, curve b'). The ratio of the dual crystal peaks is 97 : 3. The crystallization behavior of the blend further indicates the effect of PBA sequences on the thermal transition of PEO. The block copolymers crystallize at 236 and 256 K (Table II). Similar observations have been reported for di-, tri- and multiblock PS-PEO copolymers,<sup>21-23</sup> but the two crystallization temperatures are 253 and 313

K, at about 60°C apart. The occurrence of the two fusion exotherms suggests a difference in nucleation phenomenon at the two temperatures. It is suggested that only a fraction of isolated PEO-rich domains in the PBA matrix contain heterogeneous nuclei. Those domains that contain nuclei will crystallize in the usual temperature range at rather low supercooling. However, domains that do not contain any nucleus must be supercooled at a much lower temperature in order to induce some kind of homogeneous nucleation; so the crystallization at about 256 K is heterogeneously nucleated, and that at about 236 K is homogeneously nucleated.

The area of the endothermic peak in the DSC curves is proportional to the enthalpy of the fusion of PEO blocks, so the crystallinity  $X_c$  of PEO in block copolymers is calculated as follows:

$$X_c = \Delta H_f / \Delta H_f^* \quad (4)$$

**Table III** Phase Transfer Catalytic Effects of the Block Copolymers

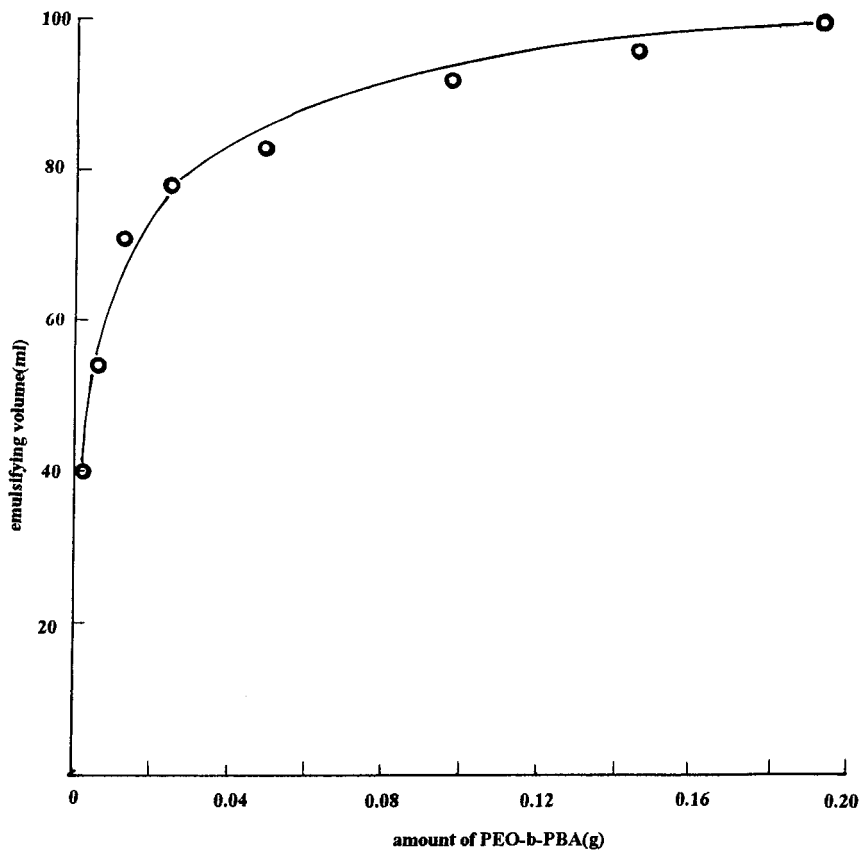
Sample	Weight (g)	$M_n$ PEO $\times 10^{-3}$	PEO (%)	Conversion <sup>a</sup> (%)
1	0.3	4	31.4	74.7
2	0.3	4	33.9	78.4
3	0.3	4	38.9	82.9
4	0.3	4	44.8	85.0
5	0.3	4	46.8	86.4
6	0.3	2	25.0	80.1
7	0.3	2	27.3	81.2
8	0.3	2	33.4	84.5
9	0.3	2	45.8	87.4
10	0.3	2	53.1	89.0
blank	—	—	—	4.2
PEO	0.3	2	100	49.2

<sup>a</sup> The conversion of potassium phenolate.

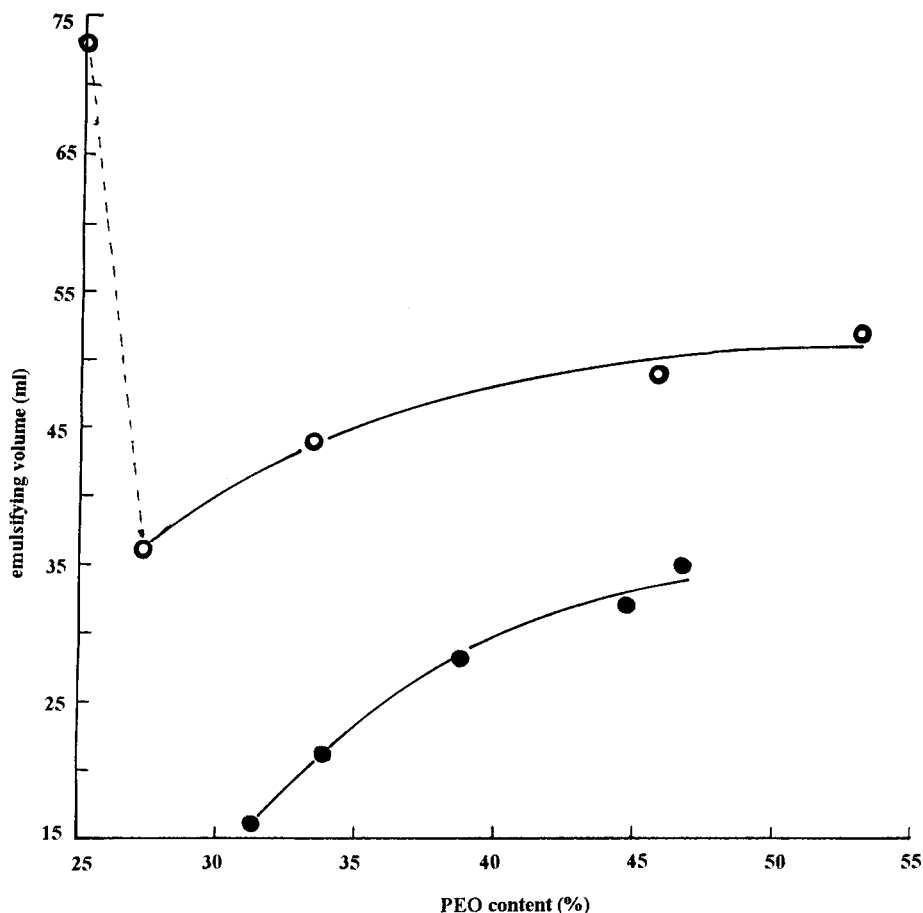
where  $\Delta H_f$  is the enthalpy of the fusion per mass unit of PEO blocks in the block copolymers, and  $\Delta H_f^*$  is the enthalpy of the fusion per mass unit

of perfectly crystallized PEO and its value is 239.8 J/g.

Table I shows the dependence of the crystallin-



**Figure 4** The influence of the amount of copolymer used on the emulsifying volume: PEO content is 46.8% and the PEO sequence molecular weight is 4000.



**Figure 5** The influence of the PEO content and PEO sequences molecular weight on the emulsifying volume. PEO sequence molecular weight: (○) 2000; (●) 4000.

ity of PEO blocks on the content of PEO in the block copolymers. Contrary to the crystallinity of HMS-MEPS copolymers,<sup>24</sup> the crystallinity of PEO-PBA block copolymers increases with the increase of the PEO content, and its value is relatively lower. The  $X_c$  increases from 13.3 to 26.5%, while the content of PEO increases from 31.4 to 46.8%.

As described by Shimura and Hatakeyama,<sup>22</sup> the molecular weight of PEO blocks ( $M_n$ ) affects the crystallinity of the block copolymers. The DSC curves indicate that there is no crystallization when the  $M_n$  of PEO sequences is 2000 (PEO-2000); however, there is obvious crystallization in PEO-4000 copolymers (Fig. 2).

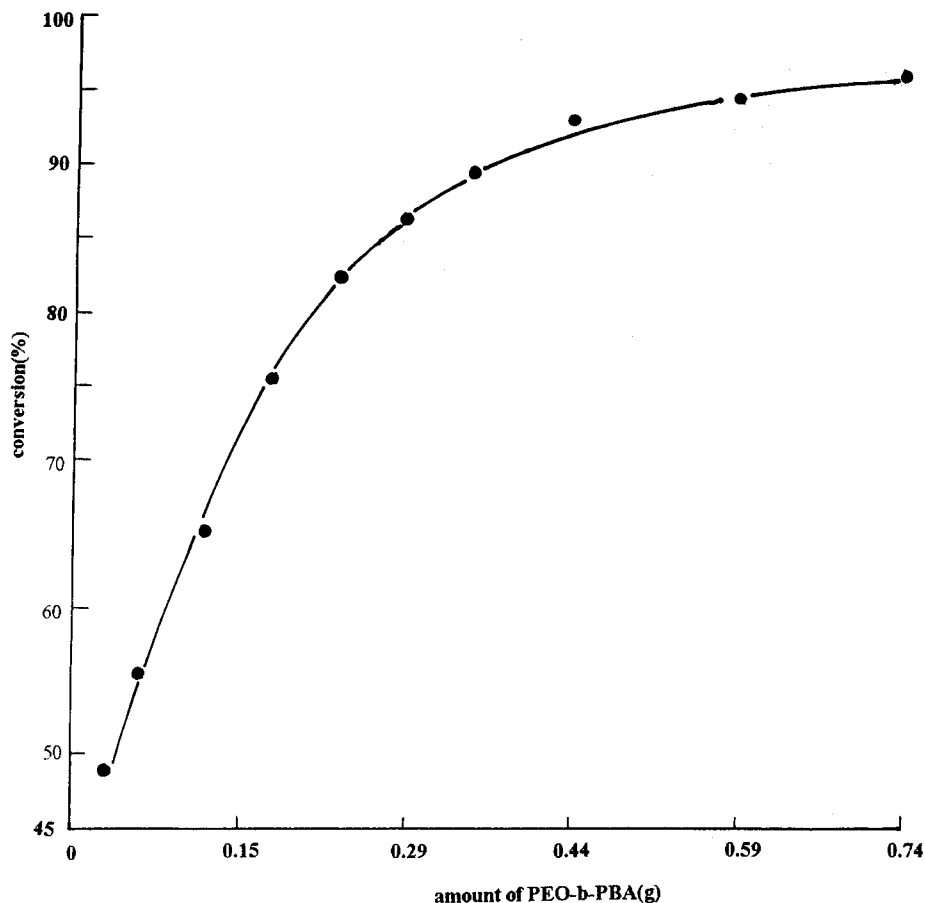
The morphology of the solvent cast films of styrene-ethylene oxide copolymers has been studied extensively.<sup>25-27</sup> It has been reported that the solvent significantly affects the morphology and crystallinity of the copolymer. Figure 3 shows the scanning electron photomicrograph of the PEG

homopolymer and the PEO-PBA copolymers. It is obvious that volume filling spherulitic films are formed and the volume of the PEO spherulites in block copolymers decreases. In the copolymer, the crystallization of PEO sequences is impeded by amorphous PBA sequences; consequently, the copolymer spherulites are smaller than that of homopolymer. More interesting, however, is that the spherulites of the tetrahydrofuran cast films are smaller but denser than that of the chloroform and toluene cast films, as shown in Table III; and the crystallinity is the highest.

## Properties of Block Copolymers

### The Emulsifying Property

The block copolymers can emulsify the water-oil system owing to the hydrophilic property of PEO sequences and the hydrophobic property of PBA sequences. Figure 4 shows the dependence of the



**Figure 6** The influence of the amount of copolymers used on the conversion of potassium phenolate. PEO content is 46.85 and PEO sequence molecular weight is 4000.

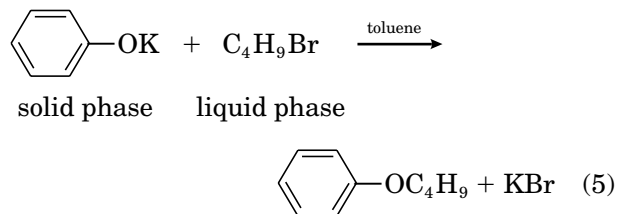
emulsifying volume on the amount of the block copolymers used in emulsifying the water-toluene system. The higher the emulsifying volume, the larger is the ability of the copolymer to emulsify. It can be seen that all of the emulsion is of the water-in-oil type. At initial stage, the emulsifying volume increases remarkably with the increase of the block copolymers, then increases slightly. When the weight of the copolymers is 0.192 g, the system is emulsified thoroughly.

Figure 5 shows the effects of the content and the molecular weight of PEO sequences on the emulsifying volume. The emulsifying volume increases with the content of PEO when the molecular weight of PEO sequences is 4000. However, in the case of PEO (2000) used, the emulsion type varies with PEO content. At a lower PEO content, the emulsion type is water-in-oil, then becomes oil-in-water with the increase of the PEO content; the emulsifying volume decreases dramatically, then increases slightly. Furthermore, the emulsi-

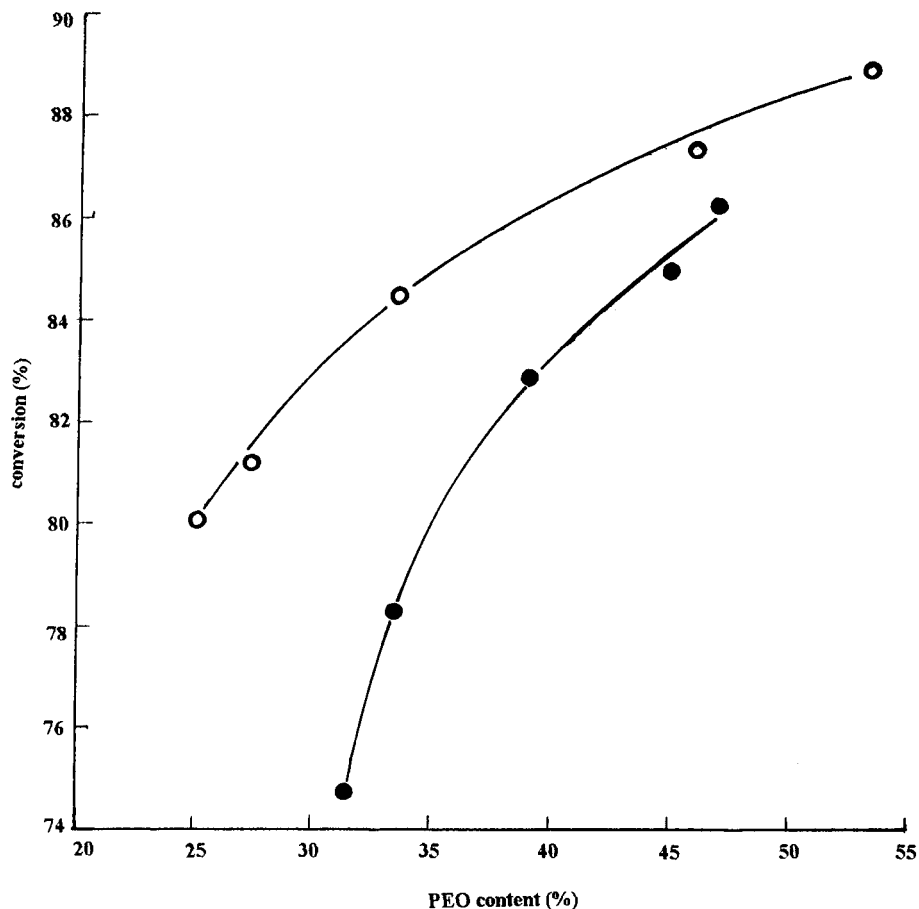
fying volume of PEO-4000 copolymers is significantly lower than that of PEO-2000 copolymer. In other words, at a fixed PEO content and amount of copolymers, the smaller the molecular weight of PEO sequences, the larger the emulsifying volume. It may be due to the number of emulsifying centers increasing with a reduction in the molecular weight of PEO sequences.

#### *The Phase Transfer Catalytic Property*

It is well known that PEO can complex with alkali salts, so the copolymers containing PEO sequences were tested as phase transfer catalysts in the Williamson reaction, as follows







**Figure 7** The influence of the PEO content and PEO sequences molecular weight on the conversion of potassium phenolate. PEO sequences molecular weight: (○) 2000; (●) 4000.

The conversion of potassium phenolate can be used to represent the yield of the reaction between solid potassium phenolate and liquid butyl bromide in toluene. As shown in Table III, the conversion is 4.2% in blank and 50% in the existence of PEG. However, for the block copolymers, it increases to more than 75%.

Figure 6 shows that the conversion of potassium phenolate increases with an increase of the amount of the block copolymers. Figure 7 shows that the conversion of potassium phenolate increases with an increase in the PEO content and decreases with an increase in the molecular weight of PEO sequences. It may be explained that, in the case of the same PEO content, the number of PEO sequence reduces with an increase in the molecular weight of PEO. It results in the reduction of the complexing sites of  $K^+$  ions; consequently, the phase transfer catalytic efficiency decreases.

## CONCLUSION

Considering the relationship among the composition, property, and structure of the amphiphilic block copolymers, it can be suggested that the crystallinity of the copolymers of ethylene oxide and butylacrylate increases with an increase in the PEO content. 2000 of the molecular weight of PEO sequences is necessary for crystallization, regardless of the molecular weight of PBA sequences. The crystallization is a dual crystallization process. The crystallinity and the spherulitic volume of the solvent cast films depend on the casting solvent.

The emulsifying ability and phase transfer catalytic efficiency of the copolymers are related to their composition too. Both the emulsifying volume and the conversion in Williamson reaction increase with increasing amount and PEO con-

tent, but decrease with increasing molecular weight of PEO sequences.

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