

# Poly(ethylene glycol)-*Block*-Poly(butyl acrylate).

## I. Synthesis

MEIDONG LANG,<sup>1</sup> GUO ZHANG,<sup>1</sup> NA FENG,<sup>2</sup> SHUHUA LI,<sup>3</sup> XINFANG CHEN<sup>1</sup>

<sup>1</sup> Institute of Materials Science, Jilin University, Changchun 130023, People's Republic of China

<sup>2</sup> Department of Chemical Engineering, Dalian Institute of Light Industry, 116034, People's Republic of China

<sup>3</sup> Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

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**ABSTRACT:** Prepolymers of poly(ethylene oxide) (Pre-PEO) were synthesized by reacting azoisobutyronitrile (AIBN) with poly(ethylene glycol) (PEG), and their structures were characterized by IR and UV. The molecular weight of pre-PEO was related to the feed ratio and reaction time. These prepolymers can be used to prepare block copolymers—poly(ethylene oxide)-*block*-poly(butyl acrylate) (PEO-*b*-PBA) by radical polymerization in the presence of butyl acrylate (BA). Solution polymerization was a suitable technique for this step. The yield and the molecular weight of the product were related to the ratio of the prepolymer to BA, the reaction time, and temperature. GPC showed that the molecular weight increased with a higher ratio of BA to pre-PEO. The intrinsic viscosity of the copolymers was only slightly dependent on reaction time, but decreased at higher reaction temperatures, as did the amount of PBA homopolymer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1667–1674, 1997

**Key words:** synthesis; prepolymer; radical polymerization; reaction condition; poly(ethylene oxide)-*block*-poly(butyl acrylate)

## INTRODUCTION

Many synthetic methods have been developed for the preparation of block polymers, such as anionic polymerization,<sup>1</sup> condensation polymerization,<sup>2,3</sup> and free-radical polymerization processes.<sup>4–8</sup> Block copolymers can be prepared by using a polymeric radical initiator<sup>9</sup> which is consecutively decomposed in a two-step procedure in the presence of two different monomers.<sup>10–13</sup> In the first step,

the polymeric initiator is partially decomposed in the presence of a monomer to prepare an azo group- or peroxygen group-containing prepolymer; then, the remaining azo groups or peroxygen groups of the prepolymer are completely decomposed in the presence of the other monomer, and the block copolymers containing some homopolymers are obtained. This synthetic method allows a combination of hard and soft blocks or of hydrophilic and hydrophobic segments.

Among block and graft polymers, amphiphilic polymers, which consist of both hydrophilic and hydrophobic segments, possess a special value in the theoretical and practical points of view. In this study, we synthesized amphiphilic block copolymers by radical polymerization in a one-step procedure. The hydrophobic segment is poly(butyl

Correspondence to: M. Lang at the Institute of Chemistry, Academia Sinica, Beijing, 100080, People's Republic of China.

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**Table I Molecular Weight of PEG Used in This Article**

	PEG(1)	PEG(2)	PEG(3)
Molecular weight	2000	3350	8000

acrylate) (PBA). The poly(ethylene glycol) containing azo groups (pre-PEO) serves both as an initiator and as a hydrophilic segment. As is well known, block copolymers can be used as a compatibilizer for blending rubber with resin.

Poly(ethylene glycol)-*block*-poly(butyl acrylate) (PEO-*b*-PBA) with different compositions were synthesized in this study. The characterization and properties of PEO-*b*-PBA will be described in the next article.<sup>14</sup>

## EXPERIMENTAL

### Materials

Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried on phosphorous pentoxide. Commercial poly(ethylene glycol) (PEG), provided by Tianjin Tiantai Chemical Co., was dried at room temperature in a desiccator. Their molecular weights are shown in Table I. The other solid reagents were used without further purification. The monomer of butyl acrylate (BA) was distilled under a vacuum prior to use. All the solvents used were analytical grade. Methanol was dried by refluxing over sodium metal and then distilled; benzene was dried in the presence of phosphorous pentoxide over 1 day and then dis-

tilled. The other solvents were purified by distillation.

### Preparation of Ethylene Oxide Prepolymer (pre-PEO)

In a three-necked round-bottom flask with a gas inlet and stirrer, 134 g (0.04 mol) of PEG (2), 6.57 g (0.04 mol) of AIBN, and 400 mL of dry benzene were stirred together until the greater part of the mixture dissolved. The flask was immersed in an ice-water bath. Dry gas of hydrogen chloride (HCl) was slowly bubbled and passed through the mixture solution to saturation. The solution was stirred under a HCl atmosphere for 25 h at 0°C, then poured into 600 mL of ice water and mixed under stirring. The mixture was kept at a static state. The portion of benzene was removed from this mixture and the aqueous layer was neutralized by sodium bicarbonate, then extracted five times with 70 mL of chloroform. The chloroform extracts were dried over anhydrous sodium sulfate overnight and the solvent was evaporated under a vacuum at room temperature; finally, 136 g of a waxy solid were obtained.

### Preparation of PEO-*b*-PBA

In a 250 mL three-necked flask equipped with a stirrer, nitrogen inlet, and reflux condenser, a certain amount of pre-PEO and BA were dissolved in 100 mL of dry benzene. The mixture solution was degassed by nitrogen for about 35 min, then heated with stirring in the thermostat. After a certain reaction time, the mixture was cooled to 40°C; then, the solvent was removed from the re-

**Table II Preparation of Pre-PEO by Reaction of AIBN with PEG**

No.	PEG		AIBN		Solvent (mL)	Reaction Time (h)	Yield (g)	[ $\eta$ ] <sup>a</sup> (mL/g)
	$M_n$	mmol	g	mmol				
1	3350	8	1.31	8	100	5	20.1	15.2
2	3350	8	1.31	8	100	10	21.2	15.6
3	3350	8	1.31	8	100	15	21.4	16.7
4	3350	8	1.31	8	100	20	20.5	18.4
5	3350	8	1.31	8	100	25	23.7	20.8
6	3350	8	0.66	4	100	25	21.5	17.0
7	3350	4	1.31	8	100	25	10.7	16.1
8	2000	20	3.34	20	200	25	33.1	11.5
9	8000	12.7	2.10	12.7	150	25	83.1	22.8

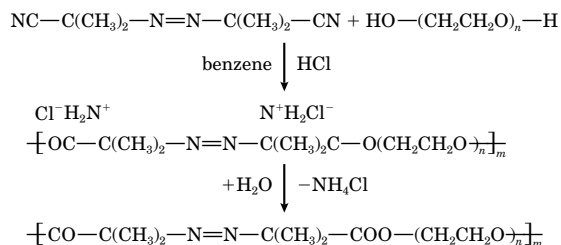
<sup>a</sup> Solvent, diethylformamide; temperature, 85°C.

action mixture under a vacuum. The crude polymer was purified with solvent extractions. PEG was removed with three water extractions at room temperature and the homopolymer of BA was removed with three mixed solvent (cyclohexane/petroleum solution 4/6 v/v) extractions at 10°C. The purified block copolymer was dried under a vacuum at room temperature.

## RESULTS AND DISCUSSION

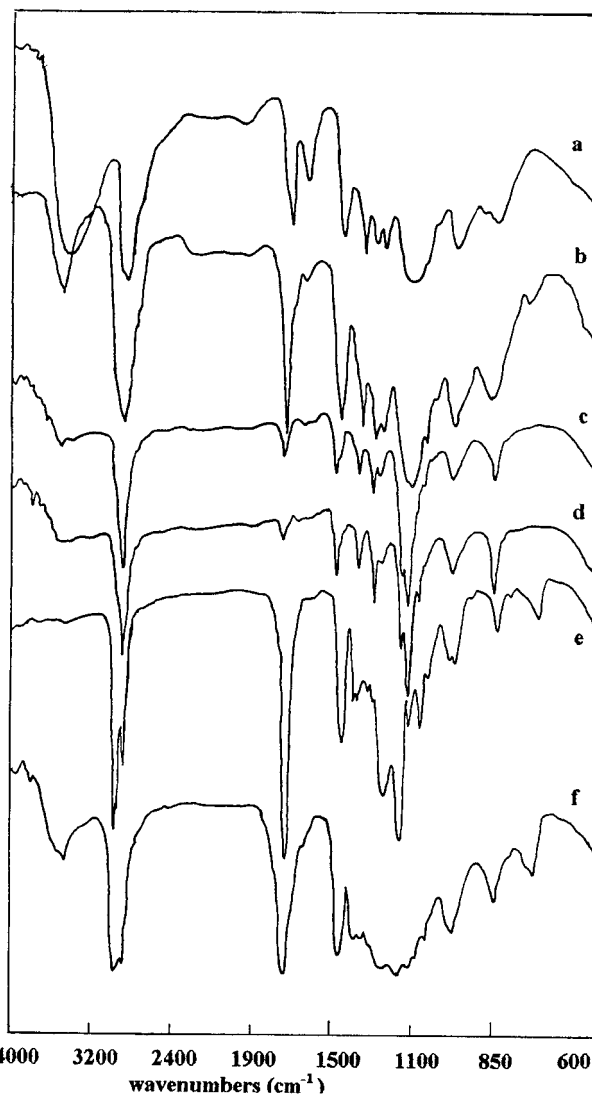
### Synthesis of Pre-PEO Polymeric Initiator

It is known that nitriles are converted to ester by reacting with a hydroxyl group in benzene/HCl (Pinner synthesis<sup>15,16</sup>). Thus, AIBN can react with PEG and be quantitatively transformed into azo(bismethyl-*i*-butyrate). The imidoester hydrochloride is a intermediate product:



According to the experimental results of Oppenheimer and Heitz,<sup>10</sup> the imidoester hydrochloride, which was prepared by reacting diethylene glycol with AIBN, was insoluble in the reaction mixture. However, in our experiment, with the gradual increase of the molecular weight of PEG, from the feculent state, the mixture become transparent. This indicates that the solubility of the imidoester hydrochloride increases with a higher molecular weight of PEG. This phenomenon may be explained as follows: With the higher molecular weight of PEG, the influence of the ion-dipole that stems from the combination of HCl with imido on the whole molecule relatively decreases, so that the molecular dipole moment decreases. Therefore, the solubility of the imidoester hydrochloride increases in the nonpolarity solvent benzene. When the molecular weight of PEG is up to 8000, the imidoester hydrochloride becomes fully soluble.

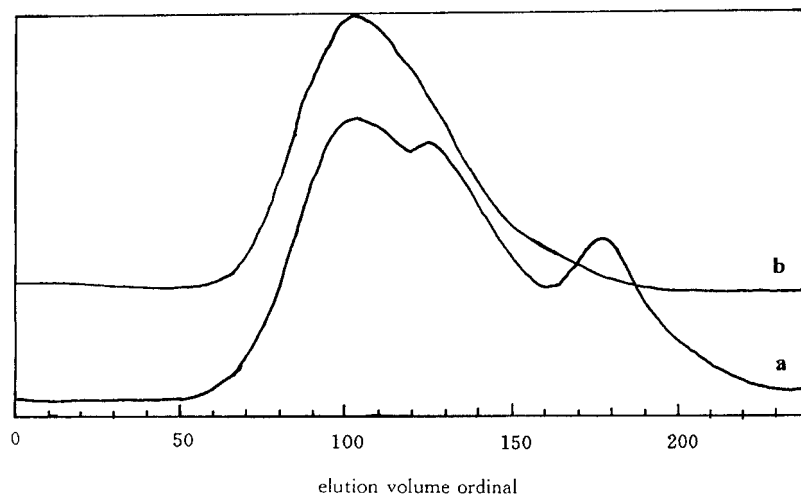
As a typical characteristic of condensation polymerization, the molecular weight of pre-PEG increases with a longer reaction time, which is dem-



**Figure 1** The IR spectra of (a) the water extract [PEG(1)], (b) pre-PEO, No. 8, (c) pre-PEO, No. 5, (d) pre-PEO, No. 9, (e) the mixed solvent extract, and (f) the purified PEO-*b*-PBA.

onstrated by the intrinsic viscosity (Table II, Nos. 1–5). In addition, the intrinsic viscosity is related to the ratio of PEG to AIBN (Table II, Nos. 5–7). Under the same experimental conditions, pre-PEO has the highest intrinsic viscosity when the feed ratio of PEG to AIBN is 1 : 1.

The absorption peaks at 1735.5 cm<sup>-1</sup> in the IR spectra of the products show the existence of carbonyl bonds of ester, and the strong absorption peaks at 1111 cm<sup>-1</sup> show the existence of ether links [Fig. 1(b)–(d)]. Meanwhile, the azo bonds are proved by the absorption peak at 360 nm in the UV spectrum. The height of the absorption



**Figure 2** The GPC curves of (a) the crude polymer and (b) the purified block copolymer.

peaks at  $1735.5\text{ cm}^{-1}$  decreases with the higher molecular weight of PEG. This phenomenon may be contributed to by the relative decrease of the content of the carbonyl with the higher molecular weight of PEG.

### Block Copolymers

Compared with the other synthetic methods of block copolymers, one characteristic of this synthesis is only a one-step procedure to prepare

block copolymers in the presence of a monomer. The polyazoester is both an initiator and a PEO prepolymer.

The IR spectrum of the water extract only has the absorption peaks of PEG:  $1111.3\text{ cm}^{-1}$  ( $\text{CH}_2\text{—O—CH}_2$ ) and  $2871.1\text{ cm}^{-1}$  ( $\text{CH}_2$ ) [Fig. 1(a)]. Instead, the IR spectrum of the mixed-solvent (cyclohexane and petroleum) extract only has the absorption peaks of PBA:  $2964.1\text{ cm}^{-1}$  ( $\text{CH}_3$ ),  $1735.5\text{ cm}^{-1}$  ( $\text{CO}$ ),  $1244.1\text{ cm}^{-1}$ , and  $1164.4\text{ cm}^{-1}$  ( $\text{CO—O—CH}_2$ ) [Fig. 1(e)]. These

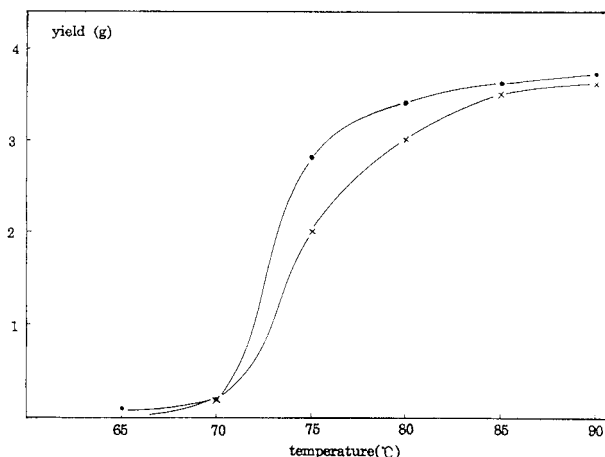
**Table III** Influence of the Reaction Temperature on the Polymerization<sup>a</sup>

No.	Temperature (°C)	Yield		[ $\eta$ ]	
		Copolymer (g)	PBA (g)	Copolymer <sup>b</sup> (mL/g)	PBA <sup>c</sup> (mL/g)
5	65	0.1	—	—	—
5	70	0.2	—	—	—
5	75	2.8	0.1	51	33
5	80	3.4	0.3	25	15
5	85	3.6	0.7	22	11
5	90	3.7	0.7	14	8
9	65	little	—	—	—
9	70	0.2	—	—	—
9	75	2.0	0.1	330	232
9	80	3.0	0.2	162	162
9	85	3.5	0.6	97	97
9	90	3.6	0.7	71	65

<sup>a</sup> Pre-PEO, 4 g; BA, 8 g; reaction time, 5 h.

<sup>b</sup> Solvent, chloroform; temperature, 20°C.

<sup>c</sup> Solvent, acetone; temperature, 25°C.



**Figure 3** The yield of block copolymers in dependence on temperature; pre-PEO, 4 g; BA 8 g; reaction time, 5 h. Pre-PEO: (●) No. 5; (×) No. 9.

phenomena demonstrate that water extracts only PEG and the mixed solvent extracts only the PBA homopolymer. Figure 2 are the GPC curves. Curve (a) is the curve of the crude polymer and curve (b) is that of the purified copolymer. GPC curves of PEO-*b*-PBA purified with three water extractions at room temperature and three mixed-solvent extractions at 10°C indicate that the peak for PEG at an elution volume ordinal of 177 disappears and the shoulder for PBA at an elution volume ordinal of 124 also disappears, while the peak at an elution volume ordinal of 100 remains unchanged (Fig. 2). These results demonstrate that after purification the copolymer contains neither PEG nor the PBA homopolymer. Therefore, solvent extraction is a suitable method to purify the crude polymer.

The IR spectrum of the purified polymer is almost the superposition of that of PBA and PEG [Fig. 1(a), (e), and (f)]. These spectra indicate that the purified product contains both PBA and PEO segments.

The influence of the reaction temperature on the polymerization is presented in Table III. When the ratio of BA to pre-PEO and the reaction time are constant, the yields of the block copolymers and homoPBA increase at higher reaction temperatures, but the intrinsic viscosity of the block copolymers decreases, as does the molecular weight of homoPBA. It is easy to understand: As is well known, the incidence of termination is more frequent at higher temperatures for the free-radical polymerization; in spite of the increase in the reaction rate constant  $k_p$  with temperature, shorter chains are grown. So, the block copolymers have a lower molecular weight and intrinsic viscosity at higher temperature. However, as the prepolymers do not decompose completely at a lower temperature for a certain time, naturally, the yield is lower. The decomposition rate of the prepolymer increases at a higher reaction temperature, so the decomposition degree of the prepolymer is higher, as is the yield. At 85°C, the prepolymer decomposes completely after a reaction time of 5 h; therefore, the yield no longer depends on the temperature, while the molecular weight and the intrinsic viscosity still decrease at a higher temperature.

The influence of the reaction time on the polymerization is presented in Table IV. When the ratio of BA to pre-PEO and the temperature are constant, the yield of the copolymer and PBA increases with a longer reaction time, while the in-

**Table IV** Influence of the Reaction Time on the Polymerization<sup>a</sup>

No.	Reaction Time (h)	Yield		[ $\eta$ ]	
		Copolymer (g)	PBA (g)	Copolymer <sup>b</sup> (mL/g)	PBA <sup>c</sup> (mL/g)
5	1	3.9	0.3	39	15.2
5	2	4.6	0.5	40	15.5
5	3	5.1	0.5	43	16.1
5	4	5.3	0.7	47	15.4
5	5	6.7	0.9	45	15.9
5	6	6.8	1.0	44	15.8

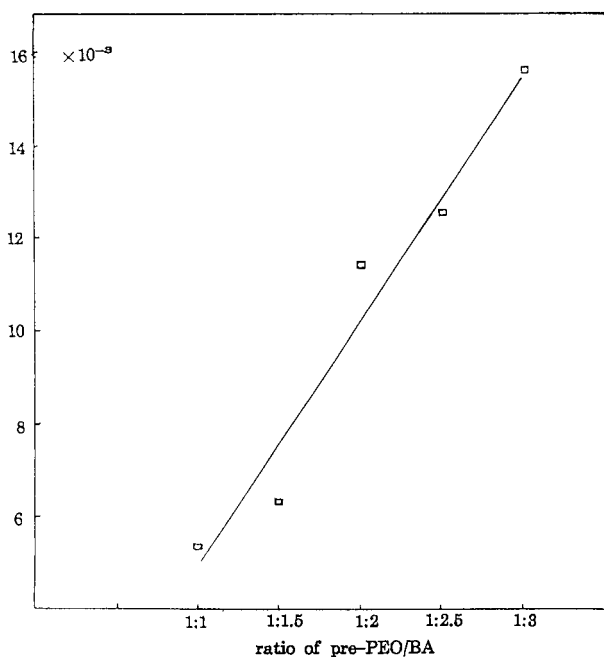
<sup>a</sup> Pre-PEO, 3.5 g; BA, 7.0 g; reaction temperature, 85°.

<sup>b</sup> Solvent, chloroform; temperature, 20°C.

<sup>c</sup> Solvent, acetone, temperature, 25°C.

**Table V** Influence of the Ratio of Pre-PEO to BA on the Polymerization<sup>a</sup>

No.	Pre-PEO (g)	Feed BA (g)	BA to Pre-PEO	Yield		[ $\eta$ ]	
				Copolymer (g)	PBA (g)	Copolymer <sup>b</sup> (mL/g)	PBA <sup>c</sup> (mL/g)
8	3.0	3.	1 : 1.0	2.4	1.9	14.1	10.5
8	3.0	4.5	1 : 1.5	3.2	2.0	15.8	11.8
8	3.0	6.0	1 : 2.0	4.1	2.5	16.9	12.3
8	3.0	7.5	1 : 2.5	4.9	3.7	19.7	12.9
8	3.0	9.0	1 : 3.0	6.5	4.7	22.2	14.0
5	3.5	3.5	1 : 1.0	1.3	0.3	30	12
5	3.5	5.25	1 : 1.5	2.0	0.5	35	13
5	3.5	7.0	1 : 2.0	3.4	0.9	52	18
5	3.5	10.5	1 : 3.0	4.5	0.4	64	22
5	3.5	12.25	1 : 3.5	5.2	0.8	70	24
9	3.5	3.5	1 : 1.0	2.2	1.0	31	11
9	3.5	5.25	1 : 1.5	2.9	1.2	44	18
9	3.5	7.0	1 : 2.0	3.5	0.4	60	25
9	3.5	8.75	1 : 2.5	4.2	0.6	78	32
9	3.5	10.5	1 : 3.0	4.6	0.4	95	39
9	3.5	12.25	1 : 3.5	5.8	0.4	120	43

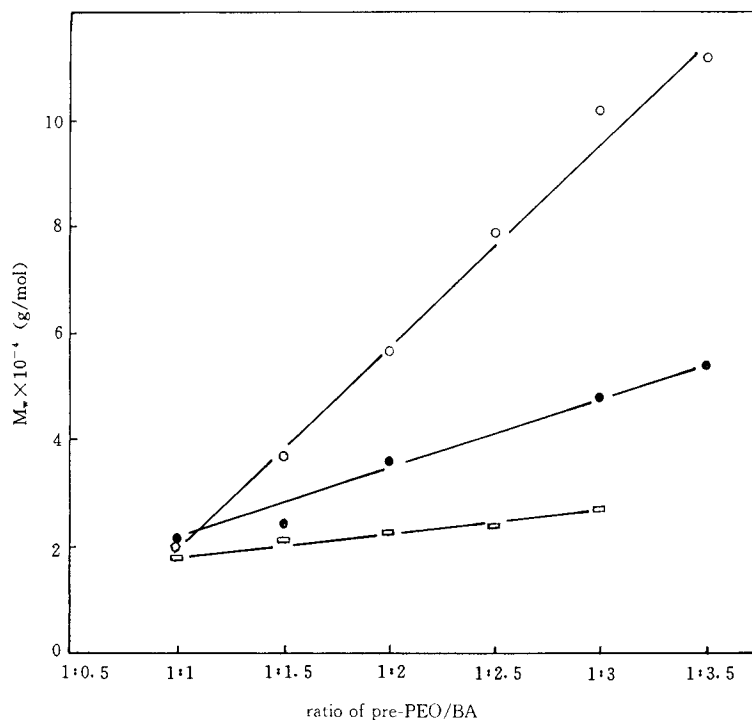
<sup>a</sup> Reaction time, 5 h; temperature, 85°C.<sup>b</sup> Solvent, chloroform; temperature, 20°C.<sup>c</sup> Solvent, acetone; temperature, 25°C.**Figure 4** The molecular weight (GPC) of block copolymers in dependence on feed ratio; reaction time, 5 h; temperature, 85°C. (□) Pre-PEO No. 8.

trinsic viscosity of the copolymer and PBA only slightly depends on the reaction time. The yield is almost unchanged after a reaction time of 5 h, which indicates the completion of the polymerization.

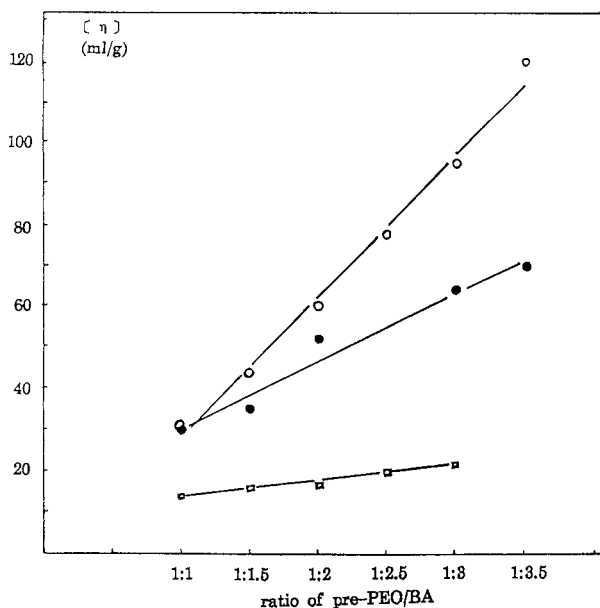
The influence of the ratio of BA to pre-PEO on the polymerization is presented in Table V. When reaction time and temperature are constant, the yield of the copolymers and PBA increases with a higher ratio of BA to pre-PEO. The molecular weight and intrinsic viscosity of the block copolymers are proportional to the feed ratio of BA to pre-PEO (Figs. 4 and 5). It is obvious that the variation of the intrinsic viscosity is related to the pre-PEO: the higher the molecular weight of PEG in the pre-PEO, the higher the increment of the intrinsic viscosity, the same as with the homoPBA (Fig. 6).

## CONCLUSION

Poly(ethylene oxide)-*block*-poly(butyl acrylate) can be prepared in a one-step procedure by radical polymerization. The effect of polymerization is related to the following reaction conditions:



**Figure 5** The intrinsic viscosity of block copolymers in dependence on the feed ratio; reaction time, 5 h; temperature, 85°C. Pre-PEO: (□) No. 8; (●) No. 5; (○) No. 9.



**Figure 6** The molecular weight of homoPBA in dependence on the the feed ratio; reaction time, 5 h; temperature, 85°C. pre-PEO: (□) No. 8; (●) No. 5; (○) No. 9.

1. The molecular weight is proportional to the ratio of BA to pre-PEO.
2. The reaction time does not influence the molecular weight, but affects the yield.
3. For certain reaction times, the yield increases at higher temperature, while the molecular weight decreases.

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## REFERENCES

1. M. Gervais and B. Gallot, *Makromol. Chem.*, **178**, 1577 (1977).
2. H. Hayashi, S. Taniguchi, H. Hamada, and T. Minami, Jpn. Kokai 7,328,078 (1973) (to Toyobo Co. Ltd.); *Chem. Abstr.*, **79**, 54537 (1978).
3. K. Dietrich, G. Reinich, and O. Metz, DDR Pat. 119,259 (1976); *Chem. Abstr.*, **86**, 56370 (1977).
4. R. B. Seymour, D. R. Owen, G. A. Stahl, H. Wood,

- and W. N. Tinnerman, *Appl. Polym. Symp.*, **25**, 69 (1974).
5. R. B. Seymour, D. R. Owen, and G. A. Stahl, *Polymer*, **14**, 324 (1973).
  6. I. Piirma and L. P. H. Chon, *J. Appl. Polym. Sci.*, **24**, 2051 (1979).
  7. J. Furukawa, S. Takamori, and S. Yamashita, *Angew. Makromol. Chem.*, **1**, 92 (1967).
  8. R. Walz and W. Heitz, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 1807 (1978).
  9. R. Walz, B. Bomer, and W. Heitz, *Makromol. Chem.*, **178**, 2527 (1977).
  10. C. Oppenheimer and W. Heitz, *Angew. Makromol. Chem.*, **98**, 167 (1981).
  11. X. Y. Qiu, W. Ruland, and W. Heitz, *Angew. Makromol. Chem.*, **125**, 69 (1984).
  12. B. Hazer, *Angew. Makromol. Chem.*, **129**, 31 (1985).
  13. T. Fang, S. Xu, and Y. Lei, *Polym. Bull.*, **22**, 317 (1989).
  14. M. Lang, G. Zhang, N. Feng, and X. Chen, to appear.
  15. A. Pinner and F. Klein, *Ber.*, **11**, 1825 (1878).
  16. R. L. Shriner and F. W. Neumann, *Chem. Rev.*, **35**, 354 (1944).