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### Block Polymers Derived from Poly(ethylene Oxide) and Hydroxy-Terminated Polybutadiene

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## Block Polymers Derived from Poly(ethylene Oxide) and Hydroxy-Terminated Polybutadiene

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### ABSTRACT

Block polymers of AB, BAB, and ABA type, derived from pre-formed poly(ethylene oxide) (PEO) of different molecular weight and hydroxy-terminated polybutadiene (HTPB) were prepared. Poly(ethylene oxide-*b*-butadiene) and poly(butadiene-*b*-ethylene oxide-*b*-butadiene) were prepared by reaction of PEO, which was previously endcapped with TDI, with HTPB at a 1:1 or 1:2 reactants molar ratio. Poly(ethylene-oxide-*b*-butadiene-*b*-ethylene oxide) were prepared by reaction of isocyanate-endcapped HTPB with PEO at a molar ratio of reactants of 2:1. High reaction yields were obtained. Correlation between tensile properties and water absorption with block polymer composition was found.

### INTRODUCTION

Block polymers containing hydrophilic and hydrophobic sequences in which the hydrophilic sequence is poly(ethylene oxide) (PEO) have diversified applications. Thus, for example, it was reported that such

block polymers having within their structure an oil-soluble segment improved the viscosity and detergent properties of lubricating oils [ 1]. Block polymers derived from vinyl polymers and PEO improved dyeability and resistance to electrical charge buildup [ 2]. Such block polymers were also suggested as polymeric surfactants [ 3] and hydrogels [ 4].

Block polymers of PEO and polybutadiene (PB) should belong to this class of block polymers. Such block polymers can be prepared by anionic polymerization. Poly(ethylene oxide-*b*-butadiene), block polymers of the AB type, were prepared by anionic polymerization from butadiene and ethylene oxide as starting materials [ 5]. These block polymers comprise an amorphous segment and a crystalline segment. The structure and the nature of their interaction with preferential solvent of one block were already reported [ 5].

The availability of preformed polymers suggests their use in the synthesis of such block polymers. By using a preformed polymer of known molecular weight, block polymers of predetermined structure may be obtained, and anionic polymerization can be replaced totally or partially by condensation polymerization. The use of a combination of these two techniques was already reported. Anionic block polymerization of ethylene oxide was initiated by hydroxy-terminated poly(butadiene) (HTPB) in the presence of alkali hydroxide. Block polymers were obtained, but block polymerization was accompanied by homopolymerization of the ethylene oxide [ 6, 7]. Elastomers derived from HTPB and hydroxy-terminated polyethers were prepared by reacting the two prepolymers in the presence of bifunctional isocyanate [ 8, 9] or by reaction of isocyanate-terminated polybutadiene with diol chain extenders [ 10]. Complete characterization of these block polymers were not always reported.

Since PEO is available in different molecular weights in the range suitable for its use as a preformed polymer, it was interesting to prepare such block polymers from preformed PEO and HTPB, in order to find out whether by the use of condensation reaction pure block polymers with a predetermined structure can be obtained. Endcapping of one polymer with isocyanate group followed by reaction with hydroxy-terminated polymer will guarantee the formation of a better organized block polymer than that obtained by block polymerization carried out in one step. By controlling the molar ratio of the isocyanate-terminated polymer and the hydroxy-terminated polymer, block polymers of AB, ABA, and BAB types can be obtained. It was already shown [ 11] that, during endcapping of PEO with toluene diisocyanate (TDI), chain extension of the PEO was minimal, and therefore the molecular weight of the PEO in the block polymer should be close to its original value. Reaction of isocyanate-terminated PEO with HTPB will lead to the formation of poly(ethylene oxide-*b*-butadiene) or poly(butadiene-*b*-ethylene oxide-*b*-butadiene), depending

on the molar ratio of reactants. Poly(ethylene oxide-*b*-butadiene-*b*-ethylene oxide) can be prepared by reaction of isocyanate-terminated PB (derived from HTPB) with PEO.

It will be of interest to find the correlation between mechanical properties and water absorption capability of these block polymers with their composition and structure.

## EXPERIMENTAL

### Materials

PEO, TDI (80/20 mixture of 2,4 and 2,6 isomers), dibutyltin dilaurate (Fluka), HTPB (Polyscience, M. W. 2130), and *n*-hexane (Merck) were used as received. Tetrahydrofuran (THF) (Frutarom) was dried by distillation from sodium benzophenone solution before use.

### Reaction between HTPB and TDI

Reaction was carried out under dry argon in a closed flask equipped with a self-sealing rubber cap. Syringes were used for the introduction of reagents and removal of samples for analysis.

A typical procedure is described. HTPB (2.13 g) was dissolved in THF (50 ml). Dibutyltin dilaurate (0.05 ml) and TDI (0.28 ml) were added, and the reaction mixture was kept at 25°C. Unreacted isocyanate groups were determined by titration with *n*-butylamine by a known procedure [9]. Reaction between unreacted isocyanate and *n*-butylamine was completed by keeping the reaction mixture for 15 min at 80°C.

### Viscosity Measurements

Viscosity measurements were carried out in a dry atmosphere by use of a Ubbelohde viscometer.

### Block Polymer Synthesis

Block polymers of the poly(ethylene oxide-*b*-butadiene) and poly-(butadiene-*b*-ethylene oxide-*b*-butadiene) type were prepared by reaction of isocyanate-terminated PEO with HTPB at a molar ratio of reactants 1:1 or 2:1. Block polymers of poly(ethylene-oxide-*b*-butadiene-*b*-ethylene oxide) were prepared using isocyanate terminated PB.

A typical procedure is described. PEO (3 g, MW 3000) was dissolved in benzene (50 ml) and was repeatedly dried by azeotropic distillation. The benzene was removed by vacuum distillation, and the PEO was dissolved in THF (50 ml); dibutyltin dilaurate (0.05 ml) and TDI (0.28 ml) were added, and the reaction mixture was kept for 1 hr at 25°C. HTPB (2.13 g) in THF (20 ml) was added, and the reaction mixture was left at 25°C for 24 hr. The THF was removed under vacuum. Unreacted HTPB was removed by extraction of the crude polymer (1 g) with n-hexane (100 ml) for 5 days, and unreacted PEO was removed similarly with water.

### Mechanical Properties

Mechanical properties were determined by using an Instron tensometer according to ASTM D 882-67. Films were cast from the reaction solution.

### Water Absorption

Films of block polymer (1.0 g) were left in distilled water (100 ml), for 5 days at 25°C. The films were dried between filter papers, and water absorption was calculated from weight increase.

## RESULTS AND DISCUSSION

Block polymers of three different types, poly(ethylene oxide-*b*-butadiene), poly(butadiene-*b*-ethylene oxide-*b*-butadiene) and poly(ethylene oxide-*b*-butadiene-*b*-ethylene oxide) were prepared by reaction between PEO and HTPB in which one of the preformed polymers was first endcapped with TDI. The first two types of block polymers were prepared by reaction between isocyanate-terminated PEO and HTPB by using molar ratio of reactants of either 1:1 or 1:2. Isocyanate-terminated PEO was prepared by endcapping of PEO with 2,4-TDI as previously described [11] and was used immediately for block polymerization. Both endcapping reaction and block polymerization were catalyzed by dibutyltin dilaurate.

For the preparation of block polymers of the poly(ethylene oxide-*b*-butadiene-*b*-ethylene oxide) type, isocyanate-terminated PB was first prepared by endcapping HTPB with 2,4-TDI. Similar reaction conditions used for the endcapping of the PEO were applied. Endcapping reaction was carried out at a molar ratio of 2:1 of TDI to HTPB. It can be seen (Fig. 1) that the presence of catalyst(dibutyltin dilaurate) is essential for completion of the endcapping reaction. The final

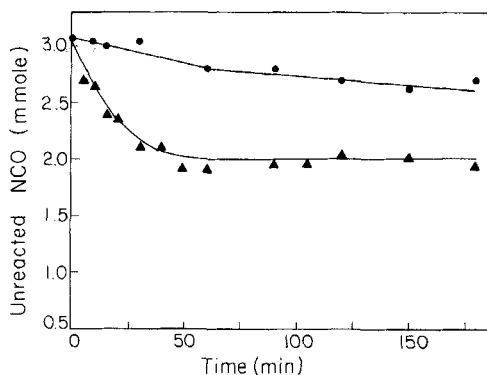


FIG. 1. Reaction between HTPB and TDI: (●) reaction carried without catalysis; (▲) reaction carried in the presence of dibutyltin dilaurate (0.05 ml). HTPB (2.13 g, MW 2130) reacted in THF (50 ml) with TDI (0.28 ml) at 25°C. Molar ratio of reactants of 1:2 was used. Unreacted isocyanate groups were determined by titration.

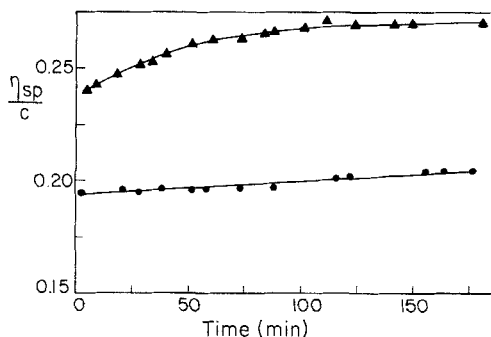


FIG. 2. Change in solution viscosity in reaction between HTPB and TDI: (▲) reaction carried without catalysis; (●) reaction carried in the presence of dibutyltin dilaurate (0.05 ml). HTPB (2.13 g, MW 2130) reacted in THF (50 ml) with TDI (0.28 ml) at 25°C. Molar ratio of reactants of 1:2 was used.

value of the unreacted isocyanate group obtained with dibutyltin dilaurate catalysis corresponds to a complete endcapping reaction. No detectable chain extension or other secondary reactions leading to a decrease in the concentration of terminal isocyanate groups were determined by this endgroup analysis. From change in viscosity of the reaction mixture (Fig. 2) it can be concluded that some chain extension did take place when reaction was catalyzed by dibutyltin dilaurate. Nevertheless, the extent of this reaction should be minimal, since it could not be detected by endgroup analysis (Fig. 1).

Block polymers of poly(ethylene oxide-*b*-butadiene) type were prepared by reaction of isocyanate-terminated PEO of molecular weight ranging between 600 to 10,000 with HTPB at a reactants molar ratio of 1:1 (Table 1). Unreacted preformed polymers were removed by extraction. Unreacted PEO was extracted by water and unreacted HTPB was extracted by *n*-hexane. The block polymers (of the three different types) were not soluble in these solvents, as was determined from the NMR spectra of the extracted polymers. When a molar ratio of reactants of 1:1 was used, high reaction yields for both preformed polymers were obtained. The ratio of PEO/PB in the block polymer indicated the formation of an AB type polymer. The variation in molecular weight of the PEO used led to the formation of block polymers with 22-81% PEO content. By using molar ratio of 1:2 isocyanate-terminated PEO to HTPB, triblock polymers, poly(butadiene-*b*-ethylene oxide-*b*-butadiene), were prepared in good yields. The ratio of PEO to PB in the block polymers indicates that the triblock polymer is contaminated by diblock polymer of the AB type. Triblock polymer of the poly(ethylene oxide-*b*-butadiene-*b*-ethylene oxide) type was prepared by reaction of isocyanate-terminated PB with PEO at a molar ratio of 1:2. Here, too, the triblock polymers obtained were contaminated by block polymers of the AB type.

Preparation of an AB type polymer by endcapping of PEO with isocyanate groups followed by block polymerization with HTPB will always lead to an organized alternate AB type block polymer in which the molecular weight of the two block segments will not be changed. Block polymers of the AB type can also be prepared by one-step synthesis, by reaction of the two hydroxy-terminated polymers in the presence of TDI at a molar ratio of reactants of 1:1:2. In such block polymers, random distribution of segments derived from the preformed polymers is expected, and the length of the PEO and PB segments in the block polymer, will vary and will be much higher than that of the original preformed polymer used. Such block polymers were obtained (Table 2), but in lower yields. The block polymers obtained contained more of the PEO segment than expected for an alternating block polymer of the type prepared by the two-step technique at a 1:1 preformed polymers molar ratio. The lower reaction yields observed may be also attributed to reaction between

TABLE 1. Reaction between Isocyanate-Terminated PEO and HTPB at Molar Ratio of Reactants of 1:1, 1:2, and 2:1<sup>a</sup>

Block polymer	PEO MW	Extent of reaction <sup>b</sup>		PEO in the block (%)	PEO/PB <sup>c</sup>
		PEO (%)	HTPB (%)		
Poly(ethylene oxide-b-butadiene)	600	97.8	90.1	22.3	1.09
	1000	90.0	80.0	34.5	1.13
	1500	93.3	95.8	40.7	0.98
	2000	98.3	95.6	49.2	1.03
	3000	95.3	92.4	59.2	1.03
	4000	94.1	88.8	66.5	1.06
Poly(butadiene-b-ethylene oxide-b-butadiene)	6000	92.4	89.2	74.2	1.04
	10000	90.5	90.9	81.0	1.00
	1000	92.4	85.9	25.3	0.54
	3000	96.1	87.7	40.0	0.55
	6000	89.7	88.3	56.4	0.51
	10000	55.2	47.9	73.0	0.58
Poly(ethylene oxide-b-butadiene-b-ethylene oxide)	1000	77.7	91.4	44.4	1.70
	3000	66.6	76.2	70.9	1.75

(continued)



TABLE 1 (continued)

Block polymer	PEO MW	Extent of reaction <sup>b</sup>		PEO in the block (%)	PEO/PB <sup>c</sup>
		PEO (%)	HTPB (%)		
Poly(ethylene oxide-b-butadiene-b-ethylene oxide)	6000	63.7	88.8	86.2	1.44
	10000	92.5	84.6	91.2	2.19

<sup>a</sup>Poly(ethylene oxide-b-butadiene) block polymers were prepared by reaction of isocyanate terminated PEO ( $10^{-3}$  mole) with HTPB (2.13 g,  $10^{-3}$  mole). Poly(butadiene-b-ethylene oxide-b-butadiene) block polymers were prepared by reaction of isocyanate-terminated PEO ( $10^{-3}$  mole) with HTPB (4.26 g,  $2 \times 10^{-3}$  mole). Poly(ethylene oxide-b-butadiene-b-ethylene oxide) were prepared by reaction of isocyanate-terminated PB (2.13 g,  $10^{-3}$  mole) with PEO ( $2 \times 10^{-3}$  mole). Reaction was carried in THF (70 ml) for 24 hr at room temperature.

<sup>b</sup>Determined after extraction.

<sup>c</sup>Molar ratio in the block polymer.

TABLE 2. One-Step Synthesis of AB Type Block Polymers<sup>a</sup>

PEO MW	Extent of reaction <sup>b</sup>		PEO in the block (%)	PEO/PB <sup>c</sup>
	PEO (%)	HTPB (%)		
1000	88.8	75.4	35.6	1.18
3000	92.6	63.9	67.1	1.45
6000	84.3	62.0	79.3	1.36
10000	86.6	69.5	84.3	1.25

<sup>a</sup>Block polymers were prepared by reaction of PEO ( $10^{-3}$  mole), HTPB (2.13 g,  $10^{-3}$  mole) and TDI (0.28 ml,  $2 \times 10^{-3}$  mole) in THF (100 ml) for 24 hr at 25°C.

<sup>b</sup>Determined after extraction.

<sup>c</sup>Molar ratio in the block polymer.

preformed polymers of the same kind leading to polymers that can be extracted together with unreacted preformed polymers.

Block polymers of PEO and PB consist of two incompatible polymeric segments. It was interesting to evaluate some of their mechanical properties. Films of different block polymers were cast from THF solution, and some of their tensile properties were determined. A more detailed study was made with block polymers of AB type prepared by reaction of HTPB of the same molecular weight with isocyanate-terminated PEO of different molecular weights (600-10,000), leading to formation of block polymers of different PEO content (22-81%).

Mechanical properties of these poly(ethylene oxide-*b*-butadiene) type block polymers are controlled by their composition. A linear relationship between the initial modulus and PEO content of the block polymer was found (Fig. 3). Increase in PEO content led to increase in the initial modulus starting with 2 kg/cm<sup>2</sup> for block polymer of 22% PEO, reaching the value of 275 kg/cm<sup>2</sup> for block polymers of 81% PEO. Similar behavior was found for the yield strength and tensile strength (Figs. 4 and 5). A linear relationship was also found for the dependence of elongation at the yield point on PEO content of the block polymer (Fig. 6). An increase in PEO content of the block polymer led to a decrease in the elongation. A more complicated behavior was observed for the elongation at break (Fig. 7). An increase in the PEO content of the block polymer led to a gradual decrease in elongation at break up to 60% PEO content (corresponds

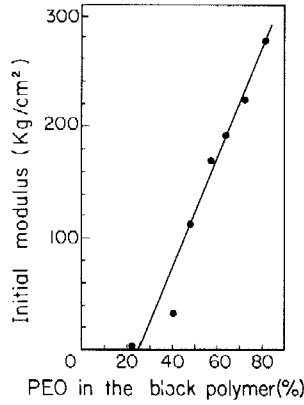


FIG. 3. Initial modulus dependence on PEO content of poly(ethylene oxide-b-butadiene).

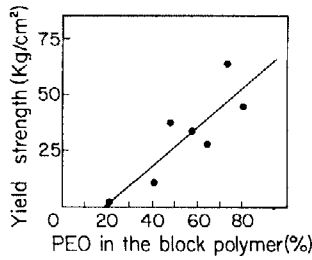


FIG. 4. Yield strength dependence on PEO content of poly(ethylene oxide-b-butadiene).

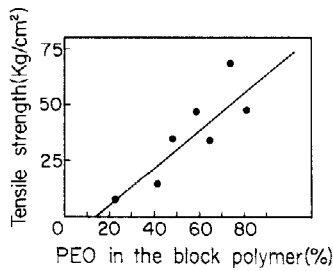


FIG. 5. Tensile strength dependence on PEO content of poly(ethylene oxide-b-butadiene).

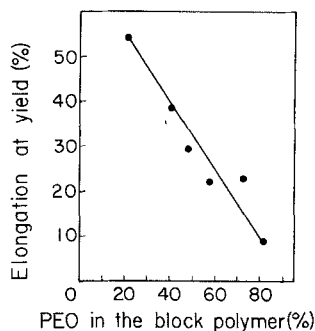


FIG. 6. Elongation at yield dependence on PEO content of poly(ethylene oxide-*b*-butadiene).

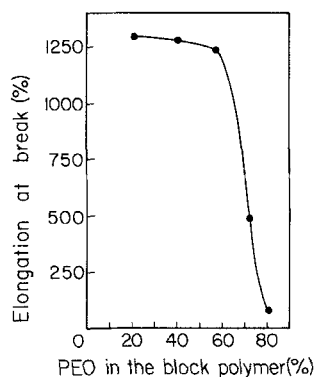


FIG. 7. Elongation at break dependence on PEO content of poly(ethylene oxide-*b*-butadiene).

to PEO of MW 3000). Further increase in the PEO content led to a drastic decrease in elongation at break.

Block polymers of similar PEO content may vary if they are not of the same type and are of different structure. It was interesting to compare tensile properties of such block polymers.

Mechanical properties of block polymers of poly(butadiene-*b*-ethylene oxide-*b*-butadiene), poly(ethylene oxide-*b*-butadiene-*b*-ethylene oxide), and poly(ethylene oxide-*b*-butadiene) prepared by

TABLE 3. Mechanical Properties of Block Polymers of Similar Composition and Different Structure

Block polymer	PEO MW	PEO content (%)	Initial modulus (kg./cm <sup>2</sup> )	Yield strength (kg./cm <sup>2</sup> )	Elongation at yield (%)	Tensile strength at break (kg./cm <sup>2</sup> )	Elongation at break (%)
Poly(butadiene-b-ethylene oxide-b-butadiene)	1000	25.3	2.62	0.33	6.2	0.43	1370
Poly(ethylene oxide-b-butadiene)	600	22.3	3.45	2.62	54.9	5.95	1316
Poly(butadiene-b-ethylene oxide-b-butadiene)	6000	56.4	129	46.7	33.0	64.8	1134
Poly(ethylene oxide-b-butadiene)	3000	59.2	170	35.1	24.0	47.6	1244
Poly(ethylene oxide-b-butadiene-b-ethylene oxide)	1000	44.4	6.7	3.7	22.7	12.6	1370
Poly(ethylene oxide-b-butadiene)	1500	40.7	37.4	11.3	37.7	14.6	1290
Poly(ethylene oxide-b-butadiene)	6000	74.2	221	64.1	69.4	26.0	492
Poly(ethylene oxide-b-butadiene) <sup>a</sup>	6000	79.3	363	53.6	55.9	8.9	338
Poly(ethylene oxide-b-butadiene)	10000	81.0	276	44.7	47.6	9.0	755
Poly(ethylene oxide-b-butadiene) <sup>a</sup>	10000	84.3	287	52.5	68.3	10.0	675

<sup>a</sup>Prepared by one-step synthesis

TABLE 4. Water Absorption by the Block Polymers

Block polymer	PEO MW	PEO in the block (%)	Water Absorption		Water absorption by the PEO in the block (%)
			Weight increase (%)	Content (%)	
Poly(ethylene oxide-b-butadiene)	600	22.3	22.7	18.5	102
	1000	34.5	27.1	21.3	79
	1500	40.7	79.5	44.3	196
	2000	49.2	117	53.8	237
	3000	59.2	170	62.9	287
Poly(butadiene-b-ethylene oxide-b-butadiene)	4000	66.5	259	72.1	388
	6000	74.2	585	74.1	384
	10000	81.0	443	81.6	547
	1000	25.3	31.5	24.0	166
	3000	40.0	106	52.3	274
Poly(ethylene oxide-b-butadiene-b-ethylene oxide)	6000	56.4	267	68.3	381
	10000	73.0	569	85.0	779
	1000	44.4	73	42.3	165
	3000	70.9	413	80.5	583
	6000	86.3	557	84.8	645

TABLE 5. Water Absorption by Block Polymers Prepared by One-Step Synthesis

PEO MW	PEO in the block (%)	Water absorption		Water absorption by the PEO in the block (%)
		Weight increase (%)	Content (%)	
1000	35.6	94	48.3	263
3000	67.1	158	61.3	271
6000	79.3	118	92.4	1482
10000	84.3	128	92.7	1513

one-step and two-step syntheses are reported and compared in Table 3. Comparison is made between block polymers of similar PEO content. It can be seen that, with both triblock polymers, mechanical properties vary with PEO content of the block. From comparison of mechanical properties of block polymers of different structure and similar PEO content, it can be seen that the structure of the block polymer contributed too to its mechanical properties.

The incorporation of hydrophilic PEO segments in the block polymer should increase its ability to absorb water. It was shown [5] that solvents, such as acetic acid, which interact specifically with PEO are absorbed by the PEO segments in the block polymer.

Water absorption by the block polymers is reported in Tables 4 and 5. It can be seen that block polymers of the AB type were converted to hydrogels with 18-82% water content. An increase in the PEO content of the block polymer led to an increase in water absorption. Assuming that water was absorbed preferentially by the PEO segments in the block, as was found with acetic acid [5], it can be seen that absorption of the PEO segment in the block polymer depends on its molecular weight. In the range of molecular weights investigated, increase of water absorption with increase in the PEO molecular weight was found. Similar results were found with block polymers of the poly(ethylene oxide-*b*-butadiene-*b*-ethylene oxide) and poly(butadiene-*b*-ethylene oxide-*b*-butadiene) types. On comparing water absorption by block polymers of similar PEO content and different structure, it can be seen that the structure of the block polymer also contributed to its capability to absorb water. It was found (Table 5) that water absorption by block polymers of AB type prepared in the one-step technique absorbed more water than the corresponding organized AB type block polymers (Table 4). This

TABLE 6. Mechanical Properties of AB Type Block Polymers Containing Water<sup>a</sup>

PEO MW	PEO in the block (%)	Water content (%)	Initial modulus (kg/cm <sup>2</sup> )	Yield strength (kg/cm <sup>2</sup> )	Elongation at yield (%)	Tensile strength at break (kg/cm <sup>2</sup> )	Elongation at break (%)
600	22.3	18.5	2.59	4.29	72.0	7.2	1330
1500	40.7	44.3	5.20	6.92	44.5	10.5	524
2000	49.2	53.8	3.46	6.39	53.1	8.9	317
3000	59.2	62.9	3.09	4.51	47.5	5.9	202
6000	74.2	74.1	3.41	4.29	40.0	5.9	183

<sup>a</sup>Block polymers were prepared by two-step synthesis.



can be attributed to the difference in their structure. Due to the possibility of finding in the block polymers PEO segments of much higher molecular weight than that of the preformed PEO used, water absorption was increased. These high values of water content and the irregular structure of these block polymers led to a complete deterioration of the films used for water absorption measurements. The films of AB type block polymers, prepared by two step synthesis, did not deteriorate in water.

Mechanical properties of AB type polymers prepared by the two-step technique and containing the maximum amount of water are reported in Table 6. It can be seen that absorption of water led to a decrease in all mechanical properties measured except for elongation at break. The dependence of these mechanical properties on PEO content of the block polymer almost disappeared at this level of water absorption.

Of the three types of block polymers prepared, poly(ethylene oxide-*b*-butadiene) and poly(ethylene oxide-*b*-butadiene-*b*-ethylene oxide) can be prepared by anionic block polymerization too, though anionic block polymerization will lead to the formation of pure block polymers with best controlled molecular weights. The availability of preformed PEO and HTPB suggests their use for synthesis of such block polymers. The two-step synthesis used led to the formation of almost pure block polymers of predetermined structure. The advantage of using preformed polymers for the synthesis of poly-(butadiene-*b*-ethylene oxide-*b*-butadiene) is obvious. With all three types of block polymers prepared, structure and composition (and thus their mechanical and water absorption properties) could be controlled.

#### REFERENCES

- [1] F. C. Schwab and L. J. Heilweil (Mobil Oil Co.), U. S. Pat. 3,867,295 (1975); *Chem. Abstr.*, **83**, 45698p (1976).
- [2] S. Katayama and H. Horikawa (Denki Onkyo Co. Ltd.), Ger. Offen. 1,928,080 (1970); *Chem. Abstr.*, **72**, 112080 (1970).
- [3] G. Reiss, J. Nervo, and D. Rogez, *Polym. Preprints*, **18**, 329 (1977).
- [4] R. D. Lundberg and N. G. Thames (Esso Res. & Eng. Co.) Ger. Offen. 2,403,934 (1974); *Chem. Abstr.*, **82**, 4942z (1975).
- [5] M. Gervais and B. Gallot, *Makromol. Chem.*, **178**, 1577 (1977).
- [6] K. Iino, H. Koda, and H. Matsui (Japan Soda Co. Ltd.), Japan. Pat. 7,134,984 (1971); *Chem. Abstr.*, **76**, 73202 (1972).
- [7] J. Niizeki, K. Iino, and H. Matsui (Japan Soda Co. Ltd.), Japan. Pat. 7,221,690 (1972); *Chem. Abstr.*, **78**, 31561 (1973).

- [ 8 ] K. M. Riches (Shell International Res.), Brit. Pat. 1,058,389 (1967); Chem. Abstr., 66, 66111 (1967).
- [ 9 ] K. Dietrich, G. Reinich, and O. Metz, DDR Pat. 119,429 (1976); Chem. Abstr., 86, 56370 (1977).
- [ 10 ] H. Hayashi, S. Tanigachi, H. Hamada, and T. Minami (Toyobo Co. Ltd.), Japan. Kokai 7,328,078 (1973); Chem. Abstr., 79, 54537 (1973).
- [ 11 ] R. Rahman and Y. Avny, J. Macromol. Sci.-Chem., A12, 1109 (1978).
- [ 12 ] S. Siggia and J. G. Hanma, Anal. Chem., 20, 1084 (1948).

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