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

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ABSTRACT

The use of preformed poly(ethylene oxide) (PEO) and carboxyl-terminated polybutadiene (CTPB) for the preparation of block polymers is reported. Block polymerization was carried out by esterification and by coupling of equimolar amounts of these polymers with 2,4-toluene diisocyanate (TDI). When esterification was carried out, conversion of the two preformed polymers and block polymer composition varied with reaction temperature, catalyst used, and molecular weight of the PEO. Full conversions were not obtained. Better results were achieved when the preformed polymers were coupled with TDI. Tensile properties and water absorption capability of these block polymers were determined. Hydrogels with high water content up to 82% were obtained.

INTRODUCTION

In a previous paper the preparation of block polymers of polybutadiene (PB) and poly(ethylene oxide) (PEO) by the use of available preformed polymers was reported [1]. These block polymers were prepared by using hydroxy-terminated PEO and hydroxy-terminated polybutadiene. Correlation between their structure and composition

with tensile properties and water absorption capability was found. It was interesting to find whether carboxyl-terminated polybutadiene (CTPB), available commercially, can be used for the preparation of similar block polymers.

The use of carboxyl-terminated polymers and hydroxy-terminated PEO for the preparation of block polymers has already been reported in literature. Various carboxyl-terminated bifunctional polyamides-11 with preselected molecular weights have been prepared [2] and used for polycondensation with various low molecular weight hydroxy-terminated PEO [3, 4]. Esterification and transesterification of the preformed polymers were carried out, and good conversions were reported. The kinetics of polycondensation of carboxyl-terminated polyamide-11 and PEO was also studied [5].

Block polymers containing both PB and polyester sequences were prepared by condensation of CTPB of low molecular weight with hydroxy-terminated polyesters [6]. These block polymers were obtained after the terminal carboxyl groups were converted to their more reactive acid chloride derivative.

Since PEO is commercially available in wide range of molecular weights, it was of interest to find out whether block polymers of AB type can be prepared either by esterification of equimolar amounts of the preformed CTPB and PEO or by coupling of these polymers with 2,4-toluene diisocyanate (TDI).

EXPERIMENTAL

Materials

PEO, TDI (80/20 mixture of 2, 4 and 2, 6 isomers, Fluka) CTPB (MW 4500 by endgroup analysis, Polyscience), and n-hexane (Merck) were used. Tetrahydrofuran (THF) (Frutarom) was dried by distillation from sodium benzophenone solution before use.

Reaction between CTPB and PEO

In a typical procedure, PEO (3.0 g, MW 3000, 10^{-3} mole) and CTPB (4.5 g, 10^{-3} mole) were dissolved in benzene and were dried three times by azeotropic distillation. Reaction was carried out at 160°C, in an oil bath under vacuum (0.2 Torr) for 48 hr. The crude product was extracted three times with water (100 ml) to remove any unreacted PEO. The insoluble polymer was extracted with THF (100 ml) in order to separate the insoluble crosslinked CTPB from the block polymer and unreacted CTPB. THF was removed under vacuum, and the unreacted CTPB was extracted from the block polymer with n-hexane.

Reaction of CTPB, PEO, and TDI

In a typical procedure, PEO (10^{-3} mole) and CTPB (4.5 g, 10^{-3} mole) were dissolved in benzene (50 ml) and were dried three times by azeotropic distillation. The polymer mixture was dissolved in dry THF (50 ml), TDI (0.28 ml, 2×10^{-3} mole) was added, and the reaction was left at room temperature for 24 hr. Films were cast directly from the reaction mixture. Unreacted PEO was removed by extraction of the crude polymer (1 g) with water (100 ml) and unreacted CTPB was removed similarly by n-hexane.

Mechanical Properties

Mechanical properties were determined by using an Instron tensometer according to ASTM D 882-67. Films of the block polymers 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

Synthesis of block polymers derived from PEO and PB by esterification of PEO with CTPB was investigated. Polymerization was carried out at different temperatures in vacuo by using equimolar amounts of the prepolymers (Table 1). PEO of 3000 molecular weight and CTPB of 4500 molecular weight were used. Unreacted PEO was removed by extraction with water, and unreacted CTPB was removed by extraction with n-hexane. The block polymers obtained were generally insoluble in these solvents, as was determined from the NMR spectra of the extracted polymers. Block polymer composition was determined from its NMR spectra.

Increase in reaction temperature led to an increase in reaction yield. Quantitative reaction yields were never obtained. The PEO reaction yields obtained are similar to those reported in literature for trans-esterification reactions of PEO. Yields of 60-80% were found in trans-esterification of methyl ester of N,N-dimethylamino-benzoic acid with ethylene glycol, di-, tri- and tetraethylene glycols as well as with PEO of molecular weights 300 and 400 [7].

CTPB conversion was always lower than PEO conversion. Pure AB type block polymers were not obtained since the preformed polymers did not incorporate in the block polymers in equimolar

TABLE 1. Reaction between PEO and CTPB at Different Temperatures

Reaction temp. (°C)	Extent of block polymerization		Crosslinked CTPB (%)	PEO in the block polymer (%)	PEO/PB ^b
	PEO (%)	CTPB (%)			
110	31.3	12.1	13.6	63.3	2.01
140	61.0	31.8	-	56.1	1.49
150	77.5	32.8	3.0	60.3	1.77
160	75.3	22.4	16.1	53.0	1.31
170	68.0	54.2	7.8	56.1	1.49
180	83.9	51.4	16.3	51.6	1.60

^aCTPB (4.5 g, 10^{-3} mole) was allowed to react with PEO (MW 3000, 3.0 g, 10^{-3} mole) for 48 hr.

^bMolar ratio in the block polymer, determined from NMR spectra.

amounts. The ratio of PEO/PB in the block polymers indicates the formation of block polymers containing more of the PB segment. The ratio PEO/PB in the block polymer prepared at 110°C indicates the formation of pure triblock polymer poly(ethylene oxide-*b*-butadiene-*b*-ethylene oxide), though in low yield. It was found that under the direct esterification conditions used, crosslinking of the CTPB also took place. The crosslinked polymer was insoluble in THF and did not contain any PEO, as was determined from its IR spectrum.

Reaction of equimolar amounts of PEO and CTPB was repeated under the same conditions with PEO of different molecular weights ranging between 600 and 10,000 (Table 2). High conversions were never obtained. When high molecular weight PEO was used, very low reaction yields were found. Generally, the preformed polymers were not incorporated in the block polymers in equimolar amounts. The extent of incorporation varied with the molecular weight of the PEO used. It was interesting to note that block polymers derived from PEO of 10,000 molecular weight were partially water-soluble. The water-extracted polymers contained 20% PB, as was determined from their NMR spectra.

The esterification reaction was repeated in the presence of a catalyst, *p*-toluenesulfonic acid. Reaction was carried out between equimolar amounts of PEO (MW 3000) and CTPB at 150°C in the presence of *p*-toluenesulfonic acid (0.05 g). Here, quantitative reaction yields were also not obtained, but PEO and CTPB conversions

TABLE 2. Reaction between CTPB and PEO of Different Molecular Weight^a

PEO MW	Extent of block polymerization		Crosslinked PB (%)	PEO in the block polymer (%)	PEO/PB ^b
	PEO (%)	CTPB (%)			
600	50.0	26.3	11.6	20.2	1.90
1000	46.0	28.7	15.3	26.2	1.24
2000	73.4	33.0	7.6	37.6	1.06
3000	75.3	22.4	16.1	53.0	1.31
6000	14.6	4.6	14.2	59.3	0.87
10000	10.0	7.6	9.6	59.9	1.58

^aCTPB (4.5 g, 10^{-3} mole) was allowed to react with PEO (10^{-3} mole) for 48 hr at 160°C .

^bMolar ratio in the block polymer, determined from NMR spectra.

were changed; 67% of the CTPB and 34% of the PEO were incorporated in the soluble block polymer, leading to PEO/PB molar ratio of 0.51. This ratio corresponds to almost pure poly(butadiene-*b*-ethylene oxide-*b*-butadiene). No change in the accompanied extent of crosslinking was observed.

Esterification of PEO and CTPB failed to lead to quantitative conversions of the preformed polymers into the corresponding block polymers and was accompanied by crosslinking of the CTPB. Though equimolar amounts of preformed polymers were used, block polymers of different segment ratios were obtained. The PEO/PB ratio in the block polymer varied with reaction temperature, molecular weight of the PEO, and the presence of a catalyst.

In order to improve reaction yields of both PEO and CTPB and thus to obtain pure block polymers and to eliminate the influence of reaction conditions and molecular weight of the PEO on block polymer composition, coupling of PEO with CTPB by 2,4-TDI was attempted (Table 3). PEO of different molecular weights, CTPB, and 2,4-TDI at 1:1:2 molar ratio were reacted in THF at room temperature. Unreacted preformed polymers were removed by extraction. Better conversions of both preformed polymers were obtained by this method. Block polymer formation was not accompanied by crosslinking of the CTPB. Nevertheless, quantitative conversions were not achieved. Conversion of PEO was higher than that of CTPB, and block polymers with higher molar amount of PEO were generally found. Conversion was dependent on the molecular weight of the PEO used.

TABLE 3. Reaction of CTPB, PEO, and TDI^a

PEO MW	Extent of block polymerization		PEO in the block polymer (%)	PEO/PB ^b
	PEO (%)	CTPB (%)		
1000	96.4	66.0	24.5	1.46
3000	80.4	53.6	50.0	1.50
6000	38.5	39.9	56.2	0.97
10000	48.5	28.1	79.3	1.73

^aPEO (10^{-3} mole) CTPB (4.5 g, 10^{-3} mole) and 2.4 TDI (0.28 ml, 2×10^{-3} mole) were allowed to react in THF (50 ml) for 24 hr at room temperature.

^bMolar ratio in the block polymer, determined from NMR spectra.

TABLE 4. Tensile Properties of Block Polymers Obtained by Reaction of PEO and CTPB with TDI

PEO MW	PEO content (%)	Initial modulus (kg/cm ²)	Yield strength (kg/cm ²)	Elongation at yield (%)	Tensile strength at break (kg/cm ²)	Elongation at break (%)
1000	24.5	88.3	20.8	7.0	21.0	58.3
3000	50.0	41.1	6.4	5.3	8.0	26.3

Almost quantitative yield of the PEO was found with PEO of 1000 molecular weight. An increase in molecular weight of the PEO led to decrease in its conversion.

The preparation of these block polymers by one-step synthesis led to less organized block polymers compared with those obtained by esterification of PEO and CTPB. During the one-step synthesis of these block polymers, chain extension of the preformed polymers also took place. As a result segments of different and higher molecular weight than those of the preformed polymer were found in the block polymer. Since in the reaction with TDI the primary terminal hydroxyl groups of the PEO are more reactive than the terminal carboxyl groups of CTPB, the extent of chain extensions with PEO is higher. Better conversions were found with this preformed polymer.

Films of these block polymers could be cast from the reaction solution. Tensile properties (Table 4) and water absorption (Table 5)

TABLE 5. Water Absorption by Block Polymers Prepared by Reaction of PEO, CTPB, and TDI^a

PEO MW	PEO content (%)	Water absorption		Water absorption by the PEO in the block polymer (%)
		Weight increase (%)	Content (%)	
1000	24.5	12.9	11.8	51
3000	50.0	90.4	47.5	180
6000	56.0	218	68.5	389
10000	79.3	468	82.4	590

^aBlock polymers (1 g) were allowed to stand for 5 days in water at room temperature.

by these polymers were determined. As with block polymers derived from hydroxy-terminated PB and PEO, these block polymers are capable of forming hydrogels. Hydrogels with up to 82% water content were obtained. An increase in PEO content of the block polymer led to an increase in water absorption. Though molecular weight of the PEO segments in the block polymer may be higher than that of the original preformed polymer used, correlation was found between molecular weight of the PEO used and water absorption by the derived PEO segment. Absorption of the PEO segment in the block polymer depends on its molecular weight. In the molecular weight range investigated, an increase in PEO molecular weight led to increase in water absorption of the derived PEO segment.

REFERENCES

- [1] R. Rahman and Y. Avny, *J. Macromol. Sci.-Chem.*, **A13**, 971 (1979).
- [2] G. Deleens, P. Foy, and E. Marechal, *Eur. Polym. J.*, **13**, 337 (1977).
- [3] G. Dellens, P. Foy, and E. Marechal, *Eur. Polym. J.*, **13**, 343 (1977).
- [4] P. Foy, G. Jungblut, and G. Deleens (Ato Chemie), *Germ. Offen.* 2,523,991 (1975); *Chem. Abstr.*, **84**, 136532 (1975).
- [5] G. Deleens, P. Foy, and E. Marechal, *Eur. Polym. J.*, **13**, 353 (1977).
- [6] C. Leriche, C. Michaud, and E. Marechal, *Bull. Soc. Chim. France*, 1977, 717.

- [7] D. P. Roelfsen, J. W. M. DeGraff, J. A. Hagendeorm, H. M. Verschoor, and H. Van Bekkum, Rec. Trav. Chim., 89, 193 (1970).

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