

Synthesis, Characterization, and Permeation Properties of Polyether-Based Polyurethanes

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Synopsis

A system of synthesis of polyether-based urethanes was developed which had sufficient flexibility in composition so that transport properties could be optimized. Mixtures of poly(oxyethylene) glycol (PEG) and poly(oxypropylene) glycol (PPG) of a variety of molecular weights were tied together by varying amounts of kinds of "hard segments." Thus, the water swell, the mechanical properties, and the size of the soft blocks and hard blocks could be varied. With a fixed content of hard segments, the water absorption decreased with decrease in the PEG/PPG ratio, demonstrating the feasibility of producing controlled changes in hydrophilicity of the polymer without significant change in the mechanical strength. Some polyurethanes based on PEG 600 and PPG 425 had a very good high value of P_w/P_s but a somewhat low value of P_w . The polyurethanes prepared by using phenylenediamines as chain extenders had markedly enhanced modulus and an extended rubbery plateau region, as anticipated.

INTRODUCTION

This work was undertaken to examine the relationship between structure and properties of polyether-based polyurethanes. The transport properties of both water and salt through the polymer membranes were of particular interest. Polyurethane elastomers are block copolymers consisting of hard and soft segments, with the former acting as physical crosslinks. The hard segments are associated by interchain hydrogen bonds to form discrete, sometimes microcrystalline domains which are separated by the soft polyether or polyester domains.^{1,2} Polyurethanes having soft segments of appropriate hydrophilicity may yield a candidate membrane for desalination by reverse osmosis.

Vieth, Douglas, and Bloch³ investigated the transport properties of a polyurethane for possible application to reverse osmosis desalination. The polymer was prepared by the reaction of tolylene diisocyanate and low molecular weight poly(oxyethylene) glycol and then crosslinking with trimethylol propane. The results did not seem too promising.

The polyether-based polyurethanes offer two features of particular interest. First, it is possible to introduce controlled change in the soft domains and hence modify the hydrophilicity of the polyurethanes. In this work, both polyethylene glycol (PEG) and polypropylene glycol (PPG)

were used to prepare the block polymers. Variation of the PEG/PPG ratios enables optimization of water permeation and salt rejection. Second, a change in the nature of hard domains modifies their constraining action on the soft domains and therefore modifies the transport properties of the polymers.

It is conceivable that both the chemical composition and the morphologic structure of the polymer membrane affect the water permeation and salt rejection. The chemical composition may profoundly affect the state of water in the membrane in the sense of water segregation and clustering. The morphologic structure, i.e., the nature of isolated domains and interconnected matrix, the molecular packing, the crystallinity, etc., would be expected to influence the mobility of free water.

The objective of the first stage of this work is to develop a system for synthesis of polyether-based polyurethanes of sufficient flexibility in composition such that transport properties can be optimized.

EXPERIMENTAL

Synthesis of Polyether-Based Polyurethanes

Carbowax 600, 1000, and 1540 (PEG 600, 1000, and 1540) and Polypropylene Glycol 425, 1025, and 2025 (PPG 425, 1025, and 2025) were used in this work. These were products of Union Carbide Corporation and were demoisturized at 60°C under a reduced pressure of nitrogen (10 mm Hg) for 24–36 hr immediately before use. Hylene W (4,4'-dicyclohexylmethane diisocyanate), a product of E. I. du Pont de Nemours and Company, was used without further purification. T 8 (dibutyltin bis-2-ethylhexonate), a product of Cincinnati Milacron Chemicals, Inc., was used as a catalyst without further purification. All solvents were carefully dried over molecular sieves (Linde Type 5A) followed by fractional distillation. All diamines were purified either by fractional distillation or by recrystallization.

The procedure of synthesis of the polyether-based polyurethanes consisted of the following three steps:

Step 1: Capping of PEG and PPG with Hylene W. The reaction of the polyether and Hylene W was carried out in methylene chloride, under agitation and nitrogen atmosphere, at room temperature, using T 8 as a catalyst. The reaction was run for 16–22 hr. Kinetics studies revealed that the reaction reached completion in 4–6 hr. The molar ratio of PEG (or PPG) to Hylene W was 1 to 4. The amount of the catalyst was 0.5 wt-% of the polyether.

The capped polyether was isolated by pouring the reaction products into petroleum ether. For purification, the capped polyethers were repeatedly dissolved into methylene chloride and precipitated by petroleum ether. Finally, the products were dried in a rotary vacuum evaporator at room temperature.

The analysis of the NCO content of the products indicated that chain extension took place during the capping reaction, yielding the products having an average of 1.5–1.8 polyether segments per molecule.

Step 2: Double Capping of the Diisocyanate-Capped PPG with Diamine. This step generally involves chain extension, when the molar ratio of the diisocyanate-capped polyether to the diamine is 1 to 1. In the present system, a 1 to 2 molar ratio was employed instead of 1 to 1, in order to double-cap the diisocyanate-capped PPG without chain extension. The reaction was run for 16–24 hr at room temperature, with agitation in a nitrogen atmosphere. Dimethylformamide was used as a solvent. The completion of the reaction was confirmed by the disappearance of the NCO band from the infrared spectrum.

Step 3: Chain Extension. The diisocyanate-capped PEG, equimolar on the basis of NCO content to the capped PPG employed in step 2, was dissolved in dimethylformamide. It was then added to the product solution of step 2 by means of a syringe, through a serum cap. The reaction was run for another 16–24 hr under the same conditions as step 2. The completion of the reaction was confirmed by the disappearance of the NCO band from the infrared spectrum.

For the preparation of polyurethanes composed of less than equimolar proportion of PEG/PPG, the diisocyanate-capped PEG was first added to the double-capped PPG. The balance was made up after 16–24 hr by adding the diisocyanate-capped PPG.

The polyurethanes thus formed were isolated by pouring the products into a mixture of petroleum ether and toluene. For purification, the polymer was repeatedly dissolved in methylene chloride and precipitated by petroleum ether. Where the polymer was insoluble in methylene chloride, it was washed with methylene chloride repeatedly and finally coagulated by petroleum ether. The polymer was dried in a vacuum oven at temperatures below 35°C.

When an equimolar ratio of PEG/PPG is used, this system of synthesis yields block copolymers whose two different soft segments, PEG and PPG, are aligned along the polymer chain in alternating order. The following are a few examples:

Example 1. 40.0 g of PEG 1000, 42.0 g of Hylene W, 0.2 g of T 8, and 100 ml of methylene chloride were placed in a three-neck flask, while 82.0 g of PPG 1025, 84.0 g of Hylene W, 0.4 g of T 8, and 200 ml of methylene chloride were placed in a separate three-neck flask. The reactions were run for 16 hr, and the products were isolated and purified according to the procedure described above; 54.0 g of capped PEG and 75.0 g of capped PPG were obtained.

In step 2, 10.000 g of the capped PPG (NCO 3.70%) dissolved in 100 ml of dimethylformamide was added to 200 ml of dimethylformamide which contained 0.53 g of ethylenediamine. After 20 hr, 9.840 g of the capped PEG (NCO 3.83%) in 100 ml of dimethylformamide was added to the solu-

tion of step 2, and the reaction was continued for 24 hr. The polymer was isolated, purified, and dried in a vacuum oven, yielding 15.4 g. This was designated polymer No. 15, whose properties are listed in Table VI.

Example 2. The capped PEG and PPG prepared in example 1 were used to prepare a polymer whose molar ratio of EO/PO was 30/70.

The capped PPG (NCO 3.70%), 10.000 g, in 100 ml of dimethylformamide was added to 200 ml of dimethylformamide containing 0.53 g of ethylenediamine. After 20 hr, 4.920 g of the capped PEG (NCO 3.83%) in 50 ml of dimethylformamide was added. The reaction was continued for 24 hr, followed by the addition of 5.000 g of the capped PPG (NCO 3.70%) dissolved in 50 ml of dimethylformamide. After 24 hr, the polymer was isolated, purified, and dried, yielding 15.7 g. This was designated polymer No. 17, whose properties are listed in Table VI.

Characterization

Viscosity. Viscosities were determined in an Ubbelohde viscometer at 25°C in dimethylformamide.

Water Absorption. Water absorption was determined by immersing strips of polymer films in water at room temperature. After 4–5 days, the swollen strips were removed, blotted with filter paper, and weighed.

Modulus-Temperature Relation. Modulus-temperature data were obtained at a constant time of 10 sec by using Gehman torsional testing apparatus.

Stress-Strain Relation. Tensile strength, Young's modulus, and elongation at break were evaluated by a Tensilon Model UTM-II (Toyo Manufacturing Co., Ltd.). Specimens were cut from the compression-molded polymer films which had a cross section of 0.25–0.35 mm × 2.5 mm and a length of 10.0 mm. The rate of strain was 40 mm/sec.

Permeabilities. Membranes were cast from a 2% solution of polymer in dimethylformamide onto glass plates which had been coated with du Pont VYDAX fluorotelomer at room temperature. The membranes were stripped from the glass after being dried.

The permeabilities of both water and salt were measured by means of direct osmosis. A piece of the membrane was supported between two stainless steel perforated plates which in turn were fastened between two cylindrical Plexiglas chambers. A 1-molar solution of NaCl was placed in one chamber and distilled water in the other. Both sides were stirred during the experiment. The entire apparatus was placed in a constant-temperature water bath kept at 25°C. Water permeability, P_w , was obtained by measuring the rate of increase in water volume on the brine side; a calibrated capillary tube was used. Salt permeability, P_s , was determined by monitoring the electrical conductance of the water side. The following equations were used for the calculation of P_w and P_s :

$$P_w = (J_w RTd/v_w \Delta\pi)$$

$$P_s = (J_s d/\Delta C)$$

where J_w and J_s are the flux of water and salt, respectively; $\Delta\pi$ is the osmotic pressure difference; ΔC is the salt concentration difference; d is the thickness of the membrane; and v_w is the molar volume of water.^{4,5,6}

RESULTS AND DISCUSSION

Comparison of Hydrophilicity of PEG and PPG

Three types of polyurethanes were made with PEG 1000 and PPG 1025. The block copolymer with alternating blocks of PEG and PPG was compared to the block copolymers having either PEG or PPG blocks alone. Table I shows the composition, where EO, PO, HW, and EDA represent the ethylene oxide unit, propylene oxide unit, Hylene W, and ethylenediamine, respectively. Table II summarizes the physical properties studied. Figure 1 shows the modulus-temperature relations.

The physical properties of No. 3 lie between the PEG-based polyurethane (No. 4) and the PPG-based polyurethane (No. 5). The modulus-tem-

TABLE I

Polymer no.	Component polyether	Composition, %			
		EO	PO	HW	EDA
3	PEG 1000 PPG 1025	38.3	29.3	29.8	2.6
4	PEG 1000	68.7	—	28.6	2.7
5	PPG 1025	—	69.6	28.0	2.4

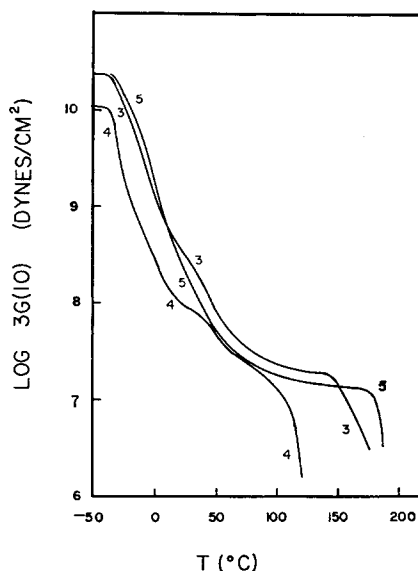


Fig. 1. Modulus-temperature relation of polymers No. 3, 4, and 5.

TABLE II

Polymer no.	Intrinsic viscosity, dl/g	Water absorption, %	Tensile strength, psi	Young's modulus, psi	Elongation at break, %
3	0.465	57.3	1300	540	750
4	0.880	105.9	1050	510	1100
5	0.750	3.6	880	1450	620

perature curves show the major transition temperatures of PEG. The hard segments, urethane and urea units, retain their glassy character, reinforcing the structure until they also pass through softening temperatures. The curves are characterized by an enhanced rubbery modulus. The three polymers had almost the same level of rubbery modulus due to the same content of hard segments.

Influence of Segmental Length of PEG and PPG

PEG and PPG molecular weights higher or lower than PEG 1000 and PPG 1025 were used for the preparation of polyurethanes. As shown in Table III, polymers No. 7, 8, and 11 have soft segments with longer PEG or PPG, or both, while polymers No. 21, 22, and 23 have shorter PEG or PPG. Polymer No. 6 is a reference polymer made of PEG 1000 and PPG 1025. As the molecular weight of PEG and PPG was increased, the weight percentage of urethane and urea groups was reduced, with a trend of lower strength and higher water absorption. Table IV illustrates the properties. The increased water absorption and lower mechanical strength of polymers No. 7, 8, and 11 could be accounted for by the reduced constraint on the soft segments due to the decreased amount of hard segments. On the contrary, the decreased water absorption and improved mechan-

TABLE III

Polymer no.	Component polyether	Composition, %			
		EO	PO	HW	EDA
6	PEG 1000 PPG 1025	37.0	32.6	28.0	2.4
7	PEG 1540 PPG 1025	39.3	33.3	25.0	2.4
8	PEG 1000 PPG 2025	25.5	51.7	21.2	1.6
11	PEG 1540 PPG 2025	29.3	50.1	18.7	1.9
21	PEG 600 PPG 425	29.3	22.6	44.1	4.0
22	PEG 1000 PPG 425	41.3	18.6	36.8	3.3
23	PEG 600 PPG 1025	36.2	27.4	33.5	2.9

TABLE IV

Polymer no.	Intrinsic viscosity, dl/g	Water absorption, %	Tensile strength, psi	Young's modulus, psi	Elongation at break, %
6	0.418	57.4	1350	640	720
7	0.445	63.6	880	360	820
8	0.293	76.7	500	470	330
11	0.236	200.5	200	45	500
21	0.502	19.3	4200	3800	600
22	0.528	70.4	2160	2040	880
23	0.523	19.2	1540	1300	320

ical strength of polymers No. 21, 22, and 23 were the results of enhanced constraint on the soft segments due to the increased content of hard segments.

Influence of EO/PO Ratio

A series of polyurethanes were prepared from PEG 1000 and PPG 1025. All polymers had the same content of hard segments (Table V), while the EO/PO ratio was changed progressively. Due to the fixed content of hard segments, the mechanical properties did not differ significantly from one another (Table VI). The water absorption decreased with the decrease in the EO/PO ratio. These results demonstrate the feasibility of introducing controlled change in hydrophilicity in the polymer without significant change in mechanical strength. It is also apparent from Table VI that the increase in water absorption is accompanied with increase in both P_w and P_s . The ratios P_w/P_s were between 10 and 20, which were too low to be of interest to reverse osmosis.

The polyurethanes prepared from PEG 600 and PPG 425, listed in Table VII, gave higher values of P_w/P_s than the polymers made from PEG 1000

TABLE V

Polymer no.	Component polyether	Composition, %			
		EO	PO	HW	EDA
15	PEG 1000 PPG 1025	33.9	34.4	29.1	2.6
16	PEG 1000 PPG 1025	29.9	38.5	29.1	2.5
12	PEG 1000 PPG 1025	26.3	42.1	29.0	2.6
13	PEG 1000 PPG 1025	22.5	46.0	29.0	2.5
14	PEG 1000 PPG 1025	19.5	49.0	29.0	2.5
17	PEG 1000 PPG 1025	16.4	52.0	29.0	2.6

TABLE VI

Polymer no.	Intrinsic viscosity, dl/g	Water absorption, %	Tensile strength, psi	Young's modulus, psi	Elongation at break, %	$P_w \times 10^6$, cm ² /sec	$P_s \times 10^7$, cm ² /sec
15	0.862	62.8	1610	550	900	3.96	3.00
16	0.680	54.8	1680	820	950	4.16	2.51
12	0.610	31.1	1880	700	920	4.50	2.07
13	0.508	26.8	1680	580	820	3.06	2.36
14	0.667	23.2	1640	700	770	1.56	1.03
17	0.487	22.8	1430	560	910	1.17	0.775

and PPG 1025. For example, No. 52 had a high P_w/P_s , although P_w was relatively low.

Influence of Aromatic Diamines

Five types of polyurethanes were prepared from PEG 1000 and PPG 1025 using various aromatic diamines in place of ethylenediamine. Table VIII shows the composition. Table IX and Figure 2 illustrate the results of characterization. Obviously, the increase in water absorption leads to high water permeation and also high salt permeation. These polyurethanes (No. 25, 26, and 27) were characterized by markedly enhanced modulus and extended region of rubbery plateau due to the greater rigidity imposed by aromatic nuclei, as illustrated in Figure 2.

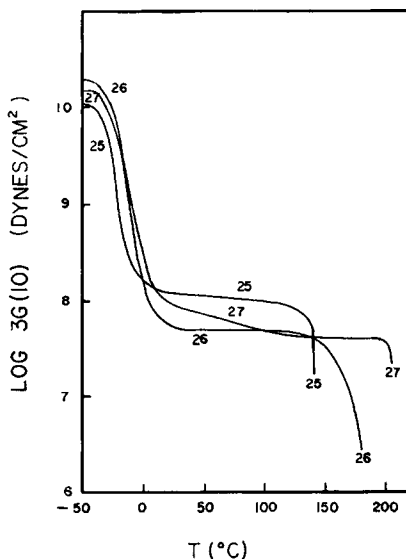


Fig. 2. Modulus-temperature relation of polymers No. 25, 26, and 27.

TABLE VII

Polymer no.	Component polyether	Composition, %			Intrinsic viscosity, dl/g	Water absorption, %	$P_w \times 10^7$, cm ² /sec	$P_s \times 10^9$, cm ² /sec
		EO	PO	HW				
50	PEG 600	32.4	21.0	43.0	0.904	21.2	6.48	12.3
	PPG 425							
51	PEG 600	26.8	25.8	43.8	1.051	18.7	1.80	2.62
	PPG 425							
52	PEG 600	20.6	30.9	44.6	0.920	14.7	0.41	0.086
	PPG 425							

TABLE VIII

Polymer no.	Composition			
	EO	PO	HW	Diamine
25	32.3	34.7	28.4	4.6 (<i>o</i> -phenylenediamine)
26	32.3	34.7	28.4	4.6 (<i>m</i> -phenylenediamine)
27	32.3	34.7	28.4	4.6 (<i>p</i> -phenylenediamine)
32	31.8	32.8	27.8	7.6 (benzidine)
33	31.5	32.5	27.7	8.3 (diaminodiphenylmethane)

TABLE IX

Polymer no.	Intrinsic viscosity, dl/g	Water absorption, %	Tensile strength, psi	Young's modulus, psi	Elongation at break, %	$P_w \times 10^6$, cm ² /sec	$P_s \times 10^7$, cm ² /sec
25	0.328	44.7	840	1250	620	—	—
26	0.658	61.5	570	520	690	5.04	3.08
27	0.350	36.2	2230	1020	750	2.17	1.72
32	0.434	76.5	650	470	910	6.48	3.97
33	0.958	78.0	1050	380	1070	7.82	8.76

CONCLUSIONS

The results of this study demonstrate the feasibility of introducing controlled changes in the hydrophilicity of the block polymers which can modify the permeabilities of water and salt. High water permeation is accompanied by high salt permeation. This is apparently the result of the ease of expansion of the membrane by swelling with water, which creates more favorable pathways through the film for both water and salt. For the purpose of developing a potential membrane for the reverse osmosis desalination process, it seems necessary to make a compromise between high water permeation and low salt permeation.

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