Preparation of Organophosphorus Polyurethane Block Copolymers

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Synopsis

The preparation of an organophosphorus polyurethane block copolymer of poly-(ethylene oxide) (PEO) and poly(bis-*p*-carboglycoxyphenyl phenyl phosphine oxide) (PCGPPO) as well as the respective homopolyurethanes is described. The properties of the prepared polymers (melting point, intrinsic viscosity, solubility, and chemical composition) have been determined. Results of thermal and infrared analyses of these polymers are also reported.

Introduction

Block copolymers are high molecular weight compounds whose macromolecules are composed of polymeric segments of either different chemical composition or different conformations. Blocks can be linked with each other directly or by low molecular weight bifunctional compounds, e.g., diisocyanate. The method of linking blocks by diisocyanate is simple, and there is no need of using either a complex apparatus or any special conditions. For these reasons the method finds many applications.¹⁻⁴

Properties of polyurethane block copolymers depend on the type of polyesters^{1,5-10} and diisocyanates used in synthesis. This interesting fact offers a possibility of preparing polymers of different properties.

Poly(ethylene oxide) (PEO) and poly(biscarboglycoxyphenyl phenyl phosphine oxide) (PCGPPO) an organophosphorus polyester, as low-molecular weight block, were used in the present work to prepare organophosphorus polyurethane block copolymers.

Experimental

PEO was purified before use in the following manner. A 30% solution of the polymer in benzene was prepared, to which adequate quantity of *o*-phosphoric acid was added to neutralize alkaline impurities of polymer; the polymer was then precipitated by diethyl ether. This procedure was repeated twice and was followed by drying under pressure of 2 mm. Hg at 110°C. The purified PEO had a melting point at 30–35°C. and molecular weight of 2100 as determined by the endgroups method. **B. LASZKIEWICZ**

PCGPPO was prepared by a method of multistage synthesis. During the first stage, phenyldi(*p*-tolylphosphine) oxide¹¹ was prepared, which was then oxidized by potassium permanganate in pyridine to give bis*p*-carboxyphenyl phenyl phosphine oxide.¹² This oxide was then esterified with methanol,¹² and the resulting bis-*p*-carbomethoxyphenyl phenyl phosphine oxide was purified by crystallization from a mixture of benzene and light petroleum. The melting point of the product was 160–165°C.

The next step was the polycondensation with ethylene glycol, equimolar quantities of reactants being used. The process was carried out for 4 hr. in nitrogen in the presence of 0.5% LiOH as catalyst. A temperature of 250°C. was reached during first hour. After 2 hr. of polycondensation, 0.2 mole of glycol was added in order to terminate the polymer with hydroxy groups. During the last hour of the process, a pressure of 1 mm. Hg was maintained.



The prepared PCGPPO was transparent and light-yellow in color. It extinguished after being removed from a Bunsen burner flame and could be dissolved in hot acetone and precipitated by addition of water. Its melting point was 140–148°C. and the molecular weight 6000, as determined by the endgroup method.

Tolylene diisocyanate used in the experiments consisted of a mixture of two isomers, the 2,4- and 2,6-tolylene diisocyanate in a percentage ratio of 80:20 \pm 2. The diisocyanates were purified before use by distillation at 10 mm. Hg, the fraction at 118–120°C. being collected ($n_{\rm D}^{25} = 1.5661$).

Preparation of Polyurethanes

All the samples of polyurethanes were prepared by the method previously described^{1,2} in a nitrobenzene solution at 170° C.

PCGPPO (15 g.), PEO (5.3 g.), and tolylene diisocyanate (0.9 g.) were put into a three-necked conical flask containing 60 g. nitrobenzene. The temperature was raised gradually to 170° C. over 3 hr. and then main-

tained for 30 min. more. The solution was stirred continuously, and nitrogen was passed over its surface. During the process an increase of viscosity was observed. After the reaction was completed the contents of the flask were cooled to room temperature. The polymer was precipitated by diethyl ether, washed several times with ether to remove nitrobenzene, and then again with hot acetone and water to remove unreacted substrates. The purified product consisted of 14.2 g. organophosphorus polyurethane copolymer. The product was resistant to flame, i.e., the combustion was extinguished after the material was removed from a Bunsen burner flame.

The same method was applied to prepare homopolyurethanes of PEO and PCGPPO, in each case about 1.1 mole of diisocynate per mole of polyglycol being used. The polyurethane based on PEO was purified by several washings with ether and water, while the PCGPPO polyurethane was washed with hot acetone.

Discussion

A comparison of properties of the polymer prepared (Table I), e.g., chemical composition, melting point, intrinsic viscosity, and solubility, indicates that the reaction between tolylene diisocyanate, PEO, and PCGPPO under the described conditions yields a block polyurethane.



In order to verify this assumption, infrared spectra of the prepared polyure thanes and model compounds were recorded in the range of 4000-700 cm.⁻¹ on a Hilger-Watts H-800 spectrophotometer by the KBr disk technique. There were found some absorption bands characteristic of the organophosphorus polyurethane block copolymer (Fig. 1). A characteristic peak of medium intensity for the P-C₆H₅ bond was found¹³ at 1435 cm.⁻¹, and that for the P=O function at 1274 cm.⁻¹, The latter is broad, and shows two distinct peaks at 1250 and 1290 cm.-1. They seem to be associated with the vibration of the three benzene rings linked with the phosphorus atom. The peaks at 1180 and 1020 cm.⁻¹ characterize the *para*-substituted benzene ring. These groups are present in the organophosphorus polyester used for the copolymer preparation. Characteristic bands of CH₂ groups in PEO blocks were observed at 843 and 2830–2850 cm.⁻¹. The vibrations of C-O-C groups were found¹⁴

			Ana	ulyses					
		Found			Calculated		Melting		
Polymer	P, %	C, %	Н, %	P, %	C, %	Н, %	°C,	a[1]	Solvents
PEO	İ	54.92	9.08	1	54.52	9.15	30-35	0.08	DMF, H ₂ O, C ₆ H ₆
PU-PEO	I	54.11	10.04	I	54.54	9.09	40-48	0.47	DMF, pyridine phenol-
PCGPPO	6.94	63.74	5.14	7.89	67.36	4.35	140-148	0.12	betracentorocentane DMF, nitrobenzene,
PU-PCGPPO	6.85	64.03	4.98	7.72	67.53	4.28	171-182	0.13	pyriaine DMF, nitrobenzene,
Polyurethane block copolymer of PCGPPO	4.37	65.31	4.80	4.42	66.61	4.67	128-139	1.21	DMF, nitrobenzene, pyridine
^a Intrinsic viscosity	determined	in DMF solu	tion at 20°C						

TABLE I

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Fig. 1. Infrared spectrum of copolyurethane based on PCGPPO and PEO.



Fig. 2. Thermograms of polyurethanes in nitrogen.

at 1100 cm.⁻¹, and that of the NH group in the urethane band, at 1660 cm.⁻¹.

Thermograms (Fig. 2) of the homopolyurethanes show endothermic peaks at 40°C. for PU-PEO and at 229°C. for PU-PCGPPO. The thermogram of the polyurethane block copolymer, however, has three endothermic peaks at 65, 115, and 202°C. and one exothermic peak at 100°C. These endothermic peaks are associated with melting of two different kinds of crystalline regions, namely, those characteristic for the PEO and PCGPPO blocks. The endothermic peak at 115°C. could be accounted for by a physical transition occurring in "hard-block," a structure characteristic of polyurethane elastomers. The sharp exothermic peak at 100°C. is associated with a cold crystallization and has been found previously in the case of poly(ethylene terephthalate).

Thus, the investigation carried out by means of differential thermal analysis confirms the formation of organophosphorus polyurethane block copolymer under the described conditions.

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Résumé

On a décrit la préparation de copolyurethanes organo-phosphoriques sequencés de poly(oxyde d'ethylene) (PEO) et poly(di-*p*-carboglycoxyphenyl) phenylophosphine oxyde (PCGPPO) et leurs homopolyurethanes. On a étudié leurs proprietés physicochimiques: la température de fusion, la viscosité intrinsèque, la solubilité et leur composition chimique. Également on a effectué des études thermiques et infrarouges de ces polymeres.

Zusammenfassung

Es wurde die Darstellung von Phosphorganischen Block-Kopoliurethanen des Poly-(Äthylenoxyd) (PEO) und des Oxyds der Poli(bis-p-Karboglikoxyphenyl)phenylphosphin (PCGPPO) und seiner Homopolyurethanen beschrieben. Die Eigenschaften der erhaltenen Polymeren, wie z.B. Schmelzpunkt, Viscositätszahl und Löslichkeit wurden untersucht und die chemische Zusammensetzung ermittelt. Es wurden auch thermische Untersuchungen dieser Polymere durchgeführt und ihre Spektren im Infrarot dargestellt.

Received April 13, 1967 Prod. No. 1628