

## 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*-carbonyloxyphenyl 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.<sup>1-4</sup>

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

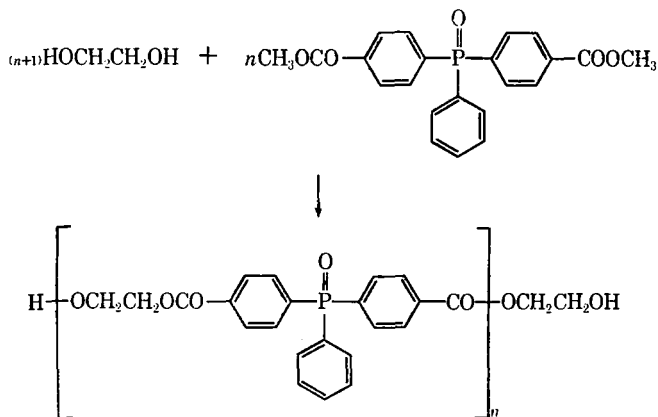
Poly(ethylene oxide) (PEO) and poly(biscarbonyloxyphenyl phenyl phosphine oxide) (PCGPPO) an organophosphorus polyester, as low-molecular weight block, were used in the present work to prepare organophosphorus polyurethane block copolymers.

### 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.

PCGPPO was prepared by a method of multistage synthesis. During the first stage, phenyldi(*p*-tolylphosphine) oxide<sup>11</sup> was prepared, which was then oxidized by potassium permanganate in pyridine to give bis-*p*-carboxyphenyl phenyl phosphine oxide.<sup>12</sup> This oxide was then esterified with methanol,<sup>12</sup> 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 ± 2. The diisocyanates were purified before use by distillation at 10 mm. Hg, the fraction at 118–120°C. being collected ( $n_D^{25} = 1.5661$ ).

### Preparation of Polyurethanes

All the samples of polyurethanes were prepared by the method previously described<sup>1,2</sup> 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-



TABLE I

Polymer	Analyses										Melting point, °C.	[ $\eta$ ] <sup>a</sup>	Solvents
	Found			Calculated				Melting point, °C.	[ $\eta$ ] <sup>a</sup>	Solvents			
	P, %	C, %	H, %	P, %	C, %	H, %							
PEO	—	54.92	9.08	—	54.52	9.15	—	54.52	9.15	30-35	0.08	DMF, H <sub>2</sub> O, C <sub>6</sub> H <sub>6</sub> , CH <sub>3</sub> OH, acetone	
PU-PEO	—	54.11	10.04	—	54.54	9.09	—	54.54	9.09	40-48	0.47	DMF, pyridine phenol-tetrachloroethane	
PCGPP0	6.94	63.74	5.14	7.89	67.36	4.35	7.89	67.36	4.35	140-148	0.12	DMF, nitrobenzene, pyridine	
PU-PCGPP0	6.85	64.03	4.98	7.72	67.53	4.28	7.72	67.53	4.28	171-182	0.13	DMF, nitrobenzene, pyridine	
Polyurethane block copolymer of PCGPP0	4.37	65.31	4.80	4.42	66.61	4.67	4.42	66.61	4.67	128-139	1.21	DMF, nitrobenzene, pyridine	

<sup>a</sup> Intrinsic viscosity determined in DMF solution at 20°C.

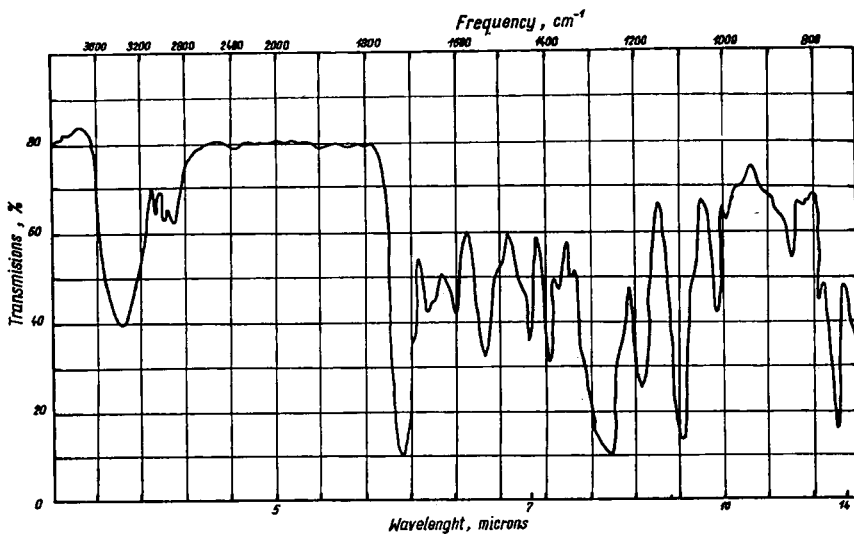


Fig. 1. Infrared spectrum of copolyurethane based on PCGPPO and PEO.

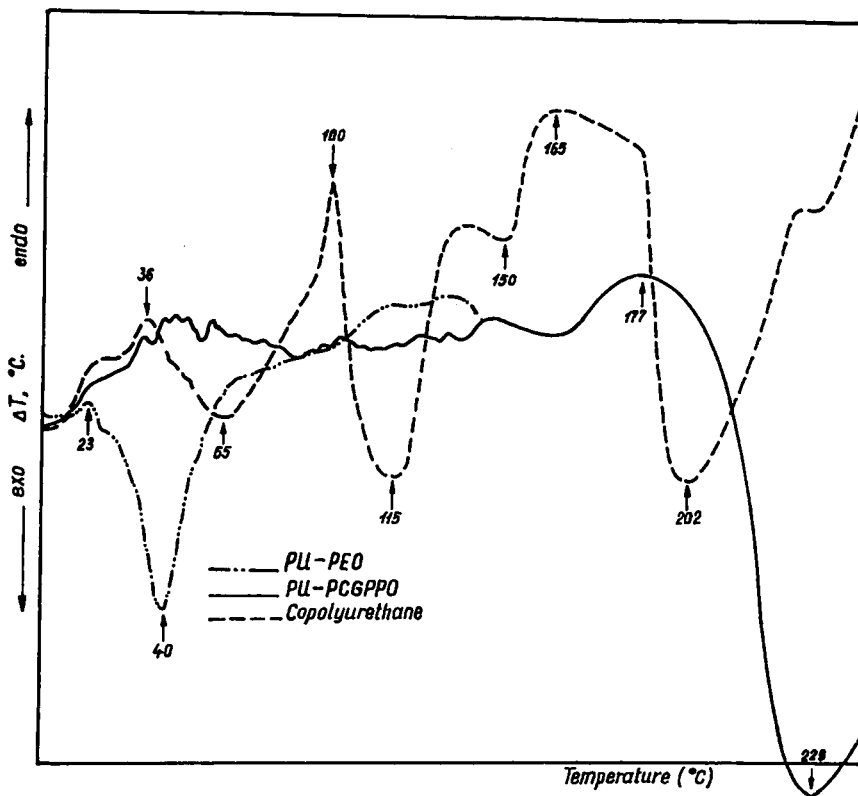


Fig. 2. Thermograms of polyurethanes in nitrogen.

at 1100  $\text{cm.}^{-1}$ , and that of the NH group in the urethane band, at 1660  $\text{cm.}^{-1}$ .

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.

### References

1. Y. Iwakura, Y. Taneda, and S. Ukhida, *J. Appl. Polymer Sci.*, **5**, 108 (1961).
2. Y. Iwakura, Japan Pat. 17596 (1960); *Chem. Abstr.*, **55**, 20504 (1961).
3. N. P. Apukhtina, A. G. Sinayskiĭ, B. Teitelbaum, E. A. Sidorovich, and E. F. Gubanov, *Plaste Kautschuk*, **34**, 212 (1966).
4. G. S. Kolesnikov and L. K. Yaralov, *Usp. Khim.*, **34**, 453 (1965).
5. E. M. Hicks, *Am. Dyestuff Repr.*, **52**, 33 (1963).
6. C. M. Cusano, E. P. Duningan, and P. Weiss, *Macromolecular Chemistry, Paris 1963 (J. Polymer Sci. C, 4)*, M. Magat, Ed., Interscience, New York, 1963, p. 743.
7. E. F. Gubanov, A. G. Sinayskiĭ, N. P. Apukhtina, and B. J. Teitelbaum, *Dokl. Akad. Nauk SSSR*, **163**, 151 (1965).
8. Neth. Appl. 6,508,294 (1965); *Chem. Abstr.*, 855 (1966).
9. B. J. Teitelbaum, J. O. Murtarina, N. P. Anoshina, L. J. Maklakov, N. P. Apukhtina, and A. G. Sinayskiĭ, *Dokl. Akad. Nauk SSSR*, **166**, 887 (1966).
10. B. M. Grieveson, *Polymer*, **1**, 499 (1960).
11. T. M. Frunze and V. V. Korshak, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1958**, 783.
12. P. W. Morgan and B. C. Herr, *J. Am. Chem. Soc.*, **74**, 4526 (1952).
13. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen, Wiley, New York, London, 1954.
14. Y. Kuroda and M. Kubo, *J. Polymer Sci.*, **26**, 323 (1957).
15. B. Ke, *J. Appl. Polymer Sci.*, **6**, 624 (1962).

### Résumé

On a décrit la préparation de copolyurethanes organo-phosphoriques séquencés de poly(oxyde d'éthylène) (PEO) et poly(di-*p*-carbogyloxyphényl) phénylophosphine oxyde (PCGPPO) et leurs homopolyurethanes. On a étudié leurs propriétés physico-chimiques: la température de fusion, la viscosité intrinsèque, la solubilité et leur composition chimique. Également on a effectué des études thermiques et infrarouges de ces polymères.

### Zusammenfassung

Es wurde die Darstellung von Phosphorganischen Block-Kopolyurethanen 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.

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