European Polymer Journal, Vol. 16, pp. 113 to 116
© Pergamon Press Ltd 1980. Printed in Great Britain

0014-3057/80/0201-0113$02.00/0

SYNTHESIS OF A SERIES OF POLYURETHANES CONTAINING PHOSPHORUS

N. GRASSIE and D. MACKERRON
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

(*Received* 2 *August* 1979)

Abstract—As a contribution to the study of fire retardance in polyurethanes by phosphorus containing compounds, polyurethanes with phosphorus incorporated in the structure have been prepared and characterized. Mol ratios P atoms/urethane linkages up to 1.108 have been obtained. Preparations were carried out in three steps: (1) formation of a phosphorus containing polyol by reaction of butane diol (BD) with phenylphosphonic dichloride, (2) end capping of the polyol with methane-bis-(4-phenyl isocyanate) (MBPI) to form prepolymer and (3) reaction of prepolymer with MBPI and BD in various proportions.

INTRODUCTION

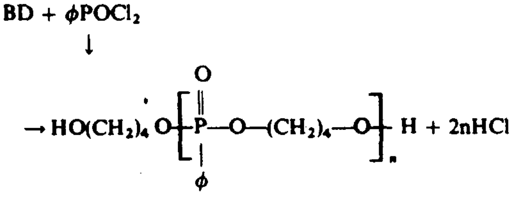
The commercial application of polyurethanes carries two closely related hazards, namely high flammability and the emission of toxic fumes from the pyrolysing material. The flammability can be controlled to some extent by additives and several types, including phosphorus containing compounds, are commonly used. Unfortunately fire retardant additives frequently influence decomposition reactions in polymers in such a way as to result in greater production of smoke of higher toxicity.

The influence of ammonium polyphosphate on the mechanism and products of thermal degradation of a relatively simple polyurethane prepared from 1,4-butane diol (BD) and methylene bis-(4-phenyl isocyanate) (MBPI) has recently been demonstrated [1, 2]. As a further contribution to the study of fire retardance in polyurethanes, it is of interest to extend these investigations to comparable materials in which the phosphorus containing structures are an integral part of the polymer molecules; this paper describes the preparation of a series of such polymers allowing the phosphorus content to be varied within wide limits.

EXPERIMENTAL

In order that the basic structures of the polymers should be as similar as possible to those previously studied [1, 2], it was decided that they should also be based upon BD and MBPI. The synthesis was carried out in the following three stages.

1. Formation of a phosphorus containing polyol by reaction of BD with phenylphosphonic dichloride (PPD),

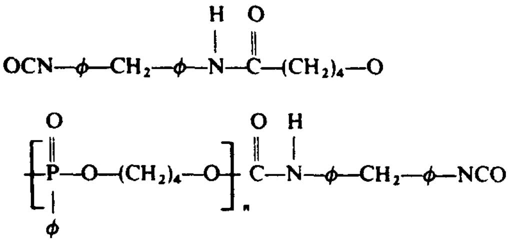


$$\mathrm{BD} + \phi\mathrm{POCl_2} \;\downarrow\; \rightarrow \mathrm{HO(CH_2)_4O}\left[\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \phi}{|}}{\mathrm{P}}}\mathrm{{-}O{-}(CH_2)_4{-}O}\right]_n\mathrm{H} + 2n\mathrm{HCl}$$

(Polyol)

2. End-capping of the polyol with MBPI to form prepolymer,

Polyol + 2MBPI



$$\mathrm{OCN{-}\phi{-}CH_2{-}\phi{-}}\overset{\overset{\displaystyle H}{|}}{\mathrm{N}}\mathrm{{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}(CH_2)_4{-}O}\left[\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle \phi}{|}}{\mathrm{P}}}\mathrm{{-}O{-}(CH_2)_4{-}O}\right]_n\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}}\overset{\overset{\displaystyle H}{|}}{\mathrm{N}}\mathrm{{-}\phi{-}CH_2{-}\phi{-}NCO}$$

(Prepolymer)

3. Preparation of polymers with a range of phosphorus/urethane ratios by reaction of prepolymer, MBPI and BD in various proportions.

These three steps will be discussed in some detail.

1. *Preparation of polyol*

Comparable syntheses have previously been described [3–6] and preliminary investigations were made to find suitable conditions for this step. High temperatures and rapid addition of the reagents resulted in discoloured products. A temperature of 10° was found to provide a satisfactory compromise between discolouration and a reasonable reaction rate in addition to high yield and low molecular weight. Polycondensations of this type may be carried out in bulk but temperature control is difficult and discolouration serious. Chloroform was found to be an appropriate solvent. The removal or neutralization of the HCl formed in the reaction is a major problem. Of the methods previously suggested [3–6], washing the chloroform solution with an aqueous solution of NaOH, as described by Maiboroda and Datskevich [4], was found to be most effective.

The preparation was carried out as follows. A mixture of freshly distilled BD (133 ml, 1.5 mol) and dry chloroform (150 ml) was placed in a 2 l. flask with dropping funnel, stirrer and N_2 inlet. The flask was immersed in a water bath at 10° and continuously flushed with dry N_2. A solution of PPD (200 ml, 1.4 mol) in dry chloroform (200 ml) was added dropwise over a period of 1.5–2 hr with rapid stirring. After stirring the mixture for a further 0.5 hr the HCl liberated was neutralized by the stoichiometric amount of aq. NaOH. After separation, the polyol was precipitated from solution by diethyl ether (1 l.), separated and redissolved in 1 l. of chloroform. Diethyl ether (200 ml) was added to precipitate fractions of higher molecular weight and anhydrous $MgSO_4$ to remove moisture. The mixture was then filtered and the solvent removed under reduced pressure by rotary evaporation.

The resulting polyol (50% yield) was characterized by proton NMR, infrared and end-group analysis [7, 8]. The molecular weight of 1036 is of the same order of magnitude as reported by Datskevich *et al.* [9].

2. *Preparation of prepolymer*

Polyols are usually end-capped by isocyanate before incorporation into a polyurethane structure. Various reports [8, 10, 13] were considered in arriving at the following procedure.

An appropriate amount of MBPI was placed in a flask equipped with stirrer and N_2 inlet. Under a continuous flow of N_2, the MBPI was heated to 80° with vigorous stirring and half the molar quantity of polyol added slowly. The temperature was raised to 110° over 20 min and the product finally cooled to ambient temperature, forming a colourless, opaque solid.

Several experiments were carried out in order to confirm that the product of the above reaction has the anticipated prepolymer structure. Results were as follows.

a. The infrared spectrum of the product has major absorptions at 3260 cm^{-1} (N–H), 2260 cm^{-1} (N=C=O), 1725 cm^{-1} (amide I) and 1540 cm^{-1} (amide II) thus confirming the formation of urethane links. Spectra of samples taken during the course of the reaction suggested that it was complete after 5 min under the conditions described above.

b. With a molar ratio, MBPI/Polyol = 2, analysis of the free isocyanate content indicated that 50% of the isocyanate groups had reacted.

c. A model compound, di-*n*-butylphenylphosphonate was synthesized [14] and heated with two molar proportions of MBPI under the above end-capping conditions. The fact that no reaction was detected may be taken as evidence that MBPI reacts exclusively with the terminal OH groups of the polyol.

Table 1. Polyurethanes containing phosphorus

Designation	Mol ratio (P: Urethane)	$\bar{M}_n$
PUP0	0	17,200
PUP11	0.110	15,600
PUP21	0.212	14,100
PUP44	0.445	10,500
PUP54	0.538	—
PUP111	1.108	—

d. Thin layer chromatography demonstrated qualitatively that small amounts of unreacted MBPI were present in the prepolymer, suggesting that small amounts of longer chain prepolymer molecules were formed by reaction of both isocyanate functions of some MBPI molecules.

e. During the reaction, traces of gases were sometimes liberated and were identified as CO_2 and tetrahydrofuran. While the amounts were so small as to have no significant effect on the overall structure of the prepolymer, they must nevertheless be accounted for.

The CO_2 could be formed in three ways. First, water present as impurity could react with isocyanate groups

$$\sim NCO + H_2O \rightarrow \sim NH_2 + CO_2$$

Second, pairs of isocyanate groups could react to form carbodiimide and CO_2 [1]

$$2 \sim NCO \rightarrow \sim N{=}C{=}N\sim + CO_2$$

Third, pairs of OH groups in the polyol could condense to form water which would lead to CO_2 as above.

The reagents used in the preparation of the prepolymer were all carefully dried and carbodiimide should only form at very much higher temperatures [1]. It therefore seems most likely that CO_2 results from the third of the above

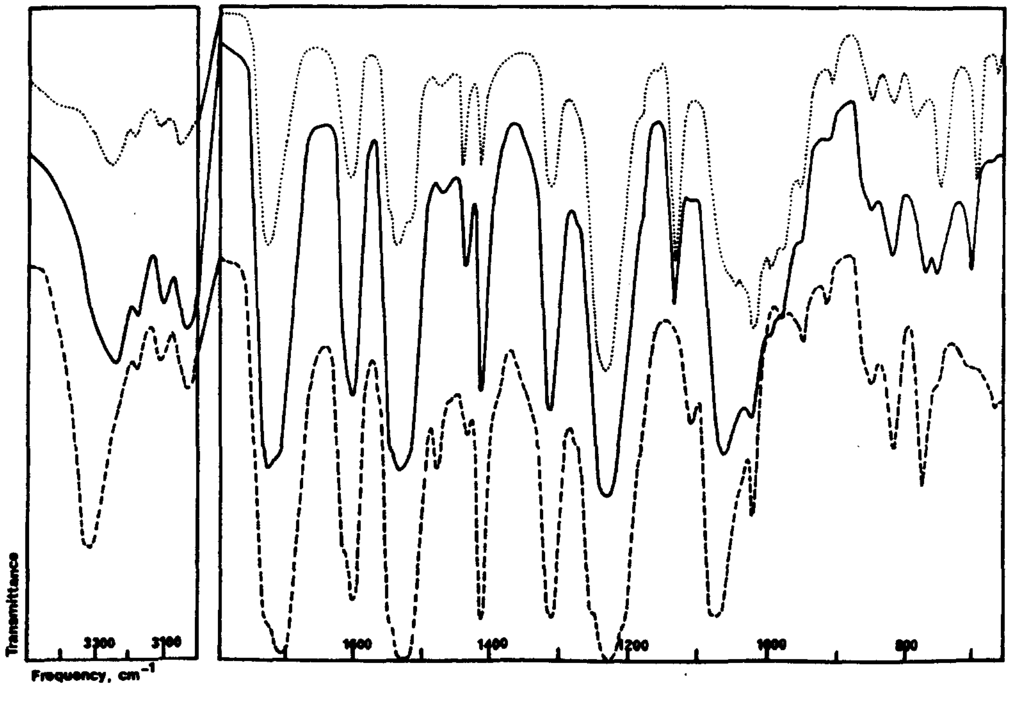


Fig. 1. Infrared spectra of polyurethanes: -----, PUPO; ——, PUP44; ·····, PUP111.

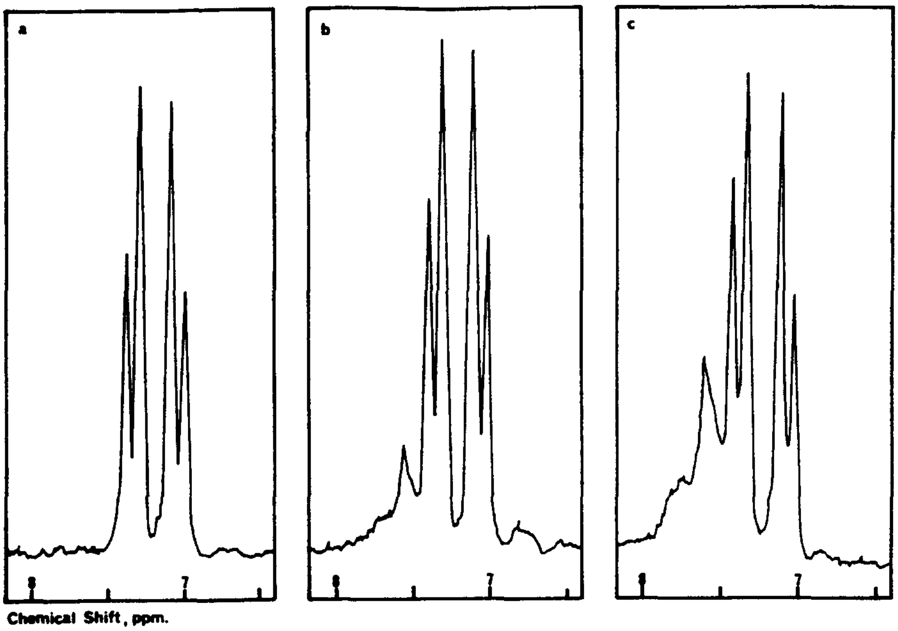


Fig. 2. NMR spectra of the aromatic region of polyurethanes: (a) PUPO; (b) PUP21; (c) PUP54.

Table 2. Infrared spectrum of phosphorus polyurethane, PUP21

Absorption (cm^{-1})	Assignment
3325	N—H stretch
1705	C═O stretch (amide I)
1600	C═C stretch
1530	amide II
1440	P—ϕ stretch
1415	C—C aromatic stretch
1230	amide III
1130	P—ϕ
1080	$\overset{O}{\overset{\|}{C}}$—O—C asymm. stretch
995	P—ϕ
820	C—H bend of p-disubstituted benzene
745	C—H bend
690	of monosubstituted benzene

alternatives. This is supported by previous work [15] and confirmed by the observation that the molecular weight of the polyol tends to increase slowly on prolonged heating at 110°. Tetrahydrofuran must result from trace decomposition of the polyol [1].

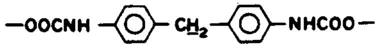
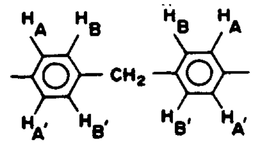
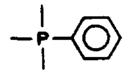
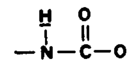
From this evidence it is reasonable to conclude that the reaction product is predominantly the expected prepolymer, with small amounts of longer chain material of similar structure and only insignificant traces of other products.

3. *Preparation of polymers*

Various reported preparations of polyurethanes [8, 16–20] were used as a guide to the preparation of the present series of polymers.

Known weights of recrystallized MBPI and freshly prepared prepolymer were dissolved in sufficient dimethylacetamide (DMA) to form a 1:1 w/v solution. The mixture, in a flask equipped with stirrer, N_2 inlet and reflux condenser with dry outlet was heated to 110° and a 1:1 v/v solution

Table 3. NMR spectra of phosphorus polyurethane PUP21

Chemical Shift (ppm)*		
1.70	Broad singlet	—$OCH_2\underline{CH_2}\underline{CH_2}CH_2O$— in P.U. and polyol
3.79	Broad singlet	
4.11	Broad singlet	—$O\underline{CH_2}CH_2CH_2\underline{CH_2}O$— in P.U. and polyol
7.20	AA′BB′ quartet	
7.56	Broad multiplet	 aromatic Protons
9.41	Sharp singlet	 $—\overset{\underline{H}}{\overset{\|}{N}}—\overset{O}{\overset{\|}{C}}—O$

* With respect to tetramethylsilane.

of the appropriate amount of BD in DMA added. Heating was continued for 80 min. The polymer (86% yield) was precipitated by distilled water, redissolved in DMF and reprecipitated by pouring into a large volume of water. Precipated polymers were filtered and dried in a vacuum oven at 40°.

Six polymers were prepared in this way with P: urethane mol ratios from zero to 1.108 (see Table 1). Molecular weights were measured osmotically using a Hewlett-Packard high speed membrane osmometer with cellophane 300 membranes. Polymers PUP54 and 111 diffused significantly through the membranes and their molecular weights were clearly less than 10,000. For the same reason the molecular weights of the other polymers may have to be modified but by no more than 5–10%.

Infrared and proton NMR spectra are illustrated in Figs 1 and 2 and the assignment of the principal peaks presented in Tables 2 and 3. The increasing intensities of the P–ϕ absorptions as the phosphorus contents of the polymers is increased, is obvious.

The absence of a signal in the chemical shift range 9.60–10.25 ppm in the proton NMR spectrum suggests [21] that the concentration of biuret linkages and therefore the amount of cross-linking in these polyurethanes cannot be significant. This is supported by the fact that no evidence of insolubility in the normal solvents for polyurethanes was ever found in the work described above.

Preliminary results have shown that the thermal degradation properties of these materials are significantly different from those of pure polyurethanes and of polyurethanes containing additive fire retardants. These investigations are being pursued in detail and will be reported subsequently.

REFERENCES

1. N. Grassie and M. Zulfiqar, *J. Polym. Sci., Chem. Ed.* **16,** 1563 (1978).
2. N. Grassie and M. Zulfiqar. In preparation.
3. F. Millich and C. E. Carraher, *J. Polym. Sci. A-1* **7,** 2669 (1969).
4. V. D. Maiboroda and L. A. Datskevich. *Polym. Sci. U.S.S.R.* **6,** 2113 (1964).
5. R. L. McConnell and W. H. Coover, U.S. 2,926, 145. C.A. **54,** 15315c.
6. A. Munoz, *Double Liaison* **125,** 37 (1966).
7. B. Dreher, *Farbe U Lack* **67,** 703 (1961).
8. W. Sorenson and T. Campbell, *Preparative Methods of Polymer Chemistry*, 2nd Edition. Wiley-Interscience, New York (1968).
9. L. A. Datskevich *et al.*, *Vysokomolek. Soedin.* 243 (1964). C.A. **61,** 5779f.
10. S. Sandler and F. R. Berg, *J. appl. Polym. Sci.* **9,** 3909 (1965).
11. S. Sandler, *J. appl. Polym. Sci.* **11,** 811 (1967).
12. T. Campbell and K. C. Smeltz, *J. org. Chem.* **28,** 2069 (1963).
13. L. A. Datskevich, *Polym. Sci. U.S.S.R.* **6,** 1662 (1964).
14. A. D. F. Toy, U.S. 2,400,577. C.A. **40,** 4745.
15. N. A. Lipatnikov *et al.*, *Sin. Fiz.-Khim. Polim.* **5,** 96 (1968). C.A. **70,** 4695y.
16. D. J. Lyman, *J. Polym. Sci.* **45,** 49 (1960).
17. G. Borisov and K. Troev, *Eur. Polym. J.* **9,** 1077 (1973).
18. K. Saotome and H. Komoto, *J. Polym. Sci. A-1* **5,** 119 (1967).
19. S. Sandler and W. Karo, *Polymer Syntheses*, Vol. 29. Academic Press, New York (1974).
20. M. L. Matuszak and K. C. Frisch, *J. Polym. Sci., A-1* **11,** 637 (1973).
21. M. Sumi *et al*, *Makromolek. Chem.* **78,** 146 (1964).