

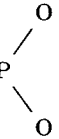
Phosphorus-Containing Polyurethanes Based on Bisphenol-AF, Prepared by *N*-Alkylation

DER-JANG LIAW* and SHIUH-PING LIN

Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan 106, Republic of China

SYNOPSIS

Phosphorus-containing polyurethanes (PU-P) based on bisphenol-AF were synthesized by *N*-alkylation in a two-step process. First, the polymer was metalated with sodium hydride; then the prepared urethane polyanion was treated with diethyl 2-bromoethyl phosphate. IR spectra exhibited characteristic absorptions at 1303 cm⁻¹ (P=O stretch), 1015 cm⁻¹

(PO—C stretch), 960 cm⁻¹ (POC—C stretch), 812 cm⁻¹ (P  deform), 2912–3020 cm⁻¹

(CH stretch), 1646 cm⁻¹ (C=O stretch), 1231 cm⁻¹ (CNH), and 1053 cm⁻¹ (CO—O—C stretch). In the ¹H-NMR spectrum of the maximum substituted PU-P, the signal of the urethane proton (NH—CO—O) at 9.87 ppm virtually disappeared as expected; new signals appeared at 1.20–1.24 ppm (POCH₂CH₃) and 3.79 ppm (POCH₂CH₃). Physical and thermal properties of the *N*-alkylated polymer were also investigated with differential scanning calorimetry (DSC), solubility, X-ray diffraction, thermogravimetric analysis (TGA), limiting oxygen index (LOI), and reduced viscosity. DSC analysis showed that *T*_g values were decreased from 81 to 43°C. The reduced viscosities of the PU-Ps were observed in the range of 0.23–0.18 dL g⁻¹. The results of TGA revealed that the thermal stability was decreased, because the phosphorus moiety in the PUs is readily dissociated thermally. The PU-Ps exhibited enhanced fire resistance because phosphorus simultaneously promoted carbonization of the polymer and inhibited combustion. The X-ray diffraction patterns of the PU-Ps showed that with increasing phosphorus content, the degree of crystallinity of the PUs decreased. *N*-alkylated PUs are soluble, not only in polar solvents such as *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone, dimethyl sulfoxide, and H₂SO₄, but also in less polar solvents such as phenol, toluene, THF, and trichloroethylene. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Modifications of polymers are used extensively to improve various typically desired properties of materials, such as enhanced thermal stability, fire retardancy, flexibility, solubility, and so on. Several authors^{1–8} indicated that polyurethanes (PUs) and polyamides can be chemically modified at labile hydrogens of the carbamate and amide groups with alkylhalogenides after preliminary metalation of the polymer with sodium hydride under suitable con-

ditions. For example, Beachell and Ngoc Son⁷ reported that the stabilization of PU to thermal degradation is improved on *N*-substitution. Espenschied and Schulz⁵ investigated the metalation and *N*-alkylation of polyamides having great flexibility and increased solubility even in less polar solvents.

Several investigators showed that polymers based on bisphenol-AF (BPAF), such as polyarylates,⁹ polyamide,^{10–12} polyphosphates,¹³ and polycarbonates,¹⁴ have improved physical and thermal properties due to the fluorine atoms. However, Minoura et al.¹⁵ reported that PUs derived from aromatic diols of small molar mass have good mechanical properties but poor processability. Sivriev et al.¹ prepared phosphorus-containing PUs (PU-Ps) by *N*-modifi-

* To whom correspondence should be addressed.

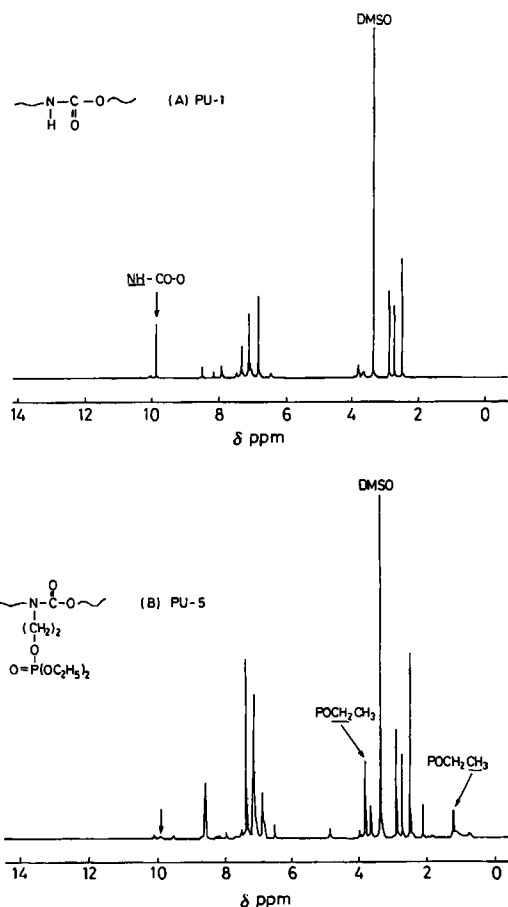


Figure 1 $^1\text{H-NMR}$ diagrams before and after *N*-modification of polyurethanes (A) PU-1 and (B) PU-5.

cation to enhance fire resistance. The influence of *N*-modification of a polymer on BPAF diol-based PUs has not been investigated so far.

The aim of the present work was to prepare PUs based on BPAF and methane diisocyanate

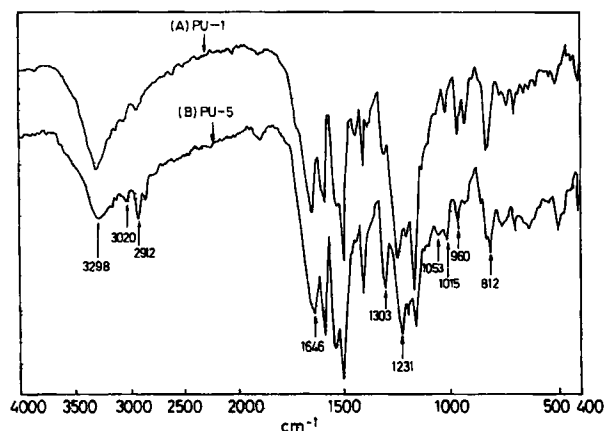


Figure 2 IR spectra before and after *N*-modification of polyurethanes (A) PU-1 and (B) PU-5.

Table I Properties of Polyurethanes Based on Bisphenol-AF

Polymer Code	Phosphorus Desired (mass %)	T_g ($^{\circ}\text{C}$)	η_{sp}/C ($\text{dL} \cdot \text{g}^{-1}$)	LOI
PU-1	—	81	0.23	26.2
PU-2	0.5	52	0.21	26.7
PU-3	1.0	49	0.20	27.0
PU-4	1.5	45	0.19	27.3
PU-5	2.0	43	0.18	27.5

(MDI), by *N*-substitution with suitable phosphorus-containing alkylhalogenide through preliminary metalation of the polymer with sodium hydride. The influence of *N*-modification of these polymers on the viscosity, thermal properties, crystallinity, solubility, and fire retardancy was investigated. IR and $^1\text{H-NMR}$ spectra were measured.

EXPERIMENTAL

Materials

Starting PUs Based on BPAF and MDI

BPAF (6.72 g, 20 mmol) was placed in a three-necked flask and dissolved in dry *N,N*-dimethylformamide (DMF; 30 mL) at 100°C . MDI (5 g, 20 mmol) was added dropwise for 30 min into the solution. After 15 h, the solution was poured into ethanol to precipitate the polymer. The product was dried in a vacuum oven at 85°C for 20 h. Diethyl 2-bromoethylphosphate was obtained from Janssen. DMF was purified by distillation over P_2O_5 and stored over 3-Å molecular sieves.

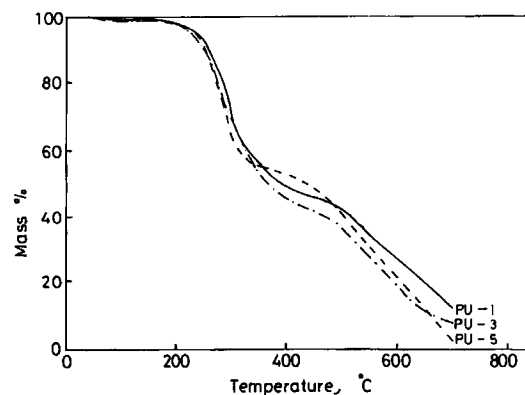


Figure 3 Thermogravimetric analysis curves of polyurethanes for PU-1, the starting polymer; PU-3, containing 1.0% phosphorus; and PU-5, containing 2.0% phosphorus conducted at a heating rate $10^{\circ}\text{C} \text{ min}^{-1}$ in air.

Table II Data of TG Analysis for Polyurethanes in Air

Polymer Code	Phosphorus (mass %)	T_d^i (°C)	$T_d^{10\%}$ (°C)	T_d^{\max} (°C)	Char Yield at 700°C (%)
PU-1	0	209	258	298	12.8
PU-2	0.5	198	254	295	8.0
PU-3	1.0	204	256	282	6.3
PU-4	1.5	199	254	284	4.9
PU-5	2.0	198	250	279	2.1

Thermogravimetric analyses conducted at a heating rate $10^\circ\text{C min}^{-1}$ in air. T_d^i is the temperature at which initial loss of mass was observed. $T_d^{10\%}$ is the temperature at which 10% loss of mass was observed. T_d^{\max} is the temperature at which maximal loss of mass was observed.

Preparation of PU-Ps

A sample (1.76 g, 3 mmol) of the PU, dissolved in dry DMF (50 mL), was placed in a three-necked flask with a glycerin seal. Sodium hydride (0.18 g, 80% suspension in paraffin, 6 mmol) was added to the solution with stirring at a temperature not exceeding 0°C . Evolution of H_2 was immediately observed; after about 15 min, the solution became deep green due to the urethane polyanion. After stirring for 2 h under these conditions in an argon atmosphere, the appropriate amount of diethyl 2-bromoethylphosphate in DMF, necessary to obtain the desired degree of substitution, was added to the mixture. After stirring for another 4 h, distilled water was added dropwise to the mixture to neutralize excess sodium hydride and to precipitate the polymer. The precipitate was washed several times with water until there was no reaction for Br^- with AgNO_3 solution, filtered, and dissolved again in DMF. It was then reprecipitated in diethyl ether; after filtration, it was dried to constant mass over P_2O_5 . The final product, which is a white powder, was obtained quantitatively.

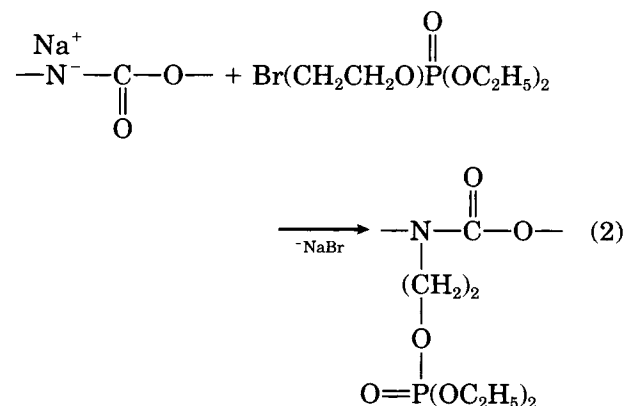
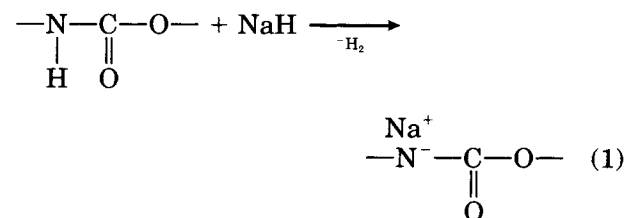
Characterization Methods

$^1\text{H-NMR}$ spectra were recorded on a $^1\text{H-NMR}$ spectrometer (Bruker EM-360L) at 400 MHz in $\text{DMSO-}d_6$. Chemical shifts (δ) were given in parts per million with tetramethylsilane (TMS) as a standard. IR spectra of KBr pellets were recorded on a spectrometer (JASCO IR-700). Thermogravimetric analysis (TGA) was performed on a TGA instrument (DuPont 2200) at a heating rate $10^\circ\text{C min}^{-1}$ in air. The glass transition temperatures were determined with a differential scanning calorimeter (DuPont 9000 DSC). Measurements were made at a heating rate of $10^\circ\text{C min}^{-1}$. The limiting oxygen index (LOI) was determined on a SUGA instrument according to JIS K7201. The viscosities were measured in an

Ubbelohde viscosimeter at $30 \pm 0.1^\circ\text{C}$; 0.5 mass % solutions of polymers in *N*-methyl-2-pyrrolidone (NMP) were used. The X-ray diffraction diagram was recorded according to the powder method with an X-ray diffractometer (Philips PW 1710).

RESULTS AND DISCUSSION

PU, prepared from MDI and BPAF, was used to carry out *N*-alkylation according to the following scheme¹:



Sodium hydride was used in the first step to abstract the labile urethane proton. Then the urethane polyanion reacted with phosphorus-containing alkoxyhalogenide, forming the PU-P. Substitution of the urethane proton in PUs leads to changes in various physicochemical and physicomechanical prop-

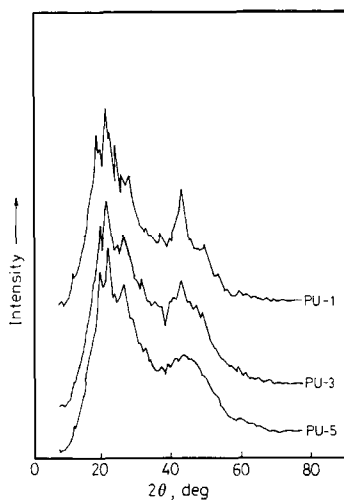


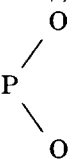
Figure 4 Effect of phosphorus content on X-ray diffraction patterns of polyurethanes for PU-1, the starting polymer; PU-3, containing 1.0% phosphorus; and PU-5, containing 2.0% phosphorus.

erties. For instance, Sivriev and coworkers¹ reported that PU modified by diethyl 3-bromopropylphosphonate acts as a short aliphatic chain to elevate the LOI remarkably, but it alters viscosity only slightly. Because the quantity of sodium hydride has a greater effect on the degree of substitution, the chosen molar ratio between PU and NaH was 1 : 2.

By total metalation of the starting PU and varying the quantity of the phosphate, one can prepare PU-P with the desired degree of substitution. *N*-modified PUs with phosphorus contents of 0.5, 1.0, 1.5, and 2.0% were obtained. The structures of the PU-P were investigated with ¹H-NMR and IR spectra. Figure 1 shows the differences between ¹H-NMR diagrams before and after *N*-modification. In the ¹H-NMR spectrum of the maximum substituted PU-P, the signal of the urethane proton (NH—CO—O) at 9.87 ppm virtually disappeared as expected; new signals appeared at 1.20–1.24 ppm (POCH₂CH₃) and 3.79 ppm (POCH₂CH₃). The decreased intensity of a signal of the NH proton and

the presence of signals for phosphorus-containing moieties are proof of *N*-alkylation of the PUs.

The same behavior is observed in the IR spectra (Fig. 2). In contrast to the starting polymer, absorption of PU-P, characteristic of the NH group at 3298 cm⁻¹ (NH stretching), decreased; and new lines, characteristic of the phosphate group, appeared at 1303 cm⁻¹ (P=O stretch), 2912–3020 cm⁻¹ (CH stretch), 1015 cm⁻¹ (PO—C stretch),

960 cm⁻¹ (POC—C stretch) and 812 cm⁻¹ (P  deform).

In all spectra, besides the NH lines, typical absorptions of PUs at 1646 cm⁻¹ (C=O stretch), 1231 cm⁻¹ (CNH), and 1053 cm⁻¹ (CO—O—C stretch) were observed. These lines are also characteristic of PU based on MDI and BPAF.

Some characteristic properties of the starting PU and of the *N*-modified PU-P are listed in Table I, showing that *N*-modification influences the properties of the PUs. Because PU has a large phosphorus content, it has a smaller content of N—H protons. This phenomenon decreases intermolecular interaction, caused by hydrogen bonds between the urethane groups, and leads in turn to a decreased glass transition temperature observed in both the present and related work.^{1-7,16} For instance, Espenschied and Schulz⁵ reported that on *N*-alkylation of polyamide, the glass transition temperature decreases with increasing length of the side chain, which acts as a plasticizer. The influence of *N*-modification on the viscosity is similar; the decreased interaction energy of the macromolecules manifests itself in a decreased viscosity. Flame resistance of polymers was measured according to their LOI values. LOI data (Table I) show that fire resistance of the PUs is enhanced with increased phosphorus content. This effect is expected because phosphorus groups promote carbonization and inhibit combustion at the same time.²

Table III Solubility of *N*-Substituted Polyurethanes

Polymer	Solvent							
	Concn H ₂ SO ₄	DMF	NMP	DMSO	Phenol	Toluene	THF	TCE
PU-1	+	+	+	+	—	—	+	—
PU-P	+	+	+	+	+	+	+	+

(+) Soluble at room temperature and (—) insoluble. DMF, *N,N*-dimethylformamide; NMP, *N*-methyl-2-pyrrolidone; DMSO, dimethyl sulfoxide; TCE, trichloroethylene.

Examples of TG curves of PUs (PU-1, PU-3, and PU-5) indicated no loss of mass below 190°C in air as shown in Figure 3. Curves of thermodestruction of these three PUs differ only slightly. Small differences are discernible in the temperature interval 198–210°C, in which *N*-modified PUs (PU-3 and PU-5) begin to decompose at slightly decreased temperatures, 204°C for PU-3 and 198°C for PU-5 compared with 209°C for the starting PU. TGA data of PUs conducted at a heating rate 10°C min⁻¹ in air are presented in Table II. The decreased $T_d^{10\%}$ and T_d^{max} were due to the ease of thermal dissociation of the phosphorus group. However, the removal of the possibility for a depolycondensation process, involving the relatively low energy N—H hydrogen transfer to the urethane oxygen of the PUs, was not found to increase the thermal decomposition temperature significantly.¹⁷

X-ray diffraction patterns of various PUs are shown in Figure 4 in terms of intensity versus 2θ (θ is the angle of diffraction (Bragg angle)). The intensity of X-ray diffraction decreased with increasing phosphorus content. Decreasing the number of hydrogen bonds and increasing the content of phosphorus groups that act as plasticizers⁵ resulted in decreased crystallinity of PU-P. The angle of maximum intensity of the diffractograms of PU-1, PU-3, and PU-5 did not shift significantly. This phenomenon may be due to weaker intermolecular forces between polymer chains derived from fluorine-containing PUs.¹³

The solubilities of *N*-substituted PUs are given in Table III. The starting polymer is soluble in polar solvents such as sulfuric acid, DMF, NMP, DMSO, and THF but insoluble in less polar solvents such as phenol, toluene, and trichloroethylene. The PU containing maximum *N*-alkylation is soluble not only in polar but also in less polar solvents. The absence of hydrogen bonding is invoked to explain this behavior.¹⁸

CONCLUSIONS

PU-Ps were synthesized by *N*-alkylation of a linear PU based on BPAF. The reaction operates in a two-step process, namely, firstly metalation of the starting polymer with sodium hydride and then treatment of the obtained urethane polyanion with diethyl 2-bromoethyl phosphate.

When the degree of *N*-substitution increased, the glass transition temperature and polarity of the PUs decreased due to weakened intermolecular interactions between the polymer chains caused by the decrease in the number of hydrogen bonds between them. A large variation of viscosity was not observed in the present work. The obtained PU-P possess a

decreased thermal stability, as shown by the slightly decreased temperatures of initial degradation. The incorporation of phosphorus in PUs led to increased fire resistance (limiting oxygen index).

Acting as a plasticizer, the increased content of phosphorus groups resulted in decreased crystallinity of the polymer. The LOI values were elevated by the introduction of phosphorus groups. This effect is expected as phosphorus groups promote carbonization and inhibit combustion at the same time.

We thank the National Science Council of the Republic of China for their financial support under Grant NSC-85-2216-E011-006.

REFERENCES

1. H. Sivriev, S. Georgiev, and G. Borissov, *Eur. Polym. J.*, **26**, 73 (1990).
2. J. A. Midroyannids, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 891 (1984).
3. G. C. Tesoro, *J. Polym. Sci., Macromol. Rev.*, **13**, 339 (1978).
4. M. Takayanagi and Tikatayose, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1133 (1981).
5. B. Espenschied and R. C. Schulz, *Polym. Bull.*, **5**, 489 (1981).
6. T. L. Cairns, H. D. Foster, A. W. Larchar, A. K. Schneider, and R. S. Schreiber, *J. Am. Chem. Soc.*, **71**, 651 (1949).
7. H. C. Beachell and C. P. Ngoc Son, *J. Appl. Polym. Sci.*, **8**, 1089 (1964).
8. H. A. Kashani, J. A. Barrie, and M. H. Gourge, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 533 (1978).
9. Y. Maruyama, M. A. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 3555 (1986).
10. T. Kiyotsukuri, K. Nakashita, and M. Nagata, *J. Soc. Fiber Sci. Technol. Jpn.*, **40**, T-72 (1984).
11. M. Nagata, N. Tsutsumi, and T. Kiyotsukuri, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 235 (1988).
12. D. J. Liaw and K. L. Wang, *J. Polym. Sci., Polym. Chem. Ed.*, to appear.
13. D. J. Liaw and P. S. Chen, *Polymer*, **36**, 4491 (1995).
14. Y. Saegusa, M. Kuriki, A. Kawai, and S. Nakamura, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 3327 (1990).
15. Y. Minoura, S. Yamashita, H. Okamoto, T. Matsuo, M. Izawa, and S. I. Kohmoto, *J. Appl. Polym. Sci.*, **23**, 1137 (1979).
16. B. S. Biggs, C. J. Frosch, and R. H. Erickson, *Ind. Eng. Chem.*, **38**, 1016 (1946).
17. S. Foti, P. Maravigna, and G. Montaudo, *Polym. Degradation Stability*, **4**, 287 (1982).
18. R. A. Weiss, R. W. Lenz, and W. J. Macknight, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1409 (1977).

Received August 24, 1995

Accepted November 4, 1995