

Synthesis and Characterization of Novel Phosphorus-Containing Polyurethane Elastomers†

WENZONG XU*, MINGYUAN REN and LIANG LIU

School of Materials Science and Chemical Engineering, Anhui Jianzhu University, 856 Jinzai Road, Hefei 230022, Anhui Province, P.R. China

*Corresponding author: E-mail: wenzongxu@sohu.com

Published online: 1 March 2014;

AJC-14764

Bis(4-aminophenoxy)phenyl phosphine oxide (BAPPO) was synthesized based on phenyl phosphonic dichloride and 4-nitrophenol and characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). Then BAPPO was used to prepare a series of phosphorus-containing polyurethane elastomers (PPUEs) with different phosphorus contents by changing the soft segments. Combustion behaviours and thermal degradation behaviours of the PPUEs and polyurethane elastomer (PUE) were investigated by thermogravimetric analysis (TGA) and microscale combustion calorimetry (MCC). Thermogravimetric analysis result shows that the thermal degradation of polyurethane elastomers is divided into two stages and the thermal stability of PPUE-1 is poorer than that of PUE. The MCC result reveals that the values of the peak heat release rate and total heat release of PPUE-1 are lower than that of PUE made by 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) when they are obtained from the same soft segment.

Keywords: Phosphorus-containing diamine, Polyurethane, Flame retardant.

INTRODUCTION

Polyurethane elastomers are widely used in various industries because they have excellent chemical, physical and mechanical properties such as antioxidation, low-temperature stability and abrasion resistance. But their flammability restricts the expansion of the scope of their application¹⁻³.

In this paper, we report the synthesis of a novel phosphorus-containing chain extender *bis*(4-aminophenoxy)phenyl phosphine oxide (BAPPO) and a series of phosphorus-containing polyurethane elastomers (PPUEs) that were synthesized by adjusting the types of soft segments. The structure of BAPPO was characterized and the thermal stability and flame retardancy of the PPUEs were investigated.

EXPERIMENTAL

Synthesis of phosphorus-containing polyurethane elastomers (PPUEs): Polyester diol was heated to 110-120 °C, stirred and vacuumed for 2 h to remove trace water. When the temperature was reduced to 70 °C, TDI was added and reacted for 2 h. The prepolymer was prepared.

The molten chain extender and prepolymer were mixed and stirred fully. Then the mixture was put into a Teflon mould at 75 °C for 2 h and 115 °C for another 2 h. Finally, the PPUEs

were synthesized. The synthesis route of BAPPO is given in **Scheme-I**.

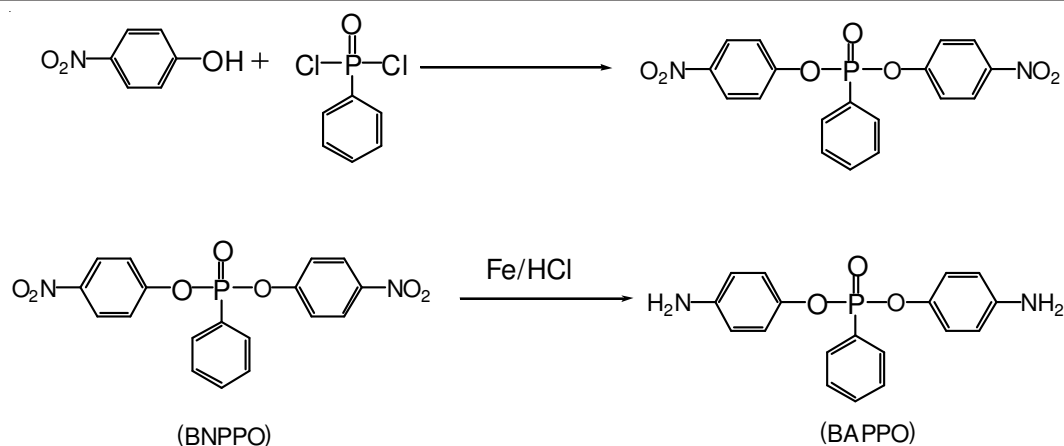
Characterization: Infrared data were obtained with a Spectrum 100 FTIR Spectrometer (Perkin Elmer) between 4000 and 500 cm⁻¹ at the resolution of 4 cm⁻¹. ¹H nuclear magnetic resonance (¹H NMR) and ³¹P NMR spectra were obtained with a Bruker AV400. A Govmark microscale combustion calorimeter (MCC-2; Farmingdale, NY, USA) was used to investigate the combustion of the PPUEs.

RESULTS AND DISCUSSION

Characterization of BAPPO: The nitro absorption peaks at 1518 and 1348 cm⁻¹ from -NO₂ asymmetric and symmetric stretching vibration absorption are found in BNPPPO and disappear in BAPPO. In BAPPO, the typical asymmetric and symmetric stretching vibration absorption peaks of primary amine are distinctly observed at 3443 and 3349 cm⁻¹ in BAPPO. All the above results indicate that BNPPPO successfully converts into BAPPO (**Scheme-I**, Fig. 1).

The ¹H and ³¹P NMR spectra of BAPPO are shown in Figs. 2 and 3, respectively. In the ¹H NMR of BAPPO (Fig. 2), the electron-donating effect of amino group and proton-donating effect of phosphine oxide group are demonstrated by the six groups of peaks: 6.43-6.52 ppm (doublet, 4H, H_a), 6.78-6.83

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China



Scheme-I: Synthesis route of BAPPO

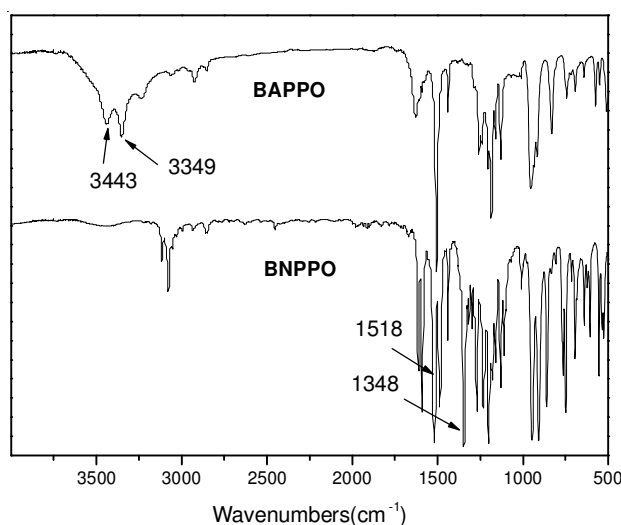
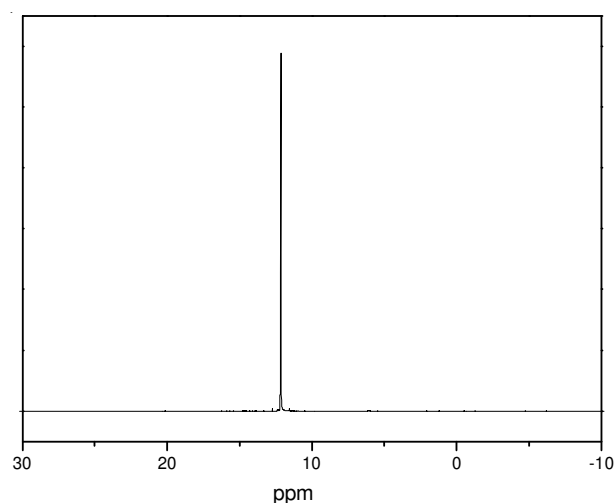
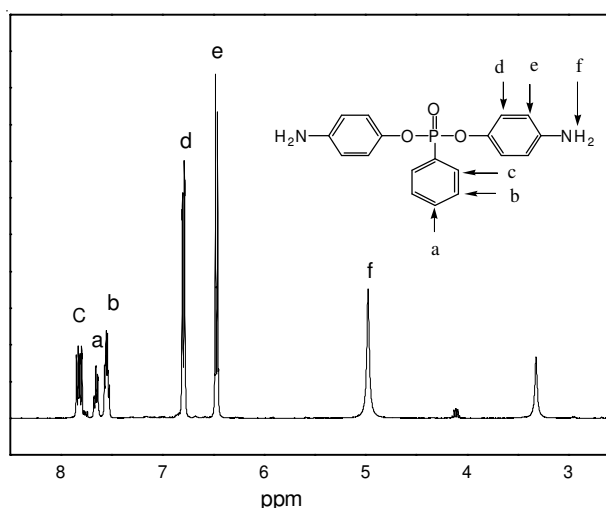


Fig. 1. FTIR spectra of BNPPPO and BAPPO

Fig. 3. ³¹P NMR spectrum of BAPPOFig. 2. ¹H NMR spectrum of BAPPO

ppm (doublet, 4H, H_d), 7.52-7.57 ppm (triplet, 2H, H_b), 7.62-7.67 ppm (triplet, 1H, H_a), 7.79-7.87 ppm (triplet, 2H, H_c) and 4.85-5.11 ppm (singlet, 4H, H_f). Furthermore, the single peak at 12.14 ppm in ³¹P NMR spectrum (Fig. 3) indicates the high purity of BAPPO.

Thermal property of PPUEs: T₅, T₅₀ and T_{max} are the temperature of 5 %, 50 % and max weight loss of the sample, respectively. The TGA curves of the PPUEs and PUE have two distinct regions of weight loss, implying at least two stages of degradation occur in these samples (Fig. 4). The T₅, T₅₀ and T_{max} of PPUE-1 are 279.0, 386.6 and 397.5 °C and those of PPUE-2 are higher and reach 281.4, 405.9 and 410.9 °C; that is to say, PPUE-2 shows better thermal stability. PPUE-1 and PUE have the same soft segment, R and chain extender coefficient, but PPUE-1 shows poorer thermal stability than polyurethane elastomer. The possible reason is that the thermal stability of phosphorus-containing extender is poor.

Flame retardant property of PPUEs: The PHRR and THR of PUE are 212 W/g and 15.9 KJ/g, respectively, but the values of PPUE-1 are 174.2 W/g and 14 KJ/g; evidently, both PHRR and THR of PPUE-1 are lower than those of PUE. PUE and PPUE-1 have the same soft segment, R and chain extension coefficient, with the only difference in the types of chain extender. It means that PPUE-1 based on chain extender BAPPO shows better flame retardation than PUE based on conventional chain extender MOCA; in other words, the introduction of phosphorus-containing chain extender enhances the flame retardation. All the PPUEs contain BAPPO, but the molecular weight of soft segments increases in the order of PPUE-1, PPUE-2 and PPUE-3 and as a result, the contents of BAPPO

TABLE-1
DESCRIPTION OF THE PPUES AND PUE

Samples	Soft segment	R*	Chain extension coefficient*	Chain extender	Hard segment content wt. (%)	P/Cl content wt. (%)
PPUE-1	Polyester diol 1213	2	0.9	BAPPO	35.4	1.5
PPUE-2	Polyester diol 1975	2	0.9	BAPPO	25.3	1.1
PPUE-3	Polyester diol 2600	2	0.9	BAPPO	19.9	0.8
PUE	Polyester diol 1213	2	0.9	MOCA	32.7	3.5

*R is the molar ratios of NCO of TDI and OH of soft segment. *Chain extension coefficient is the molar ratios of NH_2 of chain extender and NCO of prepolymer.

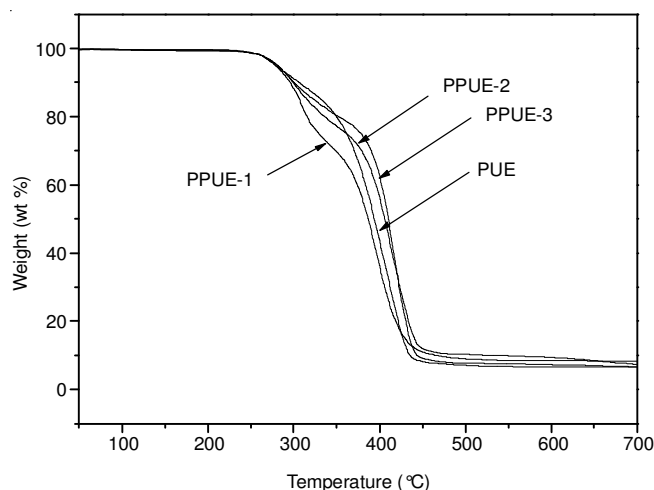


Fig. 4. TGA curves of PPUEs

in PPUEs become gradually less from PPUE-1 to PPUE-3; in other words, the phosphorus-containing contents are gradually less from PPUE-1 to PPUE-3, as we see in Table-1, from 1.5-0.8 %. From PPUE-1 to PPUE-3, the PHRR and THR increase from 174.2 W/g and 14 KJ/g to 270.9 W/g and 16.2 KJ/g, respectively. Thus, it can be seen that the increase in the BAPPO content gradually results in an increase in flame retardation.

The ignition temperature corresponds to the temperature of the maximum heat release rate. The ignition temperature for PPUE-1 is lower than that for PUE and with the BAPPO content increasing from PPUE-3 to PPUE-1, the ignition temperature decreases from 445-428.9 °C. It indicates the PPUEs have inferior thermal stability, which corresponds to the TGA result (Fig. 5).

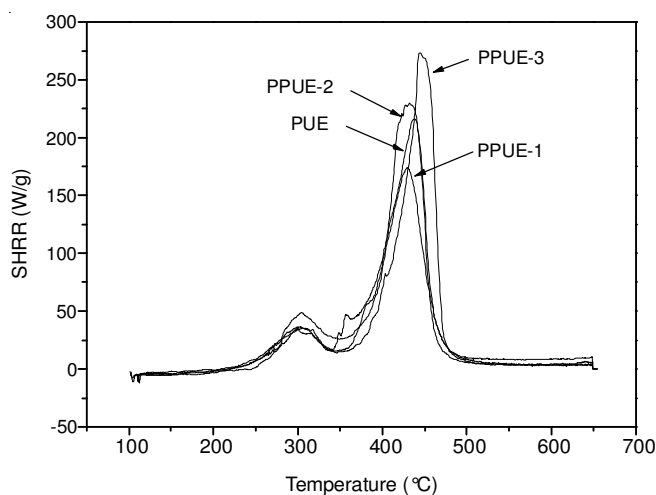


Fig. 5. Specific heat release rate curves of the PUE and PPUEs

Conclusion

Bis(4-aminophenoxy)phenyl phosphine oxide (BAPPO) was synthesized from phenyl phosphonic dichloride and 4-nitrophenol and characterized by FTIR, ^1H and ^{31}P NMR. Phosphorus-containing polyurethane elastomers were synthesized with BAPPO by two steps.

The results of FTIR, ^1H and ^{31}P NMR demonstrate that the molecular structure of BAPPO absolutely corresponds to anticipation. The flame retardant properties of PPUEs and PUE are evaluated by microscale combustion calorimetry experiments. The PHRR and THR of PPUE-1 are 174.2 W/g and 14 KJ/g and the results show the flame retardancy of PPUE-1 is better than that of PUE. The TGA results indicate that the thermal stability of phosphorus-containing polyurethane is lower than that of common polyurethane. However, the incorporation of BAPPO into polyurethane increases the char yield and a glass coating and a protective carbonized skin may be formed on the pyrolyzing phosphorus-containing polyurethanes, thus possibly leading to fire protection.

ACKNOWLEDGEMENTS

The authors thank the National Natural Science Foundation of China (No. 21004001/B040601) and the National Key Technology R&D Program (No. 2013BAJ01B05) for their financial support.

REFERENCES

1. G.B. Huang, J.R. Gao, Y.J. Li, L. Han and X. Wang, *Polym. Degrad. Stabil.*, **95**, 245 (2010).
2. D.K. Chattopadhyay and D.C. Webster, *Progr. Polym. Sci.*, **34**, 1068 (2009).
3. H. Singh, A.K. Jain and T.P. Sharma, *J. Appl. Polym. Sci.*, **109**, 2718 (2008);