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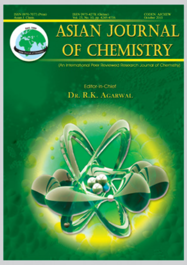

Synthesis and Thermal Degradation Behaviours of Novel Phosphorus-Containing Polyurethane Elastomers†

WENZONG XU[1,2,3], JIANGUO YIN[3], YUAN HU[1,*], BO LU[3] and WEI HUNG[4]

[1]State Key Lab of Fire Science, University of Science and Technology of China, Hefei 230026, Anhui Province, P.R. China
[2]Department of Polymer Science and Engineering, University of Science and Technology of China, 96 Jinzhai Road, Hefei 230026, Anhui Province, P.R. China
[3]School of Materials Science and Chemical Engineering, Anhui University of Architecture, 856 Jinzai Road, Hefei 230022, Anhui Province, P.R. China
[4]GuangDong Silver Age Sci & Tech. Co. Ltd., JuQi Industrial Park, HuMen Town, DongGuan City 523927, Guangdong Province, P.R. China

*Corresponding author: E-mail: yuanhu@ustc.edu.cn

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Phenyl diaminophosphate was synthesized based on phenyl dichlorophosphate and characterized by Fourier transform infrared spectroscopy and nuclear magnetic resonance. Phenyl diaminophosphate was used as chain extender to prepare a series of phosphorus containing polyurethane elastomers (PPUEs) with different phosphorus contents by changing the soft segments. The thermogravimetric analyses result reveal that the char yield of PPUEs is much higher: the char yield of PPUE1 reaches 35 % whose phosphorus content is just 1.5 %, indicating that the phosphorus contributes to the improved char-forming ability. The microscale combustion colorimeter (MCC) result shows that the PPUEs show better flame retardancy and the flame retardant of the polyurethane elastomer increases with the phosphorus content increasing. The degradation kinetics studies show that the degradation of polyurethane elastomers is divided into two stages, where the activation energy of PPUEs in their first stage is lower than that of corresponding polyurethane elastomers based on 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA), but the activation energy in the second stage is higher.

Key Words: Phosphorus-containing diamine, Polyurethane, Thermal oxidative degradation, Activation energy.

INTRODUCTION

Polyurethanes (PUs) are used worldwide on a large scale due to their excellent mechanical properties such as abrasion resistance, toughness and tensile strength. But their flammability restrict the expanding of their application. Organophosphorus compounds are widely used in polymers to improve their flame retardancy[1], sometimes they can also enhance processing ability[2] and provide plasticizing properties[3].

Early phosphorus-containing polyurethane was obtained through an additive-type phosphorus-containing flame retardant. The flame retardancy of these polyurethanes increased, but other properties such as thermal stability and mechanical properties decreased[4]. Phosphorus was introduced into the chain of polyurethanes through a molecular design to get phosphorus-containing flame retardant polyurethanes and these polyurethanes showed good flame retardant and excellent comprehensive performance.

Phosphorus-containing polyurethane can be synthesized by the reactions of diisocyanates with diols, polyesters and polyethers, while at least one of the reactants contain phosphorus. The phosphorus containing groups can be diisocyanates, chain extenders and soft segments. Liu *et al.*[5] synthesized phosphorus-containing polyurethanes by reacting phosphorus-containing diisocyanates, *bis*(4-isocyanatophenoxy)phenyl phosphine oxide (BIPPO) and *bis*(3-isocyanatophenyl)phenyl phosphine oxide (BIPPPO), with various diols. Char yield and loss on ignition (LOI) measurements demonstrated that incorporating phosphorus into polyurethanes markedly improved their flame retardancy. Park *et al.*[6] prepared two component polyurethane flame retardant coatings using phosphorus-containing lactone modified polyester (PLMPs) and polyisocyanate and results showed that various physical properties of these new flame retarding polyurethane coatings were comparable to non-flame retardant coatings. Coating with a 20 wt % dimethyl phenylphosphonate content did not burn in the vertical burning test. Comparatively, there are few reports in the literature on phosphorus-containing short-chain aromatic diamine which acts as a chain

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extender in preparing PPUEs and also the thermal degradation behaviours of phosphorus-containing polyurethane elastomers based on phosphorus-containing aromatic diamine have not been adequately investigated.

In this paper, we report the synthesis and characterization of the phosphorus-containing chain extender, Phenyl diaminophosphate (PDAP) and the synthesis of a series of PPUEs by adjusting the types of soft segment. The study of their thermal degradation behaviours illustrates the interplay between the structure and properties of PPUEs.

EXPERIMENTAL

Phenyl dichlorophosphate (99 % purity) was purchased from the Yingkou Tanyun Chemical Research Institute Corporation. N,N-Dimethylformamide (DMF) (from Sinopharm Chemical Reagent Co. Ltd.) was purified by distillation under reduced pressure from calcium chloride. Butanone (AR) (from Sinopharm Chemical Reagent Co. Ltd.) was used after drying by molecular sieves (4A). Potassium carbonate (AR) and ammonia (AR) (from Guangdong Xilong Chemical Co. Ltd.) were used without further purification. Toluene diisocyanate (TDI) was purchased from Mitsui Chemicals. Polyester diol (M_n = 1213, 1975, 2600) was obtained from Shandong Xinhuarun Chemical Co. Ltd. 3,3'-Dichloro-4,4'-diaminodiphenylmethane (MOCA) was purchased from Zhangjiagang Daily Chemical Co. Ltd.

Synthesis of phenyl diaminophosphate (PDAP): In a four-necked reactor 75 g phenyl dichlorophosphate (PDCP) were added dropwise to 210 g ammonia under constant stirring at 5 ºC. A constant flow of nitrogen gas was maintained to remove the HCl produced. The reaction solution was allowed to reach room temperature and was maintained for 6 h under these conditions to complete the reaction. The crude product was separated from the reaction mixture by filtration. Finally the product was recrystallized twice from absolute ethanol with a yield of 88 %.

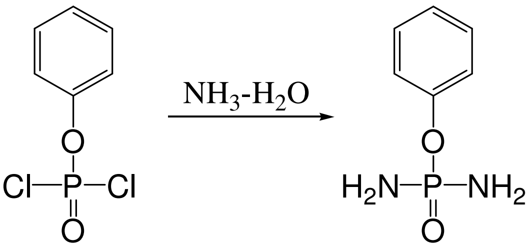
Synthesis of phosphorus containing polyurethane elastomers (PPUEs): Polyester diol was introduced into an open round-bottom 1 L glass reactor and then heated to 120 ºC. It was stirred and vacuumed for 2 h to remove the trace water. Subsequently, the vacuuming was stopped and nitrogen gas was charged into the reactor. When the temperature was cooled to 70 ºC, toluene diisocyanate (TDI) was added and reacted for 2 h. The prepolymer was made after removing bubbles by vacuum.

PDAP or MOCA were added to stirring prepolymer and the mixture was cast onto a Teflon plate, heated at 75 ºC for 2 h and 115 ºC for another 4 h. The ratio of diisocyanates, chain extenders and soft segments were varied to yield polymers with different compositions. Table-1 gives a description of the PPUEs and PUEs.

Infrared data were obtained with a Spectrum100 FTIR spectrometer (Perkin Elmer) between 4000 and 500 cm^{-1} at the resolution of 4 cm^{-1}. ^1H nuclear magnetic resonance (^1H NMR) and ^{31}P NMR spectra were obtained with a Bruker AV400 (Billerica, MA, USA). DMSO-d_6 was used as solvent and chemical shifts reported were internally referenced to Me4Si (0 ppm) and H_3PO_4 (0 ppm) for ^1H and ^{31}P, respectively. The thermogravimetric analyses (TGA) of samples were performed with a NETZSCH STA 409PC/PG (Selb, Germany) under N_2 atmosphere. A Govmark microscale combustion calorimeter (MCC-2; Farmingdale, NY, USA) was used to investigate the combustion of the FPUEs. In this system, 4-6 mg samples were heated to 700 ºC at a heating rate of 1 K/s in a stream of nitrogen flowing at 80 cm^3/min.

RESULTS AND DISCUSSION

Characterization of PDAP: The synthesis route of PDAP is shown in **Scheme-I**.



Scheme-I: Synthesis of PDAP

Fig. 1 shows the FTIR of PDCP and PDAP. In PDAP, the typical amino group stretching absorptions at 3366, 3233 cm^{-1} from N-H asymmetric and symmetric stretching and N-H bending absorption at 1573 cm^{-1} due to the amine groups[7] are found. The absorption peaks at 548 cm^{-1} from P-Cl are found in PDCP and disappear in PDAP and the peak at 1070 cm^{-1} from P-N is found in PDAP[8]. 955 and 1184 cm^{-1} from P-O can be found in both and the absorption from P=O decreases[9] from 1301 (PDCP) to 1231 (PDAP) cm^{-1} with the effect of hydrogenolysis.

The ^1H NMR of PDAP (Fig. 2) shows the proton-donating effect of Ph-O in PDAP is demonstrated by the four groups of peaks: 7.06-7.10 ppm (triplet, 1H, Ha), 7.17-7.19 ppm (doublet, 2H, Hb), 7.29-7.33 ppm (doublet, 2H, Hc), 4.3 ppm(singlet, 4H, Hd). The hydrogen peaks from Ha, Hb and Hc are in the

TABLE-1
DESCRIPTION OF THE PPUES AND PUES

Sample	Soft segment	R*	Chain extension coefficient*	Chain extender	Hard segment content wt. (%)	P/Cl content wt. (%)
PPUE-1	Polyester diol 1213	2	0.9	PDAP	29.3	1.6
PPUE-2	Polyester diol 1975	2	0.9	PDAP	20.3	1.1
PPUE-3	Polyester diol 2600	2	0.9	PDAP	16.2	0.9
PUE-1	Polyester diol 1213	2	0.9	MOCA	32.7	3.5
PUE-2	Polyester diol 1975	2	0.9	MOCA	22.9	2.5
PUE-3	Polyester diol 2600	2	0.9	MOCA	18.5	2

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

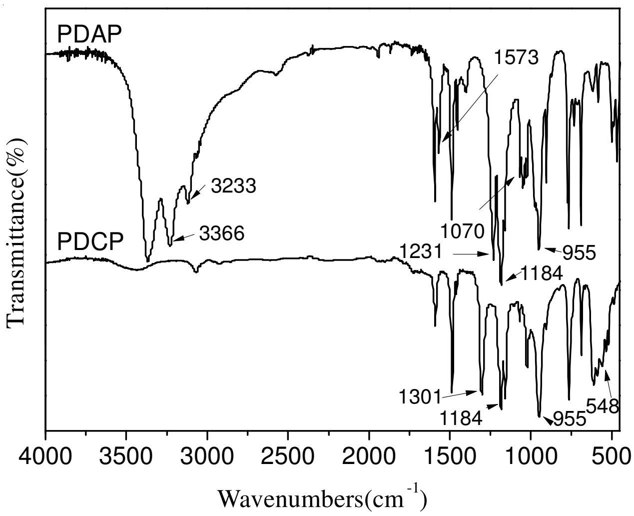


Fig. 1. FTIR of PDCP and PDAP

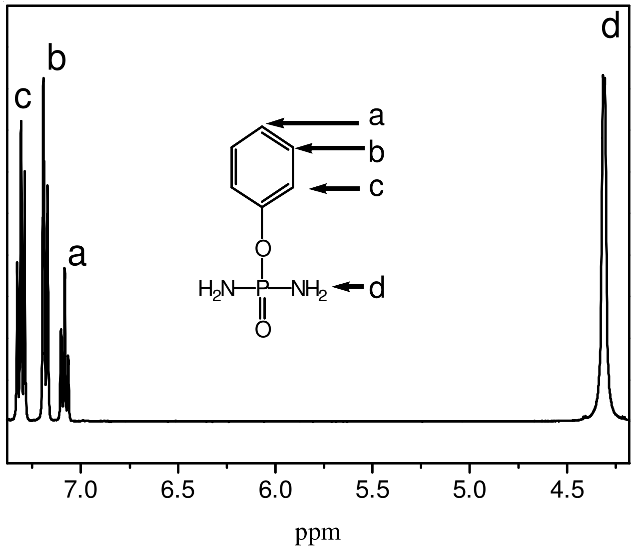


Fig. 2. ^{1}H NMR spectra of PDAP

low range due to the shielding effect of the proton-donating effect of Ph-O. The hydrogen peaks from Hc are the lowest as they are adjacent to Ph-O.

^{31}P NMR analysis provides a sharp single peak, corresponding to PDAP. Also, the sharp single peak indicates the high purity of monomers.

Thermal property of FPUEs: The TGA curves of PUE and PPUEs are shown in Figs. 3 and 4. T_5, T_{50} and T_{max} are the temperature of 10 %, 50 % and max mass loss of the sample. The T_5, T_{50} and T_{max} of PPUE-1 are 260 , 393 and 387 °C. Those of PPUE-2 are higher and reach 268, 403 and 412 °C; in other words, PPUE-2 shows better thermal stability. The possible reason is that the molecular weight of the soft segment in PPUE-2 is higher than that in PPUE-1. This is due to the fact that poorer thermal stability of biuret and urea-based carbamate is created in PPUE-1, whose initial degradation temperature is lower. PPUE-3 shows the best thermal stability of the three PPUEs as the content of less thermally stable group is the least as its molecular weight of soft segment is the highest. PUEs made from 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) show the same phenomenon.

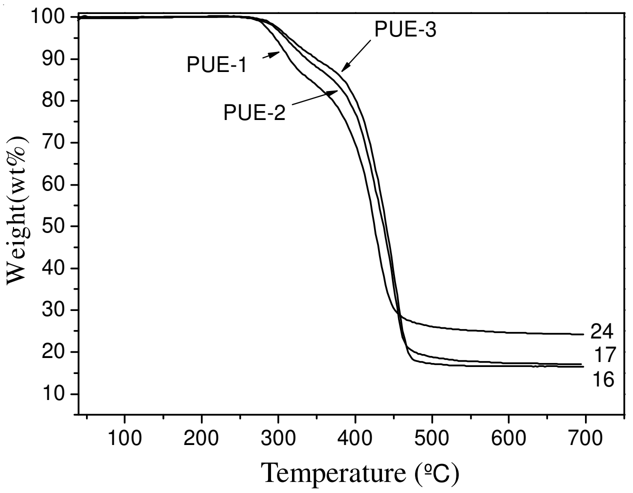


Fig. 3. TGA of PUEs

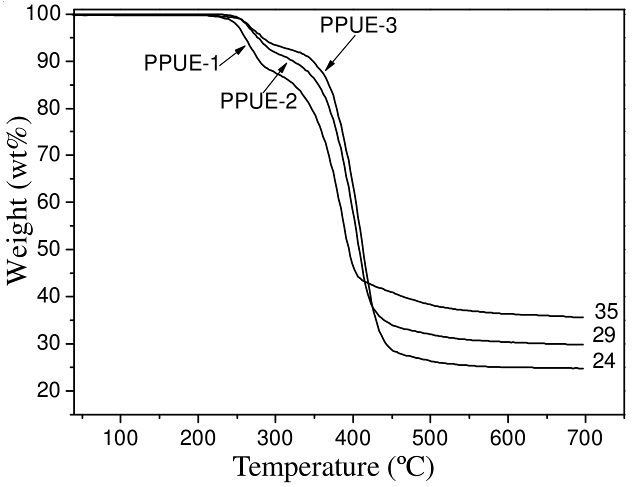


Fig. 4. TGA of PPUEs

In addition, PPUEs show poorer thermal stability than PUEs while they are obtained from the same soft segment. The possible reason is that the thermal stability of phosphorus-containing groups is poor.

The char yield of PUE-1 is 24 % which is higher than that of PUE-3 (16 %). The possible reasons for this are, first, the three PUEs made from 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) all contain chlorine which belongs to halogen. Halogen is considered to be a flame retardant. Its role is generally played through gas flames, where halogen compounds inhibit the gas chain reaction and their decomposition products of inert material can be diluted with the concentration of combustible medium; furthermore, the char yield is related to rigid groups, the increase of which (aromatic rings, *etc.*) is conducive to improving the char forming ability. Comparing PUE-1 with PUE-3, the molecular weight of the soft segments of PUE-1 is lower, so its high content of hard segments reaches 32.7 %. This means it includes more hard segments which are conducive to char forming, so the char yield of PUE-1 increases.

In PPUEs, the char yield also increases while the soft segment molecular weight decreases and the char yield of PPUE-1, PPUE-2, PPUE-3 is 35, 29 and 24 %, respectively. Increasing char formation can limit the production of combustible carbon-containing gases, thereby improving flame-retardancy[10].

The char yield of PPUE-1 is high due to the following two possible reasons. In PPUEs, phosphorus plays the role of a flame retardant. From PPUE-1 to PPUE-3, with the increase of the molecular weight of soft segment and the isocyanate index and the coefficient of chain expansion are constant, the phosphorus content in PPUEs decreases, the phosphorus content in PPUE-1 is 1.6 % and it decreases to 0.9 % in PPUE-3. Phosphorus is generally considered as a carbon accelerator, so the increase of the phosphorus content improves the performance of the material into carbon; moreover, the content of rigid groups (aromatic rings, *etc*.) which can improve the char forming ability decreases from PPUE-1 to PPUE-3 with an increase in the molecular weight of soft segments.

PPUE-1 and PUE-1 have the same type of soft segments, R and chain extension coefficient except for the type of chain extender. The char yield of PPUE-1 is 35 % and the char yield of PUE-1 is just 24 %. PPUE-2, PUE-2, PPUE-3 and PUE-3 are all made from different chain extenders (with other components being the same), respectively. The char yield of PUE-2 is 17 % and char yield of PPUE-2 increases to 29 %. The char yield of PPUE-3 is 24 %, higher than PUE-3 whose char yield is 16 %. It is obvious that the introduction of phosphorus into the polyurethane elastomers has greatly increased the amount of residual carbon.

In fact, phosphorus is thought to enhance the material's char yield, especially for oxygen containing polymers[10]. Moreover, there are P-N bonds in PDAP and a synergistic effect may exist between the two flame-retardant elements in the combustion process[11].

Flame retardant property of PPUEs: The micro combustion calorimeter (MCC) is one of the most effective bench scale methods for investigating the combustion properties of polymer materials (Table-2). The total heat release (THR) and specific heat release rate (SHRR) are good predictors of flammability[12,13].

TABLE-2
RESULTS OF MICRO COMBUSTION CALORIMETER
OF PUE-1 AND PPUES

Samples	PHRR (W/g)	THR (KJ/g)	Ignition temperature (ºC)
PUE-1	174.9	11.3	444.1
PPUE-1	82.2	7.7	381.2
PPUE-2	135.0	9.7	444.5
PPUE-3	163.0	11.1	448.0

As shown in Table-2, the peak heat release rate (PHRR) and total heat release (THR) of PPUE-1 are 82.2 W/g and 7.7 KJ/g, respectively and the two parameters of PUE-1 are both higher, up to 174.9 W/g and 11.3 KJ/g, respectively. It is believed that the phosphorus element is responsible for the decreasing heat release rate. The phosphorus content could reduce the heat release rate by providing less fuel and more char. The phenomenon could be explained by the following. From the TGA result (Tables 3 and 4), it is clear that the phosphorus can enhance the material's char yield and increasing char formation can limit the production of combustible carbon-containing gases[14], decreasing the exothermicity due to pyrolysis reactions, as well as decreasing the thermal conductivity of the surface of the burning materials, which could prevent the underlying materials from further burning and retard the pyrolysis.

TABLE-3
THERMOGRAVIMETRIC DATA OF PUE-1

Sample	β (K min^{-1})	T_{p1} (ºC)	T_{p2} (ºC)
PUE-1	10	294.2	419.2
	20	306.5	426.1
	30	318.8	433.7

TABLE-4
THERMOGRAVIMETRIC DATA OF PPUE-1

Sample	β (K min^{-1})	T_{p1} (ºC)	T_{p2} (ºC)
PPUE-1	10	258.6	383.8
	20	265.3	389.0
	30	277.5	394.7

From PPUE-3 to PPUE-1, the PHRR and THR decrease from 163.9 W/g and 11.1 KJ/g to 82.2 W/g and 7.7 KJ/g, respectively, which means that the flame retardation of PPUEs increases with the increase in the phosphorus contents. The possible reason is that phosphorus as a flame-retardant element enhances the flame retardation efficiently.

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-1. This means that PPUE-1 has the maximum flammable gas release rate. From PPUE-1 to PPUE-3, the ignition temperature increases from 381.2-448.0 ºC. The possible reason is that, with the increasing of the molecular weight of the soft segment, the hard segment and phosphorus content of PPUE-3 are the lowest, so the ignition temperature of PPUE-3 is the highest.

Kinetics of thermal degradation: Kinetic function of thermal degradation can be expressed by the Kissinger's method.

$$\ln\left[\frac{\beta}{T_p^2}\right] = \ln\left[\frac{RA}{E}\right] - \frac{E}{R}\frac{1}{T_p} \qquad (1)$$

where A represents the pre-exponential factor; E, activation energy; R, gas constant; T_p, absolute temperature at the maximum rate of reaction; β, rate of temperature increase; respectively.

Corresponding T_p is obtained at different heating rates, to ln [β/T_p^2] can get on 1/T_p drawing a straight line. Slope and intercept, respectively, can be obtained through the E and A (Table-5).

The results are identical to the range of polyurethane degradation activation energy in related literature[15,16].

Degradation of polyurethane elastomer is divided into two stages. The T_p of the first stage of PUE made from MOCA is about 30 K higher than the corresponding PPUE and the activation energy of PUE1 is 15 KJ/mol higher than the corresponding PPUE. The possible reason is that the introduction of phosphorus-containing groups results in poor thermal stability of PPUEs. The T_p of the second stage of PUE is also about 30 K higher than PPUE, but the activation energy of PPUE is higher than that of PUE in this stage: the activation energy of the former is about 286.3 KJ/mol which is about 56 KJ/mol higher than PUE. It means that in phosphorus-containing

TABLE-5
ACTIVATION ENERGY OF PUE-1 AND PPUE-1

Sample	β (K min^{-1})	T_p (K)	$1/T_p$ (1/K)	ln (β/T_p^2) (K^{-1} min^{-1})	E_k (KJ/mol)
PUE-1 (1)*	10	567.4	0.001762425	-10.37954	115.2
	20	579.7	0.00172503	-9.72929	
	30	592	0.001689189	-9.36582	
PPUE-1 (1)*	10	526.4	0.001899696	-10.22954	100.2
	20	538.5	0.00185701	-9.58184	
	30	550.7	0.001815871	-9.22118	
PUE-1 (2)*	10	692.4	0.001444252	-10.77774	230.7
	20	699.3	0.001430001	-10.10443	
	30	710.3	0.001407856	-9.73018	
PPUE-1 (2)*	10	654.4	0.001528117	-10.66485	286.3
	20	662.2	0.001510118	-9.9954	
	30	667.9	0.00149723	-9.60708	

*PUE-1(1) and PPUE-1(1) are the first peak in DTG of PUE-1and PPUE-1. *PUE-1(2) and PPUE-1(2) are the second peak in DTG of PUE-1 and PPUE-1.

polyurethane elastomer, the phosphorus-containing group is first broken down to form a protective char on the material which plays a role in isolating heat and oxygen in the further degradation of the material and increasing the activation energy, thereby protecting the materials, which demonstrates the specific performance of the condensed phase of phosphorus and the result is also corresponding to the char yield mentioned before.

Conclusion

PDAP was synthesized from phenyl dichlorophosphate and its structure was confirmed by FTIR, ^{1}H and ^{31}P NMR. Phosphorus-containing polyurethane elastomers were obtained with two-step polymerization based on PDAP.

Thermogravimetric results reveal that the thermal stability of PPUEs is a little lower than that of PUEs based on MOCA, but the char yield of PPUEs is much higher, With the content of P increasing from 0.9-1.6 % (PPUE3 to PPUE1), the char yield increases from 24-35 %, indicating that the phosphorus content increase contributes to the improved char-forming which plays an important role in flame retardation.

Microscale combustion calorimetry results show that with the same soft segment, PPUE-1 shows much better flame-retardancy than PUE-1 and the flame retardancy of PPUEs increases with the increase of hard segments.

The degradation kinetics studies show that the degradation of polyurethane elastomer is divided into two stages, where the activation energy of PPUEs in the first stage is lower than that of corresponding PUEs based on MOCA, but the activation energy in the second stage is higher.

The results demonstrate the successful synthesis of a novel polyurethane chain extender with phosphonic amide groups, which may be potential fire-retardant materials.

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