Preparation and Properties of Flame Retardant Poly(urethane-imide)s Containing Phosphine Oxide Moiety

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ABSTRACT: The preparation of new poly(urethane-imide)s (PUIs) having acceptable thermal stability and higher flame resistance was aimed. Two new aromatic diisocyanate-containing methyldiphenylphosphine oxide and triphenylphosphine oxide moieties were synthesized via Curtius rearrangement *in situ* and polymerized by various prepared diols. Four aliphatic hydroxy terminated aromatic based diols were synthesized by the reaction between ethylene carbonate and various diphenolic substances. Chemical structures of monomers and polymers were characterized by FTIR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy. Thermal stabilities and decomposition behaviors of the PUIs were tested by DSC and TGA. Thermal measurements indicate that the polymers have high thermal stability and produce high char. Polymers exhibit quite high fire resistance, evaluated by fire test UL-94. The films of the polymers were prepared by casting the solution. Inherent viscosities, solubilities, and water absorbtion behaviors of the polymers were reported in. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1329–1338, 2009

Key words: fire retardant polymers; phosphorus-containing polymers; poly(urethane-imide)s

INTRODUCTION

Polyurethanes have been extensively applied in various areas of industry, such as construction, automotive, vehicles, upholstery, medicine etc., and in many household appliances because of their excellent physical and mechanical properties. Low solvent and heat resistance are their major disadvantages. Their acceptable mechanical properties vanish above 70–80°C and thermal degradation takes place above 180°C. To overcome this disadvantages, chemically modified and thermally more stable polyurethanes have been synthesized by either blending or copolymerization. Polyurethane copolymers are commonly prepared, such as poly(urethane-imide)s (PUIs), poly(urethane-epoxie)s, poly(urethane-diacetylene)s, and poly(urethane-amide)s.[1] Polyimides are one of high-performance engineering plastics with their high thermal stability, excellent mechanical strength, high thermooxidative stability and superior electrical insulation, and chemical properties.[2,3] The polyimide materials can be processed into various material forms, such as thin films, fibers, foams, adhesive film, coatings, dry powders, and fiber-coated pre-preg, however, they have also two major shortcomings for wide application.[4] Unless carefully designed, they have inferior solubility in most organic solvents and processing difficulties due to the high melting points and/or glass transition temperatures.[5,6] To overcome these shortcomings, various attempts have been made with the aim of synthetic modifications of the rigid-chain structure by the introduction of flexible bridging linkages,[7] the distortion of molecular symmetry by meta- or ortho-oriented phenylene linkages and the introduction of bulky groups into the polymer chain without sacrificing their high thermal stability. Copolymerization is a method used to overcome these limitations. Poly(ester-imide)s,[8–10] poly(siloxane-imide)s,[11,12] PUIs,[13–15] poly(ether-imide)s,[16–19] and poly(amide-imide)s[20–23] are the well-known copolymers of polyimides. As a result, by the introduction of imide groups into the polyurethane structure, it is possible to obtain a thermally more stable and easily processable polyurethanes. Moreover, polyurethanes are easily flammable materials, widely used in construction of vehicles, such as automotive, marine, and aircraft. To improve flame resistance of polyurethanes, two approaches have been used (1) copolymerization with comonomers containing elements or groups such as P, Si, S, or X; (2) additive method, where additives containing such groups. The first method is more preferable for high-performance polymers.[24–28]

In this work, the synthesis of new PUIs having higher thermal stability and higher flame resistance was aimed. The synthesis was designed as first the preparation of diacyl azide-containing bisimide part, which has phosphorus atom and then its conversion to diisocyanate via Curtius rearrangement.[29–32] The obtained diisocyanate monomer with imide links was directly polymerized *in situ* with diols containing bromine, fluorine, and phosphorus atoms. In general, it is also preferrable that the most carbonylazides are readily converted to corresponding isocyanates *in situ*, and polyurethanes have been prepared by the reaction with hydroxylic compounds, in literature.[33–37] By this way, new poly(urethane-imide)s having highly aromatic structure and containing phosphorus and halogen atoms in would be expected to give higher thermal stability and flame resistance than the that of their related polyurethane polymers.

EXPERIMENTAL

Materials

All chemicals used in this work were purchased from Aldrich, Fluka, and Merck Chemical and were used as received. Dimethylsulfoxide (DMSO), N,N-dimethyl formamide (DMF), N,N-dimethylacetamide (DMAc) and N-methyl-2-pyrrolidinone (NMP) were purified by distillation under reduced pressure over calcium hydride and stored over 4-A° molecular sieves. Toluene and THF were purified by distillation under reduced pressure over metallic sodium and stored over 4-A° molecular sieves. All other solvents were obtained from various commercial sources and used without further purification.

Measurements

The inherent viscosities of 0.5 g/dL solution of the resulting PUIs were measured with an Ubbelohde type capillary viscometer at 25°C in NMP. FTIR spectra were recorded on a FTIR-8400 SHIMADZU spectrometer. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on a 500-MHz Bruker Avance 500 MHz spectrometer. Elementel analyses were performed by a FlashEA1112 Automatic Elemental Analyzer. DSC analyses were performed on a Perkin–Elmer DSC Pyris 1 differential scanning calorimeter at a scanning rate of 10°C/min under nitrogen purge at a rate of 30 mL/min. Data was recorded at a second run after quenching at 180°C. TGA was conducted with a Perkin–Elmer Pyris 1-TGA and the experiments were performed at a heating rate of 10°C/min both in flowing nitrogen atmosphere and in air, in a temperature range of 50–910°C. X-ray diffraction patterns were performed at room tempera-
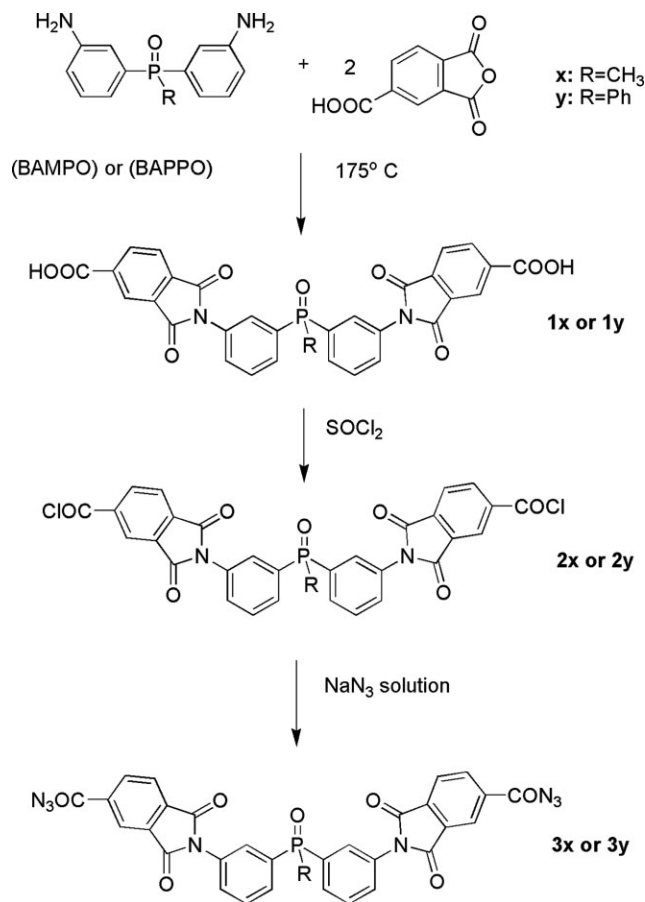
Scheme 1 Synthesis of the dicarbonylazide monomers, **3x** and **3y**.

tures with powdered specimens by aRigaku Multiflex XRD with Cu Kα radiation ($\lambda = 1.5418$ Å) in the range $2\theta = 3$–60 with a scan speed of 3°/min and a step increment of 0.02°.

Water absorbtion test was performed according to ASTM D570-98. Test samples were initially conditioned for 24 h at 50°C before immersing them in deionized water at 25 ± 0.5°C for 24 h. The water absorbtion capacities of polymer samples were calculated from the weight difference between dried and those soaked in water. Flame resistant behavior was determined on the prepared samples according to UL-94 standard.

Synthesis of the dicarbonylazide monomers

Dicarbonylazide monomers, bis[3-(N-trimellitimidoylazide)phenyl] methylphosphine oxide **3x** and bis[3-(N-trimellitimidoylazide)phenyl] phenylphosphine oxide **3y** were synthesized[29,30] as illustrated in Scheme 1. Starting diamino compounds bis(3-aminophenyl)methylphosphine oxide (BAMPO) and bis(3-aminophenyl)phenyl phosphine oxide (BAPPO) were synthesized according to the procedure

reported in the literature.[38,39] BAMPO with a yield of 65%, M.p. 154–156°C, (Lit: 154–156°C) and BAPPO with a yield of 70%, M.p. 203°C, (Lit: 203–205°C) were obtained as white powders.

Synthesis of bis[3-(N-trimellitimide)phenyl] methyl phosphine oxide 1a

A mixture of trimellitic anhydride (1.92 g, 9.8 mmol) and bis-(3-aminophenyl) methyl phosphine oxide (BAMPO) (1.37 g, 4.9 mmol) in dried DMAc (50 mL) were stirred at room temperature for 6 h. Amic acid was precipitated from methanol (300 mL), filtered and dried under vacuum for 24 h. Amic acid was obtained as a pale yellow solid with high yield, about 90%.[40] Bulk imidization was performed in an oven at 175°C for 24 h. Bisimide was purified by dissolving in DMF and reprecipitating from methanol several times. Product was obtained as a dark orange solid. Total Yield: 84%, M.p. 310–314°C, (Lit: not reported). FTIR (KBr, cm^{-1}); 3450, 1780 and 1725(C=O, imide),1484, 1425, 1377, 1188(Ar-P=O), 727. ^{1}H NMR (DMSO-d$_6$, δ, ppm): 2.1 (s, 3H), 7.5–8.6 (m,14H), 10.8 (s, 2H). Microanalysis calcd. for C$_{31}$H$_{19}$N$_2$O$_9$P MA: 593.88: C, 62.63%, H, 3.22%, N, 4.71%. Found: C, 62.46%, H, 3.36%, N, 4.79%.

Synthesis of bis[3-(N-trimellitimide)phenyl] phenyl phosphine oxide 1b

The same procedure reported in that of 1a. was conducted with bis-(3-amino phenyl) phenylphosphine oxide (BAPPO) and stoichiometrical amounts of required reagents. Product was a dark yellow solid. Yield: 88%, M.p. 305–308°C, (Lit[25]: >300°C). FTIR (KBr, cm^{-1}) 3354, 1782, and 1724 (C=O, imide), 1591, 1484, 1425, 1377, 1219, 1188(Ar-P=O), 727. ^{1}H NMR (DMSO-d$_6$, δ, ppm) 7.5–8.6 (m,19H), 10.9 (s, 2H). Microanalysis calcd. for C$_{36}$H$_{21}$N$_2$O$_9$P MA: 656.4: C, 65.33%, H, 3.10%, N, 4.21%. Found: C, 65.46%, H, 3.21%, N, 4.18%.

Synthesis of bis[3-(N-trimellitimidoylchloride) phenyl]methyl phosphine oxide 2a

Dicarboxylic acid bisimide 1a (10 g, 1.68 mmol) was refluxed with an excess amount of thionyl chloride for 10 h under nitrogen atmosphere, a few drops of pyridine was added as catalyst. Unreacted excess SOCl$_2$ was removed under reduced pressure. The residue was washed with n-hexane and dried at 90°C under nitrogen atmosphere. Crude product was purified by dissolving in dried chloroform, evaporation of solvent followed by filtration of chloroform insoluble impurities. Product is isolated as a pale yellow dust. Yield: 90%, M.p. 215–218°C, (Lit: not reported). FTIR (KBr, cm^{-1}) 3430, 1768 (CO-Cl),

1782 and 1725(C=O,imide), 1589, 1483, 1425, 1371, 1188(Ar-P=O), 723.

Synthesis of bis[3-(N-trimellitimidoylchloride) phenyl]phenyl phosphine oxide 2b

The same procedure reported in that of 2a was conducted with corresponding starting material 1b and required reagents. Yield: 90%, M.p. 227–230°C, (Lit: not reported). FTIR (KBr, cm^{-1}) 3430, 1770(CO-Cl), 1782 and 1724(C=O,imide), 1483, 1425, 1373, 1219, 1188(Ar-P=O), 895, 723.

Synthesis of bis[3-(N-trimellitimidoylazido) phenyl]methyl phosphine oxide 3a

In a three-necked round-bottomed flask equipped with a dropping funnel and a nitrogen gas inlet, 2a (10 g, 15.8 mmol) in a solution of chloroform (160 mL) was added dropwise into the solution of activated sodium azide (3.081 g, 47.4 mmol) in water (40 mL), and then stirred at 10–15°C for 48 h under nitrogen atmosphere until all the acid chloride 2a disappeared. After water (50 mL) was added, chloroform phase was separated, washed with distilled water and 5% sodium carbonate solution, respectively, and then dried under reduced pressure. Product is a pale yellow solid. Yield: 73%, M.p. >80°C. (Lit: not reported). FTIR (KBr, cm^{-1}) 3061–2980, 2144(azido group), 1778 and 1722(C=O, imide), 1680 cm^{-1} (azido C=O stretching), 1608, 1510, 1427, 1371, 1247, 1215, 1182(Ar-P=O), 1093, 754. ^{1}H NMR (CDCl$_3$, δ, ppm) 1.3(3H,s, CH$_3$), and 6.8–8.6 (14H,m,aromatic). ^{31}P NMR spectrum gave a peak for phosphorus at 13.60 ppm. Microanalysis calcd. for C$_{31}$H$_{17}$N$_8$O$_7$P MA: 644.49: C, 57.77%, H, 2.66%, N, 17.39%. Found: C, 57.89%, H, 2.78%, N, 16.91%.

Synthesis of bis[3-(N-trimellitimidoylazido) phenyl]phenyl phosphine oxide 3b

The same procedure reported in that of 3a. was conducted with corresponding starting materials and stoichiometrical amounts of required reagents. Yield: 78%, M.p. >80°C. (Lit: not reported). FTIR (KBr, cm^{-1}) 3060–2983cm^{-1}, 2144 (azido group), 1780 and 1722(C=O, imide), 1583, 1483, 1427, 1375, 1278, 1247, 1211, 1182 (Ar-P=O), 1111, 1093, 893, 750. ^{1}H NMR (CDCl$_3$, δ, ppm) 6.9–8.5(19H,m,aromatic). ^{31}P NMR spectrum gave a peak for phosphorus at 13.75 ppm. Microanalysis calcd. for C$_{36}$H$_{19}$N$_8$O$_7$P MA: 707.49: C, 61.06%, H, 2.68%, N, 15.83%. Found: C, 61.51%, H, 2.81%, N, 15.69%.

Synthesis of the diol monomers

Diol monomers 4a–d were synthesized according to the procedure reported in the literature,[41,42] the
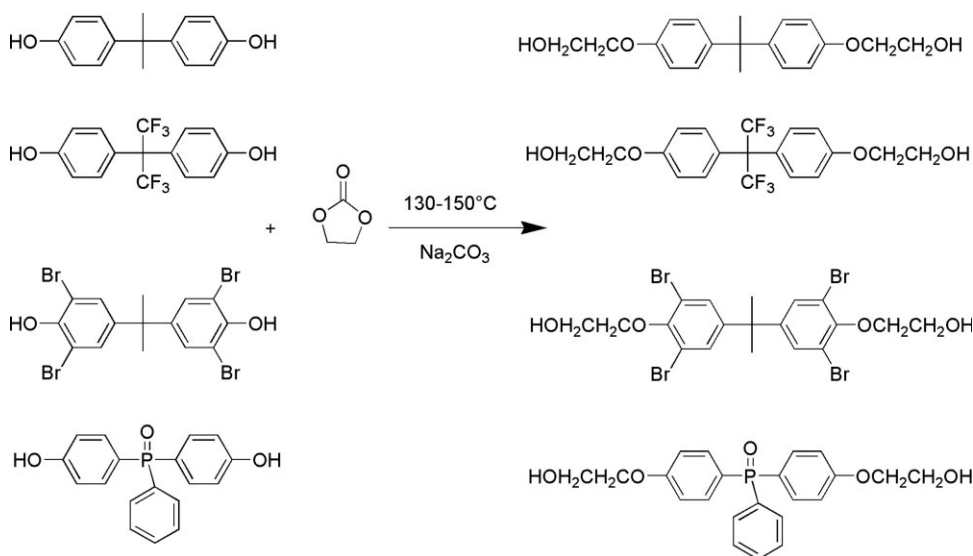
Scheme 2 Synthetic route to diol monomers **4a-d**.

method is given in Scheme 2. Three commercial diphenols, bisphenol A, hexafluoro-bisphenol A and tetrabromo-bisphenol A were used directly as received. Bis-(4-hydroxyphenyl)phenyl phosphine oxide was prepared according to the literature.[43–45] Some characteristics of the synthesized diols are given in Table I.

RESULT AND DISCUSSION

Monomer synthesis and characterization

Dicarboxylic acid azides, bis[3-(N-trimellitimidoylazido)phenyl] methylphosphine oxide **3x** and bis[3-(N-trimellitimidoylazido)phenyl] phenylphosphine oxide **3y** were synthesized by the similar route. The purification is rather difficult because of the heat-sensitive azide moieties. As well known, the purity of monomers is a vital parameter to obtain a polymer with high-molecular weight in condensation polymerizations. The chemical structure and purity of the resulting dicarboxylic acid azides were confirmed by FTIR, ^{1}H NMR, ^{31}P NMR, and elementel analysis. The FTIR spectra of the compounds showed common absorption peaks at about 2144

cm^{-1} (azido group), 1778, and 1722 cm^{-1} (C=O, imide), 1371 cm^{-1} (imide ring vibration), 1247 cm^{-1} (Ar-P=O), 1215cm^{-1}, 1182 cm^{-1} (Ar-P=O), 1093cm^{-1}. ^{1}H NMR spectra exhibited characteristic peaks at 1.3 ppm (3H,s, CH$_3$), and 6.8–8.6 ppm (m, aromatic) for **3x** and 6.9–8.5 ppm (m, aromatic) for **3y**. The presence of phosphorus atoms was confirmed by the ^{31}P NMR spectrum, which revealed a singlet resonance at 27.74 for **3x** and at 26.47 for **3y**.

Polymer synthesis and characterization

Preparation of the PUIs

Preparation of polyurethane was applied as given in literature,[29,30] synthesis was illustrated in Scheme 3. As a representative procedure, in the synthesis of PUI **5a**; diol **4a** (0.84 g, 3.7 mmol, 20% excess) in 5 mL of dried DMF was added dropwise into the dried DMF solution (5 mL) of dicarbonyl azide **3x** (2 g, 3.1 mmol) under nitrogen atmosphere at room temperature and then three drops of catalyst, dibutyltindilaurate (DBTL), was added and the temperature was raised to 90°C. After stirring the mixture for 3 h, additional dicarbonyl azide **3x** (0.6 g,

TABLE I
Synthesis and Some Characteristics of Diols 4a–d

Diol monomer	% Yield	Appearance	Melting point
4a	80	White crystalline powder	105°C (Lit: 105°C) [19]
4b	68	White crystalline powder	121–125°C (Lit: 109–125°C) [23]
4c	86	Pale yellow crystalline powder	96–97°C (Lit: 97–98°C) [19,23]
4d	70	Pale yellow powder	56–59°C (Lit: not reported)
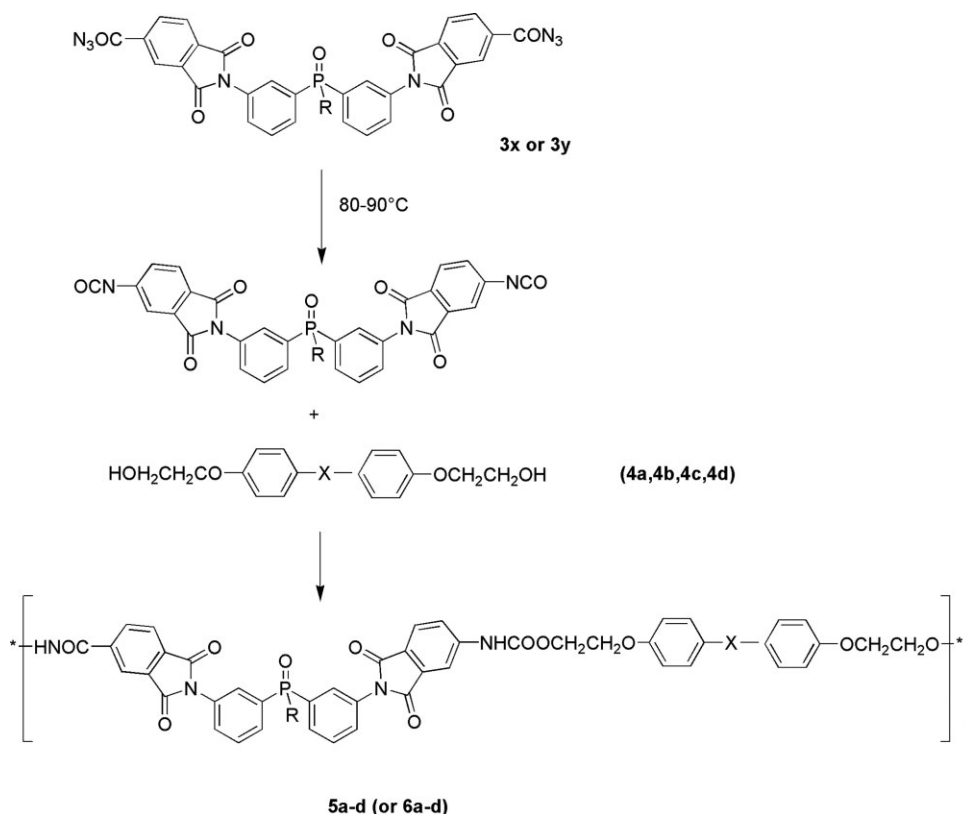
Scheme 3 Preparation of the PUIs.

0.93 mmol) was added to attain the stoichiometric amount of diisocyanate molecule for polymerization and further stirred for 4 h more at 120°C. Reaction mixture was added into MeOH : water (19 : 1) mixture (200 mL) drop by drop to allow the precipitation of polymer. Crude polymer was filtered, washed several times by hot MeOH and dried under reduced pressure. (1.54 g), total yield, including isocyanate formation and polyaddition was about: 51.8%.

PUIs **5b, 5c, 5d** were synthesized by the similar method given above. The dicarboxylic acid azide **3y** was used to prepare other four PUIs **6a–d**. Mono-

mers and their corresponding polymers are given in Table II.

The thermal decomposition of dicarboxylic acid azide via Curtius rearrangement gave the corresponding diisocyanates *in situ*. And then, these diisocyanate compounds were treated with four dihydroxylic compounds to prepare the new PUIs. Reaction was performed in dry DMF by the addition of a few drops of catalyst, DBTL. The structure of the eight PUIs **5a–d** and **6a–d** were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy.

TABLE II
Synthesis and Some Characteristics of Poly(urethane-imide)s

Polymer	Monomers	% Yield	η_{inh}[a] (dl /g)	η_{inh}[b] (dl /g)	Appearance	Film properties[c]
5a	**4a** and **3x**	51.8	0.204	0.264	Light yellow powder	Brittle,transparent light brown
5b	**4b** and **3x**	45.9	0.115	0.162	Pale yellow powder	Brittle,transparent yellow
5c	**4c** and **3x**	39.2	0.087	0.120	Yellow powder	Brittle,transparent dark brown
5d	**4d** and **3x**	42.9	0.176	0.234	Light yellow powder	Brittle,transparent dark yellow
6a	**4a** and **3y**	55.3	0.258	0.323	Yellow powder	Brittle,light brown
6b	**4b** and **3y**	48.0	0.188	0.230	Dark yellow powder	Brittle,transparent light brown
6c	**4c** and **3y**	48.0	0.124	0.161	Dark yellow powder	Brittle,dark brown
6d	**4d** and **3y**	49.6	0.175	0.260	Yellow powder	Brittle,transparent dark yellow

[a] Initial amounts of diazides/diols is equimolar.
[b] After the addition of excess diazides.
[c] The films of the PUIs were prepared by casting from the 10% solution in NMP.
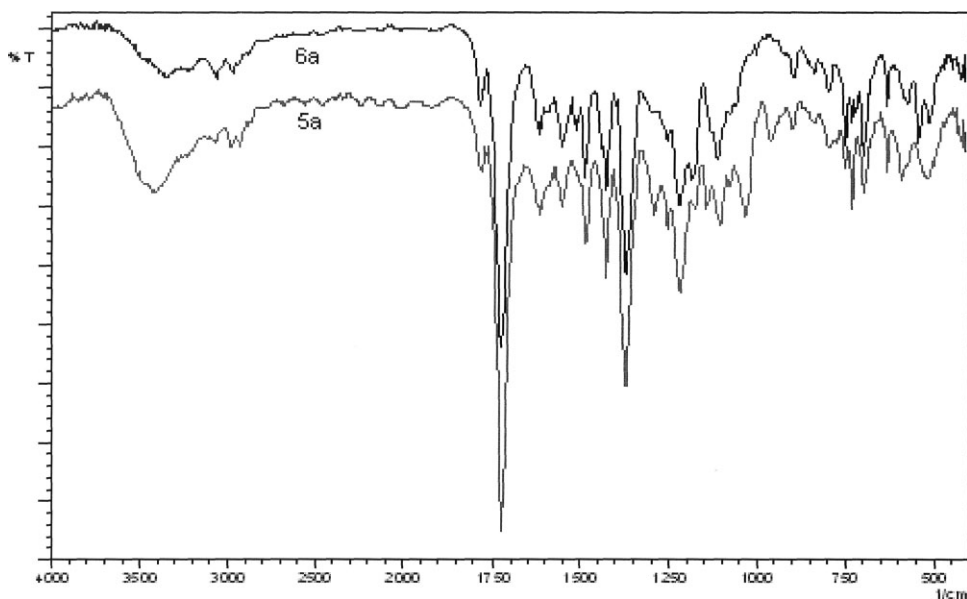The solvent was evaporated in vacuo at 40°C for 12 h, 60°C for 24 h.

Figure 1 The representative FTIR spectra of **5a** and **6a**.

The FTIR spectra of all polymers showed bands around 3360 cm^{-1} (urethane N—H bonds stretching), 1780 and 1724 cm^{-1} (imide C=O stretching), and 1184–1174 cm^{-1} (Ar-P=O stretching). Urethane carbonyl vibration, which is normally observed at about 1705–1680 cm^{-1}, did not differentiate and imide carbonyl vibration are observed together. The representative FTIR spectra of **5a** and **6a** are given in Figure 1. The chemical structure of the PUIs were further confirmed by the presence of a broad NH— proton signal at 6.6 ppm by ^{1}H NMR. The signal at 3.7–4.55 ppm (8H,m,CH$_2$CH$_2$) showed the existance of aliphatic ethylene groups on polymer chains. Isopropylidene protons (6H,s,CH$_3$CCH$_3$) of diol part and methylene

protons of methyl group bonded to phosphorus atom were detected at 1.6 and 1.3 ppm, respectively. The aromatic ring protons appeared as multiplet in the region of 6.9–8.6 ppm. The representative ^{1}H NMR spectra of **5a** and **6a** are given in Figure 2. The presence of phosphorus atoms was confirmed by the ^{31}P NMR spectrum, which revealed a singlet resonance at about 27.87 ppm for polymers **5a–c** and at 26.22 ppm for **6a–c**. Further two of the polymers **5d** and **6d** containing two different phosphorus atoms in their repeating unit, showed two signals at 27.84 and 25.52 ppm for **5d** and at 26.17 and 25.49 ppm for **6d**.

Polymers were synthesized in relatively low yields of 40 to 55%, summarized in Table II. Main reason
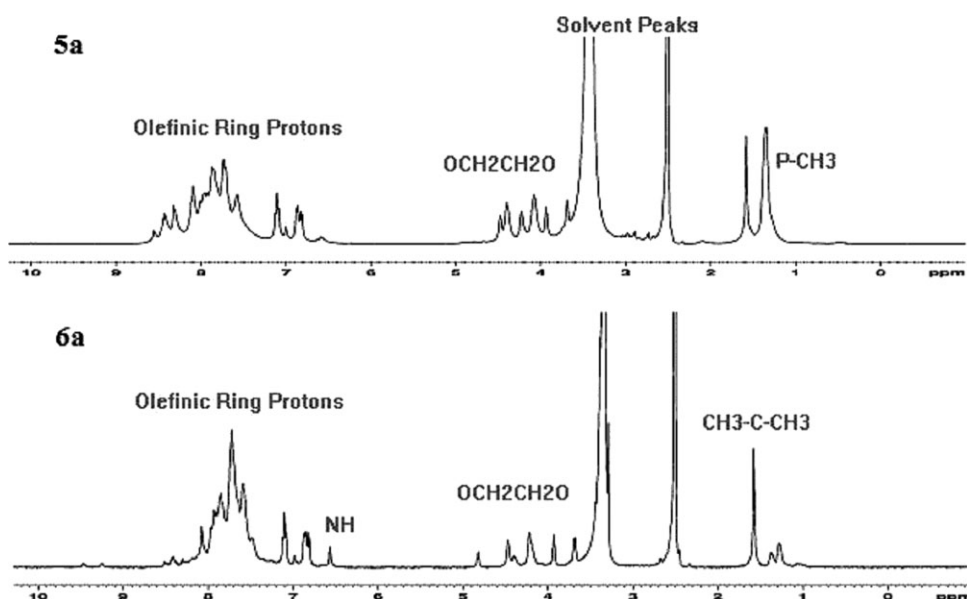

Figure 2 The representative ^{1}H NMR spectra of **5a** and **6a**.

TABLE III
Solubility and the Water Absorbtion of Poly(urethane-imide)s

Polymer	DMAc	DMSO	DMF	NMP	THF	Acetone	CHCl$_3$	% Water uptake[a]
5a	+	+	+	+	±	−	±	7.67
5b	+	+	+	+	−	−	−	6.52
5c	+	+	+	+	±	−	±	7.89
5d	+	+	+	+	±	−	±	10.38
6a	+	+	+	+	±	−	±	6.20
6b	+	+	+	+	−	−	−	6.46
6c	+	+	+	+	−	−	−	6.81
6d	+	+	+	+	±	−	±	10.30

A solution of 10 mg/mL; (+)soluble at room temperature; (±) partially soluble on heating; (−) insoluble.
[a] Acc. to ASTM D570-98.

of the low yield could be the mechanism of rearrangement reaction and applied reaction procedure. Further, several side reactions, as the ester formation between diols and diazides, might be responsible to some extent. To increase the yield together with molecular weight, a 30–50% excess amount of dicarboxylic acid azide was added during the polymerization process alternately. Unfortunately, the yield of polymers could be increased only about 5–10%, together with the increase of molecular weight. Molecular weight change was monitored by the increase in the inherent viscosity about 25–30%. Further, the method of addition of diols after heat treatment of dicarbonyl azides to convert to diisocyanate was performed to eliminate the possible reaction of ester formation between dicarbonyl azides and diol monomers. This work did not increase the yield. However, in our case, the yield of ester formation reaction is not expected as high as that of the reaction occurs by lower alcohols, as methanol.[46] The findings shows that the preparation of diisocyanate monomer via Curtius rearrangement *in situ* causes mainly the stoichiometric imbalance for the next step of polymerization. The stoichiometric imbalance results in the low yield of the PUIs and low molecu-

lar weights. The yield of low-molecular weight PUIs in such a synthetic route have also been reported previously in literature.[29,36,37] Moreover, the use of an isocyanate monomer prepared *in situ* by the Curtius rearrangement in performing a polymerization reaction results in commonly the low yield and lower molecular weight products.[47,48]

Properties of polymers

The films of the polymers were prepared by casting from the NMP solution. The PUIs films were transparent but brittle in all cases. The findings are predictable that the polymer had the fully aromatic and highly imidized rigid structure in chain as well as the low-molecular weight of the PUIs. Some characteristics of the PUIs was given in Table II. All of the polymers were soluble in polar aprotic solvents, such as DMAc, DMF, DMSO, and NMP, at room temperature. Solubility characteristics of PUIs were given in Table III. In wide-angle X-ray diffractograms of polymers, the curves had broad peaks that are characteristic of amorphous polymers. No polymers showed any sharp peaks of well-defined long-range order structure, given in Figure 3.
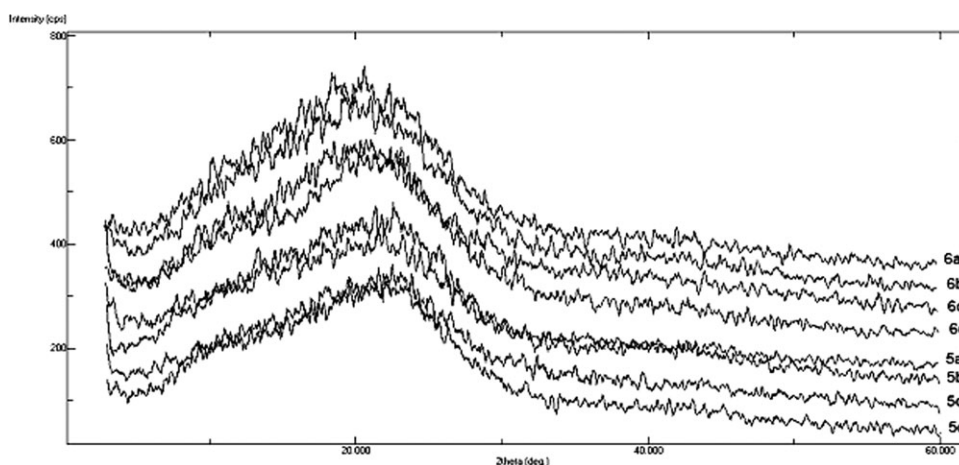

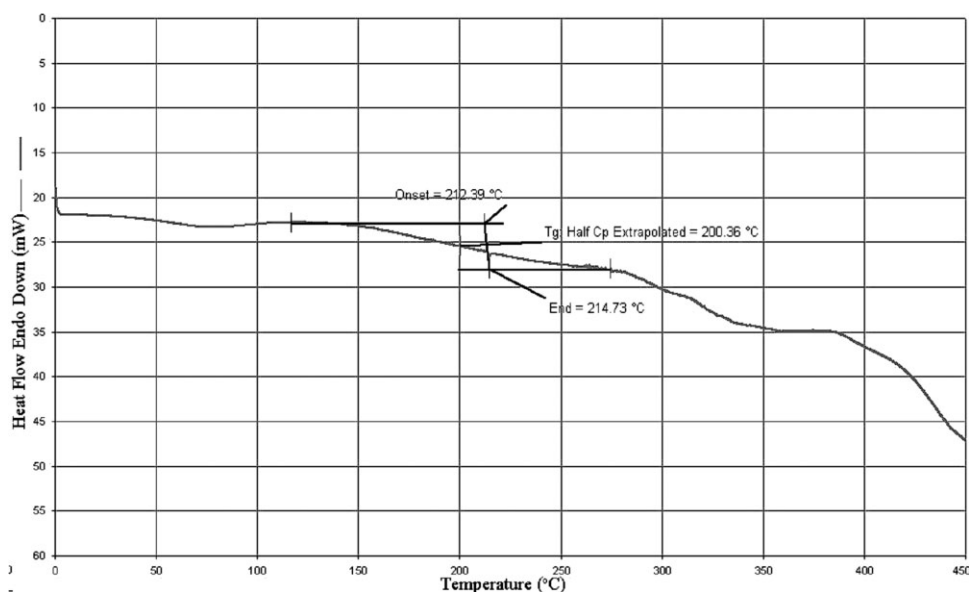**Figure 3** The WAXD spectra of polymers **5a–d** and **6a–d**.

Figure 4   The DSC thermogram of polymer **5d**.

The new PUIs absorb in a consiberable amounts of water, in the range of 5–10%, because both urethane and imide groups have a capacity of absorbing water molecules. Six of the PUIs **5a–c** and **6a–c** showed very close percentage of water absorbtion, but **5d** and **6d** containing an extra triphenylphosphine oxide moiety exhibited higher water absorbtion value than those of others.

Thermal and flame retardant properties

It was observed that eight PUIs exhibited similar trends on their thermal behaviors. The insertion of imide links into the polyurethane molecules increases T_g values up. Further, their fully aromatic structure is the other factor for an elevated T_g value. All eight PUIs have T_g values in the range of 191–211°C depending on the diol components, this matches the T_g of aromatic PUIs, found in literature.[2,29] All the PUIs synthesized exhibited lower T_g's than the aromatic polyimides and some copolyimides, such as poly(ether-imide)s, poly(amideimide)s, and the poly(ester-imide) because of the relative rigidity of imide, amide, ether and ester bonds than those of urethane linkages. However, they showed higher T_g values than the aromatic polyurethanes. Polymers 5c and 6c, containing tetrabrominated hydroxylic components, have the lowest T_g relative to the others. This might be due to the bulky bromine atoms, which prevent the close interaction between polymer chains. Further, T_g PUIs **6a–d** are somewhat higher than those of PUIs 5a–d. This could be attributed to the incorporation of extra phenyl group on triphenylphosphine moiety along the polymers backbone, which restricted the free rota-

tion of the polymer chains leading to an enhanced T_g. It is noticable that T_g values and the temperatures where the decomposition of the urethane linkages begin overlap in the same region. Frequently, it might be controversial to find a definite and correct T_g value for PUIs. A representative DSC thermogram of **5d** is given in Figure 4.

They also displayed similar thermooxidative behavior up to 300°C. New PUIs showed mainly a two-stage decomposition trend at elevated temperatures. The first stage of weight losses might be attributed to the degradation of the urethane linkages, about 25%, between 200 and 450°C. This stage involves the loss of decomposition fragments in two main parts, at 200–400 °C and 400–500°C. The second weight loss was observed above 400°C because of the breakage of imide bonds. Imide bonds of PUIs **5a–d** start to break at a relatively lower temperature (~450°C) than those of PUIs **6a–d** (~550°C).

TABLE IV
Thermal Properties of Poly(urethane-imide)s

	T_g (°C)[a]	T_{10} (°C)[b]	Char yield[c] %w at 900°C in nitrogen	Char yield[d] %w at 800°C in air
5a	211	327	50.4	51
5b	204	322	50.0	50
5c	191	326	44.8	32
5d	201	324	49.8	47
6a	220	326	49.0	44
6b	214	344	52.6	52
6c	201	326	45.4	30
6d	218	320	51.9	47

[a] DSC measurements with a heating rate of 10°C /min in nitrogen atmosphere from the second heating traces.
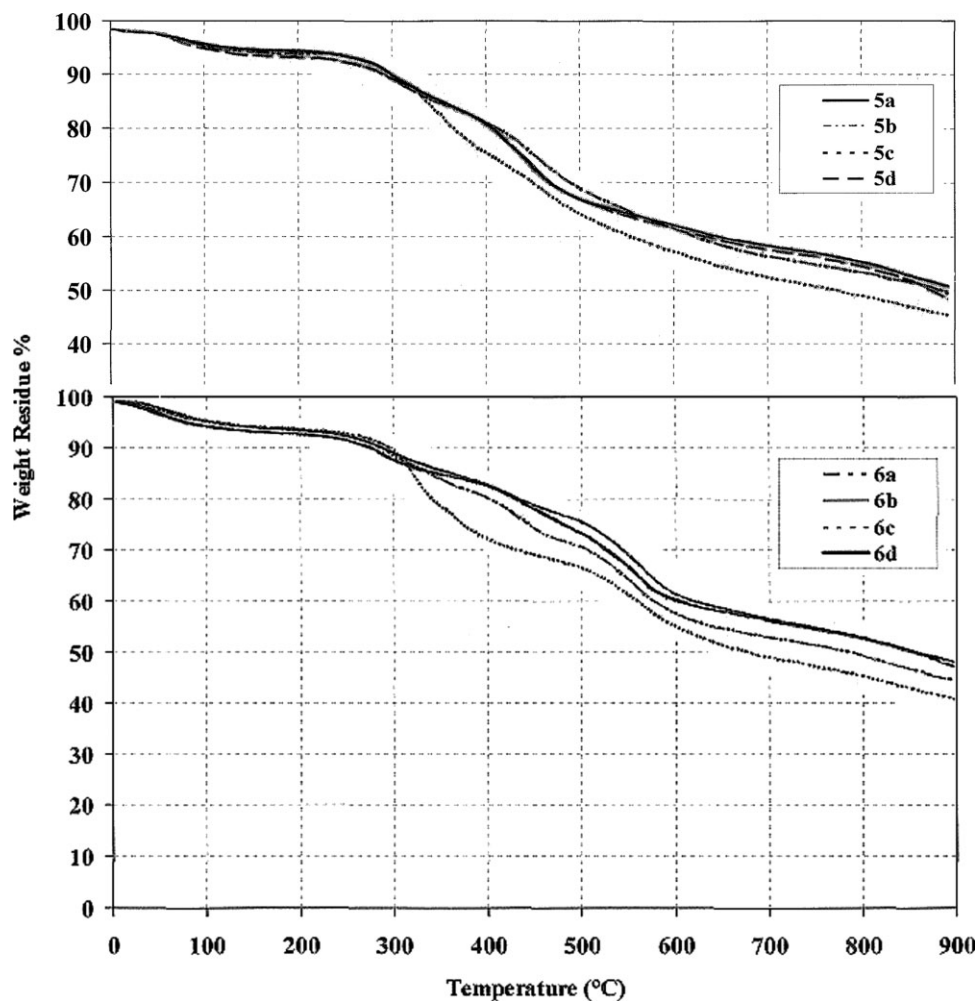[b] Temperature at which 10% weight loss was recorded by TGA in state atmosphere.

Figure 5 The TGA thermogram of polymers **5a–d** and **6a–d** in nitrogen atmosphere.

In the TGAs of PUIs, **5a–d**, it was observed that the second part of the urethane decomposition stage overlaps with the decomposition stage of imide bonds. This might be because of the early loss of methyl groups at lower temperature induces the degradation of imid links. The weaker bond strength of a methyl-phosphorus covalent bond (272 kJ/mole) relative to a phenyl-phosphorus bond (322 kJ/mole) is known. Further, an additional weight loss about 5–7% was observed in the thermograms of **5c** and **6c** bearing brominated segments due to the thermal degradation of bromine-carbon links at about 220–350°C. Furthermore, char yields of PUIs in nitrogen atmosphere and in air are found to be about 50% at 900°C and 50% at 800°C, respectively. Polymers containing brominated diol segments **5c, 6c** in chain produce lower char (about 5%) compared with others. These high char yields may imply the flame retardancy of new PUIs. The results were reported in Table IV. The TGA thermogram of polymers **5a–d** and **6a–d** were given in Figure 5.

The flame retardancy of the PUIs was examined by the test according to UL-94 standard method. All the eight PUIs belong to the burning behavior class, V-0. Test samples did not exhibit melting or burning tendency. The formation of flaming particles or drops was not observed. After flame plus after glow time for each specimen were found as ≤5 sec. During flaming, samples require a continuous flame for burning. Further polymers undergo a structural change together with the evolution of gaseous molecules by the decomposition at high temperatures, they transform a spongy, bright black porous residues.[49] This high resistance to flame might be attributed to the fully aromatic structure of polymer molecules together with the presence of phosphorus and halogen atoms in the structures. A considerable difference was not detected between the PUIs **5a–d** containing methyl group and **6a–d** containing phenyl group in the diisocyanate monomers.

CONCLUSION

The main objective of this study was to obtain new PUIs exhibiting fire resistant as well as improved solubility and the thermal stability. The synthetic

route to diisocyanate formation is not a frequently followed way because of low yield of Curtis rearrangement. The eight PUIs were synthesized successively by the reaction of two diisocyanates prepared from dicarboxylic acid azide **3x, 3y** *in situ* and four various diols. Both dicarboxylic acid azides contain phenyl-phosphorus moiety and imide functional groups. Diols **4a–d** were prepared from diphenols containing the atoms fluorine, bromine, and phosphorus. The polymers exhibited higher heat resistance in comparison with aromatic polyurethanes because of the thermally stable imide groups. In addition, they have high fire resistance because of the presence of phosphorus and halogen atoms together with highly aromatic structure. Their thermal stability and flame resistance is considerable despite their low molecular weight.

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