

## Synthesis and Characterization of Inherently Flame-Retardant and Anti-Dripping Thermoplastic Poly(imides-urethane)s

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**ABSTRACT:** A series of thermoplastic poly(imide-urethane)s (TPIUs), based on 4,4'-diphenylmethane diisocyanate (MDI) and pyromellitic anhydride (PMDA) as hard segments and poly(tetrahydrofuran) (PTMG) as soft segments, has been prepared by a two-step polymerization process. The objective of this study is to prepare a type of intrinsically flame-retardant polyurethane by incorporating PMDA as a flame retardant in the main chains. The thermal behavior and flame retardancies of the TPIUs have been characterized by thermal gravimetric (TG) analysis and limiting oxygen index (LOI), UL-94 vertical burning, cone calorimeter tests. The results indicate that the TPIUs display outstanding performance. The temperature at 5% mass loss ( $T_{5\%}$ ) and LOI value increase with the hard-segment contents, while the total heat released (THR) and peak heat release rate (p-HRR) show the opposite trend. Furthermore, the  $T_{5\%}$  of TPIU211 (molar ratio: MDI : PTMG : PMDA = 2 : 1 : 1) is 33.2°C higher than that of the conventional thermoplastic polyurethane TPU211 (molar ratio: MDI : PTMG : 1,4-butanediol = 2 : 1 : 1), and the THR and p-HRR of TPIU211 are 14.62% and 64.02% lower than the respective parameters of TPU211. In addition, UL-94 vertical burning tests show that the TPIUs exhibit excellent antidripping effects. The ultimate tensile strengths of the TPIUs reached 23.1–37.6 MPa with increasing hard segment contents, which meets the requirement of mechanical properties with regard to practical use. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40801.

**KEYWORDS:** copolymers; elastomers; polyimides; properties and characterization; thermoplastics

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### INTRODUCTION

Thermoplastic polyurethanes (TPUs) are segmented block copolymers composed of alternating hard and soft segments. They belong to one of the most versatile types of engineering thermoplastics known as thermoplastic elastomers. As TPUs exhibit many favorable properties, such as high tensile and flexural fatigue strength, excellent low-temperature flexibility, outstanding wear resistance, and abrasion resistance, as well as environmental resistance (humidity, ozone, UV-radiation, microbes), they are widely used in coatings,<sup>1</sup> films,<sup>2</sup> foams,<sup>3</sup> biomaterials,<sup>4</sup> synthetic leathers,<sup>5,6</sup> and adhesives.<sup>6</sup>

TPUs are among the most useful of commercial polymer materials, with applications in both industry and daily life. However, as they are organic polymers, their flame retardancy and thermal stability are poor, and therefore need improvement to meet industrial safety standards.<sup>7,8</sup> Their serious melt dripping behavior is also an important factor that restricts their applications.

Therefore, increased emphasis has been placed on the development of technologies that promote the flame retardancy and thermal stability of TPUs.<sup>9–11</sup>

In general, there are two methods used for achieving flame retardancy and thermal stability in polymers, namely, “additive” and “reactive” types. Additive materials include inorganic compounds,<sup>12–16</sup> as well as phosphorus,<sup>17</sup> nitrogen,<sup>18–20</sup> and silicon-containing materials.<sup>21</sup> They are widely used and generally incorporated into polymers by physical means. Their deployment provides the most economical and expeditious approach for promoting flame retardancy and enhancing the thermal properties of TPUs. Nevertheless, a variety of problems, such as poor compatibility, leaching, and deterioration in the mechanical properties of composites prepared in this manner diminish its appeal. Therefore, there has been increasing interest in the use of reactive materials. Application of reactive flame retardants involves either the design of new, intrinsically flame-retardant polymers or the modification of existing polymers through

copolymerization with a flame-retardant unit either in the main chain or as a pendant group. The modification approach is the favored method because it covalently incorporates the flame-retardant unit in the polymer backbone and thus imparts permanent flame retardancy. It also allows retention of the physical and mechanical properties of the original TPUs.<sup>22</sup>

With a view to improving the flame retardancy of TPUs, the majority of research efforts in this area have been centered on incorporating phosphorus-containing groups into the polymer backbone.<sup>22–27</sup> The results of such studies show that incorporation of such units into polymer chains at a suitable content can lead to remarkable improvements in the flame retardancy of TPUs. However, the resulting TPUs are less thermally stable than the corresponding phosphorus-free polyurethane. In 2005, Yuan et al.<sup>28</sup> prepared a kind of polyurethane that incorporated aromatic phosphate-containing cyclotriphosphazene flame retardant in the main chain, which exhibited a slightly higher initial decomposition temperature (by approximately 8°C) than the phosphorus-free polyurethane. It is necessary to prepare novel TPUs not only with excellent flame retardancy but also with better thermal stability. Our group has reported an inherently flame-retarded PUIB based on novel diol-containing imide and alkynyl groups,<sup>6</sup> which showed a V-2 ranking in UL-94 vertical burning tests. However, the PUIB exhibited poor mechanical properties and hence were of no practical value. Therefore, it is important to develop a new kind of polyurethane that not only shows excellent flame retardancy and thermal stability, but also outstanding mechanical properties.

Polyimides with inherent flame retardancy are important heterocycle-based polymers with superior mechanical properties and remarkable heat resistance. In 1985, Masiulani<sup>29</sup> introduced imide groups into polymer chains for the first time to prepare thermally stable TPUs. In recent years, there have been numerous literature reports of the thermal stability of TPUs being improved by introducing heterocyclic imide groups into their polymer chains.<sup>30–34</sup>

However, there has been relatively little research concerning the flame retardancy of TPUs incorporating imide groups. Özarslan et al.<sup>35</sup> reported the use of polyimide and triphenylphosphine oxide moieties as flame retardants in polyurethane, but the flame retardancy was only assessed by the UL-94 vertical burning test. In this study, we have incorporated different contents of pyromellitic dianhydride (PMDA) into the main chain of TPUs, and the flame retardancies of the resulting TPIUs have been systematically investigated by UL-94 vertical burning, limiting oxygen index (LOI), cone calorimeter tests. It was expected that new poly(imide-urethane)s incorporating rigid aromatic polyimides, displaying higher thermal stability and flame resistance than that of their related TPUs, would thereby be obtained. Meanwhile, the mechanical properties, thermal stability, and flame-retardant mechanism of these copolymers have been investigated and, most importantly, compared to those of conventional TPUs.

## EXPERIMENTAL

### Materials

4,4'-Diphenylmethane diisocyanate (MDI) was provided by Nipoh Polyurethane Industry and was used as received. Poly(tetrahydrofuran) (PTMG) (number-average molecular weight

( $M_n$ ) = 2000 g/mol) was purchased from Aladdin Reagent (China). PMDA was purchased from Sinopharm Chemical Reagent. 1,4-Butanediol (1,4-BDO) and dimethylformamide (DMF) were purchased from Beijing Chemical Reagents Company. PTMG and 1,4-BDO were dried in a vacuum oven at 110°C for at least 2 h prior to use.

### Measurements

Fourier-transform infrared spectroscopy (FTIR) analysis was conducted on a NICOLET 6700 IR spectrometer. The spectra were collected through 32 scans with a spectral resolution of 4 cm<sup>-1</sup>.

Thermal gravimetric (TG) analysis was performed with a NETZSCH 209 F1 thermal analyzer at a heating rate of 10°C/min under a nitrogen atmosphere, and the temperature ranged from 40°C to 600°C. Elemental analysis was performed on a Flash EA 1112 automatic elemental analyzer.

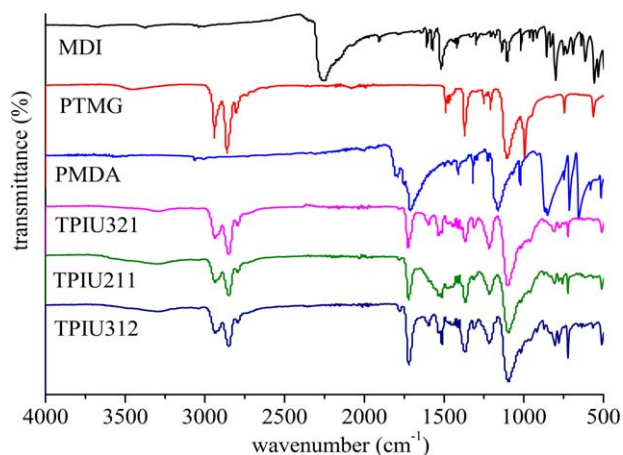
Differential scanning calorimetry (DSC) was performed on a Netzsch 200 F3 instrument (Selb, Germany). The specimens were measured starting from 20°C and heating to 220°C at a rate of 10°C/min and held at this temperature for 1 min in a nitrogen atmosphere to eliminate the effect of their thermal history. Afterwards, the specimens were quenched to -85°C at a rate of 10°C/min. Subsequently, the thermograms of the specimens were again obtained by using a heating rate of 10°C/min from -85°C to 220°C.

The viscoelastic behavior of the samples (5 × 5 × 3 mm<sup>3</sup>) was analyzed on a dynamic mechanical analysis (DMA) IV instrument (Rheometric Scientific, USA) in tensile mode at a frequency of 1 Hz and with a heating rate of 2°C/min in nitrogen atmosphere, and the temperature range of study was from -80°C to 60°C.

Dumbbell-shaped specimens of TPIUs were cut through using a metallic die and then stored at 23°C and 50% relative humidity for at least 12 h before testing. The specimens had a width of 10 mm at the neck and a thickness of 1–2 mm. Tensile tests were carried out at a cross-head deformation speed of 500 mm/min on a Universal Testing Machine Tension according to the ASTM D 638-91 method. For each plaque of TPIU, at least five specimens were tested, giving the average tensile strength with at least a 95% confidence level for statistical significance.

Gel-permeation chromatography (GPC) analysis was carried out on a Waters Breeze<sup>TM</sup> 2 HPLC system with a 2414 refractive index detector and a 1515 pump. The GPC columns were high-temperature 3, 4, and 5. Tetrahydrofuran (THF) was used as a carrier solvent, and monodisperse polystyrene standards were used for instrument calibration. The column temperature was maintained at 40°C and the flow rate was 1 mL/min. The sample was first dissolved in DMF, then diluted to 4 mg/mL in THF, and finally injected into the system. Data obtained from the detector were analyzed using Polymer Laboratories "Caliber" software.

Shore D hardness tests were conducted by employing an LX-A model apparatus, at room temperature, according to ASTM D 2240-75, in several regions of the samples. Vertical burning tests were performed according to UL-94 standard with samples of dimensions 125 × 12.5 × 3.2 mm<sup>3</sup>. In this test, the samples were classed as V-0, V-1, V-2, or unclassified according to their behavior (dripping of burning material and burning time).



**Figure 1.** The FTIR spectra of MDI, PTMG, PMAD, TPIU321, TPIU211, and TPIU312. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Combustion experiments were performed with a cone calorimeter device (Fire Testing Technology). Samples of dimensions  $100 \times 100 \times 3 \text{ mm}^3$  were exposed to a radiant cone ( $50 \text{ kW/m}^2$ ).

#### Polymer Synthesis

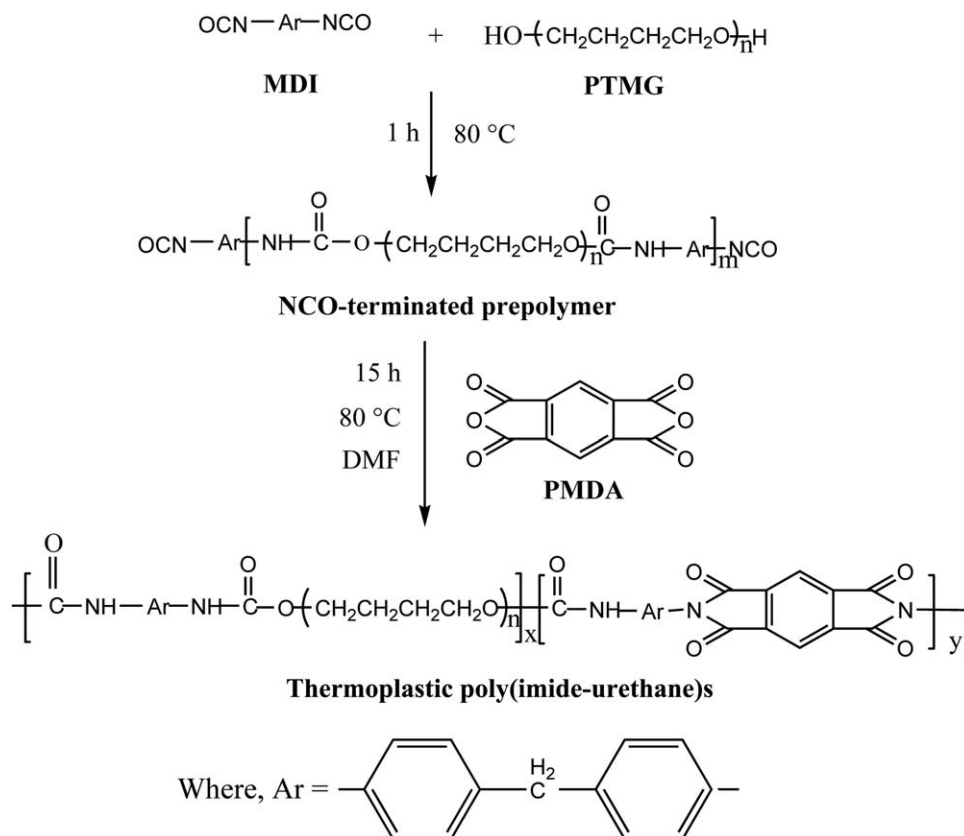
PMDA and MDI were utilized as hard segments for the fabrication of novel TPIUs with PTMG ( $M_n = 2000 \text{ g/mol}$ ) as soft segments. Each kind of MDI-based thermoplastic segmented TPIU was prepared at a molar ratio of  $\text{NCO}/(\text{OH} + \text{anhydride}) = 1.00$ , according to Scheme 1. Typically, the synthesis of TPIUs was

**Table I.** Elemental Analysis of TPIUs

Sample designation	Molar ratio (MDI : PTMG : PMDA)		Elemental analysis (%)		
			C	H	N
TPIU321	3 : 2 : 1	Calc.	66.85	9.75	1.69
		Found	67.54	9.86	1.71
TPIU211	2 : 1 : 1	Calc.	66.62	9.13	2.06
		Found	67.08	9.24	2.04
TPIU312	3 : 1 : 2	Calc.	66.25	8.17	2.64
		Found	66.84	8.53	2.79

carried out in a three-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and an  $\text{N}_2$  inlet. The mass ratio and molar ratios of reagents for various TPIUs are summarized in Table V.

An appropriate amount of PTMG was added to a flask containing a quantitative amount of molten MDI and the reaction mixture was stirred for 1 h at  $80^\circ\text{C}$ . Thereafter, the appropriate amount of chain extender (PMDA) was dissolved in DMF and the solution was added to the above flask. The total solid content of the reaction mixture was fixed at 25 wt %. The mixture was vigorously stirred under  $\text{N}_2$  atmosphere for a further 15 h. Finally, the product was poured into a poly(tetrafluoroethylene) (PTFE) mold and placed in an oven to evaporate the DMF.



**Scheme 1.** Preparation of TPIU.

**Table II.** The Compositions and Characterizations of TPIU

Sample designation	Wt % of hard segment	$M_n \times 10^4$	$M_w/M_n$	Tensile strength (MPa)	Elongation at break (%)	Hardness
TPIU321	19.5	5.04	1.65	23.1 ± 3.2	822 ± 24	68
TPIU211	26.4	5.07	1.62	34.4 ± 5.2	788 ± 28	80
TPIU312	37.3	8.86	1.80	37.6 ± 4.7	748 ± 16	94

To compare the flame retardancy of the novel TPIUs with that of conventional TPUs, 1,4-BDO-based thermoplastic polyurethane with a molar ratio of MDI : PTMG : 1,4-BDO = 2:1:1 (TPU211) was also synthesized.

The sample designation codes provide information about the category of polymers and molar ratios. For example, TPIU321 indicates that the polymer was synthesized using PMDA as a chain extender and the molar ratio of MDI : PTMG : PMDA was 3 : 2 : 1.

## RESULTS AND DISCUSSION

### FTIR Spectroscopy and Elemental Analysis

To investigate the extent of reaction for the three TPIUs, FTIR spectra of MDI, PTMG, PMDA, and TPIUs (Figure 1) were examined. The spectrum of TPIU211 is considered as a representative spectrum for the TPIU polymers, because the three spectra are very similar. In the spectrum of TPIU211, bands at 2900–2700  $\text{cm}^{-1}$  are attributable to the stretching vibration of the  $-\text{CH}_2-$  group in PTMG. The characteristic band of  $-\text{NCO}$  in MDI at about 2270  $\text{cm}^{-1}$  had almost disappeared, indicating that MDI and PTMG had been incorporated into TPIU. The spectrum of TPIU211 exhibits the characteristic absorptions of  $\text{C}=\text{O}$  stretching vibrations at 1780 and 1720  $\text{cm}^{-1}$ , as well as a  $\text{C}-\text{N}-\text{C}$  stretching vibration at 1368  $\text{cm}^{-1}$ , indicating that the imide groups had been introduced into the backbone of TPIU211 by the reaction. The band at about 1000–1200  $\text{cm}^{-1}$  in the spectrum of TPIU211 is attributed to the stretching vibration of the  $\text{C}-\text{O}$  groups. All of the aforementioned bands imply successful preparation of the TPIU polymers.

Elemental analysis values of the resulting TPIUs are listed in Table I. Because PTMG is a compound, the calculated elemental contents only can be obtained through testing by elemental analysis. The contents of C and H in PTMG are 66.54% and 11.31%, respectively. It can be seen that the calculated results of TPIUs are well consistent with the found ones.

**Table III.** Solubility Properties of TPIU

Sample designation	NMP	DMF	DMAc	$\text{CH}_2\text{Cl}_2$	THF	Acetone	<i>n</i> -Hexane
TPIU321	□, ○	□, ○	□, ○	△	△	△	△
TPIU211	□, ○	□, ○	□, ○	△	△	△	△
TPIU312	□, ○	□, ○	□, ○	△	△	△	△

□: dissolve by heating; ○: swell at 25°C; △: insoluble.

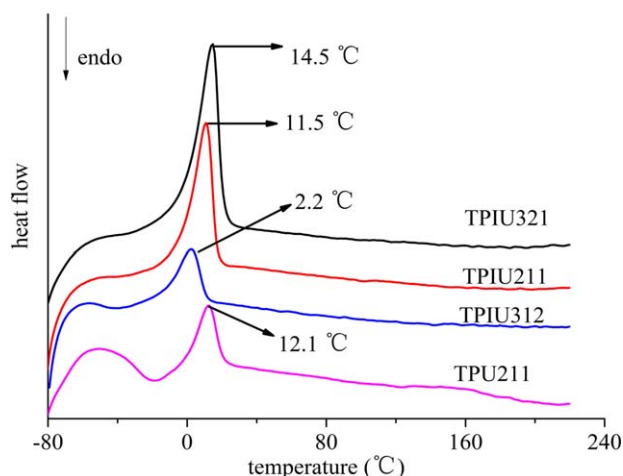
### Mechanical Properties and Molecular Weights of TPIUs

The mechanical properties and molecular weights of the TPIUs were measured on a universal testing machine and by GPC, respectively (results are shown in Table II). The data in Table II clearly indicate that the TPIU polymers display very high tensile strength because of the numerous rigid imide groups incorporated into the hard segments, imparting high chain symmetry and packing efficiency.<sup>5,36</sup> Compared with the maximum values of tensile strength of inherent flame-retardant polyurethane reported by Chen-Yang et al.<sup>22</sup> (approximately 9 MPa) and Tang et al.<sup>6</sup> (approximately 3.56 MPa), the maximum value (37.6 MPa) for the TPIUs is enhanced by more than 317.8% and 956.2%, respectively. Moreover, the tensile strength of TPIU211 is also 22.4 MPa higher than that of conventional TPU211,<sup>6</sup> which meets the requirement of mechanical properties with regard to practical use.

Furthermore, the tensile strength and hardness of the TPIU polymers increased with increasing hard-segment content (from 19.5% to 37.3%); this trend is opposite to that of the elongation at break. This phenomenon could be attributed to the increase in the number-average molecular weight ( $M_n$ ) of the TPIU polymers. The values of  $M_n$  determined by GPC (Table II) increased from  $5.04 \times 10^4$  to  $8.86 \times 10^4$ . The  $M_n$  values of the TPIU samples were in the order TPIU312 > TPIU211 > TPIU321. Although the molar content of high molecular weight of PTMG ( $M_n = 2000$ ) incorporated into the TPIU samples decreased in the order TPIU321 > TPIU211 > TPIU312, the molar content of chain extender (PMDA) increased in this order, and so could not increase the molecular weights of the polymers.

### Solubility

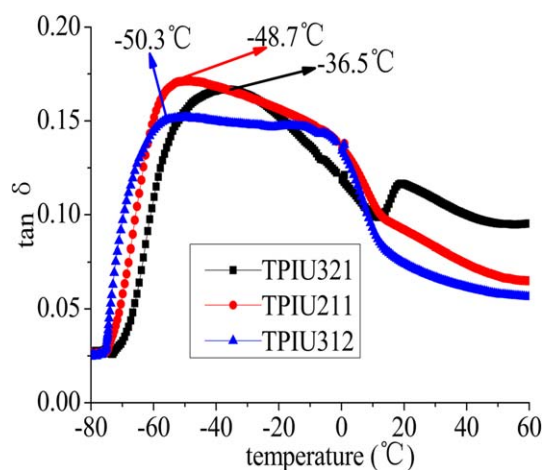
The solubility of the series of TPIUs was examined and the results are summarized in Table III. The TPIUs only swell in polar solvents such as *N*-methyl-2-pyrrolidone, DMF, and dimethylacetamide at room temperature. However, they dissolve completely upon heating at 100°C. Moreover, the TPIUs do not dissolve in THF, acetone,  $\text{CH}_2\text{Cl}_2$ , or *n*-hexane, even when heated.



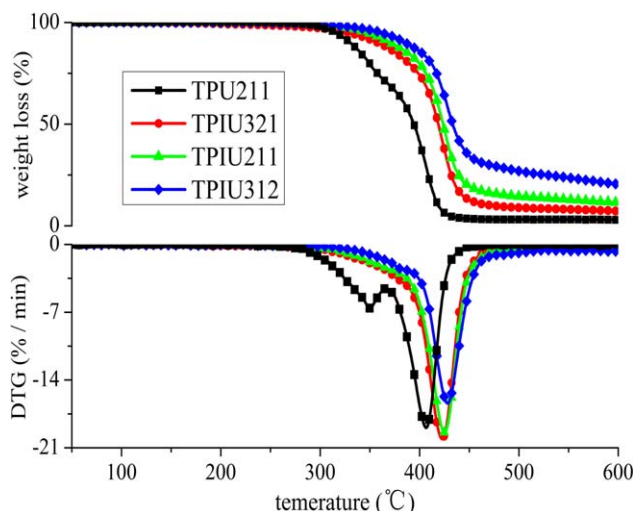
**Figure 2.** The DSC curves of TPU211 and TPIU polymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### DSC and DMA Analysis

Figure 2 shows the DSC thermograms of TPU211 and TPIU polymers with various amounts of hard segments. The DSC curves for TPU211, TPIU321, TPIU211, and TPIU312 (Figure 2) show an endothermic peak at 12.1, 14.5, 11.5, and 2.2°C, respectively. This endothermic peak could be assigned to the melting point of the soft segments. Because they have the same formulation, TPU211 and TPIU211 have similar melting points. A decrease in soft-segment content in the TPIU slightly shifted the crystalline peak areas and melting points of the soft segments to lower values. The lower values of the peak areas may be attributed to the lower contents of the soft segment. Soft segments can crystallize in the TPIU, that is, the copolymer is rich in the soft-segment phase, hence there should be a certain degree of microphase separation. Moreover, the lower melting points indicate that the hard segments have less influence on the soft segments. It can be concluded that the degree of microphase separation increases with increasing hard-segment contents.



**Figure 3.** Tan  $\delta$  curves of TPIU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** TG and DTG curves of TPU211 and TPIU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The tan  $\delta$  versus temperature curves for TPIUs with different hard-segment contents measured by DMA are shown in Figure 3. It can be seen that the curves of tan  $\delta$  gradually show a plateau with increasing hard-segment contents. This is because with increasing hard-segment contents, the molecular chains show greater rigidity and lower activity, resulting in larger friction even after the  $T_g$ , the tan  $\delta$  curves do not decrease rapidly but show a plateau. It is observed that the glass transition temperature of the soft segment,  $T_g$ , shows a slight decrease (from  $-36.5^\circ\text{C}$  to  $-50.3^\circ\text{C}$ ) with increasing hard-segment contents. This means that the compatibility between the hard and soft segments becomes poor, resulting in an increasing degree of microphase separation with increasing hard-segment content, and is consistent with the results of DSC analysis. Compared to the poly(urethane-imide)s reported by Özarşlan et al.,<sup>35</sup> the  $T_g$  of TPIU is lower by about  $240^\circ\text{C}$ , meaning that the TPIU can be used in low-temperature applications.

### TG Analysis

The thermal stabilities of TPU211 and TPIU polymers were investigated by TG performed under a nitrogen atmosphere. In Figure 4, the weight loss and weight loss rate (differential thermogravimetric, DTG) under an inert atmosphere are plotted as functions of temperature. The corresponding TG and DTG data

**Table IV.** Thermal Properties of TPU211 and TPIU

Samples designation	$T_{5\%}$ ( $^\circ\text{C}$ )	$T_{\text{maxs}}$ ( $^\circ\text{C}$ )	Char at 600 $^\circ\text{C}$ (%)
TPU211	314.5	407.1	1.9
TPIU321	328.9	422.8	7.3
TPIU211	347.7	425.8	17.0
TPIU312	363.2	432.2	27.2

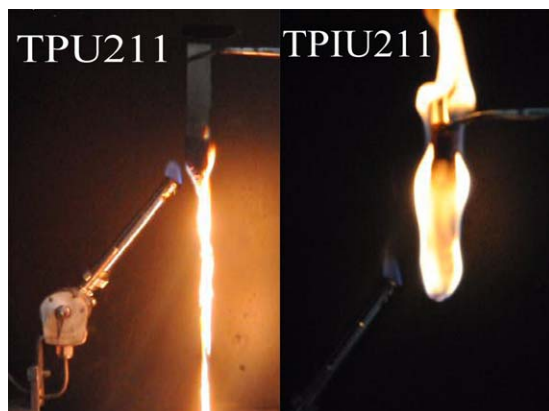
$T_{5\%}$ : defined as the temperature of the samples with the weight loss of 5%.

$T_{\text{maxs}}$ : defined as the decomposition temperature of the maximum weight loss rate.

**Table V.** Results of UL-94 Vertical Burning and LOI

Samples designation	MDI:PTMG:PMDA		Dripping (Yes or No)	UL-94 (3.2 mm)	LOI (%)
	Mass ratio (g)	Molar ratio			
TPU211 <sup>a</sup>	7.50 : 30.00 : 1.35	2:1:1	Yes, $t_1 > 30$ s	No class	19.5
TPIU321	5.62 : 30.00 : 1.64	3:2:1	Slight melting dripping, $t_1 > 30$ s	No class	19.0
TPIU211	7.50 : 30.00 : 3.26	2:1:1	No, $t_1 > 30$ s	No class	19.5
TPIU312	11.25 : 30.00 : 6.54	3:1:2	No, $t_1 > 30$ s	No class	21.0

<sup>a</sup>In TPU211, PMDA is replaced by 1,4-BDO.



**Figure 5.** Digital photos of the TPU211 and TPIU211 during the UL-94 test process. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

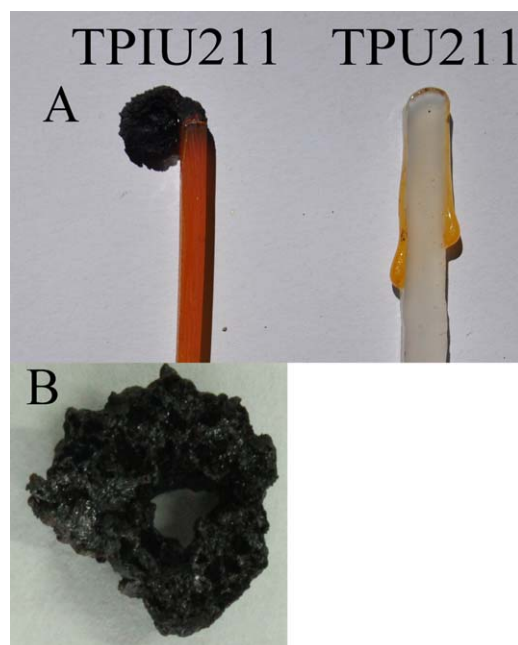


**Figure 6.** Photographs of the inner (A) and outer (B) carbon residues at the bottom of TPIU211 when the burning is up to 60 s. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

are presented in Table IV. The onset degradation temperature ( $T_{5\%}$ ) and the maximum mass loss temperature ( $T_{\max}$ ) are defined as the temperatures at 5% mass loss and the maximum mass loss rate, respectively.

Thermal decomposition of TPU211 occurred in two steps, between 287.5 and 447.7°C, as shown in Figure 4. According to

the literatures,<sup>6,37–39</sup> the first decomposition step between 287.5 and 366.4°C is due to the dissociation of the urethane bonds in the hard segments, which leads to the formation of diisocyanate and diol, as well as the subsequent release of CO<sub>2</sub>.<sup>40–43</sup> The second step (366.4–447.7°C) is ascribed to thermal decomposition of the soft segments.<sup>6,39</sup> At the end of the degradation at 600.0°C, a small amount of stable residue remained (residue, 1.9 wt %). Pyrolytic degradation of TPIU211 occurred in one step, as evidenced by comparison of the TG curve of TPU211 with that of TPIU211 in Figure 4. The TG curve exhibits an initial, smoothly decreasing slope from 300.1 to 386.5°C and rapidly decreases from 386.5 to 480.6°C (final residue at 600.0°C, 17.0 wt %). The higher  $T_{5\%}$  of TPIU211 compared with that of TPU211 (by 33.2°C) may be attributed to the large number of thermally stable heterocyclic imide groups in the main chains. These highly thermostable imide groups also considerably retard the weight loss in the first step. Furthermore, the  $T_{\max}$  of TPIU211 is higher by about 18.7°C compared with that of



**Figure 7.** Digital photos of char residue (A) and the inner carbon residues of TPIU211 (B) after LOI tests. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table VI.** Cone Calorimeter Data for TPU211 and TPIU Polymers

Samples name	TPU211	TPIU321	TPIU211	TPIU312
TTI (s)	30	35	55	65
PHRR (kW/m <sup>2</sup> )	1941.1	1491.2	700.4	524.6
THR (MJ/m <sup>2</sup> )	171.9	156.8	147.4	130.8
Mean COY (kg/kg)	0.08	0.03	0.03	0.02
Mean CO <sub>2</sub> Y (kg/kg)	6.68	3.03	2.66	2.59

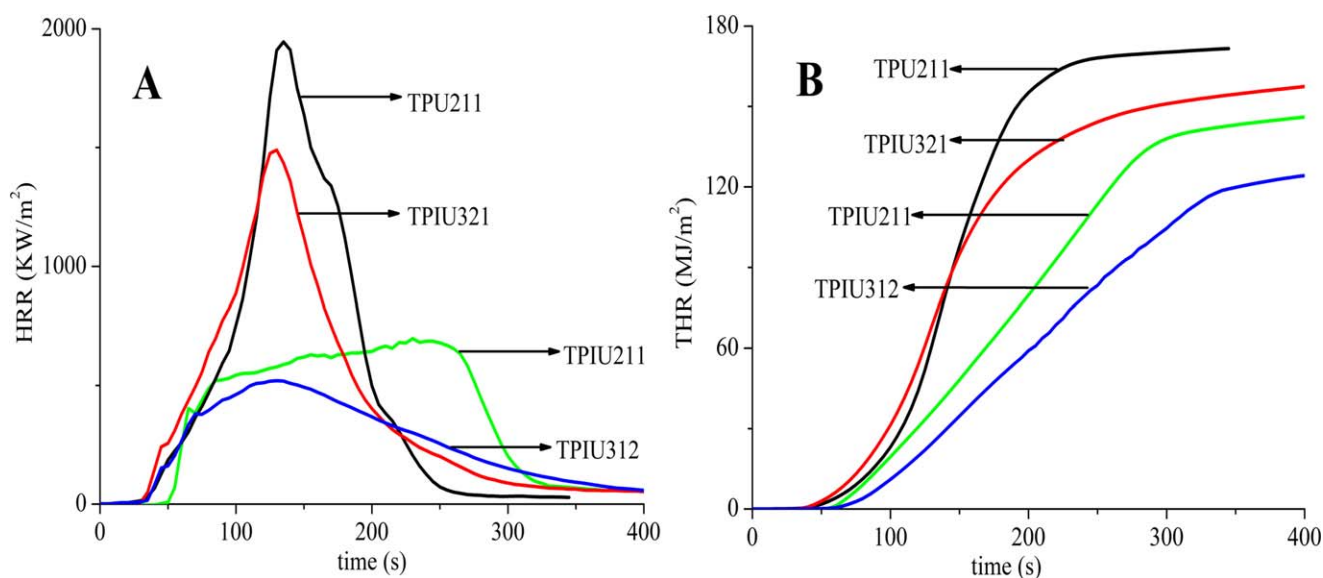
TPU211, indicating that the heterocyclic imide groups contributed to the thermostability of the soft segments.

The TG results of the TPIU polymers show an evident increase in the  $T_{50\%}$  from 328.9°C for TPIU321 to 363.2°C for TPIU312, with a corresponding increase in hard-segment content from 19.5 to 37.3 wt %. This is at variance with a lot of literature reports,<sup>6,22,44</sup> which suggest that intrinsic flame-retardant polyurethanes exhibited lower  $T_{50\%}$  with increasing contents of the flame retardant. Because the hard segments of TPIU include urethane and heterocyclic imide groups, the amount of less thermally stable urethane groups decreases with increasing PMDA content. As the amount of PMDA incorporated into the TPIU samples increases, the amount of PTMG, the soft segment, decreases, which means that the amount of urethane groups in the main chains decreases. This accounts for the increase in thermal stability of TPIU with increasing hard-segment content. Furthermore,  $T_{50\%}$  of TPIU312 is 118.1°C and 74.2°C higher than those of intrinsically flame-retardant PUIB312 (imide and alkynyl-containing flame-retardant)<sup>6</sup> and PPPZ-PU-20 (aromatic phosphate-containing cyclotriphosphazene flame-retardant),<sup>28</sup> respectively, indicating that the incorporation of imide groups leads to TPIUs with excellent thermal stability. Moreover,  $T_{50\%}$  of TPIU312 is even 19.2°C higher than  $T_{10\%}$  (the temperature of the sample at which the weight loss is

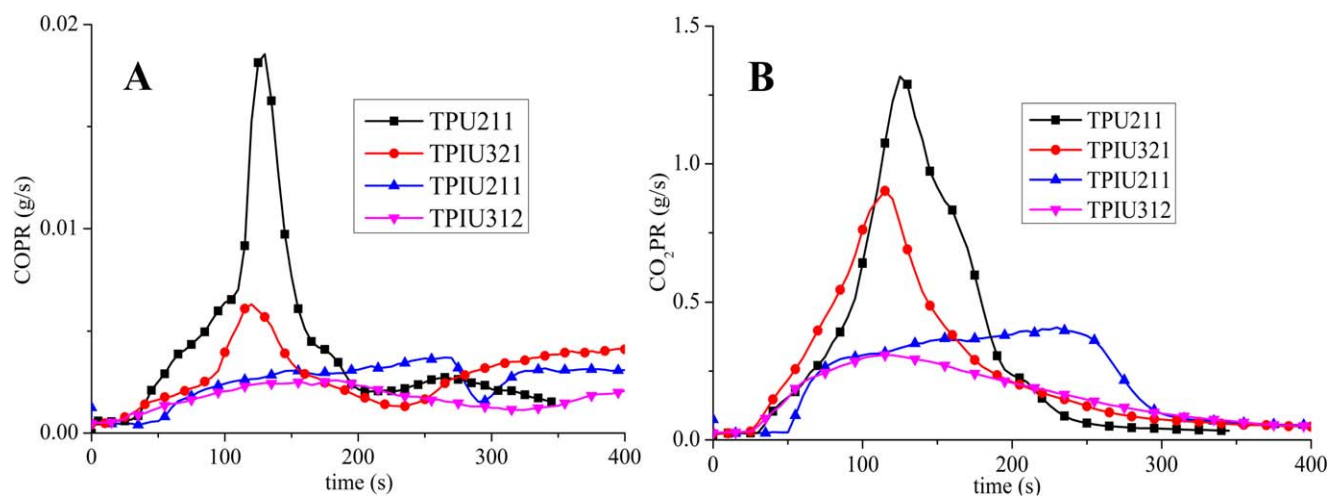
10%) of poly(urethane-imide)s.<sup>35</sup> Additionally, the results for the char residue at 600°C indicate that the amount of char increased from 7.3 to 27.2 wt % with increase in hard-segment content. Therefore, the heterocyclic imide groups contributed to the thermal stability and hence the flame retardancy of the TPIUs.

#### UL-94 Vertical Burning Test and LOI

UL-94 vertical burning classifications and LOI values for TPU211 and TPIU polymers are listed in Table V. Figure 5 shows photographs of TPIU211 and TPU211 during the UL-94 test process. TPU211 showed obvious melt-dripping behavior, and the flame burned up to the clamping. Tang et al.<sup>6</sup> reported that PUIB containing imide and alkynyl groups in the main chain also exhibited serious dripping behavior. On the contrary, although the flame for TPIU211 also burned up to the clamping and without UL-94 classification ( $t_1 > 30$  s), the sample did not exhibit dripping. However, the poly(urethane-imide)s reported by Özarlan et al.<sup>35</sup> showed a V-0 rating in UL-94 tests, which can be attributed to the presence of phosphorus and halogen atoms in their structures. When the flame burned up to 60 s, it was extinguished artificially to study the antidripping effect; photographs of the inner and outer carbon residues at the bottom of TPIU211 are shown in Figure 6. The antidripping effect may be due to the excellent char formation of the heterocyclic



**Figure 8.** The curves of HRR (A) and THR (B) for TPIU and TPU211. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9.** CO (A) and CO<sub>2</sub> (B) production rate of samples with time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

imide groups incorporated into the main chains, as shown in Figure 6. The char layer behaved as “scaffolding” and inhibited melt dripping. This result indicates that the heterocyclic imide groups imparted an excellent antidripping effect. Similarly to TPIU211, TPIU312 also showed no dripping and did not correspond to any classification in the UL-94 vertical burning test. However, TPIU321 showed slight melt dripping because of its lower imide group content. The outer surface of the char from TPIU211 was smooth and neat (Figure 6(B)), but the inner surface of the char from TPIU211 (Figure 6(A)) exhibited many honeycomb-shaped holes. Furthermore, many holes permeated the entire char residue. These holes could be attributed to the large amount of gaseous products produced during the combustion, which caused a marked expansion of the char layer.

The LOI values of the TPIU polymers slightly increased with increasing hard-segment content. When the hard-segment content reached 37.3%, the LOI value was 21.0%. Figure 7 shows photographs of the residual char after the LOI tests for TPU211 and TPIU211. When pure TPU211 was burned, it was melted completely, and at the end of the test some residue was left due to the incomplete combustion. However, the specimen of TPIU211 showed excellent char formation (Figure 7(A)). Nevertheless, it is surprising that the LOI value of TPIU211 is the same as that of TPU211. This abnormal phenomenon may be explained by the inner carbon residue (Figure 7(B)) of TPIU211 after the LOI test. Consistent with the residue of the UL-94 tests, the inner char layer also showed numerous honeycomb-shaped holes; thus, the char could not prevent the contact of oxygen with the materials and did not contribute to the LOI value. This result indicates that the heterocyclic imide groups made no obvious contribution to the LOI of polyurethane.

### Cone Calorimeter Tests

Throughout the previous literature, there have been few accounts of studies of the flame retardancy of intrinsic flame-retardant polyurethanes by cone calorimetry. Thus, to provide more data on this aspect, the flame-retardant performances of TPU211 and TPIU polymers were evaluated by cone calorimeter

tests. This test enables quantitative analysis of the flammability of materials by measuring properties such as heat release rate (HRR), peak heat release rate (p-HRR), time to ignition (TTI), and total heat released (THR). Experimental results obtained by cone calorimetry of the TPU211 and TPIU series of polymers are summarized in Table VI and Figures 8 and 9.

TTI is used to determine the influence of a flame retardant on ignitability, which can be measured from the onset in an HRR curve. Ignition occurs when the volatiles are sufficient to be ignited by a spark. As summarized in Table 6, the TTI clearly increased from 35 to 65 s with the increase in hard-segment content.

Plots of HRR versus time for TPIUs are presented in Figure 8(A). TPIU321 burned rapidly after ignition and the HRR showed a sharp peak, reaching a p-HRR of 1491.2 kW/m<sup>2</sup>. However, the p-HRR values of TPIU211 and TPIU312 were markedly lower at 700.4 and 524.6 kW/m<sup>2</sup>, respectively, as expected with the increase in hard-segment contents. Furthermore, the THR values of the TPIUs decreased with the increment in the hard-segment content, as shown in Figure 8(B). This phenomenon could be attributed to the ability of imide groups in the condensed phase to form a carbonaceous layer on the material surface after ignition. This layer insulates the polymer, retards pyrolysis, and creates a barrier that prevents gaseous products from diffusing to the flame. It also shields the polymer surface from heat and air, resulting in low HRR and THR. According to the above analyses, the heterocyclic imide groups could effectively prevent the combustion of TPIU and enhance its flame retardancy.

The curves of CO production rate (COPR) and CO<sub>2</sub> production rate (CO<sub>2</sub>PR) of the samples are shown in Figure 9(A,B). COPR (g/s) is obtained from the product of the CO yield (COY, kg/kg) and the mass loss rate (g/s). CO<sub>2</sub>PR is similarly obtained from the CO<sub>2</sub> yield (CO<sub>2</sub>Y) and mass loss rate. The COPR and CO<sub>2</sub>PR of TPIUs decreased simultaneously with the increase in hard-segment content from 19.5 to 37.3 wt % (Figure 9). CO<sub>2</sub>PR, for instance, showed a reduction of 66.7% in the peak



value. As summarized in Table VI, the mean COY and CO<sub>2</sub>Y of both samples decreased gradually with the increase in hard-segment contents. This trend may be due to the formation of more char at higher contents of imide groups, which inhibits the release of pyrolytic gases and leads to a reduction in the peak values of COPR and CO<sub>2</sub>PR (g/s). The heterocyclic imide groups with excellent char formation might have produced flame inhibition effects.

To investigate the effect of the heterocyclic imide groups on the flame resistance of TPU, the flame properties of TPU211 were compared with those of TPIU211. As summarized in Table VI and Figure 8(A), the TTI of TPIU211 is longer than that of TPU211 by 25 s. This difference may be due to the higher thermal stability of heterocyclic imide groups compared with that of urethane groups, which might delay the thermal decomposition of the TPIU211 matrix. The HRR curve of TPU211 during combustion exhibits a sharp peak, but the corresponding curve for TPIU211 shows an obvious low plateau. Furthermore, the p-HRR and THR values of TPIU211 are greatly reduced by 64.03% (from 1946 to 700 kW/m<sup>2</sup>) and 14.62% (from 171 to 146 MJ/m<sup>2</sup>), respectively. This change could be attributed to the outstanding char formation of TPIU211, which could form a char layer at the combustion surface. This layer aids in preventing the release of heat. Notably, the COPR and CO<sub>2</sub>PR curves of TPU211 (Figure 9) reach sharp peaks at 0.018 and 1.322 g/s, respectively. These values are much higher than those of TPIU211, which exhibited slow release of gases. Additionally, the mean COY and CO<sub>2</sub>Y of TPU211 are far greater than those of TPIU211 (Table VI) because only some residual TPU211 was left after burning in air and because it released large amounts of volatile products during combustion. With the violent combustion, flammable gases produced large amounts of CO and CO<sub>2</sub>.

## CONCLUSION

A series of TPIUs has been prepared by two-step polymerization from MDI, PTMG, and PMDA. The resulting thermally stable segmented TPIUs have high  $M_n$  ( $5.04 \times 10^4 - 8.86 \times 10^4$ ) and tensile strength (23.1 – 37.6 MPa) as well as excellent solvent resistance. All of these results demonstrate that the TPIUs could meet the requirements in terms of mechanical properties for engineering applications. Moreover, the TPIUs show a certain degree of microphase-separated structure, as evidenced by DSC. The  $T_{5\%}$  and LOI values of the TPIUs increased with the hard-segment content; on the contrary, the THR and p-HRR showed an obvious decrease. This phenomenon may be attributed to the excellent thermal stability and char formation of the heterocyclic imide groups. Moreover, TPIU211 and TPIU312 exhibited good antidripping effects due to the heterocyclic imide groups with good char formation; the char could serve as “scaffolding” to inhibit melt dripping. Compared with those of TPU211, TPIU211 exhibited  $T_{5\%}$  and  $T_{max}$  values higher by 33.2 and 18.7°C, respectively; meanwhile, TPIU211 also exhibited large reductions in p-HRR and THR by 63.9% and 14.2%, respectively. These results indicate that heterocyclic imide groups could improve the flame retardancy of TPU. Additionally, compared to polyurethanes with

phosphorus-containing or imide and alkynyl-containing flame retardants, the TPIUs show much better thermal stability and mechanical properties.

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