Probing Effects of Alternately-Embedded Phenoxy Phenyl Lateral Groups on Properties of Novel Aromatic Poly(ether-urea)s

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ABSTRACT: A new class of alternate aromatic poly (ether-urea)s having bulky phenoxy phenyl lateral groups was prepared by the reaction of 2,2′-bis[(*p*-phenoxy phenyl)]-4,4′-diaminodiphenyl ether (PPAPE) with two diisocyanates, isophorone diisocyanate and 2,4-tolylene diisocyanate. The limited viscosity values as well as $\overline{M}_n$ and $\overline{M}_w$ values of the resulting polymers were determined. The resulting poly(ether-urea)s could be easily cast into optically-transparent, flexible, and light color films. The cut-off wavelength values and the percentage of transmittance at 800 nm were found to be at about 415 nm and 85%, respectively. PPAPE-derived poly(ether-urea)s showed a low-crystallinity and had excellent solubility in polar organic solvents. T_{onset}, T_g, $T_{d5\%}$, and $T_{d10\%}$ values of the PPAPE-derived polymers measured from their DSC and TGA thermograms were up to 270, 280, 315, and 340°C, respectively. Surface morphology of the resulted poly(ether-urea)s were also evaluated by their scanning electron microscopy images. Excellent organo-solubility, satisfactory film quality, moderate T_g values, and good thermal stability make this class of poly (ether-urea)s promising high-performance polymeric materials. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1887–1893, 2010

Key words: polyurea; lateral group; thin films; thermogravimetric analysis; gel permeation chromatography

INTRODUCTION

The interesting properties of polyureas, which have led to their widespread application in many diversified fields, arise mainly from the nature, physical, and chemical characteristics of the urea (N—CO—N) bond. Linear polyureas are thermoplastic products are commercially very useful, as they can be used as fire-proofing polycoats, elastomers, fibers, and adhesives.[1] Therefore, this class of polymers is well-documented in the literature during recent years.[2–9] Recently, polyureas have been reported as piezoelectric and ferroelectric polymers, second-order optical nonlinear polymers, lithographic matrices, permeable membranes, biodegradable polymers, and polymer microcapsules.[10–16] A wide range of commercial polymers containing urea groups such as urea-formaldehyde resins,[17] poly(amide-urea)s,[18] poly(urethane-urea)s used as cast elastomers, and poly(ether-urea)s used as surface coating have been reported.[19] Incorporating soft and flexible linkages along with urea hard groups within the macromolecular chains may be a suitable approach for optimizing the polymer properties. This incorporation can either be in alternate form resulted from single molecules of initial monomers[20–23] or in block form (segmented) derived from a tractable prepolymer.[15,24–28] The presence of methylene groups or ether linkages associated with the urea hard domains in an aromatic polyurea have a remarkable effect on rigidity of the polymer.

In our previous studies, we tried to prepare some series of wholly aromatic polyureas from a number of structurally-modified dicarboxylic acids by one-pot polyaddition reactions.[29–31] In this study, however, we wish to report the synthesis and characterization of a novel class of alternate aromatic poly(ether-urea)s derived from an aryl ether-based diamine namely 2,2′-bis[(*p*-phenoxy phenyl)]-4,4′-diaminodiphenyl ether (PPAPE) and two diisocyanate comonomers including isophorone diisocyanate (IDI) and 2,4-tolylene diisocyanate (TDI).

Synthesis and characterization of two reference poly(ether-urea)s lacking laterally-attached phenoxy phenyl groups will be also reported. Some characteristics of the polymers obtained including solution viscosity, GPC measurements, organo-solubility, crystallinity, film transparency, thermal stability, and surface morphology will be reported and discussed.

EXPERIMENTAL

Materials

Solvents and starting materials were acquired from Merck Chemical (Germany), and used without further purification unless otherwise stated. The PPAPE was prepared starting from 4,4′-dinitrodiphenyl ether via a three-step route according to our previous work.[32] 4,4′-Diaminodiphenyl ether (DADPE) (purity $\geq$ 98%) was purified by recrystallization from ethanol before use. TDI and IDI were distilled under vacuum. Solvents used including N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) and toluene were dried by sodium before use.

Measurements

Limited viscosity values were measured by means of an Ubbelohde viscometer using polymer solutions. These values were obtained from their viscosity numbers at concentrations 0.1, 0.2, 0.3, 0.4, and 0.5 g dL^{-1} in DMAc at 30°C and were determined by extrapolation of the concentrations till zero. Melting points were determined in open capillaries with IA 9200 Series Digital Melting Point apparatus. IR spectra were recorded on a PERKIN ELMER RX I FT-IR spectrometer. The spectra of solids were obtained using KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a BRUKER AVANCE 500 NMR operated at 500 MHz for proton and 125 MHz for carbon using CDCl$_3$ and dimethyl sulfoxide-d6 (DMSO-d$_6$). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a METTLER TA 5000 system (Columbus, OH) under nitrogen atmosphere at a heating rate of 10°C min^{-1}. The DSC traces were obtained from heating, rapid cooling, and reheating of samples in a range of 50–400°C. Ultraviolet maximum wavelength (λ_{max}) values in DMSO at a concentration of 0.1 mg mL^{-1} and Cut-off wavelength (absorption edge) values (λ_0) of the prepared films were determined with a GBC model 916 ultraviolet–visible (UV–vis) instrument. Wide-angle X-ray diffraction (WXRD) patterns were performed at room temperatures with film specimens on a D8 ADVANCE BRUKER X-ray diffractometer with Ni-filtered Cu-K$_\alpha$ radiation (30 kV, 25 mA). $\overline{M}_n$ and $\overline{M}_w$ of the resulting polymers were determined by gel-permeation chromatography. This chromatography was performed on a Waters 150-C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards.

Calibration and measurements were made at a flow rate of 1 mL min^{-1}, and DMF was used as solvent. Scanning electron microscopy (SEM) images of the dry, gold-coated powders were obtained from a SEM LEO 435 VP, and magnifications up to 10,000 were obtained.

Preparation of poly(ether-urea)s

Polymerization reactions were conducted in three-necked round bottom flasks equipped with an overhead stirrer, addition funnel, and nitrogen inlet. All poly(ether-urea)s were readily prepared by reacting equimolar amounts of the corresponding diisocyanates (IPI and TDI) and the diamine PPAPE possessing laterally-attached phenoxy phenyl groups or the reference diamine DADPE without these lateral groups. The poly(ether-urea)s were technically prepared through a stepwise manner in freshly-distilled dry DMF as the reaction solvent. In the first step, PPAPE or DADPE solution was added dropwise onto the diisocyanate solution at 0°C, under strong agitation and bubbling N$_2$. After adding, temperature of the solution increased to 5°C, and then stirred under the same conditions for 2 h. In the next step, the reaction mixture was heated till room temperature, and then remained at this temperature for 6 h. The reaction precursors constituted 20% w/v of the final solution. The turbid suspension was then poured into methanol to yield the corresponding crude product. The mixture was then filtered, washed several times with methanol, and vacuum-dried overnight. Polymer films with 0.5 mm thickness were obtained by pouring a part of initial solutions into teflon molds. The molds were covered with a glass petri dish to slow down the solvent (DMF) evaporation and placed in a vacuum oven at 50°C till complete drying. The resulting films were then removed from the molds and stored under vacuum at room temperature.

Limited viscosity number values in DMAc solvent at 30°C, the data resulted from UV measurements, and the number and weight average molecular weights values ($\overline{M}_n$ and $\overline{M}_w$) measured by GPC analysis in DMF eluent will be reported and discussed in the result and discussion section.

RESULTS AND DISCUSSION

Synthesis process and characterization

Scheme 1 shows synthetic route to prepare the resulting novel poly(ether-urea)s.

A milky-colored suspension was obtained after the addition of PPAPE or DADPE solution into the diisocyanate medium. In work-up step, a stringy
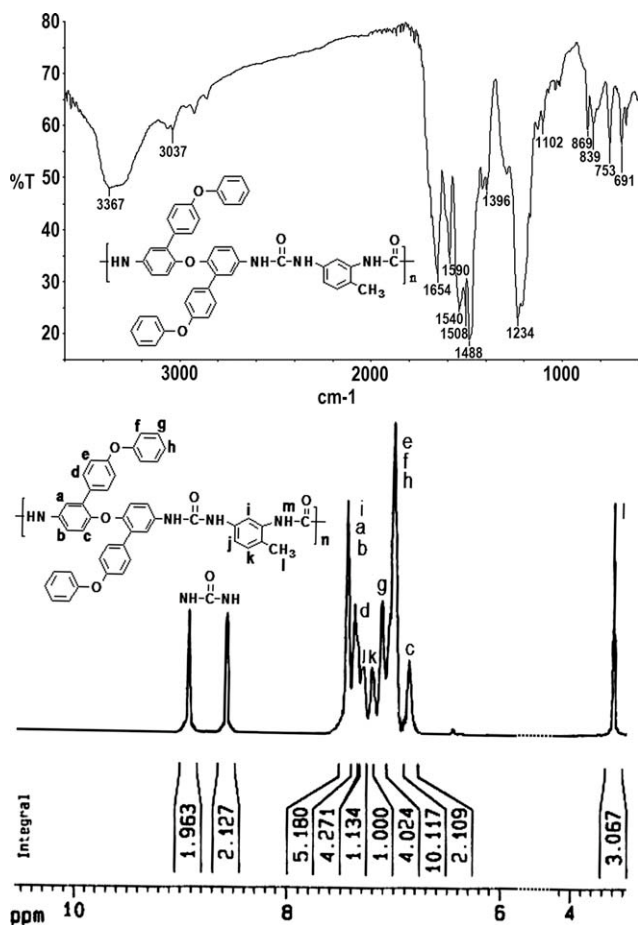
Scheme 1 Synthesis of the resulting poly(ether-urea)s.

polymer was formed when the reaction mixture was slowly poured into the vessel containing methanol nonsolvent, and the internal surface of the reaction flask (soaked by the remaining the reaction solution) became thoroughly coated by a thin film of the polymer when rinsing by methanol. The results of [η] and the results of GPC analysis are presented in Table I.

GPC analyzes showed that the number and weight average molecular weights of the resulted polymers ($\overline{M}_n$ and $\overline{M}_w$) were sufficient to prepare their flexible thin films. Some other characteristics of the resulting poly(ether-urea)s including UV maximum wavelength (λ_{max}) values in DMSO, absorption edge values (λ_0), and the percentage of transmittance at 800 nm resulted from wavelength-transmittance curves are also tabulated in Table I. In general, it should be stated that most of aromatic polymers

have strong absorption in the region of UV and visible light because of highly conjugated aromatic structures and intermolecular charge-transfer complex (CTC) formation. However, this class of aromatic poly(ether-urea)s, which have flexible ether linkages both in their backbones and in a part of their bulky pendant groups reduced the values of both the above mentioned factors: conjugation and intermolecular CTC formation. All the resulting poly(ether-urea)s had λ_0 values lower than 450 nm, and they exhibited high-optical transparency of 80–90%. Moreover, the PPAPE-derived poly(ether-urea)s produced films with λ_0 values lower than those of DADPE-derived, because of a diminished intermolecular interaction caused by the laterally-attached phenoxy phenyl groups. Details related to the films preparation and further characteristics of the prepared films will be noted in the next section.

The synthesized poly(ether-urea)s were characterized by their IR and ^{1}H-NMR spectra. In the IR spectra, characteristic absorption bands of the urea functional groups (C=O and N—H stretching vibrations) could be easily seen. The spectra of poly-(ether-urea)s showed bands around 3,350 cm^{-1} assigned to stretching vibration of the urea N—H linkages. The absorption of carbonyl groups occurred around 1,655 (urea C=O stretching) cm^{-1}. Moreover, completion of the polyaddition reactions was confirmed by the disappearance of the isocyanate absorption peak around 2,260 cm^{-1}. The ^{1}H-NMR spectra of the resulting poly(ether-urea)s showed two discrete signals attributed to N—H proton in the region of about 8.4–9.1 ppm. Moreover, the aromatic ring protons appeared in the region of about 6.75–7.80 ppm. Figure 1 shows a representative IR and ^{1}H-NMR spectra of poly(ether-urea) PPAPE/IDI.

The crystalline nature of the resulting poly(ether-urea)s was measured by WXRD at room

TABLE I
Some Characteristics of the Resulting Poly(ether-urea)s

Polymer	Formula	[η][a] (dL g^{-1})	$\overline{M}_n \times 10^{-4}$ [b] (g mol^{-1})	$\overline{M}_w \times 10^{-4}$ [b] (g mol^{-1})	λ_{max}[c] (nm)	λ_0[d] (nm)	UV$_{trans}$[e] (%)
PPAPE/IDI	(C$_{48}$H$_{46}$N$_4$O$_5$)$_n$ (758.9)$_n$	0.80	3.7	6.0	305	415	89
PPAPE/TDI	(C$_{45}$H$_{34}$N$_4$O$_5$)$_n$ (710.8)$_n$	0.87	3.3	6.2	307	411	86
DADPE/IDI	(C$_{24}$H$_{30}$N$_4$O$_3$)$_n$ (422.5)$_n$	0.76	2.1	3.4	309	429	86
DADPE/TDI	(C$_{21}$H$_{18}$N$_4$O$_3$)$_n$ (374.4)$_n$	0.69	2.2	3.5	315	418	83

[a] Measured in DMAc at 30°C.
[b] Measured by GPC in DMF with polystyrene as a standard.
[c] Measured in DMSO.
[d] Cut-off wavelength defined as the point at which the transmittance becomes less than 1%.
[e] UV-transmittance at 800 nm.

Figure 1 IR (top) and ^{1}H-NMR (bottom) spectra of the representative poly(ether-urea) PPAPE/TDI.

ages. Second, bulkiness of the attached groups, which inhibits the close packing of the polymer chains. The first factor lowers crystallinity and the second one enhances it. Consequently, density of crystallite regions of the samples under study is determined by the net effect of the two above factors. No remarkable crystal diffraction was detected for poly(ether-urea)s PPAPE/IDI and PPAPE/TDI possessing laterally-attached phenoxy phenylene groups. Therefore, incorporation of these groups along the chains of PPAPE-derived polymers resulted in a diminished crystallinity comparing with those of DADPE-derived ones.

Figure 3 shows the surface topographical structures of dry powders of two poly(ether-urea)s DADPE/IDI and PPAPE/IDI.

With a close look at these micrographs, it can be revealed that the PPAPE-derived polymer exhibits significant difference in its morphology comparing with that of DADPE-derived one. Obviously, the DADPE/IDI particles tend to agglomerate, and whereas this polymer has a rather compact and homogeneous surface, the poly(ether-urea) PPAPE/IDI is distinguished by smaller and less densely packed subdomains. A great number of irregular moieties were generated in the surface morphology of polymer PPAPE/IDI. This can be attributed to the phenoxy phenyl pendant side groups, which typically hinder a compact packaging.

Organo-solubility of the resulting poly(ether-urea)s was qualitatively determined (Table II).

Contrary to the structurally-unmodified polymers, DADPE/IPI and DADPE/TDI, poly(ether-urea)s PPAPE/IPI and PPAPE/TDI could be easily dissolved in polar organic solvents such as DMSO, DMAc, DMF, NMP, and pyridine. The phenoxy phenyl groups attached to the main chains give a structural modification that has a positive influence on the solubility, as this modification hinders the molecular packing, that is, lowers the cohesive energy. One would expect that the H-bond interactions between urea groups and oxygen atoms of
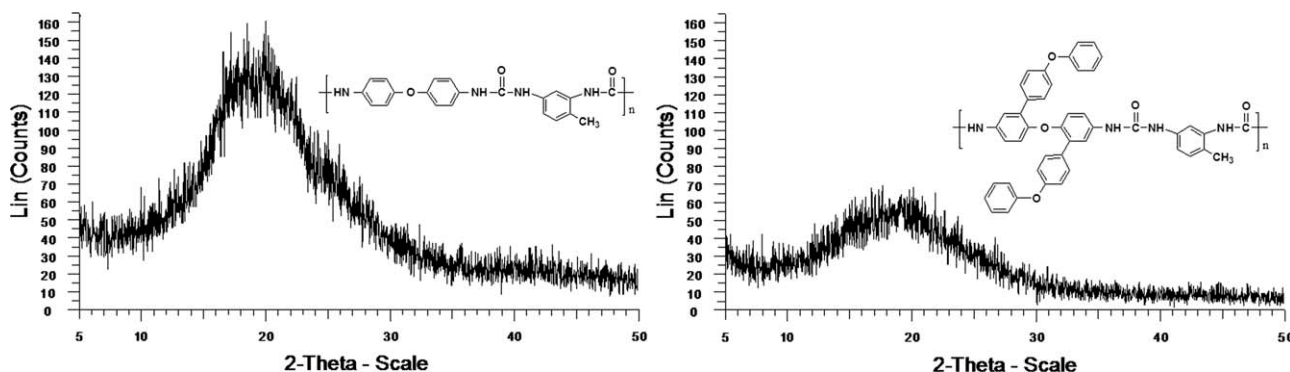
temperature. For example, Figure 2 shows the diffraction patterns of the polymers PPAPE/TDI and DADPE/TDI with 2Θ ranging from 5 to 50°.

In fact, the crystallinity of these polymers is affected by two opposite factors. First, the presence of oxygen atoms in the attached groups, which results in a further compactness, because of their direct participation in the formation of intermolecular H-bonds with hydrogen atoms of the urea link-

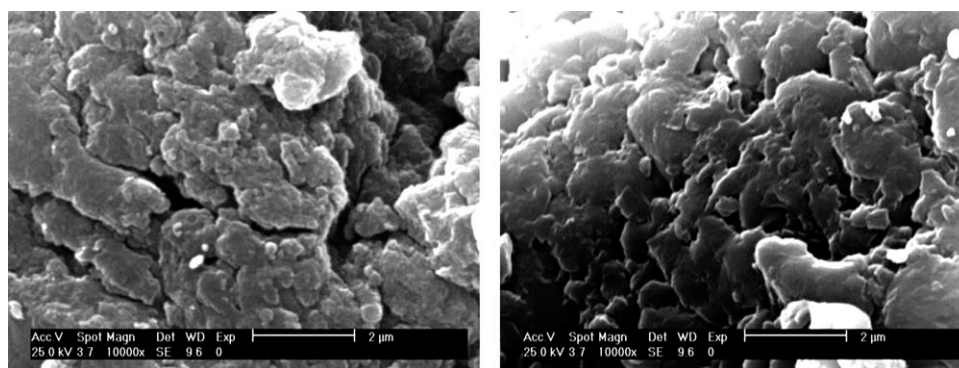**Figure 2** WXRD diffractograms of DADPE/TDI (left) and PPAPE/TDI (right).

Figure 3 SEM micrographs of DADPE/IDI (left) and PPAPE/IDI (right).

ether linkages (in addition to H-bond interaction between urea groups themselves) should impair the solubility because of further charge distribution resulted from these interactions. Moreover, the solubility of PPAPE/IPI is almost comparable with the solubility of the analogous PPAPE/TDI. This suggests that, the main role in solubility extent of this class of polymers is determined by PPAPE monomer and not IPI or TDI comonomers. Therefore, the presence of bulky pendant phenoxy phenyl groups seems to be responsible for this good organo-solubility behavior.

The optically-transparent film of PPAPE/IDI had a significant flexibility, whereas the films of poly-(ether-urea)s DADPE/IDI, and DADPE/TDI were nearly brittle in nature. Further film flexibility of the polymers resulted from PPAPE might be attributed to the presence of three flexible ether linkages as structural hinges in each repeat unit of the macromolecular chain. The films characteristics for the obtained polymers including film flexibility, film transparency, and film color are presented in Table III.

The thermal properties of the resulting poly(ether-urea)s were determined by means of DSC and TGA/DTG in nitrogen atmosphere. The thermal behavior data of the polymers including T_{onset} and T_g obtained from the second heating traces of DSC measurements in N_2 as well as 5% and 10% weight losses recorded by TGA in N_2 are summarized in Table III. Generally, the incorporation of bulky lateral units along a polymer backbone restricts the free rotation of macromolecular chains and leads to enhanced T_g values. For this class of polymers, however, this factor even intensifies by the further formation of H-bond between the oxygen atoms of phenoxy phenyl lateral groups and hydrogen atoms of the urea linkages. T_g values increase with increasing H-bond formation because intermolecular H-bonds prevent free rotation of macromolecular chains. Conversely, the presence of hinges such as ether linkages, whether within the main chain or within the structure of lateral groups attached to the main chain, lowers the polymer rigidity and reduces the T_g values. The T_g values of polymers prepared herein are influenced by the net effect of these two key factors too. As can be seen, T_g values of polymers resulted from diamine PPAPE are about 10°C greater than those resulted from diamine DADPE. TGA thermograms of the polymers showed that the resulting structurally-modified poly(ether-urea)s were stable up to 310°C. All the TGA/DTG curves of the polymers were almost similar. All poly(ether-urea)s showed a two-stage decomposition at elevated temperatures. Assuming a different stability of the urea and the other segments, the first stage of

TABLE II
Solubility of the Resulting Poly(ether-urea)s

Solvent[a]	PPAPE/IDI	PPAPE/TDI	DADPE/IDI	DADPE/TDI
DMSO	++	+	+	+
DMAc	++	++	++	++
DMF	++	++	+	+
NMP	++	++	++	+
Pyridine	+	+	±	±
THF	±	±	−	−
Chloroform	±	±	−	−
Toluene	±	±	±	−

[a] Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent.
++, soluble at room temperature; +, soluble on heating; ±, partially soluble or swollen; −, insoluble even on heating.

TABLE III
Thermal Properties and Film Quality of the Resulting Poly(ether-urea)s

Polymer	Film characteristics	T_{onset}[a] (°C)	T_g[b] (°C)	$T_{d5\%}$[c] (°C)	$T_{d10\%}$[d] (°C)	C.Y.[e] (%)
PPAPE/IDI	flexible, transparent, pale yellow	273	281	313	347	12
PPAPE/TDI	slightly brittle, transparent, khaki	272	279	311	341	27
DADPE/IDI	slightly brittle, transparent, white	263	274	319	335	8
DADPE/TDI	slightly brittle, transparent, cream	261	269	297	321	11

[a] Onset temperature, from the second heating traces of DSC measurements in N_2.
[b] Temperature of 50% transition, from the second heating traces of DSC measurements in N_2.
[c] Temperature at which 5% weight loss was recorded by TGA in N_2.
[d] Temperature at which 10% weight loss was recorded by TGA in N_2.
[e] Char yield: residual wt % at 650°C.

weight losses may be attributed to the early degradation of the urea groups. Therefore, the 10% weight loss temperatures are mainly caused by the decomposition of urea linkages. For example, typical TGA/DTG curves of representative polymer PPAPE/IDI are illustrated in Figure 4.

Furthermore, the incorporation of the laterally-attached phenoxy phenyl groups had no detrimental effect on the good thermal stability of the resulted poly(ether-urea)s. It could be observed that the values of $T_{d5\%}$ and $T_{d10\%}$ for polymers having lateral phenoxy phenyl groups were even grater than those of unmodified ones.

CONCLUSIONS

Because of the presence of bulky phenoxy phenyl lateral groups along the ether-hinged macromolecular chains of poly(ether-urea)s, the resulted poly-

mers were amorphous and could be cast into transparent and flexible films. Thermal stability of the resulting poly(ether-urea)s was essentially not decreased comparing with the unmodified DADPE-resulted poly(ether-urea)s. The presence of the mentioned pendant groups have some important effects on properties of the prepared poly(ether-urea)s such as film quality and T_g values. These bulky groups decrease the free rotation of the chains via making a difficulty in conformational interconversions. This case consequently results in a greater value of T_g and a lower amount of film flexibility. But, the film flexibility of the resulting poly(ether-urea)s was influenced by the flexible ether bonds as well. In general, good organo-solubility, satisfactory film quality, moderate T_g values, and excellent thermal stability make this class of poly(ether-urea)s promising high-performance polymeric materials.
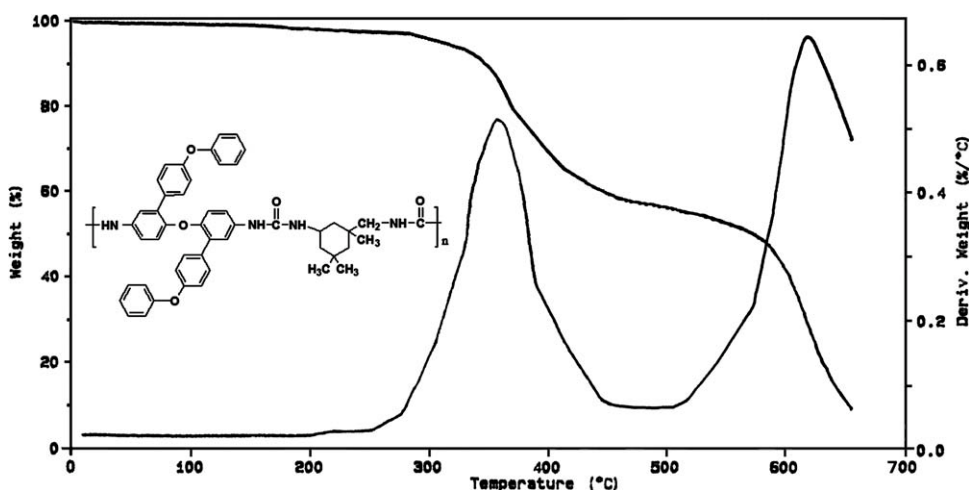

Figure 4 TGA/DTG thermogram of the representative poly(ether-urea) PPAPE/IDI.

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