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# Preparation and Properties of Thermally Stable Polyureas Containing Ether and Ketone Units

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## Abstract

The main objective of this search was to prepare novel soluble polyureas with improved thermal stability. Accordingly, a new types of polyureas was prepared through the polycondensation reaction of a prepared diamine containing ether, keto, and naphthyl groups with 4,4'-diphenylmethan diisocyanate (MDI), toluene-2,4-diisocyanate (TDI), and isophorone diisocyanate (IPDI) in N-methyl-2-pyrrolidone (NMP). Conventional spectroscopic methods and elemental analysis were used to characterize the structure of the monomer and polymers. The results showed that polyurea samples with the expected structure were synthesized. The inherent viscosity of polymers at a concentration of 0.5 g/dL in NMP at 30 °C was in the range of 0.55-0.60 dL/g. Thermal properties of resultant polyureas were investigated by differential scanning calorimetry and thermogravimetric analysis, and they indicated improved thermal stabilities in comparison with common polyureas. Physical properties of the polymers were also studied; they were soluble in common dipolar aprotic solvents. MDI-based polyurea showed highest thermal stability and lowest solubility among the prepared polymers.

***Keywords:*** *Polyurea, synthesis, characterization, polycondensation, thermally stable.*

## Introduction

Polyureas may be classified as heterochain macromolecular compounds, which contain urea groups in their structure. They are polycondensation or step-wise products in which the urea linking group occurs periodically in oligomeric or polymeric chains of otherwise different chemical structure [1-3].

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Polyureas have been prepared by several methods such as reaction of diamines with carbonate esters, carbonate alkali metals, carbon dioxides, phosgene and urea. Although a number of methods have been used to prepare polyureas, the most important method used for polyurea formation is based on the step-growth addition reaction between diamines and diisocyanates in polar aprotic solvents such as N-methyl-2-pyrrolidone (NMP). One immediate advantage of these step-growth polymerization reactions is that polyureas are formed without the evolution of condensation by-products and it can be carried out at low temperature [4-8, 10].

Linear polyureas are thermoplastic polycondensation products with aliphatic or aromatic structures. Polyureas or copolyureas containing aliphatic structures exhibit a difference of 50-100°C between melting points and the beginning of decomposition; they are used for castings. Polyureas containing aromatic structures melt near their decomposition temperatures. They are soluble in dipolar organic solvents and can be used as lacquers, varnishes and coatings [9-12]. Polyureas have been extensively studied for their good mechanical properties, hydrolytic stability, chemical resistance, unique nonlinear optical properties, etc [13-15]. In order to improve their applications in different industries, preparation of thermally stable polyureas has attracted attentions [16]. Despite their many qualities, the efficacy of polyureas is limited in many applications due to relatively simply flammability and release of toxic smoke while burning. This problem is solved by introducing other structural units into the backbone of polyureas [17, 18].

Recently, elastomeric polyureas containing flexible units such as ether, sulfur, and keto groups have received attention as protective surface coating, because of their unique features, such as fast setting, resistance to a broad range of corrosives and solvents, excellent thermo-mechanical properties, adhesion, abrasion resistance, low flammability and excellent durability, and excellent bonding properties to most materials, especially metals [19,20]. Also, ability to form stable chelates with essential metal ions and their potentially beneficial biological activities, such as antitumor, antibacterial, antiviral, and antimalarial activities have been reported for polyureas containing such functional units [21, 22].

In this research novel different polyureas containing ether and ketone units were prepared via polycondensation reactions of a synthesized diamine with different aromatic, and semi-aromatic diisocyanates.

## Experimental

### *Materials*

All of the needed chemicals were purchased either from Merck or Aldrich chemical Co.

N-Methyl-2-pyrrolidone (NMP) was purified by distillation over calcium hydride under reduced pressure (about 200 mbar). Toluene and tetrahydrofuran (THF) were dried over sodium wire by distillation. All the solvents stored over molecular sieves.

*Instruments*

Infrared measurements were performed on a Bruker-IFS 48 Fourier transform infrared (FTIR) spectrometer (Ettlingen, Germany). The $^1$H-NMR spectra were recorded in hexadeuterated dimethyl sulfoxide (DMSO-$d_6$) solution on a BrukerAvance DPX 400 MHz instrument. Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK) in air at a heating rate of 10 °C/min, from 25 to 300 °C and 25 to 700 °C, respectively. The inherent viscosities were measured at a concentration of 0.5 g/dL in NMP at 30 °C with an Ubbelohde viscometer (a local supplier in Tehran, Iran).

*Monomer Synthesis*

*Synthesis of 4-(4-nitrophenoxy) beta-naphthol (NPN)*

Into a 100 mL, three-necked, round-bottomed flask equipped with a Dean-stark trap, a condenser, a nitrogen inlet tube, a thermometer, an oil bath, and a magnetic stirrer were placed 0.01 mol(1.6017 g) of 2,7-dihydroxynaphthalene, 0.01 mol (1.4387 g) of 1-fluoro-4-nitrobenzene, 25 mL of dry NMP, and 15 mL of dry toluene. Then 0.01 mol (1.8148 g) of $K_2CO_3$ was added to the mixture and the reaction mixture was heated to 140 °C for 6 h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 160 °C by removing more toluene, and maintained at the same temperature for 20 h. The resulting reaction mixture was cooled and poured into water. Then the precipitates were isolated by filtration and the obtained product was dried in a vacuum oven at 80 °C (yield 91%).

*Synthesis of 4-(4-aminophenoxy) beta-naphthol (APN)*

0.01 mol (2.8 g) of the NPN, 0.1 g Pd/C, and 130 mL of ethanol were introduced into a three-necked flask to which 10 mL of hydrazine was added dropwise over a period of 1 h at 80 °C. After the completed addition, the reaction was continued at reflux temperature for another 4 h. To the suspension, 20 mL of tetrahydrofuran (THF) was added to dissolve the precipitated product, and refluxing was continued for 20 h. The mixture was filtered to remove the Pd-C and the filtrate was poured into water. The product was filtered off washed with hot water successively, and dried (yield 84 %).

### *Synthesis of bis(4-(4-(4-aminophenoxy)beta-naphthol)phenyl) methanone(ANPM)*

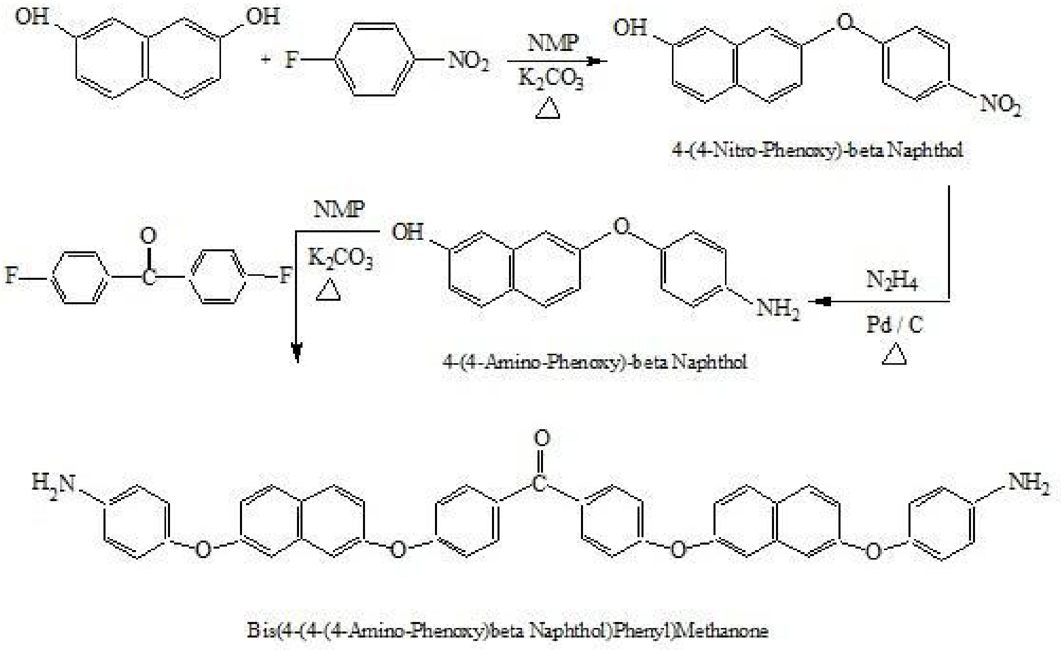
Into a 100 mL, three-necked, round-bottomed flask equipped with a Dean-stark trap, a condenser, a nitrogen inlet tube, a thermometer, an oil bath, and a magnetic stirrer was placed 0.0057 mol (1.270 g) of 4,4′-difluoro benzophenone, 0.011 mol (2.76 g) APN, 18 mL of dry NMP, and 15 mL of dry toluene. Then 0.018 mol of $K_2CO_3$ was added to the mixture and the reaction mixture was heated to 140 °C for 6 h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 160 °C by removing more toluene, and kept at the same temperature for 18 h. The resulting reaction mixture was cooled and poured into water. Then 50 mL of NaOH was added to the mixture and the mixture was washed repeatedly with a 5% NaOH solution and water. The obtained diamine was dried in a vacuum oven at 70 °C for 24 h (yield 89 %).

### *Polyurea synthesis*

The synthesis of polyureas typically was carried out as follow: Into a 100-mL, two-necked, round-bottom flask equipped with an $N_2$ inlet tube, a condenser, a magnetic stirrer, an oil bath and a thermometer was placed 1 mmol (0.664 g) of synthesized diamine (ANPM) and 3 mL of dry NMP, the reaction mixture was stirred at room temperature for a few minutes. Subsequently, a solution containing 1 mmol of diisocyanate (MDI, TDI, and IPDI) in 3 mL of dry NMP was added in one lot to the flask contents. The solution was stirred for 1 h at room temperature and for about 2 h at 60 °C, and then it was precipitated in 50 mL of water. The polymer was filtered and washed with hot water. Then it was vacuum-dried at 100 °C for 12 h.

## **Results and discussion**

The main aim of this research was preparation of novel thermally stable polyureas with improved solubility. Accordingly, the design and synthesis of a new monomer and resulting polyureas with structural modifications were considered. Aromatic diamines are valuable building blocks for the preparation of variety of polymers including polyimides, polyamides, polyureas, and so on. In this way, synthesis of a new diamine with built-in ether linkages, keton and phenyl groups were designed and prepared in three steps. In the first step, nucleophilic reaction of 2,7-dihydroxy naphthalene with 1-fluoro-4-nitrobenzene in the presence of $K_2CO_3$ resulted in preparation of NPN. In the second step, the nitro group of NPN was reduced to amino group. Thus an amino compound named as APN with built-in ether group was obtained. The final step in the preparation of a new ether keto diamine (ANPM) was the nucleophilic substitution reaction of APN with 4,4′-difluoro benzophenone in NMP solvent (Scheme 1).



**Scheme 1.** Preparation of NPN, APN, and ANPM.

Structures of NPN, APN and ANPM were characterized and the FT-IR spectra were shown in Figures 1-3, respectively and H-NMR spectra of NPN and APN were depicted in Figures 4 and 5 and the results were collected in Table 1.

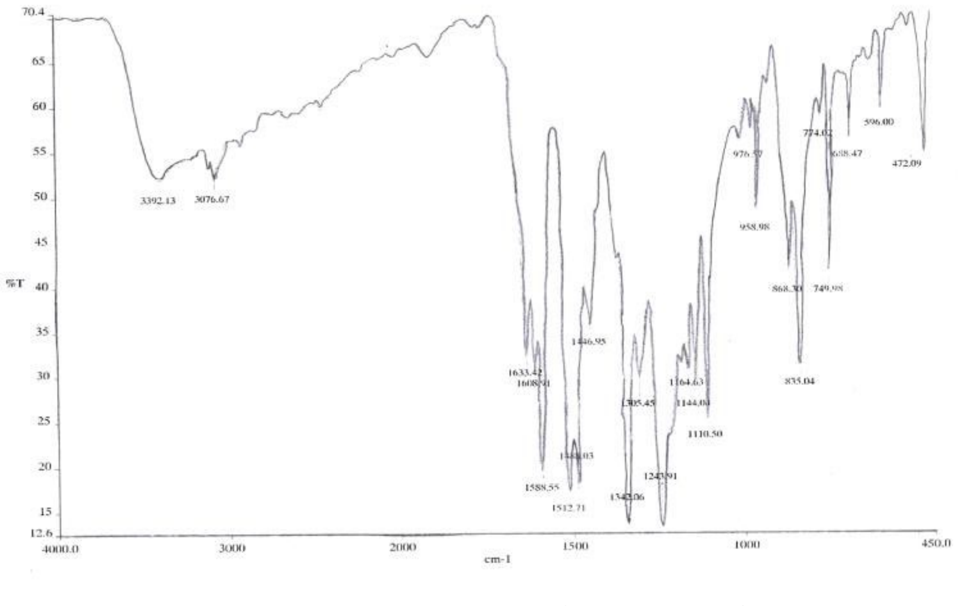


**Figure 1.** FT-IR spectrum of NPN compound.

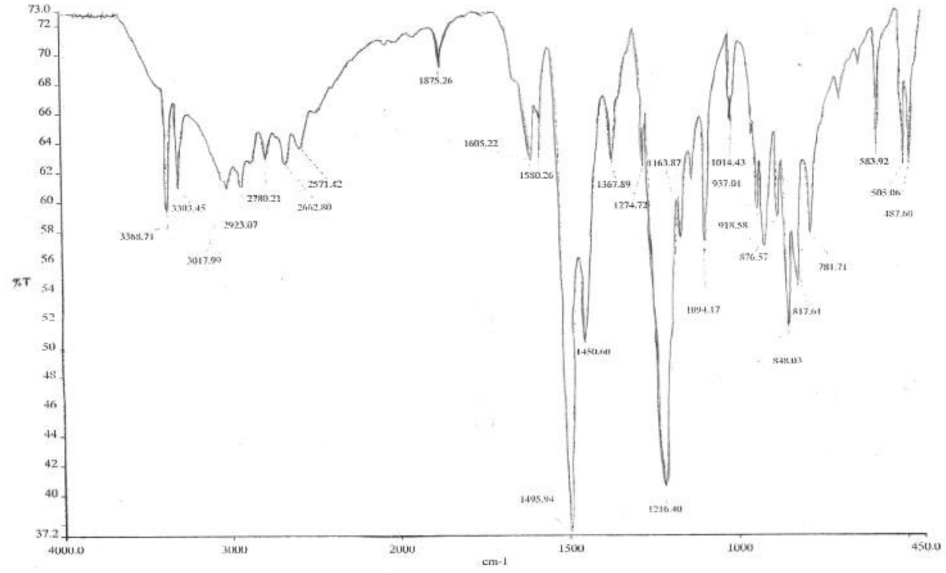


**Figure 2**. FT-IR spectrum of APN compound.

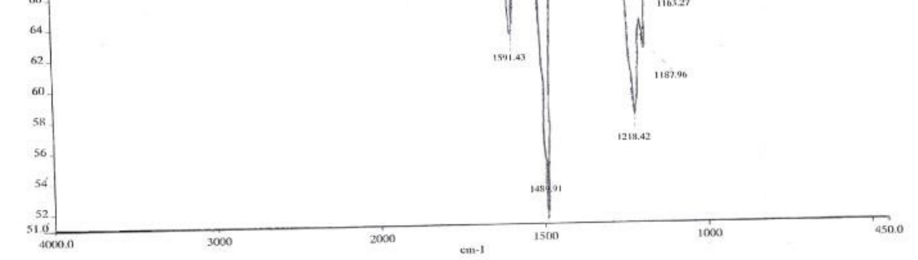


**Figure 3**. FT-IR spectrum of ANPM compound.

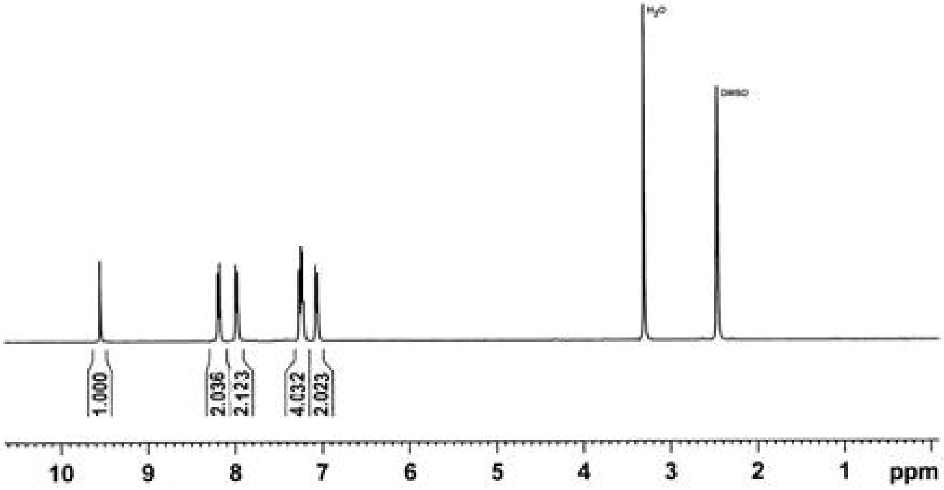


**Figure 4**. H-NMR spectrum of NPN compound.

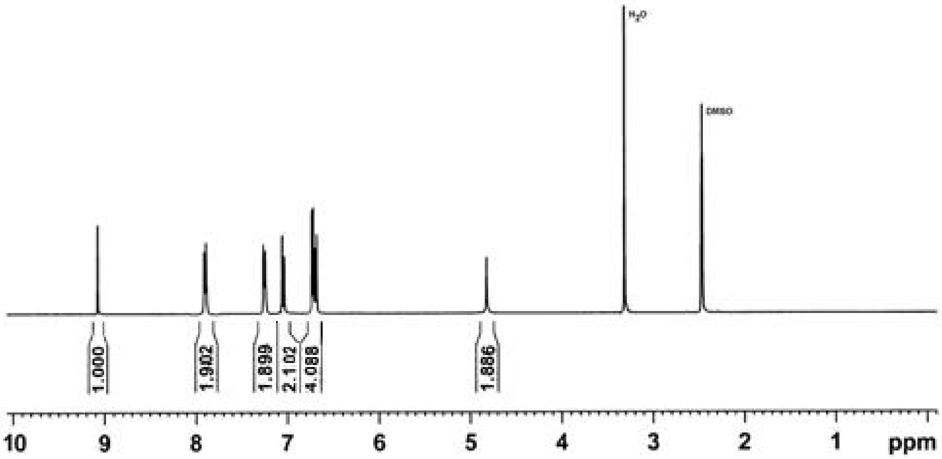
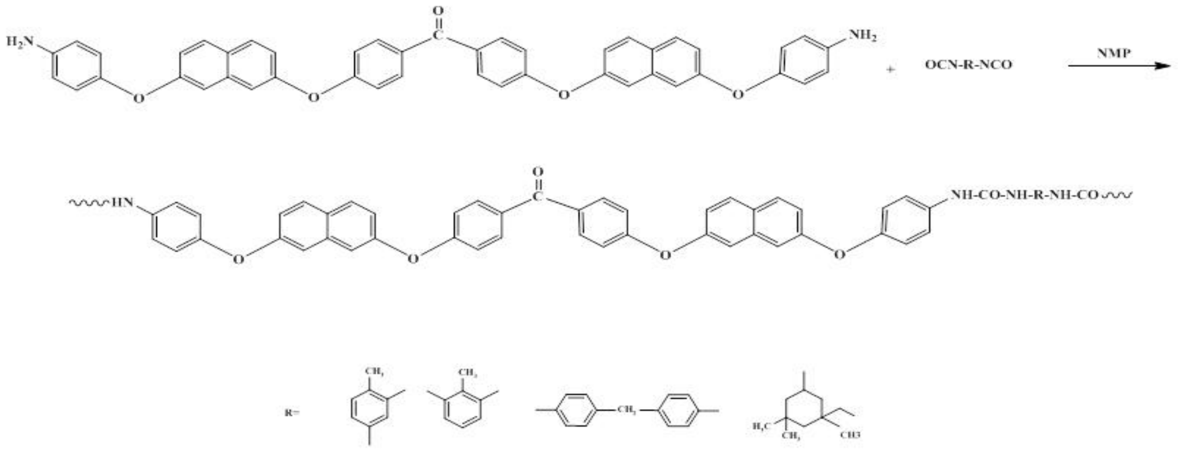


**Figure 5**. H-NMR spectrum of APN compound.

**Table 1.**Characterization of NPN, APN and ANPM.

| Compound | IR ($KBr-cm^{-1}$) | $^1H$-NMR ($DMSO-d_6$, ppm) | Elemental analysis |  |  |  |  |  | M.P. (°C) | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Calc. |  |  | Found |  |  |  |  |
|  |  |  | C | H | N | C | H | N |  |  |
| NPN | 3392, 3076, 1512, 1488, 1342, 1243 | 9.60(s, 1H, OH)<br>8.24(d, 2H, Ph)<br>7.23 (d, 2H, Ph)<br>7.09 (d, 2H, Naph)<br>7.94 (d, 2H, Naph)<br>7.27 (s, 2H, Naph) | 68.33 | 3.94 | 4.98 | 68.39 | 4.00 | 4.95 | 180-182 | 91 |
| APN | 3368, 3303, 3017,1605, 1495, 1450, 1216,1094 | 9.10(s, 1H, OH)<br>6.73 (d, 2H, Ph)<br>6.76 (d, 2H, Ph)<br>7.05 (d, 2H, Naph)<br>7.91 (d, 2H, Naph)<br>7.26 (s, 2H, Naph)<br>4.87 (s, 2H, amine) | 76.48 | 5.21 | 5.57 | 76.52 | 5.16 | 5.63 | 158-160 | 84 |
| ANPM | 3423,3038 1651,1591, 1489, 1218 | 7.74 (d, 4H, Ph)<br>7.24 (d, 4H, Ph)<br>7.05 (d, 4H, Naph)<br>7.91 (d, 4H, Naph)<br>7.26 (s, 4H, Naph)<br>6.76 (d, 4H, ph)<br>6.73 (d, 4H, ph)<br>5.03 (s, 4H, amine) | 81.31 | 4.85 | 4.21 | 81.39 | 4.92 | 4.16 | 213-217 | 89 |

Thus a novel fully aromatic diamine with ether and keton units was designed and synthesized to increase thermal stability and solubility of the final group. Polycondensation reaction of the ANPM with various diisocyanates including MDI, TDI, and IPDI led to preparation of fully aromatic and semi aromatic polyureas (Scheme 2).



**Scheme 2.** Preparation of poly(ether keto urea)s.

Structures of the polymers were characterized by IR and elemental analysis. The results were shown in Table 2.

**Table 2.**Characterization of polymers.

| **Polymer** | **IR (KBr-cm$^{-1}$)** | **Elemental analysis** | | | | | |
|---|---|---|---|---|---|---|---|
| | | Calc. | | | Found | | |
| | | C | H | N | C | H | N |
| **ANPM-MDI** | 3405, 3042<br>2926, 2861,<br>1644,1604,<br>1492, 1219 | 77.41 | 4.55 | 6.02 | 77.32 | 4.63 | 5.95 |
| **ANPM-TDI** | 3367, 3046<br>2925, 2859<br>1658, 1599<br>1493,1222 | 75.87 | 4.48 | 6.55 | 75.69 | 4.55 | 6.65 |
| **ANPM-IPDI** | 3365, 3043<br>2950, 2886<br>1650, 1599<br>1493, 1221 | 75.81 | 6.20 | 5.58 | 75.72 | 6.12 | 5.69 |

The solubility behaviors of the polymers were studied in different solvents and the results were summarized in Table 3.

**Table 3.** Solubility behavior of polymers.

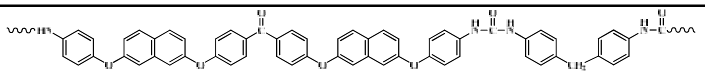
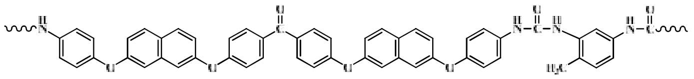
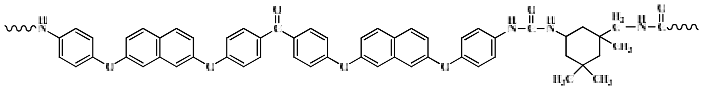
| **Polymer** | **NMP** | **DMAc** | **DMF** | **DMSO** | **THF** | **$CHCl_3$** |
|---|---|---|---|---|---|---|
| **ANPM-MDI** | ++ | ++ | + | + | - | - |
| **ANPM-TDI** | ++ | ++ | + | + | - | - |
| **ANPM-IPDI** | ++ | ++ | ++ | ++ | -+ | -+ |

Solubility: (++) soluble at room temperature; (+) soluble on heating; (+ -) partially soluble; (-) insoluble.

The polymers showed good solubility in dipolar aprotic solvents including DMF, DMAc, NMP and dimethyl sulfoxide (DMSO).This was as a result of introducing flexible ether groups and keto polar into the polymer backbone. Also, bulky naphthyl group by producing distances between chains of polymer and reducing inter-layer interactions caused improved solubility. Presence of aliphatic group in the semi aromatic IPDI-based polyurea caused increasing of solubility in comparison to aromatic polyureas.

The inherent viscosity of the polymers in NMP at a concentration of 0.5 g/dL at 30 °C was measured. The viscosity of polyureas was in the range of 0.55-0.60 dL/g (Table 4). Since, the inherent viscosity is a good criterion for estimation of molecular weight, the prepared polyureas showed reasonable molecular weights.

**Table 4.** Specifications of the polymers.

| **Polymer** | **Structure** | **Inherent viscosities[1] (dL/g)** | **Yield (%)** |
|---|---|---|---|
| **ANPM-MDI** |  | 0.6 | 92 |
| **ANPM-TDI** |  | 0.55 | 90 |
| **ANPM-IPDI** |  | 0.57 | 85 |

[1] Measured at a concentration of 0.5 g/dL in NMP at 30 °C.

The thermal behavior of polyureas was studied by differential scanning calorimetry (DSC). The glass transition temperature of polyureas ($T_g$) were found in the range of 175-203 °C. Thermogravimetric analysis (TGA) was used to study the thermal stability. They were taken in air at a heating rate of 10 °C/min. The initial decomposition temperatures ($T_0$) were about 252-286°C and the temperatures for 10% gravimetric loss ($T_{10}$) which is an important evidence for thermal stability, were in the range of 318-360 °C. The weight of polymer remaining (char yield) at 700 °C was about 38-43%. The results were collected in Table 5 and TGA curves were shown in Figure 6.

**Table 5**. Thermal analysis data.

| **Polymer** | **$T_g$ (°C)** | **$T_0$ (°C)** | **$T_{10}$ (°C)** | **$T_{max}$ (°C)** | **Char yield at 700 °C(%)** |
|---|---|---|---|---|---|
| ANPM-MDI | 203 | 286 | 360 | 430 | 43 |
| ANPM-TDI | 196 | 275 | 350 | 405 | 42 |
| ANPM-IPDI | 175 | 252 | 318 | 370 | 38 |

$T_g$: glass transition temperature, $T_0$: initial decomposition temperature, $T_{max}$: maximum decomposition temperature, $T_{10}$: temperature for 10% weight loss, Char yield: weight of polymer remained

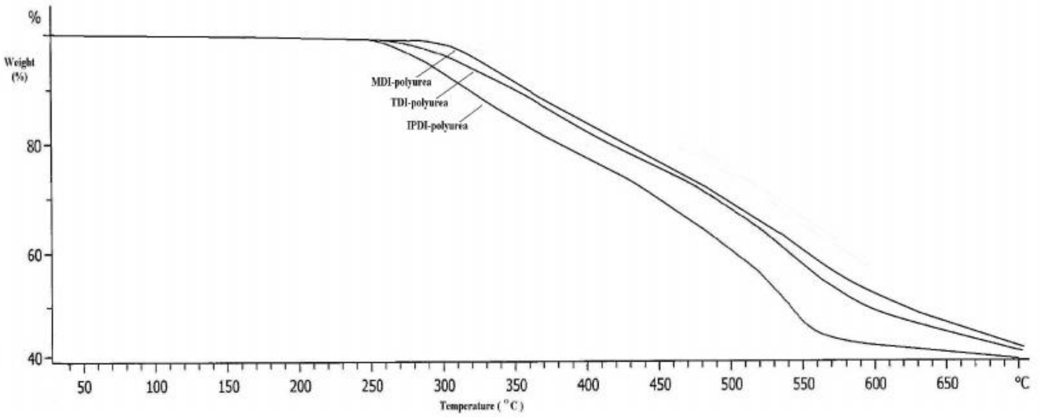


**Figure 6**. TGA curve of the polymers.

The polyureas showed good thermal stability that could be attributed to the incorporation of phenylation units into the backbone and symmetry of structures. It should be mentioned that MDI-based polyurea showed highest thermal stability and lowest solubility among the prepared polyureas due to the more rigid structure of MDI moiety.

## Conclusion

A novel keto ether diamine was prepared via three step reactions. A series of new polyureas were obtained by polycondensation of the diamine with aromatic and semi aromatic diisocyanates. The diamine and all the polymers were characterized. The obtained polymers indicated good thermal stability and improved solubility due to phenylation of backbone, avoid of weak linkages, symmetry and introduction of ether and keton groups.

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