

Synthesis, Characterization, and Properties of Novel Poly(ether urea)s

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ABSTRACT: Two diamines, 2,6-bis(4-aminophenoxy)pyridine and 2,6-bis(5-amino-1-naphenoxy)pyridine, were prepared through the nucleophilic aromatic substitution reaction of 4-aminophenol and 5-amino-1-naphthol, respectively, with 2,6-dichloropyridine. Poly(ether urea)s were synthesized through the polyaddition reactions of these diamines with aromatic, semiaromatic, and cycloaliphatic diisocyanates. All the monomers and polymers were fully

characterized, and physical properties of the polymers, including the thermal behavior, thermal stability, solubility, and solution viscosity, were studied. The polyureas showed improved thermal stability. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 961–965, 2004

Key words: addition polymerization; structure-property relations; thermal properties

INTRODUCTION

Polyureas may be classified as heterochain macromolecular compounds containing urea groups in their structure. They are polycondensation or stepwise addition products in which a urea linking group occurs periodically in oligomeric or polymeric chains of otherwise different chemical structures. The chains may be linear or nonlinear and comprise aliphatic, cycloaliphatic, aromatic, or heteroatomic structural repeat units.¹

Polyureas were initially developed because of their excellent mechanical properties and outstanding resistance to hydrolysis.² Recently, polyureas have been reported as piezoelectric and ferroelectric polymers, second-order optical nonlinear polymers, lithographic matrices, permeable membranes, biodegradable polymers, and polymer microcapsules.^{3–6}

Potentially more useful polyureas are those containing other functional groups. A wide range of commercial polymers containing urea groups, such as urea-formaldehyde resins,⁷ poly(amide urea)s,⁸ poly(urethane urea)s used as cast elastomers,⁹ and poly(ether urea acrylate)s used as surface coatings have been reported.

This article describes the preparation and properties of novel poly(ether urea)s with improved thermal stability via the addition polymerization reaction of two

pyridine-based ether diamines with different diisocyanates. Pyridine-based, ether diamines were prepared through the reaction of 4-aminophenol and 5-amino-1-naphthol with 2,6-dichloropyridine.

EXPERIMENTAL

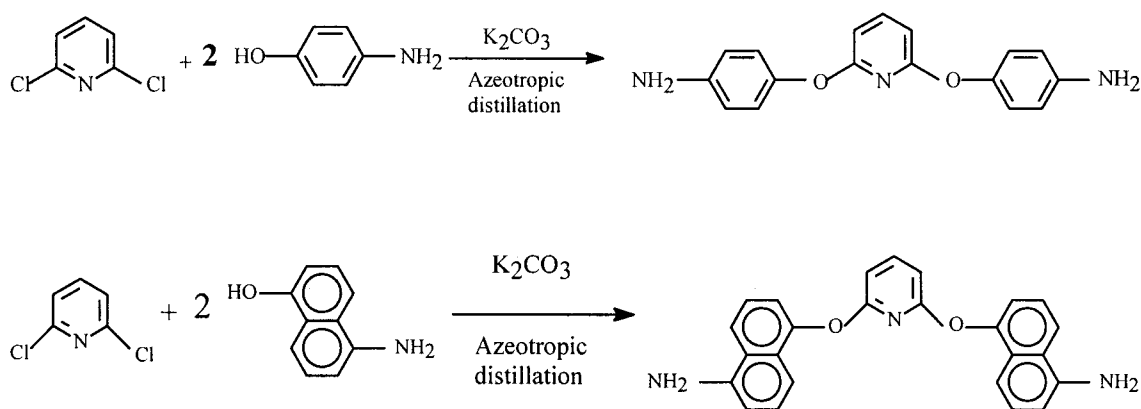
Materials

All chemicals were purchased from Merck (Darmstadt, Germany) or Aldrich Chemical Co. (Milwaukee, WI). 2,6-Dichloropyridine was recrystallized from ethanol. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and toluene were purified by distillation over calcium hydride under reduced pressure. *p*-Phenylene diisocyanate (PPDI) and 1,5-naphthalene diisocyanate (NDI) were sublimed before use. Toluene diisocyanate (TDI) and 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI) were purified by distillation.

Instruments

Infrared measurements were performed on a Bruker (Ettlingen, Germany) IFS 48 Fourier transform infrared spectrometer. The H-NMR spectra were recorded in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) solutions with a Bruker Avance DPX 250-MHz instrument. A Heraeus (Wellesley, MA) CHN-O rapid elemental analyzer was used for the elemental analyses. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton (London, England) Redcraft STA-780. Differential thermogravimetry (DTG) traces were recorded on a Polymer Lab

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Scheme 1 Synthesis of the diamines.

(London, England) TGA-1500. The dynamic mechanical measurements were performed on a Polymer Laboratories (Surrey, England) MK-II dynamic mechanical thermal analyzer over a temperature range of -100 to 200°C at 1 Hz and a heating rate of $5^{\circ}\text{C}/\text{min}$. The values of $\tan \delta$ and the storage modulus versus the temperature were recorded for each sample. The inherent viscosities (η_{inh}) were measured with an Ubbelohde viscometer.

Monomer synthesis

2,6-Bis(4-aminophenoxy)pyridine (AP) was synthesized as follows. Into a 100-mL, three-necked, round-bottom 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 of 2,6-dichloropyridine, 25 mL of dry NMP, 15 mL of dry toluene, and 0.021 mol of 4-aminophenol. Then, 0.0315 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 165°C through the removal of more toluene, and it was kept at the same temperature for 20 h. During this time, the progress of the reaction was monitored by thin-layer chromatography. The resulting reaction mixture was cooled and poured into water. Then, 100 mL of 3% NaOH was added to the mixture, and the mixture was washed repeatedly with a 3% NaOH solution and water. The obtained diamine was dried in a vacuum oven at 60°C . The yield of the reaction was about 88%.

The same procedure was repeated for the synthesis of 2,6-bis(5-amino-1-naphenoxy)pyridine (AN), but 5-amino-1-naphthol was used instead of 4-aminophenol, and the yield of reaction was about 92%, as shown in Scheme 1.

Polymer synthesis

A typical procedure for the preparation of poly(ether urea)s was as follows. A round-bottom flask equipped

with an N_2 inlet tube, a condenser, and a thermometer was charged with 0.005 mol of diamine and 10 mL of dry NMP. Then, a solution containing 0.005 mol of diisocyanate in 10 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 2 h at 60°C , and then it was precipitated in water. The polymer was filtered, washed with hot water and methanol, and dried in a vacuum oven at 100°C , as shown in Scheme 2.

RESULTS AND DISCUSSION

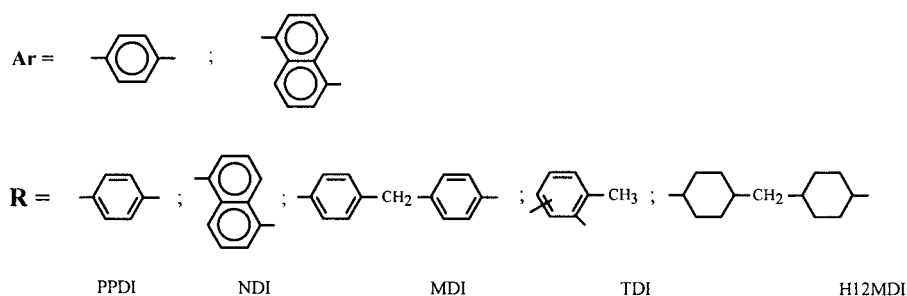
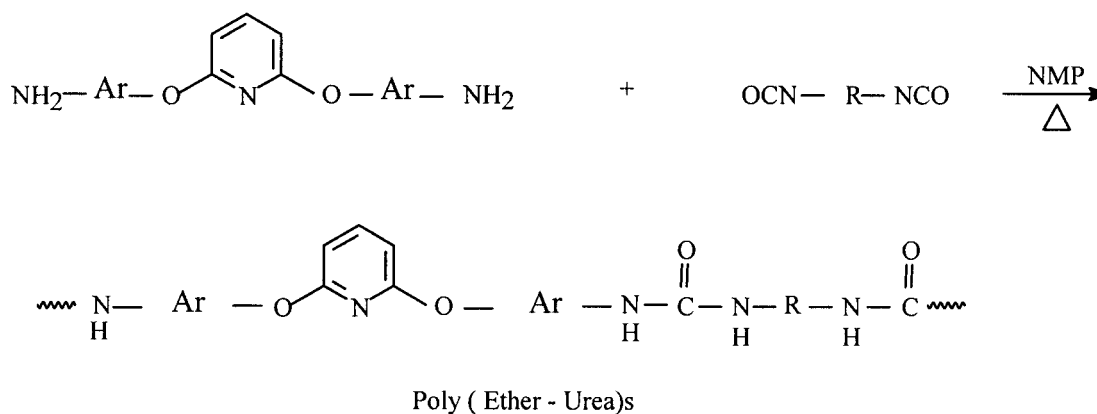
Diamines are valuable building block for the preparation of a variety of important polymers, including polyamides, polyimides, and polyureas. We prepared two fully aromatic, pyridine-based ether diamines and used them for the preparation of polyamides and polyimides.^{10,11} In this article, the synthesis of polyureas from the prepared diamines and their properties are described.

A nucleophilic aromatic substitution reaction of 4-aminophenol and 5-amino-1-naphthol with 2,6-dichloropyridine in the presence of potassium carbonate resulted in the preparation of two ether diamines, AP and AN. The structures of the two diamines are shown in Scheme 1. Spectroscopic methods and elemental analysis were applied to the characterization of the diamines (Table I).

The polyaddition reactions of five different diisocyanates (aromatic, semiaromatic, and cycloaliphatic) with the diamines afforded 10 poly(ether urea)s (Scheme 2). Conventional methods were used for the characterization of the polyureas, and the results are listed in Table II.

For the evaluation of the molecular weights, the η_{inh} values of the polyureas were measured at a concentration of 0.5 g dL^{-1} in NMP at 30°C . The η_{inh} values of the polymers were about $0.31\text{--}0.98 \text{ dLg}^{-1}$, indicating moderate to high molecular weights (Table II).

To study the thermal behavior and thermal stability of the polyureas and to study the effects of the struc-



Scheme 2 Preparation of poly(ether urea)s.

ture on these properties, we used different analytical thermal techniques, including DSC, dynamic mechanical thermal analysis (DMTA), and TGA. According to DSC (the midpoint of the change in the slope of the baseline) and DMTA (decreasing storage modulus with increasing $\tan \delta$), the polymers had glass-transition temperatures in the range of 134–183°C. The fully aromatic polyureas had higher glass-transition temperature than the others, and this was the result of higher rigidity. The initial decomposition temperatures of the poly(ether urea)s were about 146–240°C, and their temperatures of 10% gravimetric loss were 292–328°C.

For the estimation of the maximum decomposition temperatures of these polyureas, the first derivative of TGA versus the temperature (DTG) was used. It was 310–345°C. Also, the char yields of the polymers at 600°C were about 37–50% (Table III).

According to the obtained data, these poly(ether urea)s showed improved thermal stability in comparison with common polyureas.^{12–14} The phenylation of the backbone, the avoidance of weak linkages, and the symmetry of the structures, in addition to a stable pyridine heterocyclic ring, were the most important factors in improving the thermal properties. Also, the symmetry and polarity of the pyridine structure

TABLE I
Characterization of the Diamines

Substrate	IR (KBr cm^{-1})	NMR (DMSO- d_6 , δ , ppm)	Elemental analysis						Yield (%)
			Calcd			Found			
			C	H	N	C	H	N	
AP	3300–3450 1450–1600 1140	3.60 s (4H, amine); 6.34 d (2H, Py); 6.63–6.66 m (4H, Ph); 6.90–6.93 m (4H, Ph); 7.51 t (1H, Py)	69.62	5.12	14.33	69.49	5.19	14.42	88
AN	3300–3400 1460–1600 1150	5.83 s (4H, amine); 6.50 d (2H, Naph); 6.71 d (2H, Py); 7.01–7.29 m (8H, Naph); 7.75 t (1H, Py); 7.94 d (2H, Naph)	76.33	4.83	10.69	76.24	4.79	10.74	92

Py = pyridine; Ph = phenyl; Naph = naphthyl.

TABLE II
Characterization of Poly(ether ureas)

No.	Polymer	IR (KBr, cm^{-1})	NMR (DMSO- d_6 , δ)	Elemental analysis						η_{inh} (dL/g)	Yield (%)
				Calcd			Found				
				C	H	N	C	H	N		
1	AP-PPDI	3285, 3025, 1649, 1560, 1502, 1196	8.63/2H, 8.51/2H, 6.49-7.79/15H	66.22	4.16	15.45	66.01	4.06	15.62	0.98	85
2	AP-NDI	3320, 3029, 1652, 1557, 1502, 1195	8.76/2H, 8.53/2H, 6.50-8.06/17H	69.18	4.17	13.91	68.99	4.05	14.00	0.37	94
3	AP-MDI	3315, 3027, 2991, 1651, 1559, 1503, 1198	8.61/2H, 8.48/2H, 6.52-8.01/19H, 3.90/2H	70.72	4.60	12.89	70.38	4.71	12.98	0.48	91
4	AP-TDI	3366, 3030, 2989, 1659, 1547, 1504, 1200	8.62/2H, 8.56/1H, 8.52/1H, 6.50- 7.89/14H, 1.90/ 3H	66.80	4.49	14.98	66.39	4.22	15.10	0.34	90
5	AP-H ₁₂ MDI	3325, 3022, 2964, 1650, 1545, 1501, 1189	8.58/2H, 8.42/2H, 6.49-7.75/11H, 3.05/2H, 2.01- 2.07/18H, 1.26/ 2H	69.19	6.66	12.61	69.44	6.50	12.91	0.58	86
6	AN-PPDI	3277, 3019, 1642, 1555, 1510, 1218	8.95/2H, 8.76/2H, 6.52-8.47/19H	71.60	4.16	12.66	71.31	4.00	12.89	0.52	90
7	AN-NDI	3334, 3020, 1648, 1553, 1508, 1222	9.01/2H, 8.83/2H, 6.53-8.09/21H	73.63	4.14	11.60	73.19	4.39	11.34	0.32	79
8	AN-MDI	3348, 3017, 2991, 1647, 1595, 1512, 1221	8.72/2H, 8.52/2H, 6.54-8.04/23H, 3.93/2H	74.65	4.51	10.88	74.22	4.64	11.00	0.36	80
9	AN-TDI	3350, 3024, 2990, 1653, 1592, 1513, 1220	8.64/2H, 8.60/1H, 8.54/1H, 6.54- 7.92/18H, 1.91/ 3H	71.95	4.40	12.34	72.08	4.58	12.49	0.31	81
10	AN-H ₁₂ MDI	3356, 3018, 2922, 1649, 1590, 1539, 1218	8.61/2H, 8.45/2H, 6.53-7.76/15H, 3.07/2H, 2.04- 2.11/18H, 1.30/ 2H	73.28	6.26	10.68	73.01	6.04	10.92	0.40	84

TABLE III
Thermal Analysis Data

No.	T_g ($^{\circ}\text{C}$)	T_0 ($^{\circ}\text{C}$)	T_{10} ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	Char yield at 600 $^{\circ}\text{C}$ (%)
1	183	240	328	345	44
2	180	220	325	332	43
3	178	210	323	330	41
4	167	202	317	325	40
5	152	185	312	341	40
6	162	180	316	348	45
7	157	168	312	342	44
8	153	165	310	330	50
9	143	152	302	314	41
10	134	146	292	310	37

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 remaining.

caused an increase in the growth of the molecular weights, interactions, and close packing of the final polymer chains and therefore improved the thermal properties of the polymers.

The structure-property relations of these poly(ether urea)s can be explained from two points of view:

1. Diamine structures. The symmetry of the AP structure was greater than the symmetry of the AN structure. Therefore, the polymers derived from the AP monomer were more heat-resistant than the polymers derived from the AN monomer.
2. Diisocyanate structures. Fully aromatic diisocyanates (PPDI and NDI) imparted more rigidity to the final polymers, and so more thermal stability was observed than for semiaromatic [4,4'-diphenyl methane diisocyanate (MDI) and TDI] and TDI) and cycloaliphatic (H₁₂MDI) diisocyanates.

These two factors also had a reverse effect on the solubility of the polymers. Therefore, the polymers

derived from AN showed better solubility than the AP-derived polymers in dipolar aprotic solvents such as NMP, DMAc, DMF, and DMSO. The polymers derived from more flexible diisocyanates (H_{12} MDI) showed better solubility than the polymers derived from more rigid diisocyanates (PPDI).

CONCLUSIONS

Two fully aromatic pyridine-based ether diamines were synthesized through the reaction of 4-aminophenol and 5-amino-1-naphthol with 2,6-dichloropyridine. Polyaddition reactions of the prepared diamines with different diisocyanates afforded poly(ether urea)s with improved thermal stability. The phenylation of the backbone, the presence of a heterocyclic pyridine ring, and the incorporation of ether linkages were the main structural modifications used to synthesize the building block for the preparation of poly(ether urea)s with improved properties.

References

1. Allen, S. G.; Bevington, J. C. *Comprehensive Polymer Science*, 1st ed.; Pergamon: New York, 1989; Vol. 5, p 427.
2. Gopa, J.; Srinivasan, M. *J Polym Sci Polym Chem Ed* 1985, 23, 2719.
3. Yadav, S. K.; Khilar, K. C.; Suresh, A. K. *J Membr Sci* 1997, 125, 213.
4. Kurita, K.; Masuda, N. *Macromolecules* 1994, 27, 7544.
5. Hattori, T.; Takahashi, Y. *J Appl Phys* 1996, 79, 1713.
6. Segi, T.; Suzuoki, Y. *Jpn J Appl Phys* 1996, 39, 4444.
7. Meyer, B. *Urea-Formaldehyde Resins*; Addison-Wesley: New York, 1979.
8. Hayashi, K.; Harny, S.; Iwakura, Y. *Macromol Chem* 1965, 86, 64.
9. Hepburn, C. *Polyurethane Elastomers*; Applied Science: London, 1982.
10. Mehdipour-Ataei, S.; Heidari, H. *Macromol Symp* 2003, 193, 159.
11. Mehdipour-Ataei, S.; Heidari, H. *J Appl Polym Sci* 2004, 91, 22.
12. Wang, H. H.; Wu, S. P. *J Appl Polym Sci* 1999, 74, 1719.
13. Liu, J. H.; Lee, S. Y.; Tsai, F. R. *J Appl Polym Sci* 1998, 70, 2401.
14. Kwon, S. K.; Choi, K. L.; Choi, S. K. *J Polym Sci Part A: Polym Chem* 1987, 25, 1781.