Chinese Journal of Polymer Science Vol. 28, No. 1, (2010), 29–37

Chinese Journal of Polymer Science
© Chinese Chemical Society
Institute of Chemistry, CAS
Springer-Verlag 2010

HEAT-RESISTANT, PYRIDINE-BASED POLYAMIDES CONTAINING ETHER AND ESTER UNITS WITH IMPROVED SOLUBILITY

Hassan Ebadi[a] and Shahram Mehdipour-Ataei[b*]
[a] *Islamic Azad University of Shahreza, P.O. Box 81145-311, Shahreza, Isfahan, Iran*
[b] *Iran Polymer and Petrochemical Institute, P.O. Box 14965/115, Tehran, Iran*

Abstract A diamine containing ether and ester units, as basic monomer for the preparation of polyamides, was prepared *via* three consecutive reactions. Nucleophilic substitution reaction of 1,4-dihydroxy benzene with 4-nitrobenzoyl chloride produced 4-hydroxyphenyl 4-nitrobenzoate (HPNB). Reduction of nitro groups to amino groups using Fe and HCl resulted in preparation of 4-hydroxyphenyl 4-aminobenzoate (HPAB). The diamine was synthesized through nucleophilic substitution reaction of HPAB with 2,6-dichloropyridine. The precursors and diamine were fully characterized by common methods, and the diamine was polycondensed with different diacid chlorides in the presence of an acid scavenger to prepare new polyamides. The polyamides were characterized, and their physical properties including thermal stability and behavior, inherent viscosity and solubility were studied.

Keywords: Polyamide; Polycondensation; Diamine; Ester; Ether.

INTRODUCTION

Aromatic polyamides are recognized as high performance polymeric materials with outstanding mechanical properties, good chemical resistance and excellent thermal stability[1–5]. Due to the combination of these specific features, they are widely used in various industries. The demand for aromatic polyamides and other high performance polymeric materials is growing steadily because of their superior performance characteristics that are increasingly expected from engineering polymers in the aero-space, electronics, automobile and other industries[6, 7]. Due to the presence of amide linkages, they are hydrophilic polymers and can absorb water and therefore are good candidates for semi-permeable membranes[8]. These polymers (aliphatic, *meta*-aromatic and *para*-aromatic) are used as high-tech artificial fibers in the manufacturing of protective apparel for firemen, soldiers, race car drivers and gas filtration[9].

In spite of their specific structures and properties, like other heterocyclic polymers, aromatic polyamides are intractable materials, and therefore their intractability limits their applications. They have generally poor processability because of limited solubility or high softening temperatures, most of them do not melt before decomposition and can not be processed in the molten state[10, 11]. These characteristics result from the sequence of aromatic units, the inherent rigidity of the amide linkage and chain stiffness and intermolecular dipole-dipole and hydrogen bonding between amide groups[12].

New pyridine-based diamines and related polymers were previously prepared by our group[13–24] and in

---

[*] Corresponding author: Shahram Mehdipour-Ataei, E-mail: s.mehdipour@ippi.ac.ir

Received November 4, 2008; Revised December 24, 2008; Accepted December 30, 2008
doi: 10.1007/s10118-010-8212-0

continuation of these researches, here we wish to describe the synthesis and characterization of pyridine-based, heat-resistant polyamides containing ether and ester units with improved solubility. For this purpose a new diamine was designed and prepared through three consecutive reactions. Nucleophilic aromatic substitution reaction of 1,4-dihydroxybenzene with 4-nitrobenzoyl chloride using NaOH resulted in preparation of 4-hydroxyphenyl 4-nitrobenzoate (HPNB). Nitro group of HPNB was reduced to amino group and 4-hydroxyphenyl 4-aminobenzoate (HPAB) was produced. Nucleophilic substitution reaction of HPAB with 2,6-dichloropyridine led to a new diamine containing pyridine, ester and ether groups. Polycondensation reactions of this diamine with diacid chlorides yielded new polyamides that revealed heat-resistance and improved solubility which make them suitable for various applications.

EXPERIMENTAL

Materials

All needed chemicals were purchased either from Merck or Aldrich Chemical Co. 2,6-Dichloropyridine and 1,4-dihydroxybenzene were recrystallized from aqueous ethanol. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were purified by sublimation. *N*-methyl-2-pyrrolidone (NMP) and toluene were vacuum distilled over calcium hydride.

Instruments

Infrared measurements were performed on a Shimadzu IR-470 spectrometer (Tokyo, Japan). The ^{1}H-NMR spectra were recorded in DMSO-d$_6$ solution using a Bruker Avance DPX 250 MHz (GmbH, Germany). The mass spectra were recorded on a Shimadzu GC-MS-QP 1100-EX (Tokyo, Japan).

Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). Thermogravimetric analyses (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK). The dynamic mechanical measurements were recorded on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) in the bending mode at 1 Hz and a heating rate of 5 K/min (Surrey, UK). Inherent viscosities were measured at a concentration of 0.5 g/dL in NMP at 30°C by using an Ubbelohde viscometer.

Monomer Synthesis

Synthesis of 4-hydroxyphenyl 4-nitrobenzoate (HPNB)

4.95 g (0.045 mol) of 1,4-dihydroxy benzene was placed into a two-necked, round-bottomed flask, and it was dissolved in a solution containing 1.90 g of NaOH in 21 mL of H_2O. The solution temperature was maintained at 0–5°C using an ice-water bath. Then, 6.86 g (0.037 mol) of 4-nitrobenzoyl chloride was dissolved in 60 mL of tetrachloroethane and slowly added to the flask at 0–5°C. The mixture was stirred for 6 h at room temperature, and then 550 mL of 3 mol/L HCl was added to the solution and stirred for 12 h. The product was filtered and washed with hot water and methanol. It was dried in a vacuum oven at 80°C for 12 h (yield 89%).

Synthesis of 4-hydroxyphenyl 4-aminobenzoate (HPAB)

A three-necked flask containing 17.58 g of iron powder, 22 mL of ethanol, 22 mL of water and 0.3 mL of concentrated hydrochloric acid was fitted with a mechanical stirrer, a reflux condenser and a thermometer. The mixture was heated to reflux with stirring. After this mixture had been stirred for 10 min, 6.48 g of HPNB was added gradually over 20 min, and stirring was continued for another 10 min at reflux. Then the mixture was cooled down to room temperature, and 0.3 g of sodium bicarbonate was added. After three hours stirring, the mixture was filtered, and the filtrate was concentrated by vacuum distillation. The residue was dissolved in absolute alcohol, and the stoichiometric amount of 36% HCl was added to form hydrochloride salt, which was completely precipitated out of the solution by the addition of a large amount of ethyl acetate. The precipitate was filtered off and dried and then dissolved in water. HPAB was precipitated with the addition of aqueous ammonia, and the precipitated product was filtered and washed with plenty of water (yield 78%).

Synthesis of pyridine-based ether ester diamine

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 0.01 mol of 2,6-dichloropyridine, 25 mL of dry NMP, 15 mL of dry toluene and 0.021 mol of HPAB. Then 0.0315 mol of K_2CO_3 was added to the mixture by stirring, and the reaction mixture was heated to 140°C for 6 h. The generated water (reaction of HPAB with K_2CO_3 yielded the potassium salt of HPAB and by-product of water and carbon dioxide) was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 165°C by removing more toluene and kept at the same temperature for 18 h. During this time, progress of the reaction was monitored by thin-layer chromatography (TLC). 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 (yield 80%).

Polyamide Synthesis

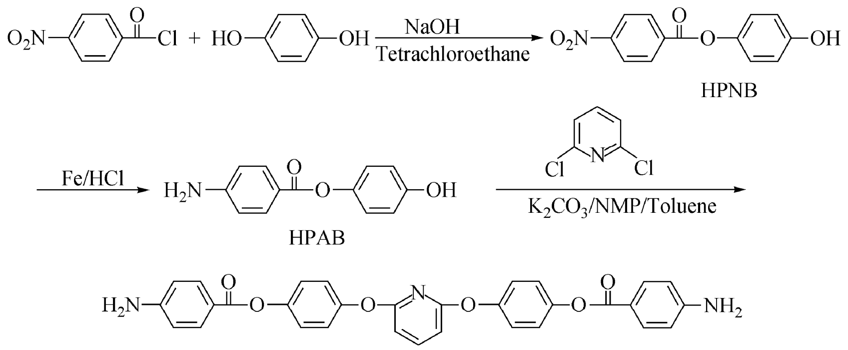
The synthesis of polyamide typically was carried out as follows: A 100 mL two-necked round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube and calcium chloride drying tube was charged with 2 mmol of the diamine and 15 mL of dry NMP. The mixture was stirred at 0°C for 0.5 h. Then about 1 mL of propylene oxide (as an acid scavenger) was added, and after a few minutes 2 mmol of diacid chloride was added and the mixture was stirred at 0°C for 0.5 h. The temperature was raised to room temperature, and the solution was stirred for 6 h. Polyamide was precipitated by pouring the flask content into water. Then it was filtered, washed with hot water and methanol and dried overnight under vacuum at 120°C (yields over 87%).

RESULTS AND DISCUSSION

Polyamides have high susceptibility and potential for application in various industrial fields, however the poor processability has limited their applications. Considerable efforts to modify polyamide structures are continuously under way to enhance their processability. Structural modifications such as the introduction of a bulky pendant substituent[25], the nature of parent chain (types of linkages and aromatic units)[26], non-coplanar biphenylene moieties[27] and flexible spacers[28] have been reported to improve the solubility and to lower the phase transition temperatures. Although most soluble polymers have been prepared by combinations of the structural modifications, it does appear that a flexible or kinked linkage is a necessary prerequisite for solubility. Generally, aromatic polymers that contain aryl ether linkages have greater tractability and chain flexibility, and lower glass transition than their corresponding polymers without these groups in the repeat units. The improved solubility and lower glass transition temperatures are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation.

In an another point of view, copolymerization is an effective approach to enhance the solubility of the polyamides and induce some useful properties to the final polymers[29–31]. Copolymers having ether and ester linkages impart flexibility to the polyamides without compromising the thermal stability. Presence of ester units retains specific physical properties in the final polymers due to the fact that polyesters have good thermal and mechanical properties. In another aspect, specific applications of poly(ester amide)s both for biomedical and pharmaceutical uses and the environmental problems result from their structural features, since they combine amide groups responsible for hydrogen bond interactions that improve properties and highly hydrolysable ester groups[32, 33].

The purpose of this study was focused on improving the solubility of the novel heat-resistant polyamides through the design and synthesis of new diamine. Therefore, for the preparation of a flexible pyridine-based diamine with built-in ester and ether groups three sequences of reactions were performed. Nucleophilic substitution reaction of 1,4-dihydroxybenzene with 4-nitrobenzoyl chloride in the presence of NaOH led to the preparation of a nitro phenolic compound (HPNB). The related amino phenolic compound (HPAB) was prepared *via* reduction of nitro group using Fe and HCl. The novel pyridine-based diamine containing ether and ester groups was obtained by nucleophilic aromatic substitution reaction of 2,6-dichloro pyridine with two moles of HPAB in the presence of potassium carbonate in NMP (Scheme 1).



Pyridine-based, ether, ester diamine

Scheme 1 Preparation of diamine

The structures of diamine and their precursors (HPNB and HPAB) were characterized and confirmed using FT-IR, ^{1}H-NMR and mass spectroscopy and also elemental analysis, and the results were collected in Table 1. The FT-IR spectra of them were shown in Fig. 1 for comparison in which the main change was observed in the position of carbonyl absorption band. For HPNB the carbonyl absorption band appeared at 1727 cm^{-1} whereas for HPAB and diamine it was observed at 1717 and 1650 cm^{-1}, respectively. This confirms reduction of double bond character of carbonyl group by conversion of HPNB to HPAB and to diamine that was resulted from electron donation character of substituents on the aromatic rings. Also, it confirms that the carbonyl group of HPAB has not been reduced using Fe and HCl reagent during reduction of nitro group.

Table 1. Characterization data of precursors and diamine

Substance	IR (KBr, cm^{-1})	^{1}H-NMR[a] (DMSO-d$_6$, δ)	Mass spectra. (m/z)	Elemental analysis			
					C	H	N
HPNB	3300–3460, 1727, 1598, 1522, 1346, 1262	9.56 (s, 1H, OH) 8.42 (d, 2H, ph.) 8.34 (d, 2H, ph.) 7.12 (d, 2H, ph.) 6.82 (d, 2H, ph.)	259	Calc.: Found:	60.23 60.08	3.47 3.34	5.40 5.62
HPAB	3200–3461, 1717, 1593, 1504, 1340, 1273, 1063	9.43 (s, 1H, OH) 7.77 (d, 2H, ph.) 6.96 (d, 2H, ph.) 6.77 (d, 2H, ph.) 6.63 (d, 2H, ph.) 6.45 (s, 2H, NH_2)	229	Calc.: Found:	68.12 67.98	4.80 4.98	6.11 5.96
Diamine	3310–3330, 1650, 1600, 1496, 1314, 1240, 1179	7.98 (d, 4H, ph.) 7.86 (dd, 1H, py.) 7.12 (d, 4H, ph.) 6.91 (d, 4H, ph.) 6.74 (d, 4H, ph.) 6.63 (d, 2H, py.) 5.80 (s, 4H, NH_2)	531	Calc.: Found:	69.79 69.39	4.32 4.16	7.88 8.02

[a] ph.= phenyl; py.= pyridine

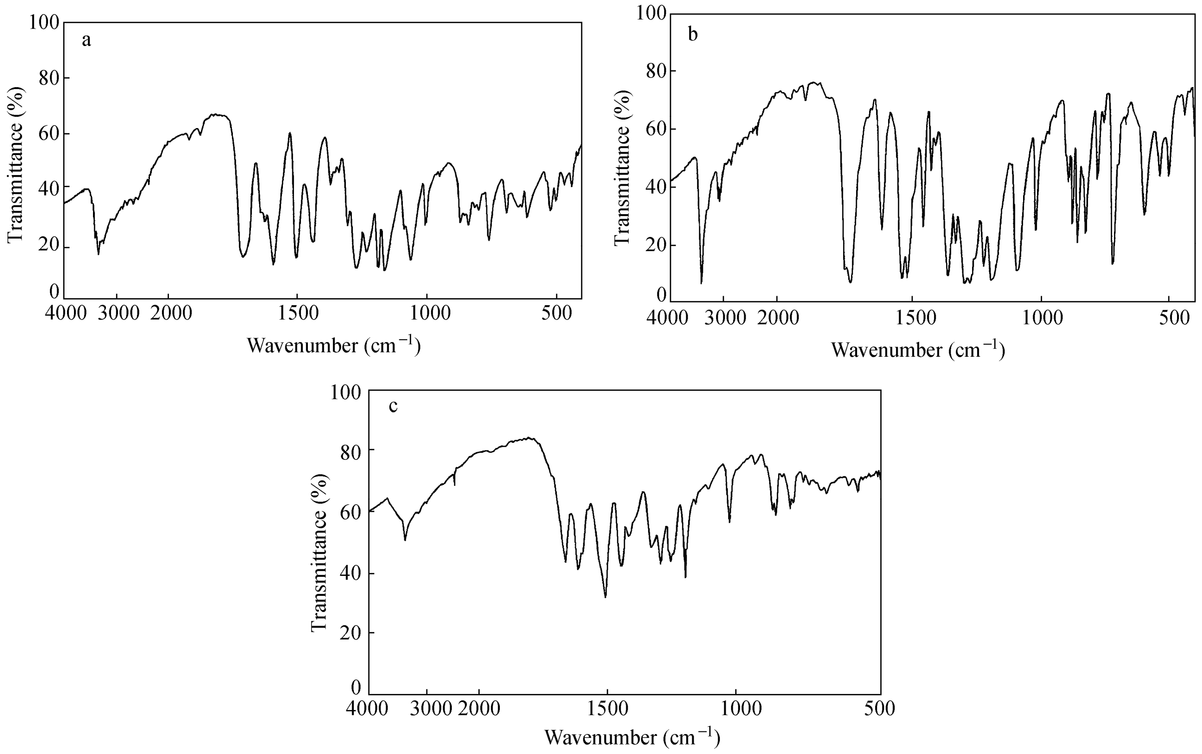
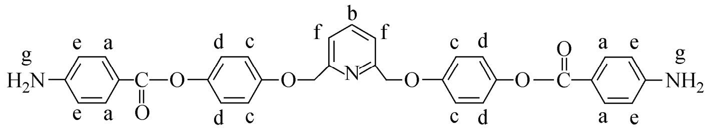
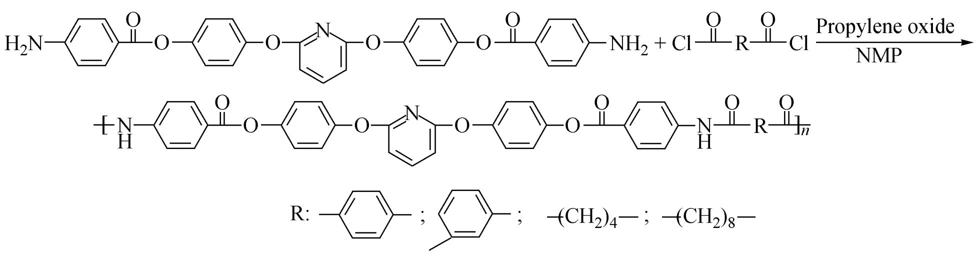


Fig. 1 FT-IR spectra of (a) HPNB, (b) HPAB and (c) diamine

Characteristic bands of diamine in the IR spectrum appeared at 3310–3330 (amine N—H stretching), 1650 (ester C=O stretching), 1600 (amine N—H bending), 1496 (C=C aromatic), 1314 (C—N stretching), 1240 (ester C—O stretching) and 1179 cm^{-1} (ether C—O stretching). Also, peaks in ^{1}H-NMR (DMSO-d$_6$) spectrum were observed at δ7.98 (d, 4H$_a$), 7.86 (dd, 1H$_b$), 7.12 (d, 4H$_c$), 6.91 (d, 4H$_d$), 6.74 (d, 4H$_e$), 6.63 (d, 2H$_f$), 5.80 (s, 4H$_g$).



Polyamides were prepared *via* low temperature polycondensation reactions of the diamine with different diacid chlorides including terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), adipoyl chloride (AC) and sebacoyl chloride (SC) in the presence of an acid scavenger (Scheme 2).



Scheme 2 Preparation of polyamides

The polyamides were characterized by using conventional spectroscopic methods including IR, ^{1}H-NMR and elemental analysis technique, and the results were tabulated in Table 2. The representative IR and ^{1}H-NMR spectra are shown in Figs. 2 and 3, respectively. In the IR spectrum, characteristic bands were observed at 3298–3330 (amide N—H stretching), 1669–1695 (ester C=O stretching), 1649–1651 (amide C=O stretching), 1598–1599 (amide N—H bending), 1496–1499 (C=C aromatic), 1312–1315 (C—N stretching), 1235–1240 (ester C—O stretching) and 1176–1183 cm^{-1} (ether C—O stretching).

Table 2. Characterization data of polymers

Polymer	IR (KBr, cm^{-1})	^{1}H-NMR[a] (DMSO-d_6, δ)	Elemental analysis			
				C	H	N
Diamine-TPC	3330, 1689, 1651, 1598, 1498, 1314, 1240, 1179	10.48 (s, 2H, NH) 8.13 (d, 4H, ph.) 8.09 (d, 4H, ph.) 7.78 (dd, 1H, py.) 7.74 (d, 4H, ph.) 7.10 (d, 4H, ph.) 6.88 (d, 4H, ph.) 6.51 (d, 2H, py.)	Calc.: Found:	70.58 70.18	3.80 3.51	6.33 6.52
Diamine-IPC	3331, 1695, 1650, 1599, 1499, 1315, 1239, 1183	10.47 (s, 2H, NH) 8.63 (d, 1H, ph.) 8.18 (d, 2H, ph.) 8.07 (d, 4H, ph.) 7.77 (dd, 1H, py.) 7.72 (d, 4H, ph.) 7.60 (dd, 1H, ph.) 7.09 (d, 4H, ph.) 6.86 (d, 4H, ph.) 6.50 (d, 2H, py.)	Calc.: Found:	70.58 70.21	3.80 3.99	6.33 6.14
Diamine-AC	3299, 2922, 1674, 1651, 1599, 1496, 1313, 1240, 1181	10.38 (s, 2H, NH) 7.99 (d, 4H, ph.) 7.74 (dd, 1H, py.) 7.70 (d, 4H, ph.) 7.05 (d, 4H, ph.) 6.83 (d, 4H, ph.) 6.47 (d, 2H, py.) 2.14 (t, 4H, CH_2) 1.60 (m, 4H, CH_2)	Calc.: Found:	69.04 68.84	4.54 4.78	6.53 6.83
Diamine-SC	3298, 2920, 1669, 1649, 1598, 1498, 1312, 1235, 1176	10.36 (s, 2H, NH) 7.96 (d, 4H, ph.) 7.73 (dd, 1H, py.) 7.69 (d, 4H, ph.) 7.03 (d, 4H, ph.) 6.81 (d, 4H, ph.) 6.46 (d, 2H, py.) 2.12 (t, 4H, CH_2) 1.55 (m, 4H, CH_2) 1.20 (m, 8H, CH_2)	Calc.: Found:	70.37 70.61	5.33 5.08	6.01 6.20

[a] ph. = phenyl; py. = pyridine

The polymers showed improved solubility (1.4–2.1 g/dL) in polar aprotic solvents such as NMP, *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and also in *m*-cresol. Incorporation of flexible ether and ester groups in addition to pyridine units into the backbone of polymers was the main factor for improving the solubility.

Inherent viscosity is a good criterion for estimation of molecular weight. The inherent viscosity of the polymers was measured at a concentration of 0.5 g/dL in NMP at 30°C. It was in the range of 0.37–0.44 g/dL that revealed reasonable molecular weights for the polymers.

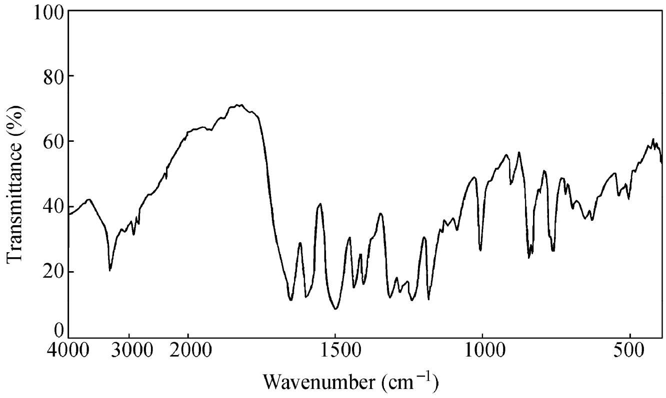


Fig. 2 FT-IR spectrum of diamine-SC polyamide

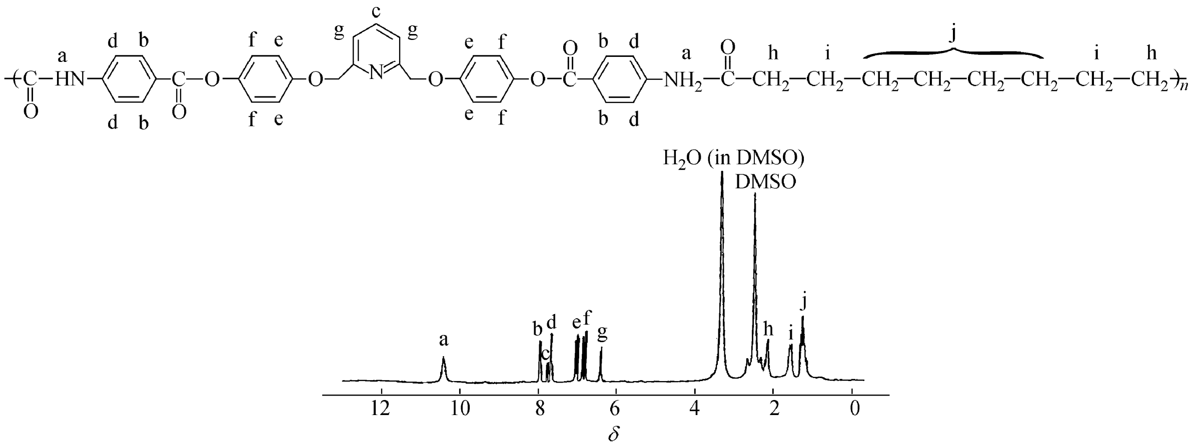


Fig. 3 ^{1}H-NMR spectrum of diamine-SC polyamide

To study thermal behavior and thermal stability of the polyamides DMTA and TGA were used. According to the DMTA analysis, the glass transition temperature (T_g) of the polymers was in the range of 183–217°C obtained from the temperature at which modulus decreased and tanδ went through a maximum (Table 3). Presence of flexible ether and alkylene groups in the polymer chains reduced the T_g values (by decreasing the energy of internal rotation) in comparison with common polyamides[11, 32].

Table 3. Thermal characteristic data of the polymers

Polymer	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Char yield at 600°C (%)
Diamine-TPC	217	274	370	503	42
Diamine-IPC	209	259	359	497	39
Diamine-AC	186	226	334	483	25
Diamine-SC	183	214	322	480	23

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

Thermogravimetric analysis (TGA) in air at a heating rate of 10 K/min was used for the evaluation of the thermal stability of the polymers. The initial decomposition temperatures (T_0) of the polymers were about

214–274°C, and the temperatures for 10% weight loss (T_{10}) that are important criterion for estimation of thermal stability, were in the range of 322–370°C. Maximum decomposition temperature ($T_{\max}$) of the polymers which was obtained from the first derivative of TGA curves was around 480–503°C, and also the weight of polymers remained (char yield) at 600°C was about 23%–42% (Table 3). The representative DMTA and TGA curves are shown in Figs. 4 and 5, respectively.

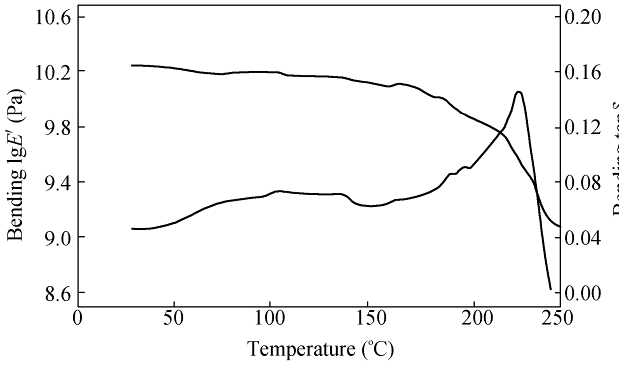


Fig. 4 DMTA graph of diamine-TPC polyamide

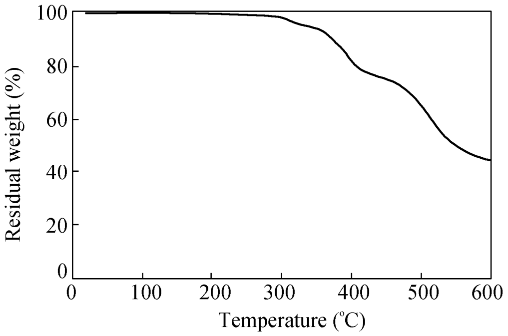


Fig. 5 TGA graph of diamine-TPC polyamide

Therefore the presence of amide, ester and phenylated units was the main factor for maintaining thermal stability, and existence of ether, pyridine and methylene groups were the main factors for improving the solubility of the polymers. Combination of these structural features led to heat-resistant polyamides with improved solubility. The most rigid and symmetric polymer (TPC-based polymer) showed the highest heat-resistant and lowest solubility while the most flexible polymer (SC-based polymer) revealed the highest solubility and lowest heat-resistant among the prepared polyamides.

CONCLUSIONS

A diamine containing ester, ether and pyridine units was prepared by three successive reactions. Reaction of 1,4-dihydroxybenzene with 4-nitrobenzoyl chloride yielded HPNB. HPAB was prepared by reduction of nitro group to amino group. The diamine was obtained through reaction of HPAB with 2,6-dichloropyridine. Polycondensation reactions of this diamine with different aromatic diacid chlorides led to a series of polyamides. Improved solubility and at the same time heat-resistance of the polymers were mainly attributed to their specific structures including existence of ether, pyridine and methylene groups from one side, and presence of amide, ester and phenylated units from the other side.

REFERENCES

1 Cassidy, P.E., "Thermally Stable Polymers", Dekker, New York, 1980, p.67

2 Liaw, D.J., Liaw, B.Y., Chen, J.R. and Yang, C.M., Macromolecules 1999, 32: 6860

3 Wu, S.C. and Shu, C.F., J. Polym. Sci. Part A: Polym. Chem., 2003, 41: 1160

4 Negi, Y.S., Suzuki, Y.I., Kawamura, I., Kakimoto, M.A. and Imai,Y., J. Polym. Sci. Part A: Polym. Chem., 1996, 34: 1663

5 Liaw, D.J., Liaw, B.Y. and Yang, C.M., Macromolecules, 1999, 32: 7248

6 King, F.A. and King, J.J., "Engineering Thermoplastics", Dekker, New York, 1985, p.83

7 Yang, C.P. and Hsiao, S.H., J. Appl. Polym. Sci., 1986, 31: 979

8 Frazer, A.H., "High Temperature Resistant Polymers, Polymer Reviews", Vol. 17, Interscience, New York, 1968, p.78

9 Prestone, J., de Winter, W.F., Black, W.B. and Hofferbert, W.L., J. Polym. Sci. Part A: Polym. Chem., 1969, 7: 3027

10 Yang, H.H., "Aromatic High-Strength Fibers", Wiley, New York, 1989, p.15

11 Ferreiro, J.J., de la Campa, J.G., Lozano, A.E. and de Abajo, J., J. Polym. Sci. Part A: Polym. Chem., 2005, 43: 5300

12 Horta, A., Coca, J. and Diez, F.V., Adv. Polym. Technol., 2000, 19: 120

13 Mehdipour-Ataei, S. and Heidari, H., Macromol. Symp., 2003, 193: 159

14 Mehdipour-Ataei, S. and Heidari, H., J. Appl. Polym. Sci., 2004, 91: 22

15 Mehdipour-Ataei, S. and Amirshaghaghi, A., Eur. Polym. J., 2004, 40: 503

16 Mehdipour-Ataei, S. and Amirshaghaghi, A., Polym. Int., 2004, 53: 1185

17 Mehdipour-Ataei, S., Sarrafi, Y. and Pirjel, M.A., J. Appl. Polym. Sci., 2004, 93: 961

18 Mehdipour-Ataei, S., Malekimoghaddam, R. and Nami, M., Eur. Polym. J., 2004, 40: 2523

19 Mehdipour-Ataei, S., Malekimoghaddam, R. and Nami, M., Eur. Polym. J., 2005, 41: 1024

20 Mehdipour-Ataei, S. and Amirshaghaghi, A., J. Appl. Polym. Sci., 2005, 96: 570

21 Mehdipour-Ataei, S., Mosslemin, M.H. and Shafieezadeh, M., React. Funct. Polym., 2006, 66: 403

22 Mehdipour-Ataei, S., Amirshaghaghi, A. and Bahri, N., Eur. Polym. J., 2006, 42: 2646

23 Mehdipour-Ataei, S., Tadjarodi, A. and Babanzadeh, S., Eur. Polym. J., 2007, 43: 498

24 Mehdipour-Ataei, S. and Babanzadeh, S., React. Funct. Polym., 2007, 67: 883

25 Oishi, Y., Takado, M., Yoneyama, M., Kakimoto, M.A. and Imai, Y., J. Polym. Sci. Part A: Polym. Chem., 1990, 28: 1763

26 Hsiao, S.H. and Yang, C.P., J. Polym. Sci. Part A: Polym. Chem., 1990, 28: 2169

27 Liaw, D.J., Hsu, P.N. and Liaw, B.Y., J. Polym. Sci. Part A: Polym. Chem., 2001, 39: 63

28 García, J.M., Álvarez, J.C., de la Campa, J.G. and de Abajo, J., J. Appl. Polym. Sci., 1998, 67: 975

29 Kricheldorf, H.R., Schmidt, B. and Delius, U., Eur. Polym. J., 1990, 26: 791

30 Aducci, J., Chapoy, L.L., Jonsson, G., Kops, J. and Shinde, B.M., Polym. Eng. Sci., 1983, 28: 2069

31 Aducci, J., Chapoy, L.L., Jonsson, G., Kops, J. and Shinde, B.M., Polym. Eng. Sci., 1981, 21: 712

32 Rodriguez-Galan, A., Fuentes, L. and Puiggali, J., Polymer, 2000, 41: 5967

33 Gonsalves, K.E. and Mungara, P.M., Trends Polym. Sci., 1996, 25: 4