Colloid Polym Sci (2007) 285:1749–1754
DOI 10.1007/s00396-007-1768-8

SHORT COMMUNICATION

Soluble aromatic polyamide bearing ether linkages: synthesis and characterization

Sonia Zulfiqar · Zahoor Ahmad · Muhammad Ilyas Sarwar

Received: 31 July 2007 / Revised: 15 August 2007 / Accepted: 23 August 2007 / Published online: 16 October 2007

Abstract Soluble aromatic polyamide chains were prepared by reacting 4–4′-oxydianiline with isophthaloyl chloride in dimethylacetamide. To quench the HCl produced during the polymerization reaction, a stoichiometric amount of triethylamine was added. The precipitates formed were separated leaving behind clear polyamide resin. Thin and transparent film was obtained by evaporating the solvent and was subjected for Fourier transform infrared (IR), nuclear magnetic resonance (NMR), gel permeation chromatography, thermogravimetric analysis, differential scanning calorimetry, water absorption, and mechanical analyses. The transparent film was found to be soluble in dimethylacetamide, dimethyl sulfoxide, and dimethylformamide. IR and NMR spectroscopic analyses confirmed the structure of the polyamide while the gel permeation chromatography revealed the formation of a high-molecular-weight polymer. Thermogravimetry, differential scanning calorimetry, water absorption, and mechanical testing were also performed to further verify its physical properties. A soluble aromatic polyamide was successfully synthesized by solution polymerization and characterized. The polyamide has film-forming property, and the film is transparent, mechanically strong, and thermally stable.

Keywords Aromatic polyamide · Spectroscopic analysis · GPC · Mechanical properties · TGA · DSC

Introduction

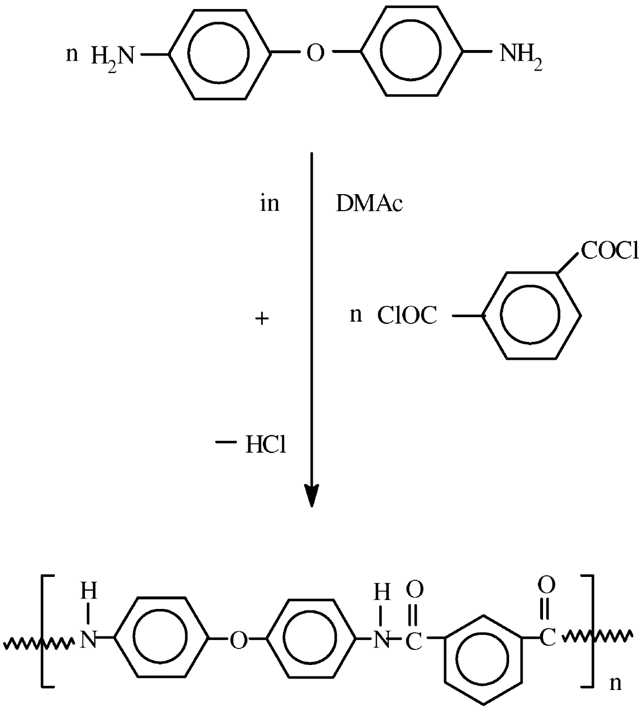
Aromatic polyamides are the modern high-temperature-resistant polymers. In fact, they were the first aromatic linear polymers that could be considered thermally stable and constitute the most important family of functionalized polyphenylenes [1–3]. Moreover, polyimides and fluorinated polymers are more vital for their production, and consumption are concerned than aromatic polyamides when thermally stable polymers are considered [4]. Aromatic polyamides like other aromatic and heterocyclic polymers are quite intractable materials because they are infusible and insoluble in organic solvents. Purely aromatic polyisophthalamides, for instance, are soluble only in a few aprotic polar solvents containing dissolved inorganic salts. Therefore, much effort has been invested to modify the backbone and the structure of aromatic polyamides by chemical means to improve their solubility (processability) without severely sacrificing their outstanding thermal properties [5–7].

Regular aromatic polyamides derived from symmetrical monomers can develop high degrees of crystallinity, a factor that works against solubility and processability. A lot of efforts have been directed toward structural modifications designed to disturb regularity and chain packing, thus providing better solubility. Several other approaches have been made through synthetic modification by the incorporation of ether groups or other flexibilizing linkages [8, 9] into the main chain generally leads to a significant improvement in the solubility and/or thermo-plasticity of aramids. It has been recognized that the incorporation of aryl-ether linkages generally imparts an enhanced solubility, processability, and toughness of the polymers without substantial diminution of thermal properties. Such flexibility in these polymers leads to their excellent solubility in polar, aprotic solvents such as *N*-methylpyrrolidone, dimethyl-

---

S. Zulfiqar · M. I. Sarwar (✉)
Department of Chemistry, Quaid-i-Azam University,
Islamabad 45320, Pakistan
e-mail: ilyassarwar@hotmail.com

Z. Ahmad
Department of Chemistry, Faculty of Science, Kuwait University,
P.O. Box 5969, Safat 13060, Kuwait



Scheme 1 Formation of aromatic polyamide chains

formamide (DMF), dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO). Aramids containing ether linkages or asymmetrical groups are significantly more flexible and soluble than conventional aramids [10–12]. Different hybrid materials based on these soluble aramids have been reported [13–19]. Another attractive synthetic approach to achieve structural modifications is the incorporation of bulky substituents as pendent groups along the polymer backbone. If the pendent groups are carefully chosen, it is possible to promote solubility without impairing thermal and mechanical properties to any great extent. Some useful modifications can also be achieved by the use of chemical and stereochemical copolymers. In fact, many polymers, such as polyterephthalamides [20], polyterephthalates [21], polyimides [22], and other polyheterocycles [23] have been chemically modified by polycondensation or co-condensation of monomers bearing bulky pendent groups.

In this paper, a diamine containing an ether group was condensed with isophthaloyl chloride (IPC) to produce soluble aromatic polyamide resin. The polymer chains were prepared by the reaction of 4-aminophenyl ether with IPC in DMAc. The polyamide had a film-forming property, and the dried film was easily soluble in DMSO. This improved solubility facilitates for its further characterization and to establish the structure–property relationship of the polyamide. The synthesized aromatic polyamide was characterized by Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), stress–strain, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and water absorption measurements.

Experimental section

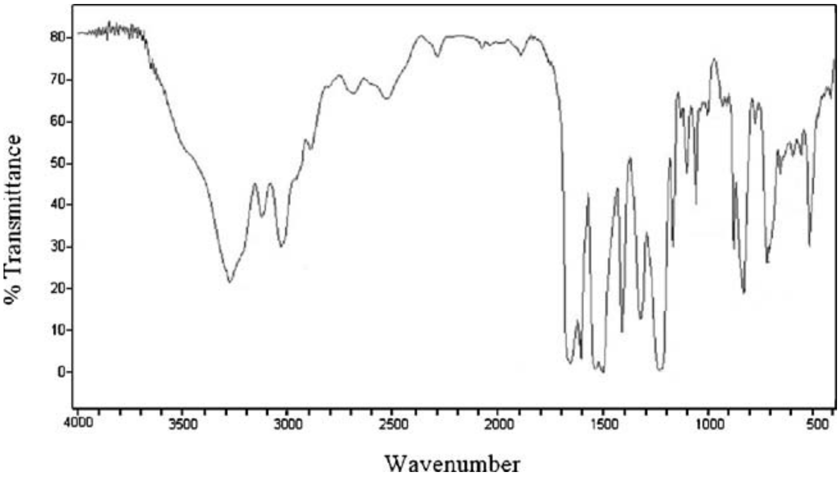
Materials

4–4′-Oxydianiline, IPC, triethylamine (TEA), DMSO, and absolute *N*, *N*-DMF was obtained from Fluka and used as such. *N*, *N*-DMAc was procured from Aldrich and dried over molecular sieves before use.

Synthesis of aromatic polyamide

A soluble aromatic polyamide was synthesized by the condensation of aromatic diamine and diacid chloride at low temperature. For the preparation of polyamide, a known amount of 4, 4′-oxydianiline was placed in the flask followed by the addition of DMAc as a solvent under an

Fig. 1 FT-IR spectrum of neat aromatic polyamide film at 25 °C



inert atmosphere. After initial mixing of the diamine, a stoichiometric amount of IPC was added to the reaction flask. The reaction is highly exothermic, and a low temperature is necessary to avoid any side reactions. Therefore, the reaction contents were cooled to 0 °C. For the solution polymerization of aromatic polyamide, however, no organic solvent is sufficiently powerful to keep the polymer in solution as the molecular weight of the polymer builds up. Therefore, DMAc and HCl (produced during the polymerization reaction of diamine and diacids chloride) give the desired salt–solvent combination with increased solubility for polyaramids. Moreover, the HCl salt concentration increases as the polycondensation proceeds, thereby increasing the solvating power of the solvent as the molecular weight of the polymer is building up. The polymer reaction after initial mixing of monomers was allowed to come to ambient temperature after 1 h. Although the reaction between diamine and diacid chloride is extremely fast, however, further 24 h were given to the reaction mixture for its completion [24]. The reaction mixture is highly viscous and golden yellow in color. The chemical reaction leading to the formation of aromatic polyamide chains is shown in Scheme 1. To remove the HCl from the aramid solution, stoichiometric amount of TEA was added with constant stirring for 3 h. The precipitates formed were centrifuged, and the pure aromatic polyamide was separated by decant method.

Film preparation

The pure aromatic polyamide solution was poured into a Petri dish placed on a leveled surface in an oven at 80 °C for 6 h to evaporate the solvent. The polyamide film was removed from the Petri dish and further dried in vacuo at 60 °C for 72 h. The film obtained was about 0.5 mm thick and was used for the complete characterization of the aromatic polyamide.

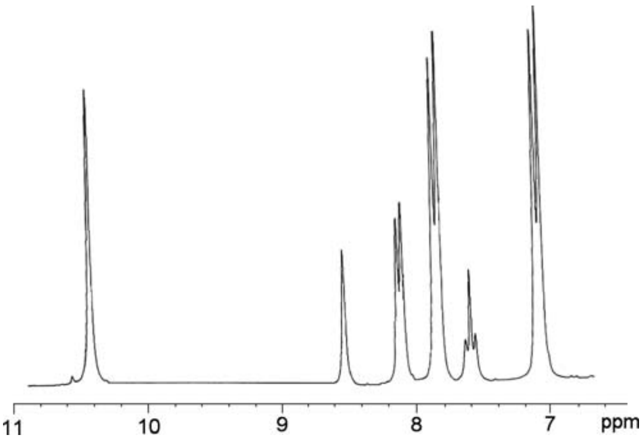


Fig. 2 ^{1}H NMR spectrum of neat aromatic polyamide in DMSO-d_6

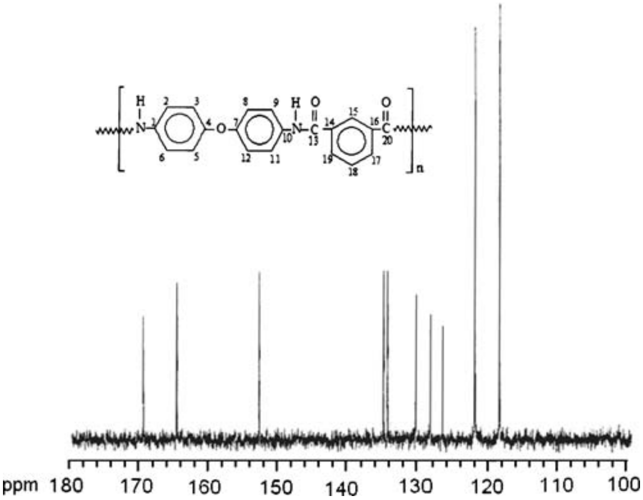


Fig. 3 ^{13}C NMR spectrum of neat aromatic polyamide in DMSO-d_6

Characterization

The FT-IR spectrum of the thin transparent film of neat aromatic polyamide was recorded at 25 °C over the range 4,000–400 cm^{-1} using Excalibur series FT-IR spectrometer, Model no. FTSW 3000MX manufactured by BIO-RAD. The ^{1}H and ^{13}C NMR spectra of neat aromatic polyamide were recorded on a Bruker Avance 300 MHz NMR Spectrometer in deuterated DMSO (DMSO-d_6). Tetramethylsilane was used as an internal reference. Weight-average (M_w) and number-average (M_n) molecular weights and polydispersity of aromatic polyamide was determined by a GPC equipped with Waters 515 pump. Polystyrene was employed as the standard. A combination of three columns (GRAM 10,000, 1,000, and 100 in a series supplied by Polymer Standard Service, Mainz (Germany) were used for GPC analysis. Absolute *N*, *N*-DMF was used as an eluent with a flow rate of 1.0 ml min^{-1} at 60 °C. One hundred and 50 µl of polymer solution in DMF were injected, and the eluents were monitored with an refractive index (RI) detector (RI 101) and UV detector (UV S3702 at 270 nm), respectively. Tensile properties of the polyamide

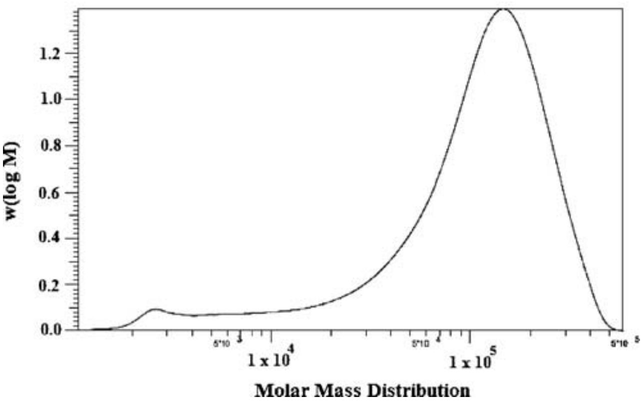


Fig. 4 GPC distribution of aromatic polyamide monitored with an RI detector (RI 101)

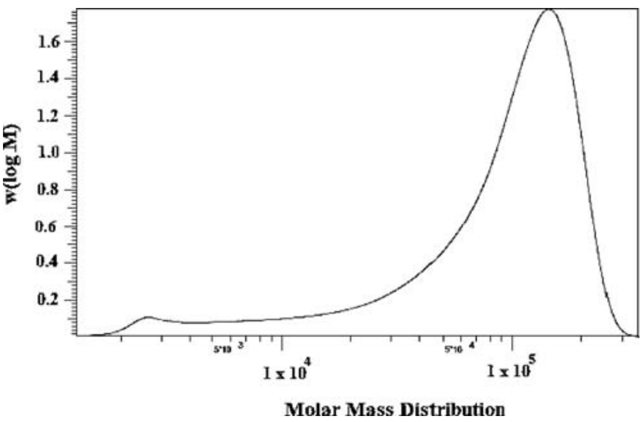


Fig. 5 GPC distribution of aromatic polyamide monitored with UV detector (UV S3702 at 270 nm)

film was measured according to DIN procedure 53455 having a crosshead speed of 5 mm min^{-1} at 25 °C using Testometric Universal Testing Machine M350/500, and a typical stress–strain curve obtained has been reported that is used to calculate its related mechanical properties. The thermal stability of the aromatic polyamide was determined using a METTLER TOLEDO TGA/SDTA 851^{e} thermogravimetric analyzer using 1–5 mg of the sample in Al_2O_3 crucible heated from 25 to 900 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere with a gas flow rate of 30 ml min^{-1}. Thermomechanical property of aromatic polyamide was characterized using a METTLER TOLEDO DSC 822^{e} differential scanning calorimeter. For determining the glass transition temperature, sample of 5–10 mg was encapsulated in an aluminum pan and heated at a ramp rate of 10 °C min^{-1} under a nitrogen atmosphere. The water absorption study of the polyamide was carried out following ASTM D570-81 procedure. The film was placed in a vacuum oven at 80 °C till the film attained a constant weight and then immediately weighed out to the nearest 0.001 g to get the initial weight (W_o). The film was completely soaked in a container of deionized water maintained at 25 °C. After 24 h, the film was removed from water and then was quickly placed between sheets of paper to remove the excess water and film was weighed immediately. The film was again immersed in water. After another 24-h soaking period, the film was removed, dried, and weighed for any weight gain. The procedure was repeated till the film almost attained the constant weight. The total soaking time was 168 h, and the sample was weighed at regular 24-h time intervals to get the final weight (W_f). The percentage of increase in weight of the sample was calculated to the nearest 0.01% by using the formula $(W_\mathrm{f}-W_\mathrm{o})/W_\mathrm{o}$.

Results and discussion

The thin film obtained from pristine aromatic polyamide was transparent and golden yellow in color. The different kinds of analyses employed for the characterization of synthesized polyamide are discussed below.

FT-IR spectroscopy

To elucidate the structure of aromatic polyamide, an IR spectrum of its thin and transparent film was recorded at 25 °C and various IR bands appeared in the spectrum are presented in Fig. 1. The bands at 3,269 and 1,605 cm^{-1} can be assigned to the N–H stretching and bending vibrations, respectively. The band at the 3,058 cm^{-1} is due to the aromatic C–H stretching. Band at 1,655 cm^{-1} is ascribed to the C=O group. The broadening of the band shows the C=O in different environments, i.e., amide C=O both free and combined. The group of closely related bands at 1,536 cm^{-1} can be attributed to aromatic C=C stretching. The sharp bands at 1,231 and 1,059 cm^{-1} can be represented to the –C–O–C– asymmetric and symmetric stretching, respectively.

NMR spectroscopy

The ^{1}H NMR spectrum of aromatic polyamide in DMSO-d$_6$ was recorded and analyzed according to chemical shifts for various functional groups present in the polymeric structure (Fig. 2). The various NMR signals observed include signals for −NH− protons at 10.43 ppm and for amide proton at 8.53 ppm as a singlet confirming the amide linkage in the structure. The characteristic chemical shifts of aromatic protons can be observed in the range from 7.02 to 8.15 ppm. The formation of aromatic polyamide is confirmed by the NMR data, and all the protons in the polyamide have been identified by intensity and multiplicity pattern and the total numbers of protons calculated from the integration curve are in agreement with the expected molecular structure.

Table 1 GPC data of aromatic polyamide in DMF with a flow rate of 1.0 ml min^{-1} at 60 °C

Detector	M_n (g/mol)	M_w (g/mol)	D (M_w/M_n)	V_p (ml)	M_p (g/mol)	Area (ml × V)
RI 101	38587.90	134986.0	3.50	20.80	152169.0	0.08
UV S3702	33839.80	108640.0	3.21	20.87	146964.0	0.51

The ^{13}C NMR spectral data for the aromatic polyamide in DMSO-d_6 was recorded and presented in Fig. 3. The ^{13}C resonances are well resolved due to the presence of all unique carbon atoms in the polyamide chain: δ_C=135.1 (C-1, C-10); 122.1 (C-2, C-6, C-9, C-11); 118.6 (C-3, C-5, C-8, C-12); 152.9 (C-4, C-7); 164.8 (C-13); 134.5 (C-14, C-16); 130.5 (C-15); 128.5 (C-17, C-19); 126.9 (C-18); 169.5 ppm (C-20). The carbon resonances were assigned by comparison of experimental chemical shifts with those calculated from incremental method and with the literature values.

Molecular weight and molecular weight distribution

The primary objective of any GPC measurement is to obtain the molecular weight distribution accurately. Although both RI and UV absorption could be used for detection, however, the later provides a much better S/N ratio. GPC profiles of the aromatic polyamide monitored with an RI detector (RI 101) and UV detector (UV S3702 at 270 nm) are described in Figs. 4 and 5, respectively. The GPC data obtained through both the detectors is demonstrated in Table 1. The polydispersity, M_w, and M_n were calculated using the universal calibration with polystyrene standards and absolute DMF as solvent. The molecular weight distribution is unimodal. The values of M_n and M_w of the aromatic polyamide were found to be 38,587.90 and 134,986.0 g/mol with the RI detector, while 33,839.80 and 108,640.0 g/mol with UV detector, respectively. The corresponding polydispersity values of aromatic polyamide were found to be 3.50 and 3.21 using RI and UV detectors, respectively. These values of polydispersity are typical for condensation polymers and also indicated that the aromatic polyamide had relatively broader molecular weight distribution.

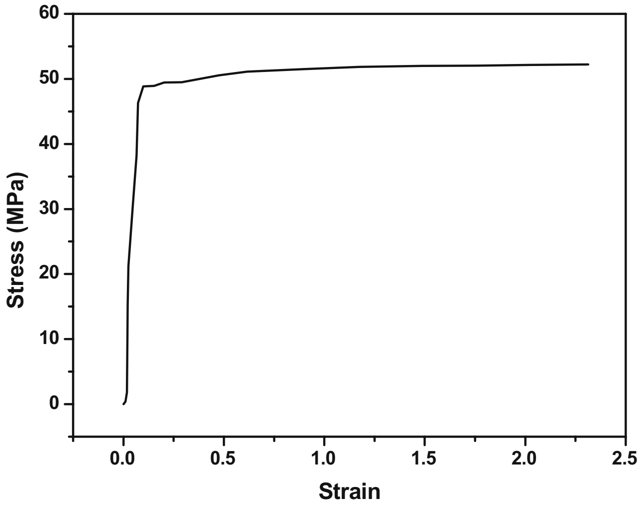


Fig. 6 Typical stress–strain curve for aromatic polyamide

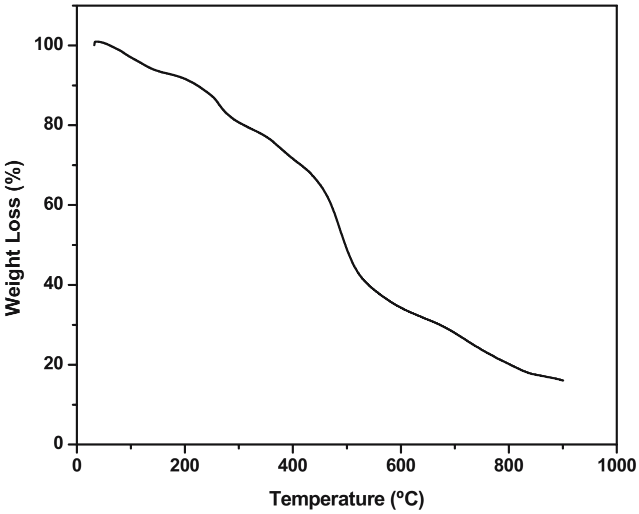


Fig. 7 Thermogram for aromatic polyamide at a heating rate of 10 °C min$^{-1$} under nitrogen

Mechanical properties

Mechanical testing on the rectangular strip of the pure polyamide was carried out at 25 °C. The typical stress–strain isotherm of the polyamide is shown in Fig. 6. The polymer shows a maximum tensile strength of the order of 52.2 MPa, while elongation at break point 2.3. The young modulus calculated from the initial slope of the linear portion of the stress–strain isotherm gives a value of 179 MPa. Toughness of this material was determined by integrating the area under the stress–strain curve up to the maximum extension, which corresponds to the energy or work required for rupture. The value of toughness is found to be 117 MPa. The aromatic polyamide shows good tensile strength, but it is relatively low as compared to certain high-performance polyamides; however, the pattern of this polymer is similar to the latter ones. This may be due to the flexible and less

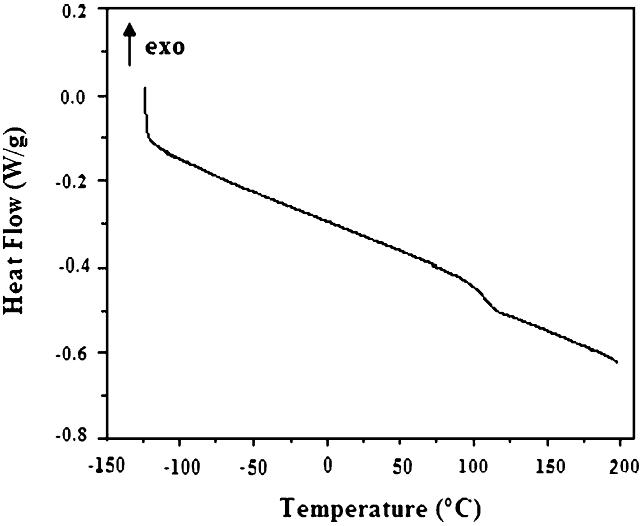


Fig. 8 Typical DSC curve for aromatic polyamide

crystalline structure of the polyamide because the mechanical properties are largely dependent on the microstructure and intermolecular forces operative among the chains.

Thermogravimetric analysis

Thermogravimetry carried out for pure aromatic polyamide under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} is shown in Fig. 7. The thermogram for this system shows a thermal decomposition temperature in the range of 300–400 °C. The thermogravimetric result indicates that the polymer is thermally stable.

Differential scanning calorimetry

Below glass transition temperature, a polymer is glassy solid because its segments do not have enough energy for rotation. Upon heating, gain in volume and energy of a polymer takes place, and chains start flowing, in this way a polymer glassy state is converted into a rubbery state. With increase in temperature, segmental motions start with an increase in the baseline when the polymer changes from the glassy to rubbery region giving a glass transition. The temperature at which polymers are transferred from a rigid form to a flexible form is called glass transition temperature (T_g). The heat flow plotted against temperature gives the glass transition behavior (Fig. 8), and the T_g value is noted to be 105 °C.

Water absorption measurement

The water absorption measurement of the pure aromatic polyamide was performed, and the amount of water absorption by polymer under saturation conditions for 168 h is 5.7%. This may be due to the abundant exposure of amide groups to the surface of polymer where water molecules develop secondary bond forces with these amide groups. Water absorption studies are necessary as the polyamide chains possess polar amide groups that have a tendency to absorb water through hydrogen bonding; this is obviously important because it can adversely affect the mechanical and dielectric properties.

Conclusions

A soluble aromatic polyamide was successfully prepared by step polymerization. After purification and drying, the polyamide was found to be soluble and had a film-forming property. These characteristics of the polyamide provide a facility to monitor its related physical properties as well. The spectroscopic techniques confirmed the formation of the polyamide, and the molecular weight determined by GPC depicts a broader molecular weight distribution. The film-forming property of the material permits to study the mechanical behavior easily. TGA and DSC measurements were also successfully carried out to find out the thermal stability and glass transition temperature of the soluble aromatic polyamide.

Acknowledgments We appreciate the financial support provided by the Higher Education Commission of Pakistan (HEC) through project research grant 20-23-ACAD (R) 03-410 and under "International Research Support Initiative Program" to pursue research work at Max Planck Institute for Polymer Research (MPI-P), Mainz, Germany. Special thanks are due to Prof. Dr. Gerhard Wegner, Director, MPI-P, for providing the characterization facilities for the completion of this work.

References

1. Lee H, Stoffey D, Neville K (1967) New linear polymers. McGraw-Hill, New York
2. Cassidy PE (1980) Thermally stable polymers: synthesis and properties. Marcel Dekker, New York
3. Yang HH (1989) Aromatic high-strength fibres. Wiley, New York
4. Hergenrother PW (1990) Angew Chem Int Ed Engl 29:1262
5. Preston J (1988) Aromatic polyamides. In: Mark HF, Bikales NM, Overberger CG, Menges G (eds) Encyclopaedia of polymer science, vol. 11. Wiley, New York, p 381
6. Chaudhuri AK, Min BY, Pearce EM (1980) J Polym Sci Polym Chem Ed 18:2949
7. de Abdjo J, de Santos E (1983) Angew Makromol Chem 111:17
8. Spiliopoulos IK, Mikroyannidis JA, Tsivgoulis GM (1998) Macromolecules 31:522
9. Liaw DL, Liaw BY, Tseng JM (1999) J Polym Sci A Polym Chem 37:2629
10. Yang CP, Hsiao SH, Jang CC (1995) J Polym Sci A Polym Chem 33:1095
11. Yang CP, Lin JH (1996) J Polym Sci A Polym Chem 34:341
12. Hsiao SH, Yang CP, Chen SH (2000) Polymer 41:6537
13. Wang S, Ahmad Z, Mark JE (1993) Polym Bull 31:323
14. Ahmad Z, Sarwar MI, Mark JE (1997) J Mater Chem 7:259
15. Ahmad Z, Sarwar MI, Mark JE (1997) J Appl Polym Sci 63:1345
16. Ahmad Z, Sarwar MI, Wang S, Mark JE (1997) Polymer 38:4523
17. Ahmad Z, Sarwar MI, Mark JE (1998) J Appl Polym Sci 70:297
18. Rehman HU, Sarwar MI, Ahmad Z, Krug H, Schmidt H (1997) J Non-Cryst Solids 211:105
19. Sarwar MI, Ahmad Z (2000) Eur Polym J 36:89
20. Jadhav JY, Preston J, Krigbaum WR (1989) J Polym Sci Polym Chem Ed 27:1175
21. Kricheldorf HR, Schwarz G (1989) Makromol Chem Rapid Commun 10:243
22. Korshak VV, Rusanov AL, Batirov I, Kazarava RD, Nijazi FF (1978) Faserforsch Text Tech 92:649
23. Tsai T, Arnold FE (1986) Polym Prepr 27(2):221
24. Preston J, Dobinson F (1964) Polym Lett 2:1175