

Synthesis and Characterization of Polyamides from Diamine Containing Amide Linkages in the Main Chain

Satish S. Deokar*

Department of Chemistry, S.M.College, Akulj,
Dist- Solapur- 413114 M.S. (India)

Abstract

A novel aromatic diamine, *N,N'* bis-(4'-aminobenzoyl) benzene 1,4 diamine (BABD) containing amide linkages in the main chain was synthesized and characterized by FT-IR, NMR (¹H, ¹³C, DEPT ¹³C) and Mass spectrometry. A series of novel aromatic polyamides was synthesized from BABD and IPC/TPC in various mole proportions using low temperature solution polycondensation method. All the polyamides were obtained in very good yields and were characterized by FT-IR spectroscopy, viscosity measurements, solubility tests, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and X-ray diffraction (XRD) techniques. The inherent viscosities (η_{inh}) of these polyamides were in the range 0.27-0.41 dL/g in DMAc at 30 ± 0.1 °C; indicating moderate to high molecular weight buildup. The polyamides showed solubility in aprotic polar solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), dimethyl sulphoxide (DMSO) and *N,N*-dimethylformamide (DMF). The XRD results showed that the polyamides were partly crystalline. The glass transition temperature (T_g) of these polyamides were in the range 234 to 244°C. The thermogravimetric analysis of all polymers showed no weight loss below 412 °C whereas the char yields at 900°C were in the range 15 to 60 % indicating high thermal stabilities of these polymers. Thus these polymers meet high temperature resistant requirements and could find applications as special materials in aerospace, military and microelectronics industries. The structure-property correlation among these polyamides is discussed.

Keywords: *N,N'* bis-(4'-aminobenzoyl) benzene 1,4-diamine; inherent viscosity; XRD; thermal stability.

1. Introduction

Aromatic polyamides have attracted much attention of researchers all over the world as a class of high temperature resistant polymers. They have high temperature resistance and excellent mechanical

strength. Hence efforts were devoted to the synthesis of new, thermally stable polymers. However infusibility and limited solubility in organic solvents, restrict their applications [1-5]. Therefore, many efforts have been made with the aim of designing the chemical structure of the rigid aromatic back bone with some aliphatic or heterocyclic linkages to obtain aramids that are processable by conventional techniques [6-11]. Attempts in this area include introducing flexible linkages, bulky substituents, non coplanar conformation, *m*, *m'*-linkages and bulky pendant groups into polymer chain, which leads to a reduction in crystallinity [12-16]. These modifications lower the melting temperature and lead to soluble and amorphous polymers which may open applications in the areas of films, gas separation membranes, coatings, engineering, plastics, polymer blends and composites [17-18].

Studies have been focused on introducing both ether and bulky pendant groups along the aramides backbone with some aliphatic linkage to minimize the tradeoff between the processability and useful properties of aramides. The introduction of ether linkages is known to enhance the processability and toughness of aromatic polymers without a significant reduction in thermal stability [19-22]. Furthermore, the incorporation of bulky pendant groups can decrease hydrogen bonding and inter chain interactions in polyamides and generally disturb the coplanarity of aromatic units to reduce packing density and crystallinity [23-26]. This should enhance solubility and maintain a high glass transition temperature (T_g) through controlled segmental mobility [27-28].

It has been suggested that introduction of heterocyclic moieties, pendant groups, and asymmetric structure onto the molecular chains of polymers could improve the processability and / or glass transition temperature (T_g) and solubility in organic solvents [29-31].

Here we report synthesis and characterization of new aromatic diamine; *N,N'* bis-(4'-aminobenzoyl)

benzene1,4-diamine BABD and novel polyamides therefrom. To increase their thermal stability and solubility in common organic solvent, again various functional groups have been introduced into their backbones, through further copolymerization.

2. Experimental

N-Methyl-2-pyrrolidone (NMP), N, N-dimethyl acetamide (DMAc) were purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves 4 Å. Pyridine was refluxed over potassium hydroxide pellets under nitrogen, distilled and stored over 4 Å molecular sieves. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were synthesized and purified by reported procedure. 1, 4-diaminobenzene and 4-nitro benzoic acid E.Merk product was recrystallized from alcohol and vacuum dried. LiCl was dried under vacuum at 15 °C for 6 hours. Triphenyl phosphite (Aldrich) was used as received.

2.1 Synthesis of N,N'bis-(4'-nitrobenzoyl) benzene1,4-diamine (I)

A 250 mL three necked round bottom flask equipped with a water condenser, a calcium chloride guard tube, a magnetic stirrer, a nitrogen gas inlet and a thermowell was flame dried under flow of nitrogen gas. N-Methyl-2-pyrrolidone (NMP) 50 mL, pyridine 25 mL, benzene 1,4-diamine (PPDA) 10 g (0.05 mol) and 4-nitrobenzoic acid 16.7 g (0.1 mol) were charged into the flask. Triphenyl phosphate (TPP) 31.26 mL (0.12 mol) was added and the reaction mixture was heated to 110°C under stirring, for 12 h. The reaction mixture was then cooled and poured into excess methanol, to precipitate the N,N'bis-(4'-nitrobenzoyl) benzene1,4-diamine which was filtered on Buckner funnel, washed with hot water and then with methanol (3 x 100 mL) and was dried under vacuum at 80 °C.

Yield: 24 g (91%), M.P.: 1810C

2.2 Synthesis of N,N'bis-(4'-aminobenzoyl)benzene 1,4-diamine, BABD (II)

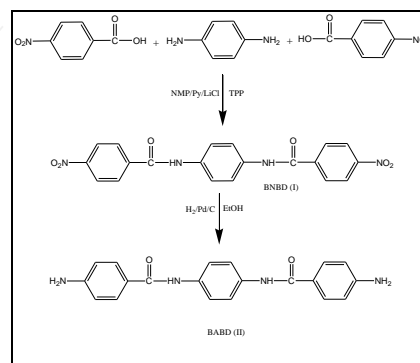
Into a 250 mL three necked round bottom flask N,N'bis-(4'-nitrobenzoyl) benzene1,4-diamine (0.020mol, 8.12 g) and 10 % Pd/C (0.4 g) were suspended in 200 mL ethanol. The suspension solution was heated to reflux and 99 % hydrazine monohydrate (20 mL) was added dropwise over 1 h. After additional 8 h of refluxing, the resultant clear, dark solution was filtered while hot to remove catalyst, Pd/C and the filtrate was subjected to distillation to remove part of solvent. The concentrated solution was poured into 150 mL water with stirring, giving rise to an off white BABD (II), which was filtered, washed with water till

free from hydrazine hydrate. The BABD (II) was recrystallized from aqueous ethanol and vacuum dried. Yield: 6.5 g (93.36 %); M.P.165°C.

2.3 Polymer Synthesis: (PA-1)

In a 100 mL three-necked round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet and a calcium chloride guard tube were placed BABD, 0.346 g (1mmol) and DMAc, 3 mL stirred to form homogenous solution and cooled to -15 °C in ice-salt bath. To the reaction mixture solid IPC, 0.203 g (1 mmol) was added in small lots over a period of 1 h and stirring was continued for additional 2 h at 0°C and then at room temperature for 12 h. The viscous solution was poured into methanol, 200 mL with rapid stirring. The precipitated polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 h. Yield 0.568 g (98.5%); η_{inh} 0.27 dL/g. Other polyamides, PA-2 to PA-5 were synthesized by similar procedure.

Scheme: I: Synthesis of N,N'bis-(4'-aminobenzoyl) benzene1,4-diamine BABD (II)



Scheme: II: Synthesis of polyamides from BABD and IPC/TPC by low temperature solution polycondensation

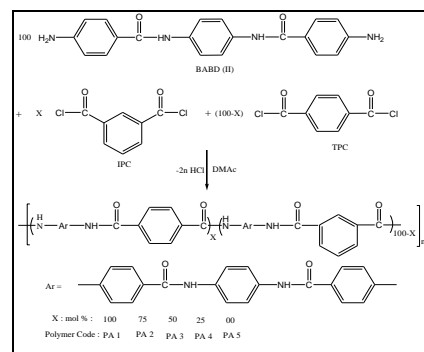


Table-1: % Yield and inherent viscosity of polyamides^aPA-1 to PA-5 from BABD (II) and IPC/TPC

Sr. No	Polymer Code	mol %		Yield (%)	η_{inh} (dL/g)
		IPC	TPC		
1	PA-1	100	00	96	0.27
2	PA-2	75	25	98	0.29
3	PA-3	50	50	97	0.33
4	PA-4	25	75	98	0.28
5	PA-5	00	100	96	0.41

^a Polymerization was carried out with 1mmol each of BABD (II) and [IPC/TPC]

^b Measured at concentration of 0.5 g/dL in DMAc at 30°C.

^a Polymerization was carried out with 1mmol each of BABD (II) and [IPC/TPC]

^b Measured at concentration of 0.5 g/dL in DMAc at 30°C.

^c BABD (II), N,N'-bis-(4'-aminobenzoyl) benzene 1,4-diamine

Table-2: Thermal properties of polyamides^a PA-1 to PA-5 from BABD (II) and IPC/TPC

Sr. No.	Polymer Code	T _i ^b (°C)	T ₁₀ (°C)	T _{max} ^c (°C)	Residual wt. at 900 °C (%)	T _g ^d (°C)
1	PA-1	439	498	670	60	242
2	PA-2	412	505	647	40	244
3	PA-3	435	477	576	55	238
4	PA-4	519	555	633	15	243
5	PA-5	440	503	585	53	234

^aThermo gravimetric analysis was conducted at a heating rate of 10 °C/min under Nitrogen.

^bT_i, temperature at which initial loss of mass was observed.

^cT_{max}, temperature of the maximum rate of decomposition from derivative T_g.

^dDetermined by DSC measured at a heating rate 20 °C/min.

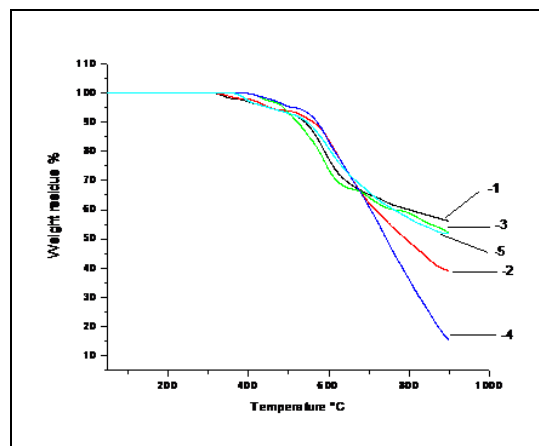


Fig.1: TGA Curves of PA-1 to PA-5

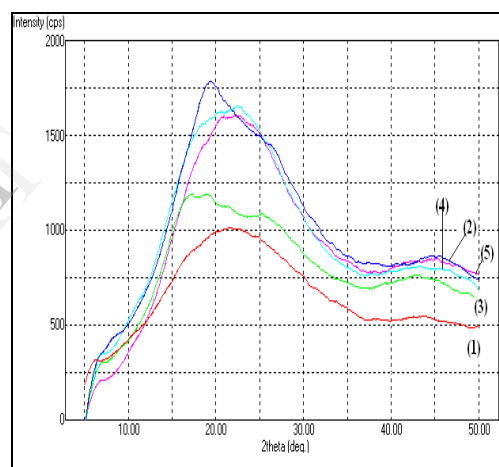


Fig.2: XRD Curves of PA-1 to PA-5

3. RESULTS AND DISCUSSION

The structure of monomer was confirmed by FT-IR, NMR (1H and 13C) and mass spectrometry. The dinitro compound BNBD (I) showed IR band at 1560 and 1345 cm⁻¹ due to -NO₂ group while diamine compound BABD (II) showed band at 3413 and 3320cm⁻¹ due to -NH₂ group which indicates the total conversion of nitro group into amino group. The PMR spectrum of showed a peak at 3.63 δ corresponding to -NH₂ group, 9.5 δ corresponding to -NH₂ group and 6.5 to 7.8 δ corresponding to aromatic protons. Elemental analysis of BABD (II) for C, H and N % was in good agreement with those calculated.

Aromatic polyamides were synthesized by low-temperature solution polycondensation of BABD (II) with isomeric aromatic diacid chlorides, namely IPC or

TPC in DMAc. In a similar manner, co-polyamides were also prepared from BABD (II) and a mixture of IPC and TPC in different mole proportions.

The results of synthesis of polyamides are presented in Table-1. All the polymers were obtained in more than 96 % yields. These polyamides exhibited inherent viscosities in the range 0.25 to 0.41 dL/g showing that the resultant polymers were of moderate molecular weights. Inherent viscosity of polyamide PA-5, based on TPC was highest (0.41 dL/g) among the series. This was attributed to the higher reactivity of TPC compared to that of IPC. In the present study copolyamides; PA-2 to PA-4; derived from a mixture of TPC and IPC showed lower viscosity than corresponding PA-5, probably due to mixed reactivity of IPC and TPC.

The inherent viscosities (η_{inh}) of these polyamides were in the range 0.27-0.41 dL/g in DMAc at $30 \pm 0.1^\circ\text{C}$; indicating moderate to high molecular weight build up. The polyamides showed solubility in aprotic polar solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), dimethyl sulphoxide (DMSO) and N,N-dimethylformamide (DMF), Pyridine, THF and m-Cresol.

The Tg of polymers were in the range of 234 to 244 °C. Thermal stability of polyamides was evaluated by TGA under nitrogen atmosphere and all the polymers showed no weight loss below 412 °C; indicating good thermal stability (fig.1). The X-ray diffraction pattern of all polymers exhibited partly crystalline nature of these materials (fig.2).

4. CONCLUSIONS:

Synthesis of a new diamine containing amide unit, namely N,N'-bis-(4'-aminobenzoyl)benzene 1,4-diamine BABD (II) was successfully accomplished and it was characterized by IR, NMR and mass spectrometric techniques. A series of polyamides was synthesized by copolymerization of the BABD (II) and IPC/TPC in various mole proportions. Viscosity values of these polymers were in the range of 0.27 to 0.41 dL/g indicating built up of moderate molecular weights. The solubility of polymers was tested in different solvents. The Tg of polymers were in the range of 234 to 244 °C. Thermal stability of polyamides was evaluated by TGA under nitrogen atmosphere and all the polymers showed no weight loss below 412 °C and residual weight at 900 °C is 15-60 % indicated very good thermal stability of polymers. The X-ray diffraction pattern of all polymers exhibited partly crystalline nature.

REFERENCES:

1. Yang, H. H., "Aromatic high strength fibers", John Wiley and Sons Publication, NewYork (1989).
2. Maglio, G; Paiumbo, R.; Vignola, M. C. *Macromol. Chem. Phys.* 196, 775 (1995).
3. Sowrirajulu, B.; Muthusamy, S. J. *Polym Res.* 14, 261 (2007).
4. Shadpour, M.; Zahra, Rafiee. *Polym. Adv. Techno.* 19, 1474 (2008).
5. Guey, S. L.; Hung, Yi. L. *Macromolecules*; 42, 125 (2009).
6. Hsiao, S. H.; Chang, Yu. M.; Chen, H. W.; Liou, G. S. J. *Polym. Sci. Polym. Chem.* 44, 4579 (2006).
7. Hsiao, S. H.; Yang, H. Y. J. *Polym. Sci. Polym. Chem.* 34, 1421 (1996)
8. Liou, G. S.; Kakimoto, M. A.; Imai, Y.; J. *Polym. Sci. Polym. Chem.*, 31, 3265 (1993).
9. Abajo, J. D.; De la Campa, J. G.; Lozano A. E.; *Macromol. Symp.*, 199, 293 (2003).
10. Preston, J.; *Encyclopedia of Polymer Science and Technol.*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley Interscience, NewYork, 11, 381 (1988).
11. Lin, J; Sherington, D. C.; *Adv. Polym. Sci.*, 111, 177 (1994).
12. Chang, G.; Lao, X.; Zhang, L.; Lin, R.; *Macromolecules.* 40, 8625 (2007)
13. Imai, Y.; Maldar, N. N.; Kakimoto, M. J; *J. Polym. Sci. Polym. Chem.* 22, 2189 (1985).
14. Jadhav, A. S.; Maldar, N. N.; Vernekar, S. P. *Polym. Int.* 32, 5 (1993).
15. Volbracht, L.; *In Comprehensive Polymer Sci.*; Allen G.; Bevington, J.; Eds.; Pergamon, Wheaton and Co.: Exeter, England, 5, 375 (1989).
16. Yang, H. H.; *Aromatic High-Strength Fibers*; Wiley Interscience, NewYork, 202 (1989).
17. Jadhav, A. S. Ph.D. Thesis submitted to Shivaji University, Kolhapur. (1997).
18. Espeso, J. F.; De la. Campa, J.G.; Lozano, A. E.; De Abaso, J. J. *Polym. Sci. Polym. Chem.* 38, 1014 (2000).
19. Espeso, J. F.; Ferrero, E.; De-La. Campa. J.G.; De Abajo, J.; Lozano, A. E. J. *Polym. Sci. Polym. Chem.* 39, 475, (2001).
20. Hsiao, S. H., Chang, C. F.; *J. Polym. Sci. Polym. Chem.* 20, 1528 (1999).
21. Hsiao, S.; Huci, T.; Lin, H. J. *Polym. Sci. Polym. Chem.* 40, 947 (2002).
22. Hsiao, S. H.; Chen, Y. J. *J. Polym. Res.* 7, 205 (2000).
23. Yamazaki, N ; Higashi, F ; Kawabata, J ; *J. Polym. Sci. Polym. Chem.* 12, 2149 (1974).

24. Yamazaki, N.; Matsumoto, M.; Higashi, F. J. Polym. Sci. Polym. Chem. 13, 1373 (1975).
25. Ghaemy, M.; Barghamadi, M. J. Appl. Polym. Sci. 110, 1730 (2008).
26. Basutkar, P. H.; Joshi, M. D.; Lonikar, S. V.; Maldar, N. N.; Idage, B. B. J. Appl. Polym. Sci. 68, 1523 (1998).
27. Liou, G. S.; Hsiao, S. H. J. Polym. Sci. Polym. Chem. 40, 459 (2002).
28. Shockravi, A.; Abouzari, L. E.; Atabaki, F. Euro. Polymer. J. 45, 1599 (2009).
29. Pino, P.; Lorenzi, G. P.; Suter, U. W.; Casartelli. P. G.; Steinmann A.; Bonner, F. J.; Quiroga, J. A. Macromolecules. 11, 624 (1978).
30. Sutter, U. W.; Pino, P.; Macromolecules. 17, 2248 (1984).
31. Allen, S. G. "Comprehensive Polymer Science." Plenum. New York. 5, 97 (1989).

IJERT