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Synthesis and Spectral Studies of Some Azo Polyimides

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Ten polyimides based on *p,p*'-aromatic diamines and 3,3',4,4'-azo benzenetetracarboxylic dianhydride were synthesized by high temperature solution imidization method. The polymers were characterized by viscosity, solubility, UV-Visible, IR, Raman spectroscopy and thermogravimetry.

Key Words: Synthesis, Characterization, Spectra, Thermal analysis.

INTRODUCTION

The commercial kapton[1] H, PRD and Arimid[2] PM polyimide fibres are well known for their high temperature resistance and good mechanical properties. In recent years attention has been given to the synthesis of polyimides which are leading candidates for aerospace applications due to their excellent thermo oxidative stability, good adhesion to metals and good mechanical properties over a wide range of temperature[3]. Micro electronic devices such as printed circuit boards and multichip packages are also rely on good adhesion between polyamide-polyimide and polyimide-metal interfaces[4,5]. There are many references in the literature on the synthesis of polyimides from a variety of aromatic diamines and aromatic tetra carboxylic dianhydride[6]. However, there appears to be no data on the synthesis of azopolyimides. This gave us, therefore, the impetus to prepare certain azopolyimides from 3,3',4,4'-azobenzenetetracarboxylic dianhydride and several *p,p'*-diamines and to characterize them by solubility, viscocsity, IR and UV-Visible spectroscopy and thermal studies. Further interest in the azopolyimides is due to the *trans* configuration of azo linkage in azobenzenetetracarboxylic dianhydride which would lead to an extended-chain structure with aromatic *p,p'*-diamines. These polymers which are easily processable have an excellent balance of mechanical and electrical properties and good resistance to solvent attack. The presence of azo group in the main chain of a polymer increases chain rigidity leading to close packing of the polymer chains and better thermal stability. Earlier reports from this laboratory dealt with the synthesis and characterization of new polyhydrazides, polyamides and polyamide-imides[7].

EXPERIMENTAL

N,N-Dimethylacetamide (Fluka-puriss) was kept over KOH overnight, filtered and distilled over P_2O_5 (b.p 161-162 °C). 1-Methyl-2-pyrrolidone (Koch-light, pure) was dried, first over KOH pellets, then over P_2O_5 and finally distilled over freshly added P_2O_5 (bp 196-197 °C). Anhydrous LiCl (Lancaster) was obstained by drying LiCl over P_2O_5 in vaccum at 100 °C.

Monomers used: 1,4-Diaminobenzene, benzidine, 4,4'-diaminoazobenzene, 2,2'-dimethyl-4,4'-diaminoazobezene, 2,2'-dichloro-4,4'-azo benzene, 2,2'-dimethoxy-4,4'-azobenzene, 3,5-dimethyl-4,4'-diamino azobenzene, 4,4'-diamino benzanilide, 4,4'-diamino diphenyl ether and 2,2-*bis*[(4-(*p*-aminophenoxy)phenyl] propane.

3,3',4,4'-Azobenzenetetracarboxylic dianhydride (m.p. 329-331 ºC) was synthesized[8] from phthalic anhydride.

Polymerization: The following procedure was followed for the preparation of azopolyimides by solution imidization method.

A mixture of diamine (one equivalent), dianhydride (one equivalent), 1-methyl-2-pyrrolidone (25 mL) and *o*-dichlorobenzene was heated at 180 °C for 24 h with stirring under nitrogen. The polymer was precipitated in methanol, filtered washed and dried. The polyamic acid formed was then converted to polyimide by refluxing 24 h in 1-methyl-2-pyrrolidone: *o*-dichlorobenzene (5:1) at 180 °C, polyimide formed was dried in vaccum oven.

Characterization: The following physical properties have been studied using the azo polyimides synthesised.

Inherent viscosity: Viscosity measurements were made at 25 °C using conc. H_2SO_4 as solvent for all polymers in an ubbelohde viscometer. The concentration used was 0.5 g/dL throughout for all the measurements.

Solubility: Solubility of the polyimides was determined in various solvents. A 10 % solution was prepared and allowed to stand for few hours. If insoluble in cold the solution was heated.

Thermal analyses: TGA and DTA were recorded in nitrogen for all the polymers using STA-409C model simultaneous recorder. About 20 mg of the sample was heated at a heating rate of 5 °C/ min for all the polymers.

RESULTS AND DISCUSSION

Properties of the polymers such as colour, inherent viscosity and UV-visible spectral data are presented in Table-1.

From the Table-1, it is evident that polyimides derived from azodiamines show higher viscosities than that of polyimides derived from non-azodiamines. This may be due to the rigid nature of (high strength/high modulus) the azo linkage which is in *trans* form. Comparing the viscosities of polyimides derived from non-azodiamines, the following order has been observed.

TABLE-1
PROPERTIES OF POLYIMIDES

Polyimides	Yield (%)	η_{inh} (g/dL)	UV-Visible (nm)		Colour
			UV	Visible	
ABTD-Bz	60	0.78	190, 231, 279	485.0	Black
ABTD-Biph	65	0.98	235, 285	510.0	Brown
ABTD-Az	85	1.22	221, 302	477	Dark brown
ABTD-MeAz	90	1.45	217, 268	460.3 505.2	Brown
ABTD-CIAz	70	1.02	260	417.0 518.1	Yellowish brown
ABTD-MeOAz	70	1.17	200.6 245.2	409.6 534.0	Golden yellow
ABTD-DiMeAz	50	0.72	250.6 286.2	536.5	Light yellow
ABTD-BzAni	55	1.04	241	402.0	Yellow
ABTD-Dipheth	80	1.12	244.0	410.1	Pale yellow
ABTD - BAP	90	1.14	190, 232, 271	420.6	Pale yellow

Conc. = 0.5 g/dL in conc. H_2SO_4 at 25 ºC.

Bz < Biph < Bz Ani < Dipheth < BAP

Also more basic diamines with electron releasing substituents (methyl or methoxy) on the phenylene rings have fairly higher viscosities than those derived from less basic diamines with electron withdrawing (chlorine) substituents[9].

Solubility tests showed that all the polyimides are insoluble in common organic solvents such as acetone, THF, chloroform but soluble in conc. H_2SO_4, NMP/LiCl, DMAc/LiCl. In general both methyl and chloro substituents are known to increase the solubility because of their capacity to disrupt the chain.

UV Spectra: The bands in the visible region are due to n-π* transition whereas those in the UV region are associted with π-π* transitions. All the polyimides absorb at 220-230 nm in the UV region and at 470-535 nm in the visible region.

IR Spectra: Specturm of ABTD-BZ showed C-N stretching at 1550 cm^{-1}. Imide absorption bands were observed at 1780 and 1720 cm^{-1} (imide-1), 1375 cm^{-1} (imide II), 1120 cm^{-1} (imide III) and 720 cm^{-1} (imide IV) in the cyclodehydrated samples. All those bands were very strong and were absent in the polyamic acid. Spectra of imide I band is attributed to the stretching vibrations of weakly coupled carbonyl groups. The imide, II, III and IV bands have been assigned to axial, transversed and out-of-plane vibrations of the cyclic imide structures.

IR and Raman spectra: The IR spectra of polyamic acid of ABTD-Biph, ABTD-Az and ABTD-BAP show the bands at 3260, 1411 and 1320 cm^{-1} (due to N-H stretching, O-H in-plane deformation and C-O stretching, respectively). These bands disappeared after cyclodehydration, thus confirming that in polyimides the amido-acid group was absent.

The assignments made on FT IR are well supported by Raman spectra. IR spectra are studied in conjunction with Raman to get information about the molecular structure.

Relatively neutral bonds such as C–C, C=C *etc.* suffer large changes in polarisability during a vibration. The dipole moment is not affected and vibrations that predominantly involve this type of bonds are strong Raman scatterers but weak in IR. ABTD molecule has a centre of symmetry and hence modes active in Raman spectra are inactive in IR spectra and *vice versa*. The point group may be C_2h. Not all Raman lines have their corresponding IR bands and all IR bands do not have their corresponding Raman lines.

There are three common frequencies observed in all the three polymers which are IR active but Raman inactive. The IR active frequencies are 3447 cm^{-1} (O-H stretch), 2360 cm^{-1} and 2342 cm^{-1} (cyclic anhydride), 843 cm^{-1} (benzene ring), 668.72 cm^{-1} (C-N symmetric stretch). All these indicate common diamine part present in the polymers. But for a complex molecule that may not have any symmetry, same identity normal vibration modes are allowed both in Raman and in IR. Thus in our study all the three polyimides exhibited certain common lines in IR and in Raman though of different intensities. Considering all these factors, a Cs point group may be assigned to the macro molecule as a whole.

^{13}C NMR Spectra: ^{13}C NMR spectrum (with proton coupling) was assigned to the respective carbons based on long range ^{1}H coupling patterns. ^{13}C NMR spectrum of ABTD-AZ polymer shows a peak at 152 ppm as a long range doublet (J = 10.5 Hz) which confirms that the carbon containing the azo group in ABTD "sees" only one *meta*-proton. This fixes the C-5 position. The order of coupling constants in aromatics is $^1J_{CH} >> {}^3J_{CH} > {}^2J_{CH} > {}^4J_{CH}$. Usually one does not observe $^2J_{CH}$ (in the order 1-2 Hz). The peak at 138 ppm is a triplet with two *meta*-protons, thus assigned to C-10, 13.

The peak at 135 ppm is C-14, 18 (doublet with two *meta* protons). The signal at 118 ppm is assigned to C-16, 18 because it shows only $^1J_{CH}$ and no observable $^3J_{CH}$, C-16, 18 are the carbon atoms without any *meta* proton. The assignment of C-15, 17 to the peaks at 114 ppm is obvious. The peak at 166.11 ppm is assigned to carboxyl carbon of ring B and this one at 165.96 ppm is to carboxyl carbon of ring A, since shielding effect is more for ring B than A.

Stability of polymers: Stability of ABTD-BAP, ABTD-AZ, ABTD-MeAZ and ABTD-ClAZ has been studied in conc. H_2SO_4 since these polyimides have excellent fibre forming capacity. ABTD-ClAZ has the maximum stability towards conc. H_2SO_4. The order of stability among the four polyimides is

$$ClAZ > MeAZ > AZ > BAP$$

Thermal analysis (Table-2) of the polymers were carried out in a nitrogen atmosphere to evaluate their relative thermal stability. The thermograms show minimum three stages of weight loss. In the first stage, an initial weight loss of 1-2 % occurs in the temperature range of 100 °C which may be due to the removal of absorbed moisture. A weight loss around 200 °C is likely due to the chain extension that may take place by the condensation of end groups resulting in the elimination of water. The second stage of weight loss occurring at about 500 °C corresponds to a steep fall in the TG curve. In the third stage, above 800 °C there is a gradual weight loss as evidenced from the TG curves.

TABLE-2
THERMAL ANALYSES (TGA AND DTA)

Polymer	Weight loss (%)					Tmax (°C)	No. of stages of wt loss	Exotherm temp. (°C)
	10	20	30	40	50			
ABTD-Bz	202	405	580	780	1180	585	3	360.4, 420, 985
ABTD-Biph	205	410	600	830	1195	600	4	352.6, 394,9 646.8, 689.6, 787.8
ABTD-Az	210	425	538	7258	1210	176, 520	4	340, 402, 810
ABTD-MeAz	208	430	535	710	1205	188, 560	4	425, 526, 690, 1035
ABTD-CIAz	220	445	540	725	1215	190, 585	4	430.0, 528.0 695.0, 1040.0
ABTD-MeOAz	218	438	543	710	1220	205, 570	4	421, 515.0, 1035.2
ABTD-DiMeAz	207	402	510	640	995	201, 510	3	385, 410, 980.7
ABTD-BzAni	205	395	505	628	1102	184	3	360, 384, 1008
ABTD-Dipheth	211	400	480	625	1006	180	3	310, 325.2, 960.6
ABTD - BAP	190	440	530	720	1150	180, 510	4	421.4, 523.7 692.6, 1030.6

Heating rate = 5 °C/min

Among the substituents the order of thermal stability is as follows:

$$Cl > OCH_3 > CH_3 > DiMe$$

In our work, 10 % decomposition is noticed around 200 °C and 20 % weight loss is often in the range 450-500 °C. The chemical moietics that decrease the thermal stability of polyimides are (i) aliphatic or benzylic protons (ii) steric factor due to bimethyl groups or hydroxyl group and (iii) other thermally less stable functionalities.

DTA thermograms showed a strong endotherm indicating glass transition (Tg) at 450 °C for the polyimides ABTD-Biph and ABTD-BAP. The other polyimides do not show very sharp Tg. This behaviour can be attributed to the transformation of highly rigid nature of the polyimide to glassy form. It is obvious that the first exotherm temperature in DTA corresponds to the 20 % thermal decomposition of TGA and the successive exothermic peaks represent the second phase, third phase *etc.* In some cases like ABTD-BzAni and ABTD-Dipheth, the number of DTA peaks are not identical to the number of phases in the TG curves due to overlapping of peaks. The very low 20 % decomposition temperature of ABTD-Dipheth (390 °C) can be seen as a sharp peak in the DTA curve. As noted in TGA, the last and penultimate peaks are the most significant one describing crystallization, melting, cross-linking and thermal decomposition or vapourization.

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