

Studies on Fibres of Some Azoaromatic Polyimides

T.V. RAJENDIRAN* and C. ANBUSELVAN

Department of Chemistry, Pachaiyappa's College, Chennai-600 030, India

E-mail: dr_v_r@yahoo.co.in

Three new azoaromatic polyimides were synthesized by condensing 3,3',4,4'-azobenzene tetra carboxylic dianhydride and 4,4'-diaminodiphenyl/4,4'-diaminoazobenzene/2,2-bis(4-*p*-aminophenoxy) phenyl]propane. These polyimides were drawn into fibres with different experimental conditions. Their physical, mechanical and morphological properties were studied. The structure of polyimides were also confirmed by pyrolysis-GC-mass spectra.

Key Words: Polyimide fibres, Mechanical, Morphological studies.

INTRODUCTION

Polyimides are widely used in electronic field such as wafer fabrication, adhesion, chip packaging and assembly^{1,2}. They also serve as insulators which prevent 'cross-talk' between conducting vias and as adhesives between polymer-polymer and polymer-metal interfaces. Nanjan and Sivaraj³ synthesized poly(*bis*-imides) based on several diamines and maleic anhydride or citraconic anhydride³ and fibre glass cloth reinforced laminate was also studied. Synthesis of several polyimides, polyamides, polyamide-imides and polyhydrazides from this laboratory^{4,5}. In present studies, synthesis of three new azo aromatic polyimides are reported.

EXPERIMENTAL

Monomers: 3,3',4,4'-Azobenzene tetra carboxylic dianhydride was prepared from 4-nitrophthalic acid⁶. The different diamines used were (i) benzidine (ii) 4,4'-diamino azobenzene and (iii) 2,2-bis[4-(*p*-amino phenoxy)phenyl]propane⁷.

Polymerization: Three new azoaromatic polyimides were synthesized following the solution imidization method⁸. A mixture of diamine (1 mol), dianhydride (1 mol), NMP (25 mL) was heated at 30 °C for 24 h with stirring under nitrogen atmosphere. The polyamic acid was precipitated in methanol, filtered, washed and dried. The polyamic acid formed was then converted to polyimide by refluxing 24 h in NMP: *o*-DCB (5:1) at 180 °C. Polyimide formed was dried in vacuum.

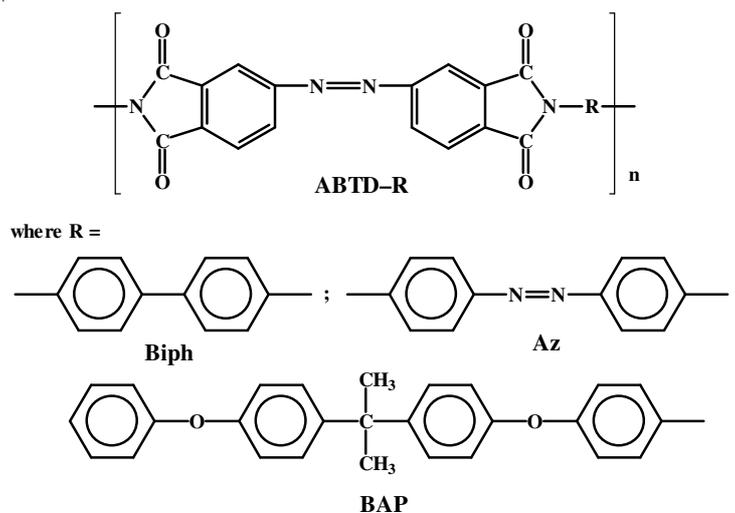
Fibre studies: Fibres were drawn from a laboratory scale spinning unit. The tensile properties were determined on an Instron 1112 model instrument using pneumatic clamp jaws (gauge length 4 cm, cross head speed 0.5 cm/min, full scale load calibration 50 g and chart speed 30 cm/min).

*Present Address: Academic Officer, Meenakshi University, Chennai-600 078, India.

SEM study was investigated with a stereo scan model 440 scanning electron microscope. The fibres were coated with a thin film of gold in the polar on SC 500 sputter coater prior to SEM examination to eliminate 'local charging' and to make them electrically conductive. X-ray diffraction patterns were recorded with a shimadzu XD-D1 X-ray Diffractometer. A 35 KV and 25 mA nickel filtered $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation was employed. Dielectric constant was measured at 9.1 GHz using cavity perturbation technique. The cavity used was TE_{105} mode reflection type rectangular cavity. The instrument used was HP 8720A microwave rector network analyzer. Polyimide samples were heated to 280 °C and mass spectral analysis were carried out using QP 2000 Shimadzu.

RESULTS AND DISCUSSION

Three new azoaromatic polyimides were synthesized following solution imidization method⁶ from 3,3',4,4'-azobenzenetetracarboxylic dianhydride (monomer) and benzidine/4,4'-diaminoazobenzene/2,2'-bis[(4-*p*-amino phenoxy phenyl)]propane. The code and structure of the polyimides are given below:



Fibres were drawn from these polyimides with different experimental conditions and the results are given in Table-1.

Effect of jet stretch: It is observed that fibres spun at higher jet stretch did not cyclize satisfactorily (Fig. 1). The optimum jet stretch is found to be 5. If jet stretch ratio is increased, a reduction in denier as well as percentage elongation is noticed.

Effect of hot drawing: In this work, tenacity and initial modulus of all the fibres improved on hot drawing at the expense of elongation at break (Table-2). The increased tensile strength as hot drawing is due to the attainment of enhanced orientation through stretch at temperature sufficient to cause molecular mobility. This is also corroborated with the dynamic TGA in nitrogen which showed that fibres were stable upto 400 °C.

Comparing the effect of jet stretch (Table-1) and the change in spinning condition (*i.e.* dope 25 %, jet stretch 5, $\eta_{inh} = 1.4$ g/dl) in Table-3. ABTD-Az polyimide as polyamic acid and cyclodehydrated shows that the cyclodehydrated undrawn fibres had higher percentage extensions at break and could be hot-drawn upto a draw ratio of 2.5. The higher draw ratios possible under these conditions yielded polyimide fibres with better mechanical properties (tenacity = 2.86 g/denier).

TABLE-1
EFFECT OF JET STRETCH ON THE MECHANICAL
PROPERTIES OF POLYAMIC ACID FIBRES

As-spun fibre	Jet stretch	Denier	Mechanical properties		
			Tenacity (g/denier)	Elongation (%)	Initial modulus (g/denier)
ABTD-Biph	22.0	16.2	1.98	15.1	37.05
ABTD-Az	16.0	24.1	1.95	19.2	24.50
ABTD-BAP	5.0	32.0	1.60	26.0	21.80

Dope conc. = 20 % bath composition (H₂O:H₂SO₄): 80:20

TABLE-2
EFFECT OF HOT-DRAWING ON THE MECHANICAL PROPERTIES OF
POLYIMIDE FIBRES BASED ON SAMPLE ABTD-Az

ABTD-Az sample	Temp. (°C)	Draw ratio	Denier	Tenacity (g/denier)	Elongation (%)	Initial modulus (g/denier)
1	30	0	58	1.65	38	19.10
2	150	2.0	34	2.40	12	34.25
3	200	2.5	26	2.95	10	36.15

TABLE-3
MECHANICAL PROPERTIES OF POLYIMIDE
FIBRES AT THE FOLLOWING SPINNING CONDITIONS:

Dope conc. 25 %, Bath composition (H₂O:H₂SO₄) 80:20, Jet stretch 5; $\eta_{inh} = 1.40$ (g/dl)

Samples	Draw ratio	Denier	Mechanical properties		
			Tenacity (g/denier)	Elongation (%)	Initial modulus (g/denier)
ABTD-Az					
1	0	42	1.75	42	14.80
2	2.0	38	2.60	16	41.80
3	2.5	32	2.82	10	52.10

Viscosity: Spinning was made with polymers having inherent viscosities of 1.35 and 1.40 with a dope concentration of 30 %. A comparison of sample 1 in Tables 3 and 4 indicates that tenacity as well as initial modulus of fibres prepared under identical conditions depends on the viscosity of the polymers. Higher tenacity and initial modulus fibres were obtained with the polymers of higher viscosity.

The tenacity (1.55 g/denier) of the resulting undrawn (draw ration is zero) polyimide fibres did not change with the dope concentration (fibre samples 2 and 3 in Table-4). However, when these undrawn fibres were subjected to drawn at optimum temperature, the tenacity increases. Table-4 indicates that optimum coagulation bath is found to be 80:20 (H₂O:H₂SO₄) and change in composition of water to either 70:30 or 60:40 decreases the % elongation but increases tenacity (Fig. 2).

TABLE-4
EFFECT OF COAGULATION BATH

Samples of ABTD-Az	Dope conc. (%)	Bath composition H ₂ O:H ₂ SO ₄	Draw ratio (hot-drawn)	Mechanical properties			
				Denier	Tenacity (g/denier)	Elongation (%)	Initial modulus (g/denier)
1	25	80:20	0.0	41.2	1.71	40	14.1
2	25	70:30	0.0	41.0	1.55	108	11.2
			2.5	30.0	2.02	14	47.8
3	30	70:30	0.0	38.0	1.55	70	15.2
			2.5	29.0	2.06	9	49.4
4	30	60:40	0.0	36.0	1.62	122	12.2
			2.0	31.0	2.40	14	32.2
			2.5	28.0	2.86	12	34.9

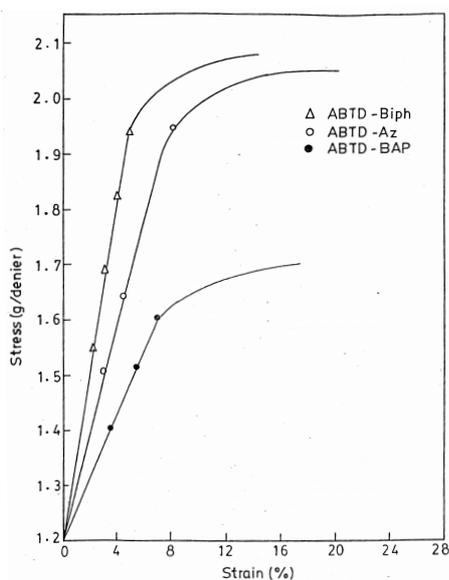


Fig. 1. Stress-strain curves of polyamic acid fibres (effect of jet stretch)

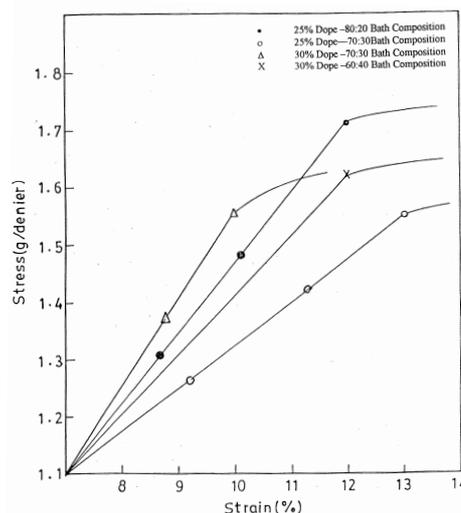


Fig. 2. Stress-strain curves of polyamic acid fibres (effect of coagulation bath)

Comparison of ABTD-Az fibre as polyamic acid (as spun) in Table-1 and polyimide (as spun or undrawn) results in extension as high as 19.2 and 38 %, respectively at the point of break. In the case of polyamic acid, the curve shows a local yielding maxima between 5 to 13 % strain *i.e.* tenacity is 1.95 for polyamic acid and 1.65 for polyimide of ABTD-Az. After yielding the maxima, the fibre begins to undergo a permanent deformation. The hot-drawn fibres have high breaking stress (2.95 g/denier) at relatively small elongations (10 %). It is observed that tenacity and initial modulus are increased with the cyclodehydration of polyamic acid to polyimide. Infact, after cyclodehydration, a considerable rearrangement in

the internal structure of the fibre takes place resulting in more compact (striking) of chains to give higher tenacity. The increase in percentage extension may be due to the absence of intermolecular hydrogen bonding which is present in the polyamic acids. The as-spun fibres were hot-drawn at various draw ratios (2.0, 2.5). The draw ratio 2.5 results with a tenacity of 2.95 g/denier at 200 °C.

Rigidity and mechanical property: Rigid chains are preferred for fibre formation while flexible chains make better elastomers. The flexibility of a polymer depends on the ease with which the backbone chain bonds can rotate. High flexible chains will be able to rotate easily into the various available conformations, while the internal rotations of bonds in a stiff chain are hindered and impeded. Comparison of ABTD-Biph and ABTD-BAP polymers (Table-1) shows that the flexible polymer (latter) yields 26 % elongation while the rigid polymer (former) yields 15.1 % elongation.

Blends: An attempt has been made to prepare some blend of LDPE and a polyimide based on either Biph, Az or BAP diamine of present work. Following the procedure of dry blending, three different blended polyimides were prepared in the ratio of 75:25 (LDPE: polyimide) and subjected to melt spinning, to hot drawn fibre formation in a hot pressed single holed spinnerette at 450 °C. Fig. 3 shows the change in mechanical properties. Considering the tenacity, the order can be given as ABTD-BAP>ABTD-AZ> ABTD-Biph. Due to linear flexible chain in BAP unit, the percentage elongation is increased appreciably. Initial modulus is also increased to 35.5 for ABTD-BAP which shows that the fibre is too strong, stiff and tough. Total area under stress-strain curve is proportional to the ultimate energy resistance

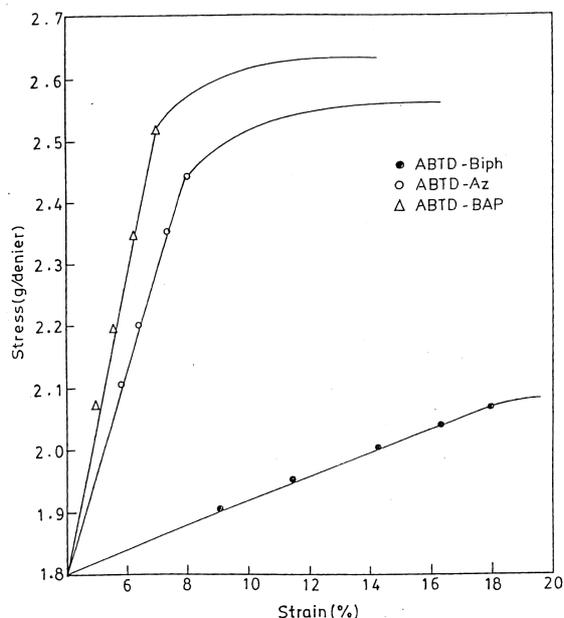


Fig. 3. Mechanical properties of blended polymers

or the work done on the material to deform it up to the breaking point which is called toughness of the material. Azo group can not be stretched to a long distance. This is reflected in the % elongation. But there is an increase in the mechanical property (tenacity 2.42×10^3 psi). It sustains load or pressure to a greater extent than the ordinary (pure) polyimides or even LDPE.

Dielectric constant: Dielectric constant of polyimides are known to decrease gradually with increasing frequency. The magnitude of the dielectric constant is dependent upon the ability of the polarizable units in a polymer to orient fast enough to keep up with the oscillations of an alternating electric field.

At optical frequencies where only electronic polarization occurs, the dielectric constant, ϵ' is related to the refractive index (n_{ref}) by Maxwell's identity.

$$\epsilon' = (n_{\text{ref}})^2$$

The introduction of free volume in a polymer decreases the number of polarizable groups per unit volume, resulting in lower values for ϵ_{atomic} and $\epsilon_{\text{dipolar}}$. Using cavity perturbation technique⁹ at 9.1 GHz, dielectric constant values for the fibre samples were calculated and presented in Table-5. ABTD-BAP fibre has very low dielectric constant *i.e.* the insulation property is more compared to the other polymers.

TABLE-5
DETERMINATION OF DIELECTRIC CONSTANT

S. No.	Sample	f_0 (GHz)	f_1 (GHz)	Q_0	Q_1	ϵ'	ϵ''	σ (ohm ⁻¹ cm ⁻¹)
1	ABTD-Biph	9.515	9.1480	1410.10	1406	1.7149	0.0018698	2.86×10^{-8}
2	ABTD-Az	9.515	9.1475	1410.10	1375	1.8171	0.0168304	2.59×10^{-8}
3	ABTD-BAP	9.515	9.1490	1410.10	1305	1.5105	0.0533079	8.21×10^{-9}

Length of the fibre: 0.36 cm; Thickness of the fibre = 0.02 cm.

As per Clausius - Mosotti relationship,

$$\epsilon = \epsilon_{\text{electronic}} + \epsilon_{\text{atomic}} + \epsilon_{\text{dipolar}}$$

At optical frequencies (10^{14} Hz) only the lowest mass species (electrons) are efficiently polarized.

The dielectric constant (ϵ') data were evaluated using the formula:

$$(\epsilon' - 1) = V_c / 4V_s \left(\frac{f_0^2}{f_1^2} - 1 \right)$$

where $V_c = A_c \times b$ [A_c = area of cross-section of cavity, b = breadth of cavity], $V_s = A_s \times b$ [A_s = area of cross - section of sample], f_0 = resonance frequency of the cavity without sample, f_1 = resonance frequency of the cavity with sample.

Similarly, the dielectric loss (ϵ'') can be determined using the formula:

$$\epsilon'' = V_c / 4V_s \left(\frac{f_0^2}{f_1^2} \right) \left(\frac{1}{Q_1} - \frac{1}{Q_0} \right)$$

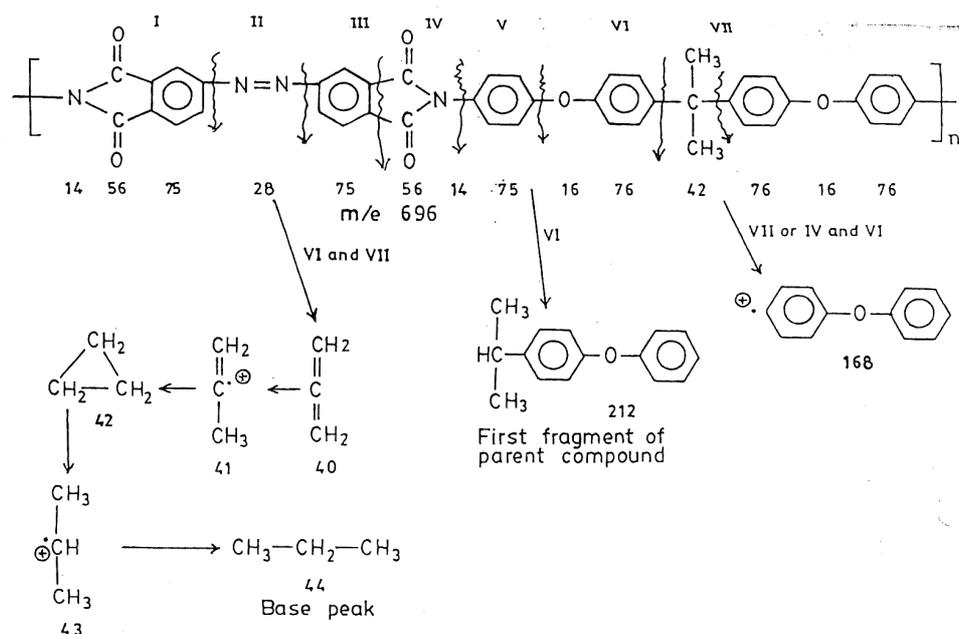
where Q_0 = quality factor without sample, Q_1 = quality factor with sample.

The conductivity (σ) is measured using the expression:

$$\sigma = \frac{\epsilon'' \epsilon'}{2\pi f_1}$$

The quantities f_0 , f_1 , Q_0 and Q_1 are determined using the instrument HP 8720 A, Microwave Vector Network Analyzer and the results are given in Table-4.

Mass spectral studies: The pathways through which a polymer degrades thermally can be investigated by pyrolysis-GC-mass spectra. ABTD Biph, ABTD-Az and ABTD-BAP have a parent peak at m/e 149, 369 and 212, respectively. Fragmentation pattern of ABTD-BAP is given in **Scheme-I** and m/e 369 indicates that the dianhydride moiety can be easily cleaved whereas azo moiety in diamine part cannot. *i.e.* N=N group is stronger than -C-N bond of the end phenyl group (*i.e.* breakage at scission II). All the m/e values fit in well with this spectral data of the three polyimides and hence confirm the structures.



Scheme-I: Fragmentation pattern of ABTD-BAP

Morphological properties

Scanning electron microscope (SEM): In the present work, ABTD-Biph, ABTD-Az and ABTD-BAP were studied and the SEM photographs of the cross-sections of the 'as-spun' (at room temperature) and 'hot drawn' fibres at 150 and 200 °C were presented in plates 1, 2 and 3, respectively. These photographs show that some of the fibers are porous in nature whereas others are smooth and void-free. 'Hot-drawn' fibres are having larger voids than the undrawn fibres. ABTD-BAP

fibres show expansion of voids at 200 °C compared to that of 150 °C. Therefore, it is desirable to choose optimum temperature for fibres drawn depending on the nature of the polymer. The formation of voids and their concentration (number of voids) in the fibers may be explained interms of the rate of coagulation of the extruded polymer dope in the non-solvent used, polymer-solvent interaction, spinning conditions, *etc.* Coagulation (rapid mass transfer) increases the voids concentration in wet-spinning methods. If more voids are formed, it indicates that during the formation of fibre, either oxygen is occluded or the molecules are not orienting towards the fibre drawing axis.

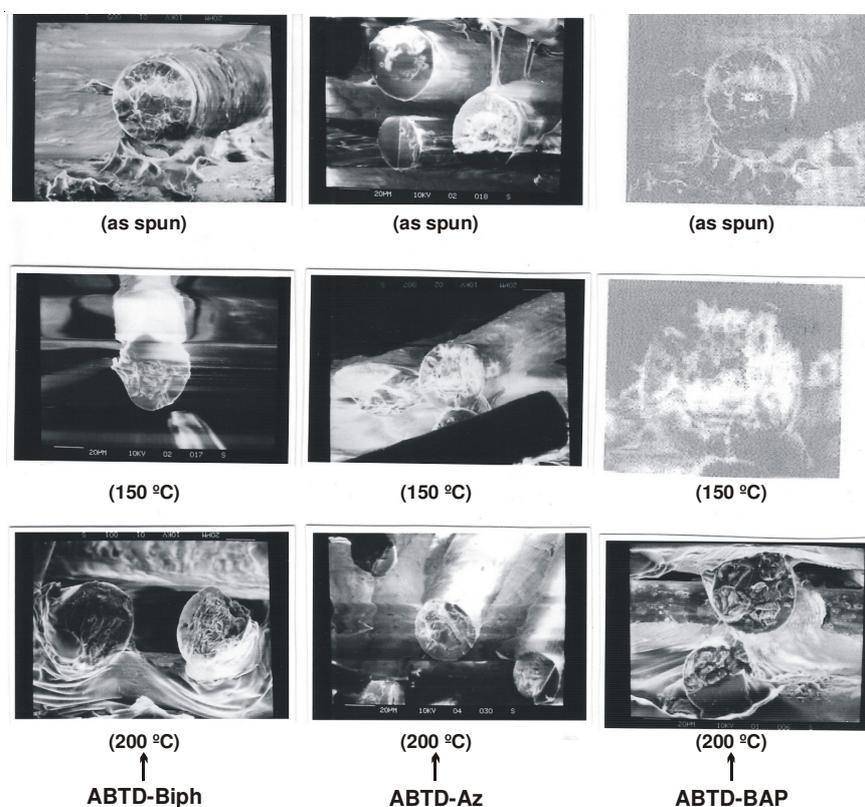


Fig. 4. Scanning electron microscopic photographs of ABTD-Biph, ABTD-Az and ABTD-BAP

In this study, since dilute sulphuric acid is used as a coagulant, as soon as the fibres from spinnerette touches the acid, more heat is evolved and it leads to voids formation on the outer surface and less effect is felt at the interior. However, numbers of voids and their size are the important factors to decide the mechanical properties of a fibre. SEM shows higher voids in ABTD-BAP fibres and small sized voids in ABTD-Biph and ABTD-Az is in the middle order.

Fig. 4 reveals that voids formation leads to less stability due to less close packing. These voids are formed by the following reason: (i) non-close packing of the substance (ii) geometry of the polymer (iii) either crystalline or amorphous (iv) concentration of polymer dope (v) effective stirring (vi) occlusion of oxygen atom (*i.e.*) oxidation of -N=N- group to $\begin{array}{c} \text{-N=N-} \\ \downarrow \\ \text{O} \end{array}$ (azoxy) which is evidenced from the change in colour after long standing (vii) drawing speed of the fibres and (viii) coagulation bath (*i.e.*) spinning conditions.

X-ray diffraction studies: The diffractograms (Fig. 5) do not indicate sharp and high intensity peaks, indicating very little orientation in these polyimides. All the three polyimides exhibit partial crystalline and partial amorphous nature. This crystalline study (WAXS pattern) leads to explain the mechanical properties interms of orientation of molecules.

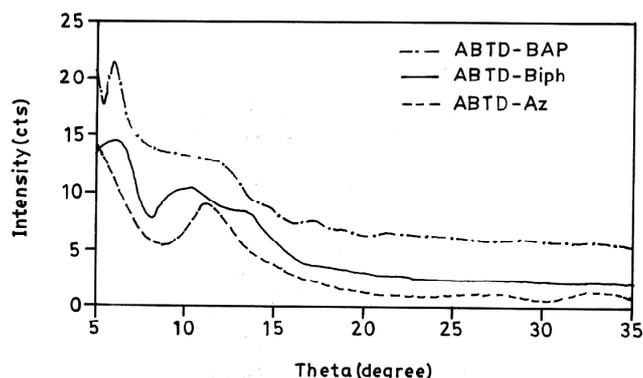


Fig. 5. X-ray diffraction patterns of polyimides

ACKNOWLEDGEMENTS

The authors thank U.G.C. New Delhi for the financial help under minor research project.

REFERENCES

1. C.P. Wong, *Mater. Chem. Phys.*, **42**, 125 (1995).
2. S.D. Bluestein, D.P.Y. Bramono, I.N. Miaoulis and P.Y. Wong, *Mater. Res. Soc. Symp. Proc.*, **445**, 185 (1997).
3. M.J. Nanjan and K. Sivaraj, *J. Polym. Sci. Part A, Polym. Chem.*, **27**, 375 (1989).
4. V. Rajendran and M.J. Nanjan, *J. Poly. Sci., Poly. Chem.*, **25**, 829 (1987); *J. Appl. Polym. Sci.*, **37**, 3281 (1989).
5. V. Rajendran and S.M. Thayumanaswamy, *Iran. Polym. J.*, **4**, 257 (2002).
6. R.L. Hansen, Rosevila, minn. U.S. Pat 3,476-505 (1969).
7. J. Sugano, M. Abe and T. Takenslei, Tap. Pat. 6,723,340 (1967).
8. C. Anbuselvam, Ph.D. Thesis, University of Madras, India, February (2004).
9. V.R. Murthy and R. Raman, *Solid State Commun.*, **80**, 847 (1989).

(Received: 1 December 2008; Accepted: 10 March 2010)

AJC-8505