Asian Journal of Chemistry Vol. 22, No. 7 (2010), 4976-4984

Film Studies of New Aromatic-Aliphatic Polyimides

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Three new aromatic-aliphatic polyimides based on 3,3',4,4'-azobenzene tetracarboxylic dianhydride and the aliphatic diamines *viz.*, ethylene diamine, 1,4-butane diamine and 1,8-octane diamine were synthesized and the films were cast. Film studies were carried out by scanning electron microscope, dielectric constant, microwave and X-ray diffraction pattern. The results were correlated with structure and orientation of the molecules.

Key Words: Polyimides, Azo linkage, Film studies, Dielectric property.

INTRODUCTION

In recent years, attention has been given to the synthesis of polyimide films because it shows wide applications from domestic purpose to industrial purpose. First polyimide films (Kapton) was introduced by Dupont. Polyimide films are high performance with a range of properties including high thermal stability, resistance to chemical attack. Lower dielectric constant can withstand temperatures as low as -269 ºC and as high as 400 ºC and still retain its properties. Polyimide films used primarily as insulation for aircraft and spacecraft wiring. Thin and light weight polyimide films can withstand flexing without developing cracks or tears shows electronic application[1]. Photo sensitive polyimide precursor and its photocuring behaviour for lithography applications were studied by Nguyen *et al.*[2]. Reflective and conductive silvered polyimide films are shown wide applications in space[3]. A study on dielectric properties of a new polyimide films suitable for interlalyer dielectric materials in microelectronics applications were reported by Kuntman[4]. In this article we report the synthesis of polyimide films based on aromatic dianhydrides and aliphatic diamines.

EXPERIMENTAL

3,3',4,4'-Azobenzene tetracarboxylic dianhydride is prepared from 4-nitrophthalic acid and it is purified by dioxane.The aliphatic diamines used are: 1,2-diamino ethane (ethylene diamine) (DAE), 1,4-diamino butane (1,4-butane diamine) (DAB) and 1,8-diamino octane (1,8-octane diamine) (DAO).

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The polyimides were synthesized by imidization method which involves two step process. In the first step monomers are condensed to form polyamic acid. In the second step, conversion of polyamic acid into polyimides was followed by three methods *viz.*, chemical, solution and thermal imidization methods.

Polyimide films were prepared by condensing 3,3',4,4'-azobenzene-tetracarboxylic dianhydride (ABTD) with one of the following aliphatic diamines *viz.* diamino ethane, 1,4-diamino butane and 1,8-diamino octane. Polyimides ABTD-DAE, ABTD-DAB and ABTD-DAO were chosen for casting films onto a glass plate using 0.5 % *p*-toluene sulfonamide as plasticizer. A fixed thickness of 0.015 cm was taken in these cases.

The X-ray diffraction patterns were recorded with a SEIFERT JSO Deblyfelex 2002 X-ray diffractometer. A 40 KV and 30 mA copper target (λ -1.54 Å) radiation was employed. The films were fixed in the sample holder and mounted perpendicular to the X-ray beam and diffraction patterns were recorded by the usual method. The polyimide films (0.015 cm thickness) obtained from 25 and 30 % dopes (with plasticizer) ABTD-DAB and ABTD-DAO were exposed for various time intervals (1 to 16 min) using 930 W morphy AC 2000-II microwave oven. The frequency selected for microwave dielectric heating is 2.45 GHz (wavelength = 12.2 cm) which is in the region between infrared and radiowave (K band) wavelengths in the electromagnetic spectrum.

Dieletric constant of the films was measured directly using circular film samples (dia = 1 cm) coated both sides with a collodial silver paste. The capacitance and loss factor (tan δ) of the circular film samples were measured using a Zentech 1061 LCZ capacitance measuring assembly in the frequency range 1 to 200 KHz at room temperature.

The polyimide was heated at two different temperatures *i.e.*, 170 and 250 °C for 0.5 h. The residue obtained was subjected to mass spectral analysis using QP 2000 Shimadzu mass spectrometer by the direct inlet probe technique.

RESULTS AND DISCUSSION

Scanning electron microscopic (SEM) studies: The SEM micro photographs of the images of polyimide films *viz.*, ABTD-DAE, ABTD-DAB and ABTD-DAO are shown in Fig. 1. These polyimide films were treated at different temperatures and the magnification is X2000 (lower) and X5000 (higher).

The uniform distribution of plasticizer *p*-toluenesulfonamide of 20 nm size within the polyimide matrix was observed in all cases. It can clearly observe that the degree of surface roughening or imperfection increases with temperature. The surface of heat treated polyimide is observed to consist of globules, cavities, blisters and voids of various sizes. This may be attributed to scissoring and cross-linking on the surface of the polyimide film. The scissoring is responsible for the evolution of gases from the surface and to respective erosion/sputtering rate can vary with the position on the polyimide surface. Such uneven evolution of gases may lead to significant surface roughening. Secondly, some of the scissioned polymer chains may further cross-link. This may change the free volume on the surface, due to which the surface appears imperfect after thermal effects.The top skin layer consists of closed packed polymer nodules (Fig. 1.1). These nodules are not artfacts of the gold sputter coating of the membranes and are a feature of the top layer microstructure, since SEM images of TiO_2 and ZnO thin films on glass using the same sputtering technique and instruments do not show these nodules[5,6]. Many holes are distributed throughout the bulk material on the nanometer scale, perhaps formed by the removal of solvent when the polyamic acid was dried *via* imidization at 300 ºC.

As the temperature increases, the uniformity of thin films also increases. Increase in defect of polyimide films increases the electrical resistivity[7]. Fig. 1.1 shows bigger voids in ABTD-DAE compare to other two polyimides *viz.*, ABTD-DAB and ABTD-DAO (Figs. 1.3 and 1.4). Nevertheless, number of voids and their size are the important factors that decide the mechanical properties of a film where initial modulus and percentage elongation vary appreciably. Fig. 1.4(b) demonstrated that the absorption of polar organic molecules or solvents or filler or air in polyimides were curled and entangled in the polymer matrix.

ABTD-DAO polyimide film, at higher magnitude permits a better close packing of the chains, because of the long CH_2 linkage, there is a possibility of forming coil structure and air or nitrogen gas may be occluded and therefore, there are large voids [Fig. 1.4(b)] in the films during the formation itself. The films cast from DAO based polyimide are weak and thick, perhaps due to the high mass transfer in short times.

Fig. 1.3(b) shows that loss of crystallinity results in changes to the spherulitic textures and lamellae, with cracks often appearing in the amorphous region of these structures. Large dimensional changes can be induced by radiation that distorts the object and changes the image. This is quite serious because it might be overlooked and misinterpreted[8].

X-Ray diffraction studies: Of the ten polyimides, based on homologous series starting from diamino ethane (R_2) to 1,10-diamino decane (R_{10}) and 1,12-diaminododecane (R_{12}), ABTD-DADo has the highest crystalline order. An increase in the length of the methylene units in the diamine component, the intensities of X-ray diffraction peaks increased for aliphatic-aromatic polyimides films. Two diffraction peaks have been observed for all the polyimides suggesting some ordered structure due to the symmetric structure of monomers. The intensities of the peaks become higher with increasing length of methylene chain in diamine component, suggesting that a flexiable, longer methylene chain reduces the distortion of the network structure. It is observed that polyimides containing even number of methylene units in the diamine moiety is more crystalline than the corresponding odd number of methylene units (Fig. 2). In addition, the polyimides based on even numbered aliphatic diamines all rapidly crystallize from the melt whereas the PIs based on 1,7-diaminoheptane and 1,9-diaminonanane stay amorphous upon cooling from the melt. This odd-even effect was found in this homologus series of polyimides too[9].

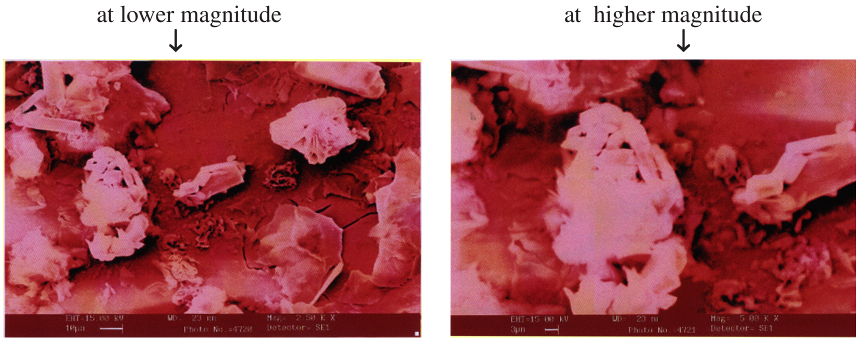


Fig. 1.1. SEM photographs (perpendicular to the surface of the film of ABTD-DAE)

(at very high temperature)

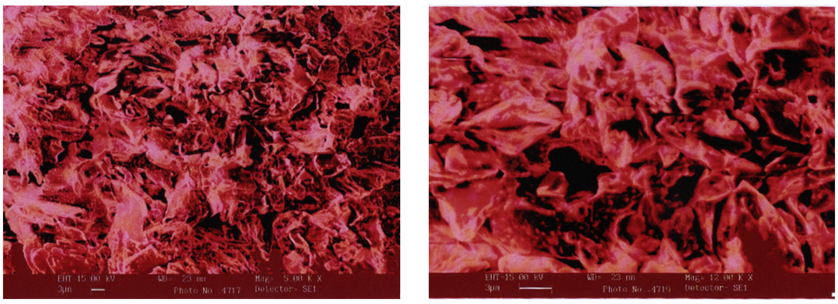
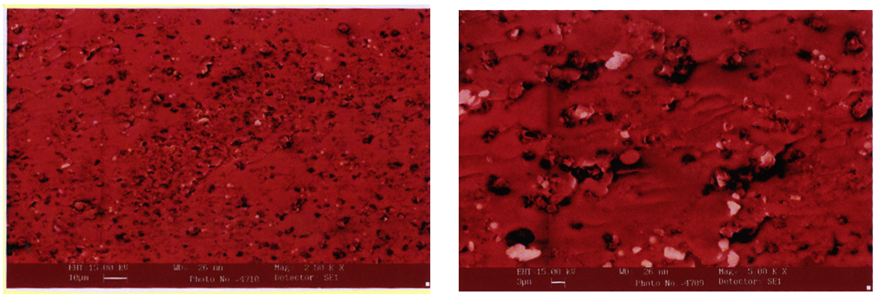


Fig. 1.2. SEM Photographs showing liquid crystalline behaviour at moderate temperature of ABTD-DAE(parallel to the surface of the film)



(a) (b)

Fig. 1.3. SEM photographs of ABTD-DAB at lower and higher magnitude

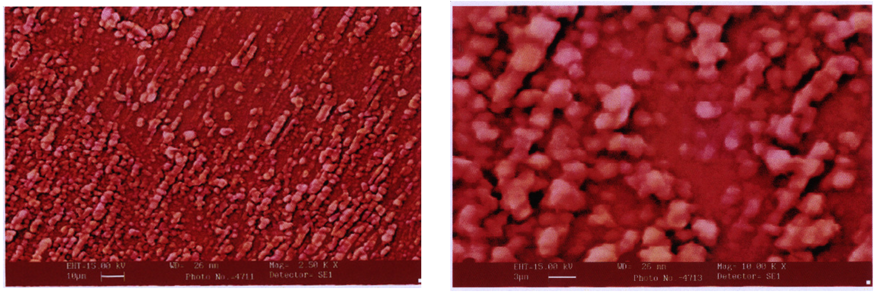


Fig-1.4 SEM photographs of ABTD-DAO at lower and higher magnitude

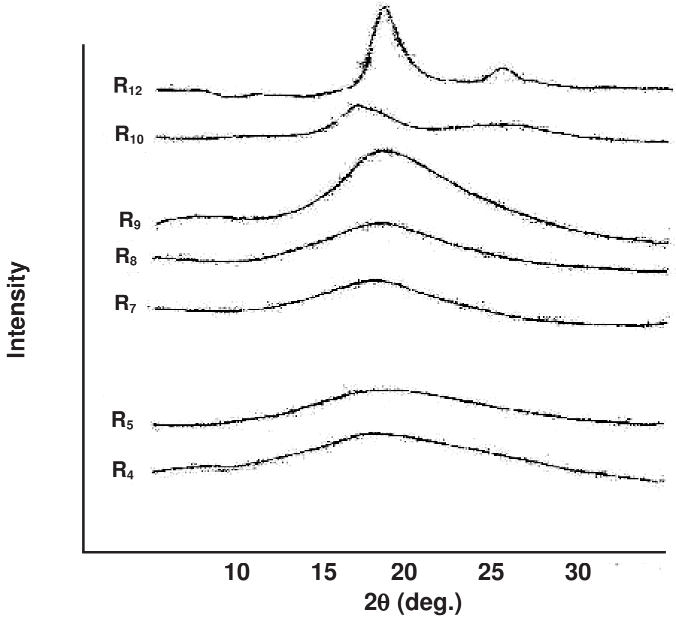


Fig. 2. X-ray diffraction pattern of polyimides

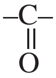
Microwave study: The IR spectra recorded before and after microwave treatment shows that the film is not affected by microwave. It has been noticed that absolutely there is no change in IR frequencies or peak areas. No physical change could be noticed on the films. The penetration depth (Dp) of microwave on the polymeric film has been studied based on the following equation:

$$\tan\delta = \frac{\varepsilon'}{\varepsilon''} \text{ (or) Dxf and } Dp = \lambda\overline{\varepsilon'/\varepsilon''}$$

where D = dissipation factor, f = frequency, λ = wavelength of microwave radiation, ε' = relative permittivity which is a measure of the ability of a molecule to be polarized by an electric field, ε'' = dielectric loss which is indicative of the ability of a medium to convert dielectric energy into heat, tan δ = dielectric loss tangent which defines the ability of a material to convert electromagnetic energy into heat energy at a given frequency and temperature.

From Table-1, it is clear that as the concentration of polymer dope increases from 25 to 30 %, both tan δ and Dp value increase. However, plasticized polymer film has lower tan δ and Dp value compare to unplasticized one. It has been found that the value of tan δ depends on the following factors: (i) frequency of electromagnetic waves (ii) temperature (iii) physical state and (iv) composition of the mixture.

The results of microwave experiments can be correlated with the thermogravimetric data. The difference between microwave cured and theremally cured polymers have been rationalized in terms of the temperature profile during the initial stages of the reaction or specific activation. This will be the cause of the occurrence of cross-linking reactions or intra-molecular reaction. This reaction was followed by IR spectroscopy. This effect was thought to be caused by temperature 'hot-spots' at a molecular level.

Microwave study reveals the fact that the polymer film is transparent to microwave and it acts as an insulator. There is no identification of ene or isomerization (in *trans*) reactions though –N=N– and  $-\underset{\underset{\displaystyle O}{\|}}{C}-$ groups are present.

Microwave reaction involves selective absorption of microwave energy by polar molecules whereas, non-polar molecules being inert to microwave dielectric loss. This study in useful in: (i) polymer curing (ii) effect of rapid heating (iii) hot spots surface effects (iv) Dielectric heating or temperature effect (v) kinetically and/or thermodynamically controlled reactions and (vi) solvent free organic synthesis *i.e.* under dry reaction conditions.

Dielectric constant: Dielectric properties have been studied for two aromatic polyimides *viz.*, ABTD-DAB and ABTD-DAO. The dielectric properties *i.e.*, dielectric constant (ε) and loss factor (tan δ) of the films are measured as a function of low range frequency from 1 to 200 KHz at room temperature (25 ºC). The dielectric constant and dissipation factor of the two films *viz.*, ABTD-DAB and ABTD-DAO are shown in Table-1.

TABLE-1
DIELECTRIC CONSTANT AND MICROWAVE DATA OF FILMS

Polymer	Conc.		Frequency (KHz)							Microwave study at frequency = 2.45 GHz	
			1	5	10	25	50	100	200	tan δ	Dp
ABTD-DAB	25 % Dope	A	1.95	1.78	1.55	1.38	1.19	1.12	1.01	9.80	35.60
		B	9.92	9.70	9.26	9.08	8.90	8.71	8.50		
		C	8.45	1.940	0.926	0.363	0.1798	0.00871	0.00425		
	30 % Dope	A	2.08	1.91	1.62	1.42	1.36	1.29	1.20	10.0	37.20
		B	10.02	9.98	9.38	9.24	9.01	8.90	8.75		
		C	8.80	1.96	0.98	0.42	0.22	0.009	0.006		
ABTD-DAO	25 % Dope	A	1.79	1.58	1.35	1.15	1.01	0.78	0.56	19.45	53.10
		B	19.51	19.36	19.20	19.00	18.05	17.0	15.94		
		C	9.52	3.872	1.920	0.760	0.361	0.170	0.0797		
	30 % Dope	A	1.34	1.18	1.01	0.86	0.75	0.59	0.42	9.82	26.40
		B	8.81	8.01	7.89	7.75	7.65	7.48	7.02		
		C	4.30	1.60	0.789	0.310	0.153	0.075	0.035		

A = ε; B = tan δ; C = Dissipation factor D; Dia: Thickness of the film = 1 cm: 0.015 cm

The dielectric constant dependence of frequency for both polyimide films at room temperature is shown in Fig. 3. It is seen from these figures that ε_1 decreases with increasing frequency when temperature is kept constant[10]. Also, the addition of plasticizer lowers the dielectric constant compare to unplasticized one. This behaviour can be attributed to the frequency dependence of the polarization mechanisms. When frequency increases, the orientation polarization decreases since the orientation of dipole moments need a longer time than electronic and ionic polarizations. This causes the dielectric constant ε_1 to decrease. The increase of ε_1 towards the low frequency region is also observed. This may be attributed to the blocking of charge carriers at the electrode[11]. On application of the field, charges in the dielectric films migrate because of the impedance of their motion at the electrodes and space charge and hence macroscopic distortion results. However, comparing the two polyimides, ABTD-DAB and ABTD-DAO, from Fig. 4, it has been found that ABTD-DAB has more dielectric constant as well as less loss factor than ABTD-DAO.

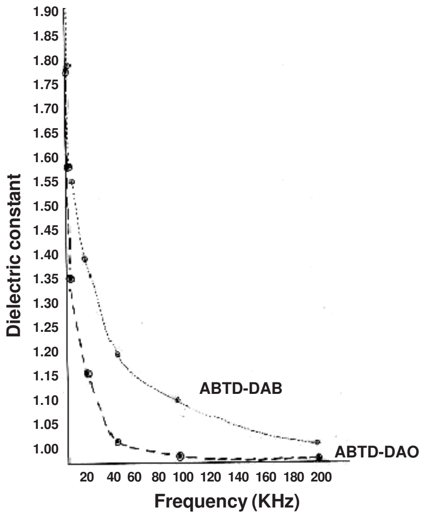


Fig. 3. Dielectric constant curve of ABTD-DAB and ABTD-DAO

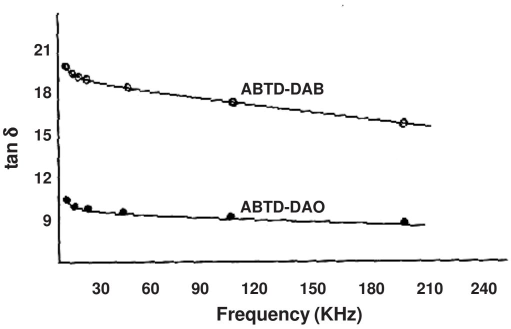


Fig. 4. Loss factor curve of ABTD-DAB and ABTD-DAO (25 % dope)

Pyrolysis-mass spectral studies: The mass spectra are recorded at 200 ºC for the polymide films ABTD-DAE, ABTD-DAB and ABTD-DAO are recorded. Fig. 5 shows the mass spectrum of polyimide ABTD-DAB. The pathways through which a polymer degrades thermally can be investigated by pyrolysis-mass spectral studies. The spectra are seem to be complex due to the presence of a number of peaks at lower m/e values with low intensity. The peaks at higher m/e values are found to be significant and they are considered mainly for arriving at degradation mechanisms.

All polymers exhibit the major step as hydrolytic scission. Water is probably not a direct product of pyrolysis but its origin could be, either due to the absorbed moisture held by hydrogen bonding in the polymer main chain or due to the reaction between the amino and carbonyl/anhydride end groups of the polymer chain. Dehydration of a primary amine, formed during pyrolysis, may also lead to nitrile which yields water molecule. The formation of carbon dioxide is suggestive of the hydrolytic type of degradation, hydrogen abstraction reaction is found to occur normally in the fragmentation patterns. The hydrogen can be abstracted from water. All these data confirm the structure of polyimides.

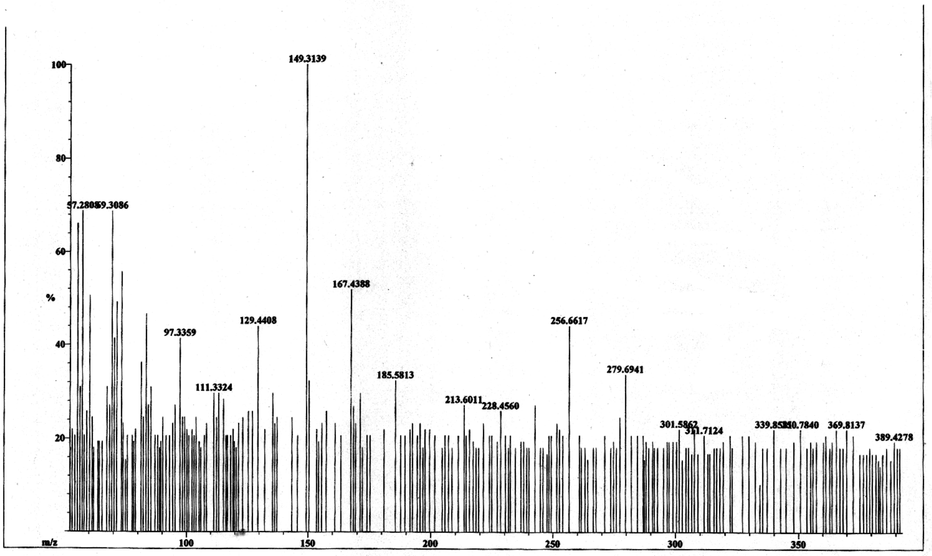


Fig. 5. Mass spectrum of ABTD-DAB

TABLE-2
COMPARISON OF m/z VALUES OF POLYMERS

DAE		DAB		DAO	
363	**174**	391	188	444	**162**
360	**163**	389	**174**	430	**161**
349	**151**	388	166	392	166
346	**149**	356	**149**	377	**149**
332	147	342	146	374	146
324	146	328	137	324	**135**
318	**135**	**318**	**135**	321	128
314	132	256	131	**318**	**123**
311	131	**239**	**123**	274	**105**
242	**123**	218	**105**	272	**104**
239	**105**	216	73	201	73
188	56	213	72	177	56
176		212	**56**	**174**	

Values (in bold) refers to common peaks observed in all polymers.

ACKNOWLEDGEMENTS

The authors are thankful to U.G.C, New Delhi for financial help under Minor Research Project.

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(*Received*: 1 December 2008; *Accepted*: 10 March 2010) AJC-8504