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New Azopolyimides: Synthesis and Film Studies

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Aromatic azopolyimide films were prepared from 3,3′,4,4′-azobenzenetetracarboxylic dianhydride condensed with four different diamines by thermal imidization method. Diamines used were (i) 4,4′-diaminodiphenyl ether, (ii) 4,4′-diaminodiphenyl methane (iii) 4,4′-diamino benzanilide and (iv) 2,2-*bis*[4(*p*-amino phenoxy)phenyl]-propane. These polyimide films were characterized by scanning electron microscope, X-ray diffraction, pyrolysis-mass spectra and dielectric constant.

Key Words: Azopolyimide films, Mass spectra, Dielectric constant.

INTRODUCTION

Polyimides have many desirable characteristics such as excellent mechanical properties, low dielectric constant, low relative permitivity, high breakdown voltage, intertness to solvent and radiation resistance. They are distinguished from other high performance polymers by the solubility of poly (amic acid) precursor form which can be casted into uniform films and quantitatively conversion to polyimide. Due to these prior properties polyimides have been especially used widely in micro-electronic, film, adhesive and membrane industry[1-4]. One of the most important applications of polyimide thin films is in the inter level dielectric insulators. The polyimide films that are widely used in the microelectronic industry with low relative permitivity (dielectric constant) have values[4] in the range of 2.9-3.4 *i.e.* the low dielectric constant and high dielectric breakdown voltage of polyimides. In electronics packing, low dielectric materials minimize cross talk and maximize signal propagation speed in devices. Hence, the development of polyimides with low dielectric constant[5] has been the focus of several investigations[5,6]. Polyimides are now available as electrical insulating materials, capable of demonstrating performance at temperatures up to 600 K. There is an increasing use of polyimides as interlevel dielectrics and as passivators in integrated circuits[7].

EXPERIMENTAL

3,3′,4,4′-Azobenzenetetracarboxylic dianhydride (ABTD) monomer was synthesized by reported method[8,9]. 4,4′-Diaminodiphenyl ether (m.p. 191-192 ºC) and 4,4′-diaminodiphenyl methane m.p. 86-87 ºC. Aldrich, Germany were recrystallized from aqueous methanol and aqueous alcohol, respectively, 4,4′-diaminobenzanilide (m.p. 239 ºC)[10] and 2,2-*bis*[4-(*p*-aminophenoxy)phenyl]propane were synthesized[11]. These polyimides were cast into films using conc. H_2SO_4 solvent.

Characterization

Scanning electron microscope (SEM): The surface of the film was investigated with a stereo scan model 440 scanning electron microscope. The film was coated with a thin film of gold in the polaron SC500 sputter coater prior to SEM examination to eliminate 'local charging' and to make them electrically conductive.

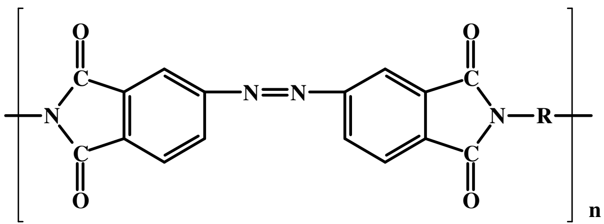
X-ray diffraction of film: These were recorded with a Seifert JSO Deblyfelex 2002 X-ray diffractometer. A 40 KV and 30 mA copper target (λ = 1.54 Å) radiation was employed. The films were fixed in the sample holder perpendicular to the X-ray beam and diffraction pattern were recorded.

Pyrolysis-GC-mass spectra: The polyimides were heated at two different temperatures *i.e.*, 170 and 250 ºC for 0.5 h. The residue obtained was subjected to mass spectral analysis using QP 2000 Shimadzu mass spectrometer by the direct inlet proble technique.

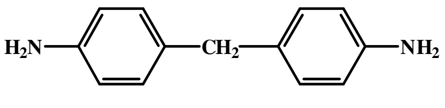
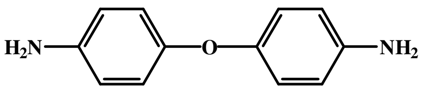
Determination of dielectric constant: The capacitance (or) electrical resistance and loss factor of the representative films ABTD-DiphyMe and ABTD-Diphyeth sample were measured using Zentech 1061 LCZ capacitance measuring assembly in the frequency range 1 to 200 KHz at room temperature. From the capacitance (C) and loss factor values (tan δ), the dielectric constant (ε), dissipation factor and the conductivity (σ) have been calculated.

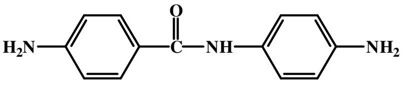
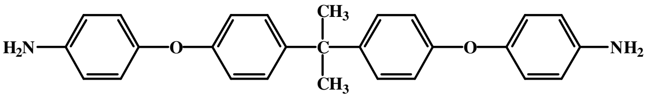
RESULTS AND DISCUSSION

The following four polyimides were synthesized and cast films.



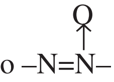
ABTD-R

where the following diamines were used for R	Code	Inherent viscosity (in conc. H_2SO_4)
1.  **4,4'-Diamino diphenylmethane**	DiphyMe	1.32
2.  **4,4'-Diamino diphenylether**	Diphyeth	1.18

3.	 **4,4'-Diamino benzanilide**	BzAni	1.10
4.	 **2,2'-*Bis*[4-(*p*-aminophenoxy)phenyl)propane**	Oxalk	1.28

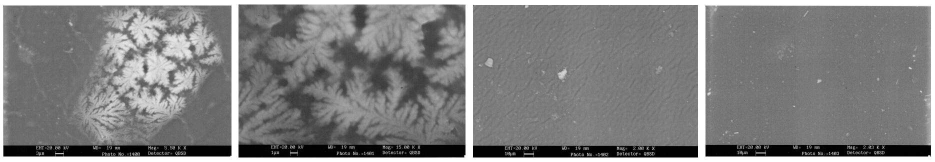
Scheme-I

SEM: The morphology of ABTD-DiphyMe, ABTD-Diphyeth, ABTD-BzAni and ABTD-Oxalk were studied and the scanning electron micrographs are presented in Figs. 1 to 4, respectively. These voids are formed by the following reasons: (i) non-close packing of the substance, (ii) geometry of the polymer either in *cis* or *trans* form. In other words orientation of molecules along the stretching axis, (iii) nature of polymer either crystalline or amorphous, (iv) concentration of the polymer dope, (v) effective stirring, (vi) occlusion of oxygen atom (*i.e.*) oxidation of



$-N=N-$ group to $-N=\overset{\overset{O}{\uparrow}}{N}-$ (Azoxy)

which is evidenced from the change in colour after long standing in air or oxygen and (vii) drawing speed of the films and coagulation bath.

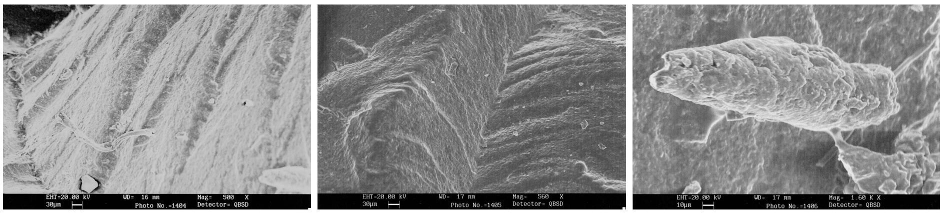


(a) (b) (c) (d)

SEM micrograph showing liquid crystalline behaviour at 200 ºC (parallel to surface of the the film) SEM

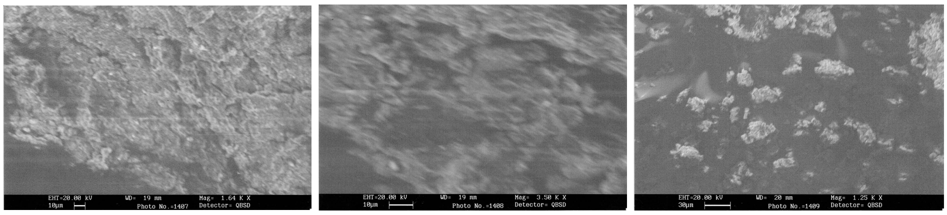
SEM micrograph of ABTD-DiphyMe film (Perpendicular to surface of the film)

Fig. 1.



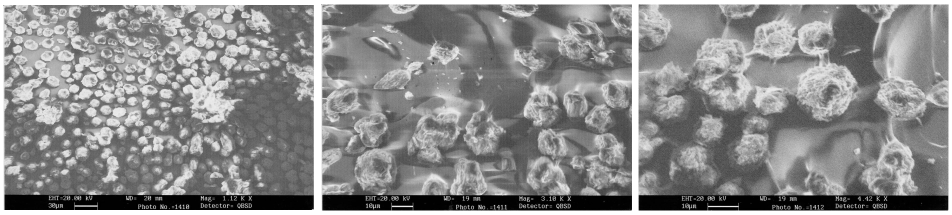
(a) (b) (c)

Fig. 2. SEM of a fracture of a liquid crystalline polymer molded part



(a) (b) (c)

Fig. 3. Fracture surface of the polyimide after peeling



(a) (b) (c)

Fig. 4. SEM image of polyimide microporous membrane showing a thick granular texture and cracks due to Au coating

If more voids are formed, it indicates that during film casting either oxygen is occluded or the molecules are not orienting towards the film drawing axis. In this study, since water is used as coagulant, as soon as the film is immersed and peeled, more heat is evolved and it leads to voids formation on the outer surface and less effect is felt at the interior. However, number of voids and their size are the important factors that decide the mechanical properties of a film. SEM shows bigger voids in ABTD-Oxalk and small sized voids in ABTD-Diphyeth, ABTD-DiphyMe and ABTD-BzAni (in the middle order). All these voids factors will reflect in the mechanical properties where initial modulus and percentage elongation vary appreciably if studied.

X-Ray study: X-ray diffractogram recorded for the above films were presented in Fig. 5. The diffractograms do not indicate sharp and high intensity (240 and 200) peaks for ABTD-Oxalk, indicating a little orientation. ABTD-BzAni, ABTD-Diphyeth diffractograms indicate medium, sharp and intensity peaks because of medium orientation of molecules. However, a comparison of the sharpness of peaks and their intensity leads to the following conclusions: (i) above three films exhibit crystalline nature (ii) of the three films, the ABTD-Oxalk film is found to be more crystalline than ABTD-BzAni, ABTD-Diphyeth films.

Dielectric property: 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-DiphyMe and ABTD-Diphyeth are shown in Table-1.

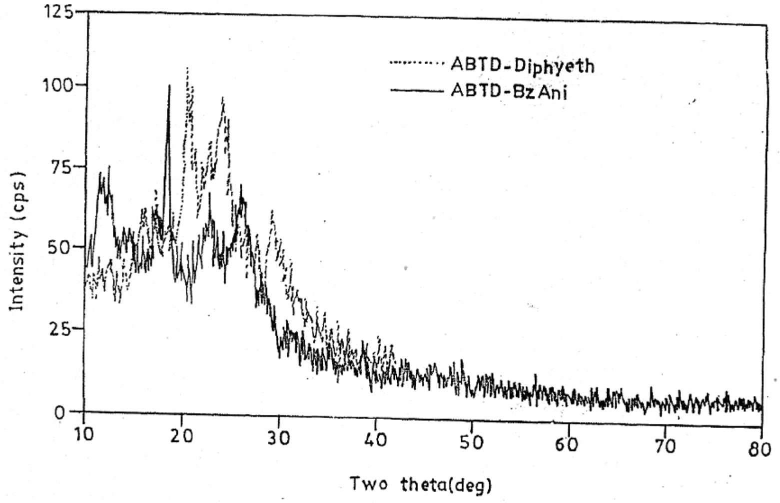


Fig. 5. X-ray diffraction curves

TABLE-1
DETERMINATION OF DIELECTRIC CONSTANT

ABTD-Diphyeth	Frequency KHz	1	5	10	25	50	100	150	200
	E	3.3501	3,2230	3.0280	2.2647	2.0801	1.7380		1.5780
	Tan δ	0.6510	0.6010	0.5813	0.4123	0.3972	0.3123		2.2203
	Dissipation factor D	0.6510	0.1202	0.05813	0.0164	0.0079	0.00312		0.0010
ABTD-DiphyMe	Frequency KHz	1	5	10	25	50	100	150	200
	E	2.8960	2.1257	1.9750	1.8434	1.6854	1.4747	1.3693	1.3167
	Tan δ	0.5310	0.3452	0.3172	0.2910	0.2203	0.1821	0.1427	0.1378
	Dissipation factor D	0.5310	0.06904	0.08172	0.01164	0.00440	0.001821	0.00095	0.000689

Area of the film = 0.64 cm^2. Thickness of the film 0.015 cm.

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[2]. For polar polymers the dielectric constant increase with increasing temperature[12]. For many microelectronic applications, dielectric materials with stable dielectric constant and dissipation factor values across large frequency and temperature range are highly preferred. Despite polyimide have the same frequency and temperature dependence, the dielectric constant of the polyimides have lower values. This result confirms the restriction on orientation and relaxation of polar groups by the formation of network stability. In addition to this, another factor affecting the dielectric behaviour of a material is its chemical structure which influences charge distribution and thermal motion of dipolar. Comparing the two polyimides, ABTD-Diphyeth has more dielectric constant as well as more 'loss factor' than ABTD-DiphyMe.

Mass spectra: The mass spectra of the polymers are recorded at 200 ºC for ABTD-Diphyeth, ABTD-DiphyMe, ABTD-BzAni. The pathways through which a polymer degrades thermally can be investigated by pyrolysis-mass spectral studies. The formation of carbon dioxide is suggestive of the hydrolytic type of degradation. Hydrogen abstraction (may be from water) is found to occur normally in the fragmentation pattern.

The pyrolysis-mass spectra of the three polyimides are given in Fig. 6 for ABTD-DiphyMe, ABTD-Diphyeth and ABTD-BzAni, respectively. Common peaks showing the fragmentation of ABTD are observed in ABTD-DiphyMe from m/z values 63 to 484, ABTD-Diphyeth = 52 to 486 and ABTD-BzAni = 51 to 530. All the three polyimides have a parent peak at m/z 484, m/z = 486 and m/z at 530, respectively and confirm the structures.

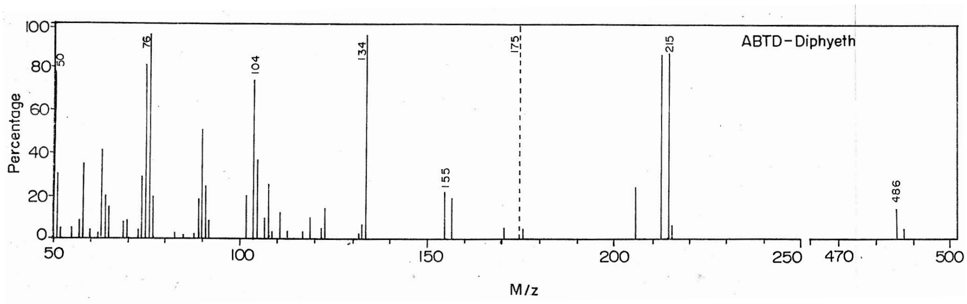


Fig. 6. Pyrolysis-mass spectrum of ABTD-Diphyeth

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