Synthesis of a Novel Polyesterimide

SWAPAN KUMAR DOLUI, DHANANJAY PAL, and SUKUMAR MAITI, *Polymer Division, Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India*

Synopsis

A new polyesterimide has been synthesized from trimellitic acid anhydride, diaminodiphenylsulfone, and bisphenol-A following three different routes. Solubility behavior in different solvents, solution viscosity, density, crystallinity, and thermal and electrical properties of the polyesterimide have been discussed. Results indicate that the polyesterimide thus prepared has medium thermal stability.

INTRODUCTION

Polyesterimides are well known for their thermal resistance coupled with processing ease.[1-3] In our program for development of processable thermostable polymers, we reported earlier a few polyesterimides.[3-5] General methods of synthesis of these polymers include the following: (a) direct condensation between trimellitic acid or its derivative with a diamine and a diol,[2] (b) reaction between a dicarboxylic acid containing imido group with a diol,[2,3] and (c) reaction between a dianhydride containing ester group with a diamine.[6]

In the present communication we report the synthesis and properties of a polyesterimide using trimellitic acid anhydride (TMA), bisphenol A, and diaminodiphenyl sulfone (DADS).

EXPERIMENTAL

Reagents

TMA was obtained from Amoco Chemical Corp. and was used without further purification. Bisphenol A, acetic anhydride, concentrated sulfuric acid, and potassium acetate (E. Merck, India) were AR grades and used as received. DADS (Wilson Laboratories, India) was used as received. *N*-methylpyrrolidone (NMP) (E. Merck, India) was used after necessary purification. All solvents were AR grades and used after purification.

Synthesis of Monomers

Synthesis of Bisphenoldiacetate (BPDA). Typical charge consists of 20 g (0.087 mol) bisphenol A, 60 mL (0.54 mol) acetic anhydride, and 8 drops of concentrated sulfuric acid. The reactants were taken in a 250 mL three-necked flask equipped with a stirrer, a thermometer, and a reflux condenser. The reaction mass was heated and stirred for 30 min at the reflux temperature of acetic anhydride. After the reaction was over, the product was

CCC 0021-8995/85/093867-12$04.00

isolated by precipitating the content of the flask into ice-water, filtering and washing the precipitate with caustic potash solution to free it from acid and then with cold water repeatedly till neutral to litmus, and finally drying in vacuum; crude yield 21 g.

Preparation of N,N'-(4,4'-Diphenylsulfone) Bis (trimellitimide) (DID-CA). Similar reactor as used in preparation of BPDA was used in this case also. At first 15.36 g (0.08 mol) of TMA was dissolved in 50 mL of NMP at 50°C. Next, 9.92 g (0.04 mol) DADS was added to the reactor after cooling to room temperature and was left for 5 h at room temperature reaction. After this period, the temperature was raised to 180°C and kept for 4 h under stirring condition to complete the reaction. DIDCA was isolated by precipitation in 500 mL water, filtered, washed repeatedly with water, and dried in vacuum at 60°C; crude yield 19 g.

Preparation of 2,2-Bis(p-Trimellitoxyphenyl)Propane Dianhydride (TMPDA). A typical charge consists of 15.6 g (0.05 mol) BPDA, 19.2 g (0.1 mol) TMA, and 0.2 g potassium acetate. The reactants were taken in a reaction vessel fitted with a stirrer, a thermometer, and a nitrogen purging tube. The reaction was allowed to proceed in the following steps: (i) charge was melted by heating at about 180°C under nitrogen, (ii) acetic acid was stripped off when pressure in the vessel was reduced to 100 mm Hg at 180°C, and (iii) after 1.5 h of reaction a Liebig condenser was connected to the vessel for distilling out the acetic acid under vacuum. Pressure was further reduced to 10 mm Hg, when the temperature was raised to 210°C. At this stage acetic acid was removed completely. The solid reaction product was recrystallized from acetic anhydride; yield of the impure dianhydride (TMPDA) 30 g.

Synthesis of Polymers

Synthesis of Polyesterimide (Method A). Polycondensation was carried out in a similar vessel as described earlier[7]; instead of a 1500-mL reaction kettle, we used a 500-mL four-necked round-bottom flask fitted with a nitrogen purging tube, a mechanical stirrer, a thermometer, and a vacuum arrangement through the water-cooled condenser. A typical charge consists of 7.68 g (0.04 mol) TMA, 4.96 g (0.02 mol) DADS, and 4.56 g (0.02 mol) bisphenol A, a mixture of 0.001 g Sb_2O_3 and 0.001 g $Zn(OAC)_2$ as catalyst along with 50 mL NMP as solvent. TMA was dissolved in NMP in the reaction kettle and DADS was added after addition of bisphenol A. The content of the flask was continuously stirred for 4 h at room temperature. Then the temperature was raised to 130°C and kept constant for 1 h. Next, the temperature was raised slowly to 190°C when the catalyst mixture was added. At this stage the temperature was kept constant for 5–6 h. During the last 1 h, vacuum was applied to facilitate the polycondensation reaction. The reaction mixture was cooled to room temperature, and the polyesterimide was isolated by precipitation in cold water; crude yield 12 g.

Synthesis of the Polyesterimide (Method B). In the reaction vessel as mentioned earlier 2.98 g (0.005 mol) imidodicarboxylic acid (DIDCA) and 1.140 g (0.005 mol) bisphenol A were added along with 30 mL of NMP. Stirring was continued for 2 h at room temperature to get a homogeneous solution. Temperature was then increased to 170°C in 1 h when the mixture

of catalysts [0.005 g Sb_2O_3 and 0.005 g $Zn(OAC)_2$] was added. The temperature was kept constant for 4 h at 170°C and for 9 h 190°C. Vacuum was applied to the system during the last hour to facilitate polycondensation reaction. The content of the kettle was cooled to room temperature and crude polyesterimide was isolated by precipitation in cold water; crude yield 2.9 g.

Synthesis of the Polyesterimide (Method C). In the reaction vessel, 8.640 g (0.015 mol) dianhydride (TMPDA) and 3.720 g (0.015 mol) DADS were added to 100 mL NMP. Stirring was continued for 5 h at room temperature to obtain a homogeneous solution in the kettle. The temperature was then slowly raised to 180°C and kept constant for 4–5 h and vacuum was applied to the system during the last hour of the reaction. System was cooled to room temperature and content of the reaction vessel was poured over cold water to isolate the polyesterimide; crude yield 10 g.

Purification of the Samples. BPDA was recrystallized from petroleum ether. DIDCA was purified by washing with ethanol to free it from DADS and with aceton to free from TMA. TMPDA was recrystallized from acetic anhydride. The polyesterimide samples were made free from any free amine by repeated washing with ethyl alcohol and further purified by dissolving the dry polymers in NMP and reprecipitating by ethyl alcohol. The polymers were dried in vacuum oven at 60°C.

Characterization of the Monomers and the Polymer

IR and NMR Spectra. IR spectra of the monomers and the polymer were recorded on a Perkin-Elmer Model 257 Spectrophotometer in nujol. NMR spectra were obtained from a Varian A 90 MHz spectrometer in DMSO-d_6.

Viscosity Measurements. 0.5% (g/mL) solutions of the polyesterimides in NMP were used to measure the inherent viscosity (dL/g) at 30°C using a Ubbelhode viscometer.

Density Measurements. The density of the polymer materials was determined by using a pycnometer in ethyl alcohol at 30°C.

Thermal Analysis. Differential thermal analysis (DTA), thermogravimetric analysis (TGA), and derivative thermogravimetry (DTG) curves of the polymer samples were obtained from a Hungarian Mom Derivatograph of the Paulik–Paulik–Erdey system. The measurements were done in air at a heating rate of 10°C/min. Isothermal aging of the polymer samples was done in a forced air circulated aging oven at 250 ± 2 and 330 ± 3°C.

X-Ray Diffraction Study. This was recorded with a Dron I(USSR) X-ray diffractometer using Zr-filtered MoK$_\alpha$ radiation (λ = 0.711 Å).

Electrical Measurements. The electrical properties of the polyesterimide sample were measured at room temperature (30 ± 1°C) with a pellet 2.14 cm in diameter and 0.12 cm in thickness. The measurements were recorded by a General Radio Capacitance Bridge (type 716 C) and a Q-meter (Marcony Circuit Magnification-Meter (type 329 G) at 4×10^2 to 4×10^6 Hz.

Hydrolysis of the Polyesterimide. All three polyesterimide samples obtained by methods A–C were hydrolyzed by refluxing with a 10% (w/v)

caustic soda solution for 48 h. The diamine (DADS) and unreacted polymer were filtered after cooling the content of the flask after hydrolysis. The residue after drying was leached with ethanol when DADS went into solution. This was obtained from the filtrate when it was allowed to crystallize. This was identified by its melting point (175°C). The original filtrate after removing the unhydrolyzed polymer and DADS contained sodium salts of trimellitic acid and bisphenol-A. Acidification of the filtrate with concentrated hydrochloric acid gave a precipitate containing trimellitic acid and bisphenol A. The presence of the acid and bisphenol A in the mixed sample were identified by IR spectroscopy.

RESULTS AND DISCUSSION

Synthesis of Monomers and Their Characterization

DIDCA was synthesized from TMA and DADS by condensation [eq. (1)]. TMPDA was synthesized from TMA and BPDA by a similar condensation reaction [eq. (2)]. All these reactions are represented in reaction scheme I:

(1)
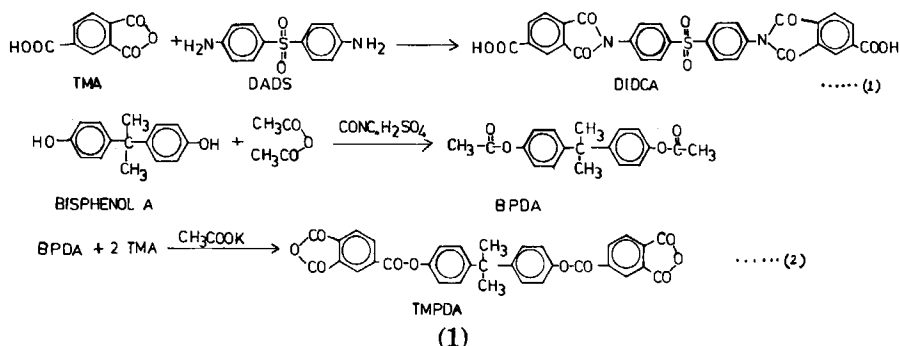
The properties of these monomers are given in Table I. The formation of the diimidodicarboxylic acid results most likely through the formation of amic acid in the first step and then its condensation to DIDCA by elimination of water.

The IR spectrum of DIDCA shows characteristic imide bands at 1725 and 725 cm^{-1} that are due to carbonyl stretching and ring carbonyl deformation,

TABLE I
Properties of the Monomers

Monomer	Yield (%)	Physical state	Melting point (°C)	Elemental analysis (%)			
					C	H	N	S
BPDA[a]	87.0	White crystal-line	78	Calcd	—	—	—	—
				Found	—	—	—	—
DIDCA	79.7	Yellowish white powder	>280	Calcd	—	—	4.69	5.36
				Found	—	—	4.36	5.25
TMPDA	85.0	Deep brown powder	192	Calcd	68.75	3.46	—	—
				Found	68.40	3.36	—	—

[a] This was characterized by its literature melting point only.

respectively. The absorptions at 1300 and 1625 cm^{-1} are due to the carbonyl stretching of —COOH.

In the spectrum of TMPDA, C—O stretching vibration band of the ester group occurs at 1745 cm^{-1} and its C—O stretching appears at 1290 cm^{-1}. C—O stretching vibration of the anhydride occurs at 1800 cm^{-1}, and that of its C—O group occurs at 1205 and 925 cm^{-1}.

TMPDA was also characterized by proton counting from its ^{1}H NMR spectra. In the spectrum 14 aromatic protons appeared in the region of 5.5–9.5 ppm (δ) and six aliphatic protons in the region of 0.5–3 ppm.

The properties of the monomers are given in Table I. The results of elemental analyses are in agreement with the structural formulae of DIDCA and TMPDA (Table I).

Synthesis of Polymers and their Characterization

Reaction scheme II represents the polycondensation reactions in various routes leading to the formation of the polyesterimide:
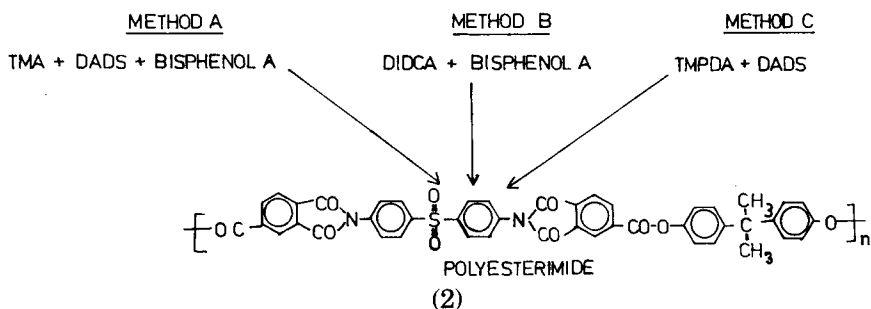

A mixture of Sb_2O_3/$Zn(OAC)_2$ is used as the catalyst for the esterification reaction involving the —COOH and —OH groups in both the routes (A and B). Route C does not need addition of any catalyst.

The general characteristics of the polymer synthesized through various routes are described in Table II.

Polymer Characterization

The polyesterimide synthesized through different routes was characterized by elemental analyses, IR spectra, and chemical analysis (hydrolysis with 10% NaOH solution). Results of chemical analysis and characteristic IR bands for different groups present in the polymer are presented in Table II. The IR spectra for the polyesterimide synthesized by the three different methods are given in Figure 1. The spectra show imide bands at 1785 and 1775 cm^{-1} due to the symmetrical carbonyl stretching for the polyesterimide. Bands at 1725 cm^{-1} appear for asymmetric carbonyl stretching and those at 727, 700, and 725 cm^{-1} appear for the ring carbonyl deformation of the imide group. C—O stretching bands of arylester group appear at at 1175, 1225, 1250, and 1255 cm^{-1}. Bands at 1300 and 1295 cm^{-1} appear for symmetrical stretching of $-S\underset{O}{\overset{O}{<}}$ groups and those at 1125 and 1155 cm^{-1} are due to asymmetric stretching of the same.

TABLE II
Properties, IR Spectral Characteristics and Elemental Analysis of Polyesterimide

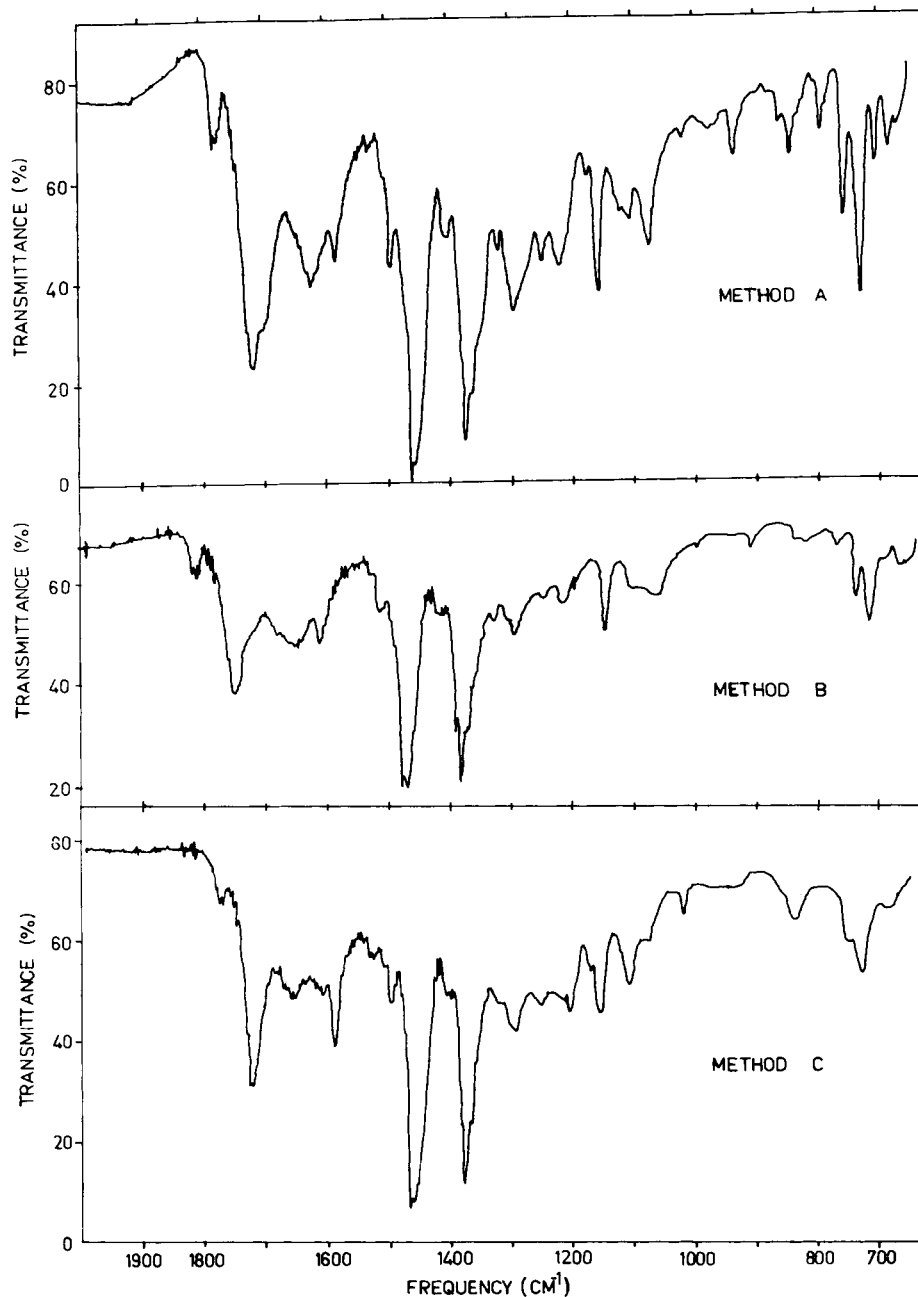| Polymerization method	Yield (%)	Inherent viscosity (dL/g)	Density (g/cm³)	IR spectral bands at cm⁻¹			Elemental analysis (N and S) (%)		
				Imido, C=O	Arylester, C=O	Sulfonyl, $-S(=O)(=O)-$		N	S
Method A	71.21	0.17	1.296	1785(w) 1725(s) 727(s)	1175(w) 1250(w)	1155(s) 1300(s)	Calcd Found	3.55 3.75	4.06 3.92
Method B	67.10	0.09	1.2167	1785(w) 1725(s) 700(s)	1175(w) 1225(w)	1125(s) 1300(w)	Calcd Found	3.55 3.85	4.06 3.89
Method C	80.11	0.18	1.246	1775(w) 1725(s) 725(s)	1175(w) 1255(w)	1155(s) 1295(m)	Calcd Found	3.55 3.10	4.06 4.16

Fig. 1.   IR spectra of the polyesterimide synthesized through different methods.

It is very difficult to characterize polyesterimide by its IR spectra since the strongest band of the ester group is that of the carbonyl group, which unfortunately coincides with the strong imide absorption band at 1725 cm^{-1}. To overcome this difficulty, the polyesterimide was hydrolyzed by aqueous alkali. Presence of carbonyl stretching absorptions at 1300 and 1625 cm^{-1}

indicates the acid (i.e., trimellitic acid) in the hydrolyzed product, and thus the ester group in the original polymer may be confirmed.

Polymer Properties

Solubility Behavior

All the polyesterimide samples were found to be soluble ($< 2\%$ w/v) only in polar solvents like N,N-dimethyl formamide (DMF), NMP, m-cresol, dimethylsulfoxide (DMSO), concentrated sulfuric, and formic acid.

Solution Viscosity

The inherent viscosity of the polyesterimide prepared by method C is the highest and that by method B is the lowest. The polymer prepared through method A exhibits a very close inherent viscosity to the polymer prepared by method C. Thus the molecular weight of the polyesterimide prepared by method A or C is nearly same, but the polymer prepared through method B exhibits a very low molecular weight.

Density and Molecular Crystallinity

Like inherent viscosity, the density of the polyesterimide prepared by method B is the lowest of the polymers prepared by other two methods. Density of the polyesterimide prepared by method A is highest and that for the polymer prepared by method C is intermediate of the other two varieties.

X-ray diffraction diagrams of the polymers are given in Figure 2. This analysis shows that all these three polymer varieties are amorphous in nature.
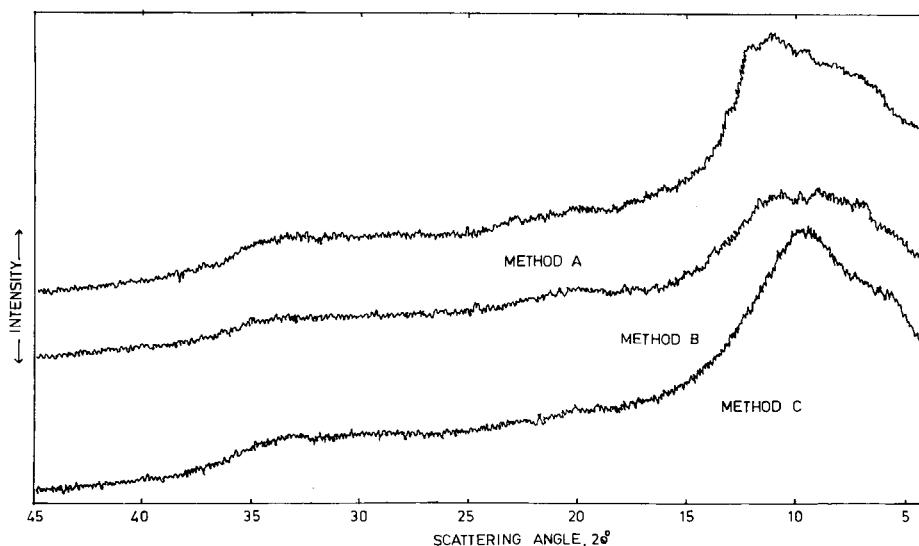

Fig. 2. X-ray diffraction diagrams of the polyesterimide synthesized through different methods.

Thermal Behavior

Thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG), and differential thermal analysis (DTA) curves of all the three varieties of the polyesterimide are given in Figure 3. DTA curves of the polymer samples indicate that the polyesterimide so prepared by different routes has nearly identical glass transition temperatures (T_g), though the polymer prepared by method A exhibits a bit higher T_g. The situation is also similar in case of crystalline melting temperature (T_m) of the three varieties of the polymer where all have nearly the same T_m values, although polymer prepared by method C exhibits slightly higher T_m. Initial weight loss up to 200°C as evident from the TGA curves of the polymeric samples is due to the loss of entrapped moisture, solvent, monomeric components, or further polymerization of residual monomers, if any. In all the polymer varieties, thermo-oxidative degradation completes in three consecutive stages and starts immediately after melting. Thermal properties of the three polymeric samples are given in Table III. It is observed that the first stage of degradation starts within 380–410, second stage within 430–445, and final stage within 520–550°C.

Isothermal aging data for the three varieties of the polyesterimide are given in Table IV. They exhibit nearly the same weight loss at both the temperatures, viz., 250 and 330°C. Thermal analysis data reveal that the thermal stability range for the polyesterimide is 290–325°C.

It appears from the chemical and thermal behavior of the polyesterimide prepared by the above three methods that there is very little difference in the polymers. This indicates that there is perhaps no significant difference in the structure of the macromolecule. However, slightly lower thermal stability of the polymer prepared by method B may be explained by the relatively low molecular weight of the polymer as evident from viscosity values. Method A is a one-step process whereas other two methods are two-step processes. As such preparation of the polymer by method A appears to be economical in comparison with the other two-step methods. It may be noted, however, that there is about 9% higher yield obtained by method C over method A.

Electrical Properties

Variation of electrical properties of the polyesterimide like dielectric constant (ϵ') and dielectric loss (tan δ) with frequency (f) has been presented in Figure 4. The dielectric constant of the polymer gradually decreases with increase in frequency. This is due to the fact that, with increasing frequency of the applied alternating electric field, the polar groups in the polymer find little time for orientation in the direction of the applied field, and at very high frequency they become hardly able to orient and thus the polymer exhibits a low dielectric constant.

The curve representing the variation of tan δ vs. log f shows two maxima at 1×10^2 and 1×10^5 Hz. A high dielectric loss of the polymer can be accounted for the orientation polarization of the polar groups in the macromolecular chain in the direction[8] of the applied electric field. The relaxation time (τ) calculated at these maxima is 1.57×10^{-3} s at 10^2 Hz and
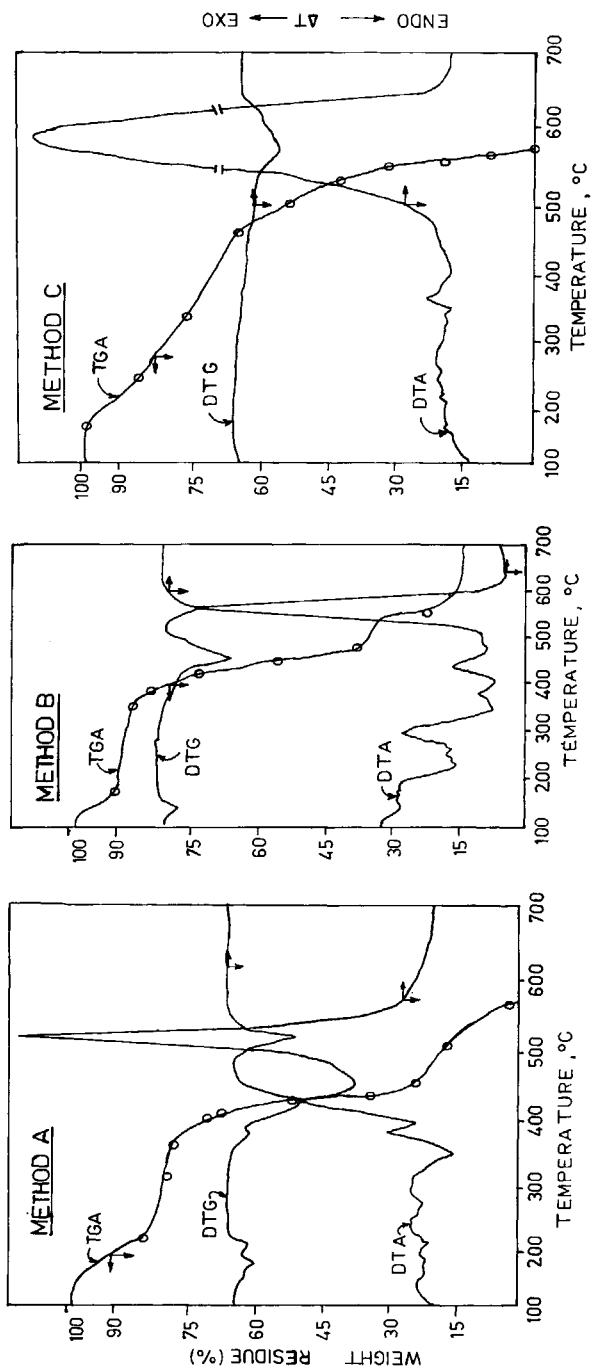
Fig. 3. Thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG), and differential thermal analysis (DTA) curves of the polyesterimide synthesized through different routes.

TABLE III
Thermal Properties of the Polyesterimide

Properties	Method A	Method B	Method C
T_g (°C)	270	265	260
T_m (°C)	350	350	360
Thermal stability range (°C)	<320	<290	<325
Degradation stages (peak temperature) (°C)			
Stage I	400	380	410
Stage II	430	440	445
Stage III	520	550	550

TABLE IV
Isothermal Aging Properties of the Polymers in Air

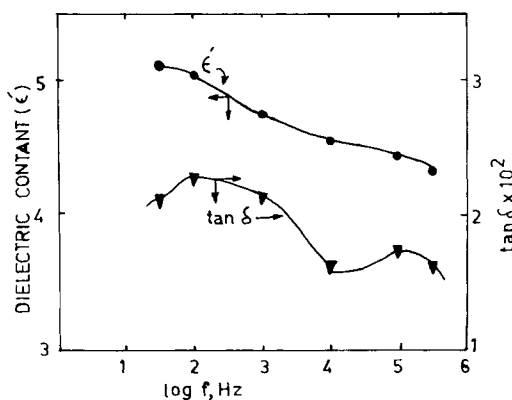| Polymer	Aging temperature (°C)	% Weight loss on aging (h)							
		2	4	6	8	12	24	30	48
Method A	250 ± 2	12.0	12.1	13.1	—	13.3	15.0	15.0	24.0
	330 ± 3	24.0	27.8	28.4	36.0	42.0	42.5	—	—
Method B	250 ± 2	00.0	2.2	3.0	—	4.0	4.9	4.9	14.3
	330 ± 3	21.2	27.4	30.6	31.0	42.3	46.0	—	—
Method C	250 ± 2	10.0	12.8	14.0	—	14.0	15.0	15.0	26.0
	330 ± 3	25.0	30.6	33.0	36.0	47.0	52.8	—	—

Fig. 4. Variation of dielectric constant (ϵ') and dielectric loss (tan δ) with frequency (f) for the polyesterimide prepared through method A.

1.57×10^{-6} s at 10^5 Hz. τ was calculated from equation $2\pi f_{max}\tau = 1$. This time is the average or most probable relaxation time determined by a set of structural unit of different mobility.[9,10]

References

1. D. F. Loncrini, *J. Polym. Sci. Part A-1*, **4**, 1531 (1966).
2. S. Maiti and S. Das, *Annual Report*, Allied Resins and Chemicals Ltd., Calcutta, 1978.
3. S. Maiti and S. Das, *Angew. Makromol. Chem.*, **86**, 181 (1980).
4. S. Maiti and S. Das, *J. Appl. Polym. Sci.*, **26**, 957 (1981).
5. S. Maiti and A. Ray, *Makromol. Chem.*, **183**, 2949 (1982).
6. G. F. Redfern & Co., Brit. Pat. 1,070,364 (1964).
7. S. Das and S. Maiti, *J. Macromol. Sci. Chem.*, **A17**, 1177 (1982).
8. A. X. Schmidt and C. A. Marlies, *Principles of High Polymer Theory and Practice*, McGraw-Hill, New York, 1948, p. 442.
9. A. Tager, *Physical Chemistry of Polymers*, Mir, Moscow, 1978, p. 314.
10. M. Kryszewski, *IUPAC, Macromol. Prepr., Boston*, **1**, 208 (1971).