Processable Heat-Resistant Polymers. XIII.
Structure–Property Relationship in Polyamideimides

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Synopsis

Novel isomeric polyamideimides were synthesized by reacting the diacid chloride of 2-(4-carboxy phenyl)-1,3-dioxoisoindoline-5-carboxylic acid and o-, m-, and p-phenylenediamine at 30–70°C using polar solvents. The reactivity of the isomeric amines in the polycondensation reaction was studied. The isomeric effects on the physical, chemical, thermal, and electrical properties of the polymers were also studied. The polymers were found to be soluble in highly polar solvents such as DMF, DMAC, NMP, DMSO, m-cresol, etc. Thermal analysis indicated that polymers were thermostable and that their thermal stability follows the order para > meta > ortho. X-ray diffraction data revealed that para polymer is crystalline in nature. Dielectric properties with the variation of frequency at room temperature indicated that the dielectric constant and dielectric loss of the polymers follow the order ortho > meta > para.

INTRODUCTION

To develop successfully any material, particularly polymers, and to meet the demands of the end uses, an understanding of how the structure of the material influences its properties and behavior is essential. The study of structure–property relationship therefore is becoming increasingly important in the development of new polymers required for modern technology.

In our program of development of processable heat-resistant polymers, we have already reported the structure–property relationship in polyesterimides.[1] We now wish to report such studies for polyamideimides.

EXPERIMENTAL

Reagents

Trimellitic acid anhydride (TMA) was obtained from Chemalog, U.S.A., and used after crystallization from acetic anhydride.[2]

Meta- and p-phenylenediamine (BDH, England) and o-phenylenediamine (VEB Lab., West Germany) were purified by the usual procedure.[3] p-Amino-benzoic acid (E. Merck, India) was used after crystallization from ethanol. Thionyl chloride was freshly distilled before use.

N,N-Dimethylformamide (DMF) (E. Merck, India) was dried over phosphorus pentoxide and distilled under reduced pressure (~20 torr). All other solvents used were of pure grade.

Monomers

Preparation of 2-(4-carboxyphenyl)-1,3-dioxoisoindoline-5-carboxylic acid (CPDCA).[4] CPDCA was prepared by condensing TMA and p-amino-benzoic acid in DMF by the procedure of Maiti et al.[1]

Preparation of the diacid chloride of CPDCA.[4] The diacid chloride of CPDCA was prepared by reacting CPDCA and thionyl chloride for 14 h. The details of the experimental procedure have been reported elsewhere.[5]

Polymer Synthesis

Isomeric polyamideimides were prepared by reacting the diacid chloride of CPDCA and o-, m-, and p-phenylenediamine. A typical example is as follows: 3.48 g (10 mmol) diacid chloride of CPDCA was dissolved in 30 mL N-methyl-2-pyrrolidone (NMP) in a three-necked flask fitted with a stirrer, a thermometer, and a nitrogen purge tube. The solution was cooled to 0°C when 1.08 g (10 mmol) p-phenylenediamine and 1.58 g (20 mmol) pyridine were added to the solution with stirring. The reaction mixture was stirred at room temperature for 2 h, at 40–50°C for 6 h, and finally at 60–70°C for 2.5 h. At the end of the reaction, the mixture was poured into ice/water and filter immediately. It was washed several times with chloroform and dried under vacuum at 50°C for 10 h.

Characterization of Polyamideimides

Purification of polyamideimides. Polymer samples were purified by repeated precipitation from a solution in DMF using methanol as a nonsolvent. The precipitated polymer was isolated by filtration, washed several times with methanol, and dried under vacuum at 70–80°C for 10 h.

Viscosity measurements. These were carried out in 0.5% (g/mL) solution in DMF at 30°C using a Ubbelhode suspended-level viscometer. For determining the course of the polycondensation reaction by viscosity measurements, the polymer samples from the reaction flask were removed at different time intervals. The polymer samples were immediately precipitated in methanol, isolated, washed, and dried. The solution viscosity for all the samples was measured in DMF at 30°C.

Density measurements. The density of the polymer samples was determined by means of a small pycnometer in dry benzene at 30°C.

IR spectroscopy. Infrared spectra of all the polymer samples were recorded on a Perkin–Elmer 237B spectrophotometer on a KBr pellet.

X-ray. X-ray diffraction diagram was recorded with a Dorn I (USSR) X-ray diffractometer using Ni-filtered CuK_α radiation.

Solubility Characteristics

Polyamideimide samples (0.02 g) were placed in 2 mL of various solvents and allowed to stand for two weeks.[6] The polymers were then observed in order to judge solvent effects such as swelling or dissolution. A plot of solubility parameter (δ) against hydrogen bonding index (γ) was prepared. The midpoint

of the solubility parameter range was chosen as the solubility parameter of the polymer.

Thermal Analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of polymers were made simultaneously with a Mom Derivatograph of a Paulik Paulik–Erdey system. The measurements were recorded in air at a heating rate of 10°C/min.

Isothermal Aging

Polymer samples 500 mg each were heated in a specially designed air circulating aging oven (Thermogravimetric Analyzer, Planning and Development Division, Fertilizer Corporation of India) at 200°C. The weight loss in air was recorded at different time intervals.

Electrical Behavior

The electrical properties of the polymers were measured at room temperature (~30°C) with a pellet 1.253 cm in diameter and thickness 0.197, 0.201, and 0.186 cm for o-, m-, and p-polyamideimides, respectively. The measurements were recorded by a General Radio Capacitance Bridge (type 716C) and a Q-Meter (Marcony Circuit Magnification Meter, type 329G) at $4 \times (10^2–10^7)$ Hz.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

The polycondensation reaction between the diacid chloride of CPDCA and o-, m- and p-phenylenediamine is, in fact, a polyamidization reaction involving a diacid chloride and a diamine. The synthesis of polyamideimides from imidodicarboxylic acid chloride with diamines was reported by Abajo et al.,[7] Lindberg et al.,[8] Fontal,[9] and Strul et al.[10] The reaction scheme for the synthesis of isomeric polyamideimides is shown in Figure 1.

The polycondensation reaction proceeds in anhydrous polar solvents in the presence of pyridine as an acid acceptor. However, triethylamine may be used instead of pyridine. Depending on the end use of the polyamideimides, the
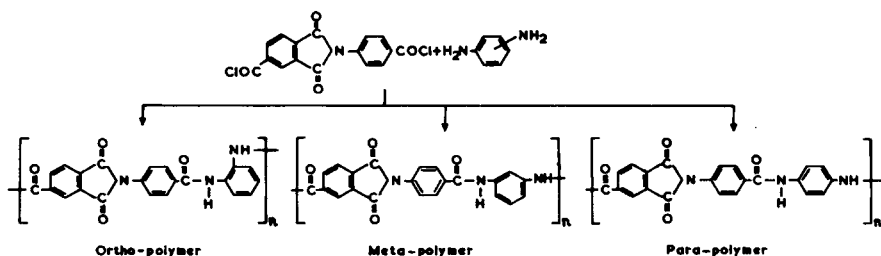

Fig. 1. Scheme for synthesis of the isomeric polyamideimides.

polycondensation reaction may be controlled by changing reaction conditions and solvents, and preferably by the use of a suitable catalyst.

The general characteristics of the resulting polyamideimides are presented in Table I. It appears that the yield (based on purified polymer in each case) of the meta polymer is highest, followed by the para and ortho polymers. The highest yield of the meta polymer is probably due to the highest reactivity of the m-phenylenediamine among the three isomeric diamines. Eventually, the lowest yield of the ortho polymer may be explained on the basis of lower reactivity and steric hindrance arising from the inherent structure of o-phenylenediamine, which makes the amine group less available to react further with the acid chlorides. Table I shows that the inherent viscosity of the para polymer is greater than that of meta polymer, and the latter is greater than ortho polymer. This is probably due to the fact that the molecular weight of the para polymer is the highest of all the isomers. Bower and Frost[11] and Maiti et al.[1,12] have also observed the highest inherent viscosity in solution of para-substituted polymers.

Effect of Time on the Polycondensation Reaction

In our earlier communications,[5,13–15] we reported that the polymer prepared by low-temperature polycondensation possesses low inherent viscosity, but that at 30–70°C relatively higher-molecular-weight polymers are obtained. At lower temperatures, the increase in molecular weight with time is not appreciable, indicating probably that the rate of polymerization at this condition is not significant. The change in inherent viscosity with time during the course of polymerization reaction at 30–70°C of the three isomeric polyamideimides is shown in Figure 2. It is evident that the inherent viscosity of the polymers gradually increases with the time of the polycondensation reaction. The inherent viscosity of the meta polymer attains its maximum value earlier than those of para and ortho polymers. This is probably due to the highest reactivity of m-phenylenediamine among its isomers. The highest yield of the meta polymer also agrees with this fact. A similar observation has also been made with other polymers.[1,12]

TABLE I
Physical Properties of the Polyamideimides

Polymer	Solvent	Yield, %	Inherent viscosity,[a] dL/g	Density, g/cm^3	T_g,[b] °C	Nitrogen, % Calc.	Found
Ortho polymer	DMF	60–66	0.16	1.15	—	10.96	10.76
	NMP	68–72	0.19 (0.24)[c]	1.16	215	10.96	10.82
Meta polymer	DMF	80–82	0.24	1.21	—	10.96	10.67
	NMP	83–86	0.29 (0.31)[c]	1.22	240	10.96	10.73
Para polymer	DMF	71–73	0.27	1.27	—	10.96	10.88
	NMP	77–79	0.32 (0.34)[c]	1.27	275	10.96	10.69

[a] Measured in DMF (0.5 wt % solution) at 30°C.
[b] Calculated from the DTA curves (Fig. 8).
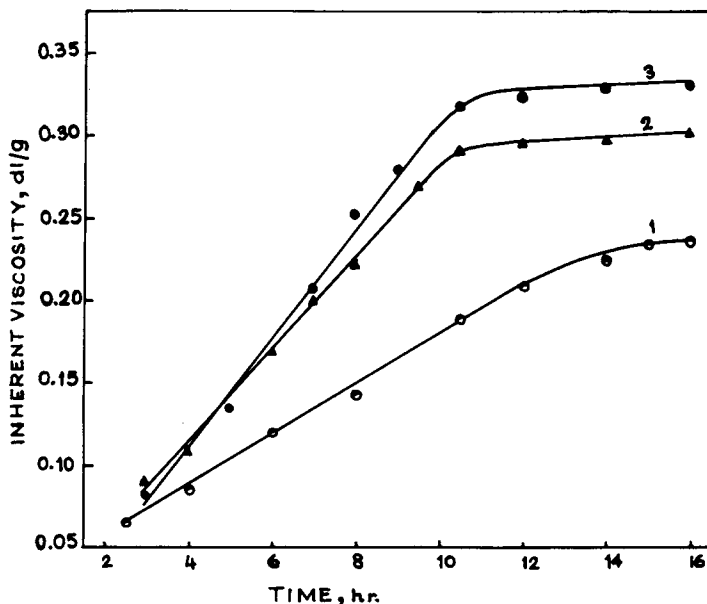[c] Obtained after 24 h of reaction.

Fig. 2. Variation of inherent viscosity with time of polycondensation reaction: 1, ortho polymer; 2, meta polymer; 3, para polymer.

Polymer Characterization

The isomeric polyamideimides were characterized by nitrogen analyses and IR spectra. The IR spectra of the polymers are shown in Figure 3. The IR spectra show the characteristic imide bands near 1785 and 1720 cm^{-1} due to symmetrical and asymmetric carbonyl stretching vibration at 725 cm^{-1}, possibly due to the ring carbonyl deformation. The presence of the amide groups is indicated by the band near 1690 cm^{-1} due to carbonyl stretching. A broad band near 3300–3400 cm^{-1} is possibly due to the $>$N—H stretching band of amides.

Thus, from nitrogen analyses and IR spectra, the structure of the repeat unit may be represented as follows:
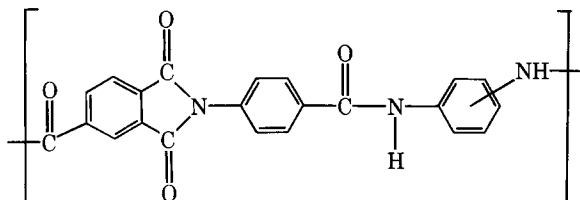
Solubility Characteristics

The solubility of isomeric polyamideimides is summarized in Table II. Polyamideimides are found to be soluble in highly polar solvents. The solubility characteristics of the polymers follow the order ortho polymer > meta polymer > para polymer. The para polymer is found to be insoluble in most of the solvents (Table II) except in DMF, dimethyl sulfoxide (DMSO), N,N-dimethyl-
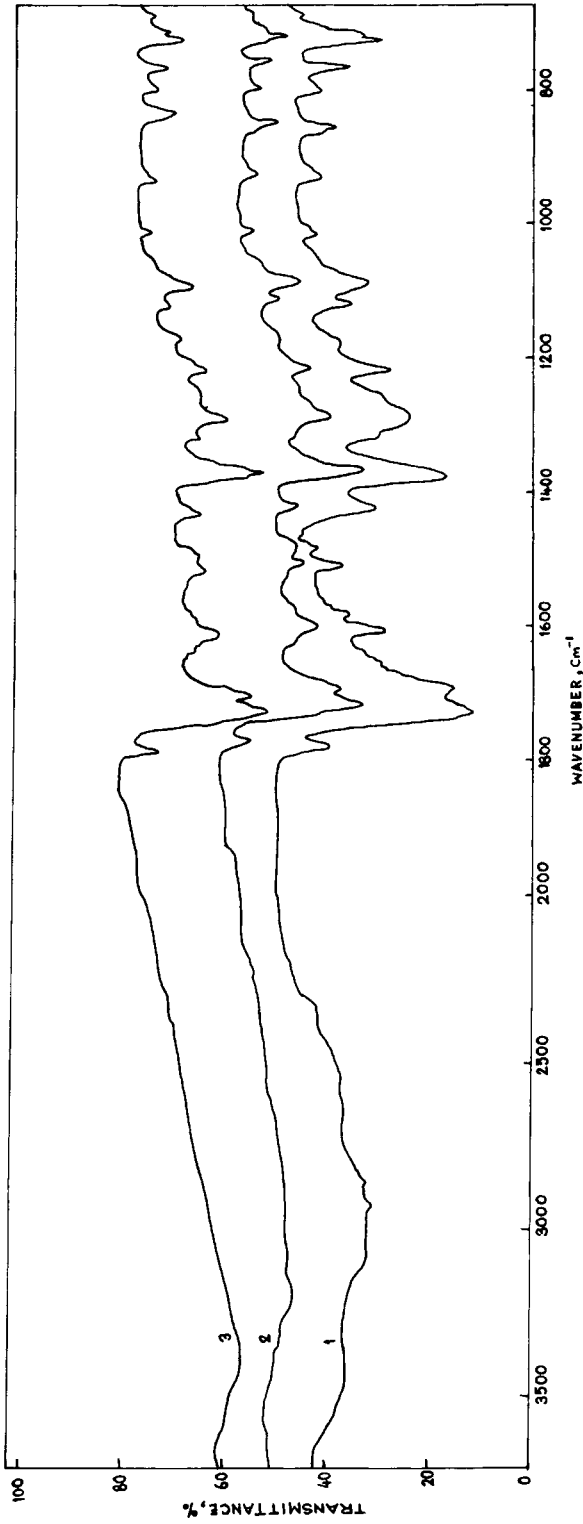
Fig. 3. IR spectra of the polyamideimides: 1, ortho polymer; 2, meta polymer; 3, para polymer.

TABLE II
Solubility Behavior of the Polyamideimides

Solvent	Solubility parameter δ	Hydrogen bonding index γ	Solubility[a]		
			Ortho polymer	Meta polymer	Para polymer
Benzene	9.16	2.2	−	−	−
Nitrobenzene	10.00	2.2	−	−	−
Chloroform	9.16	2.2	−	−	−
Carbon tetrachloride	8.55	2.2	−	−	−
N,N-Dimethylformamide	11.79	6.4	+	+	+
N,N-Dimethylacetamide	10.80	−	+	+	+
N-Methyl-2-pyrrolidone	11.00	5.6	+	+	+
Dimethyl sulfoxide	13.00	5.0	+	+	+
Formic acid	12.10	−	+	±	−
Tetrahydrofuran	9.10	5.3	±	−	−
Dioxane	10.13	5.7	−	−	−
n-Pentane	7.02	2.2	−	−	−
n-Hexane	7.27	2.2	−	−	−
Cyclohexane	8.19	2.2	−	−	−
Cyclohexanone	10.42	6.4	±	±	±
Cyclopentanone	10.53	5.2	±	±	±
m-Cresol	10.20	−	+	+	+
Ethyl methyl ketone	9.45	5.0	±	−	−
Methyl acetate	9.46	5.2	−	−	−
Diacetone alcohol	9.77	6.9	−	−	−
Acetone	9.62	5.7	−	−	−
Ethyl acetate	8.91	5.2	−	−	−
Toluene	8.93	3.8	−	−	−
Methylene dichloride	9.88	2.7	−	−	−
Ethylene dichloride	9.86	2.7	−	−	−
Chlorobenzene	9.67	2.7	−	−	−
Decane	7.74	2.2	−	−	−
Methyl isobutyl ketone	8.40	5.0	−	−	−
Conc. H_2SO_4	−	−	+	+	+

[a] +, Soluble; ±, partially soluble or swelling; −, insoluble.

acetamide (DMAC), N-methyl-2-pyrrolidone (NMP), m-cresol, and concentrated sulfuric acid. The poor solubility of the para polymer appears to be due to the higher chain symmetry and higher molecular weight compared with the other two isomers. Similar solubilities have been reported for polyamideimides by Kurita et al.[16] as well as Maiti and his co-workers.[13-15] The higher solubility of these polymers compared with the polyimides of similar structure may be explained by the fact[17-19] that the presence of large polar groups in a macromolecular chain increases the polymer solubility. This is due to the decrease of chain symmetry and consequently the degree of crystallinity which in turn increases the solubility of the polymers. These polyamideimide polymers closely resemble polyesterimides in their solubility characteristics.[1,20,21]

Solubility Parameter

A plot of solubility parameter (δ) vs. hydrogen bonding index (γ) for various solvents is shown in Figure 4. The solubility parameter may be calculated from
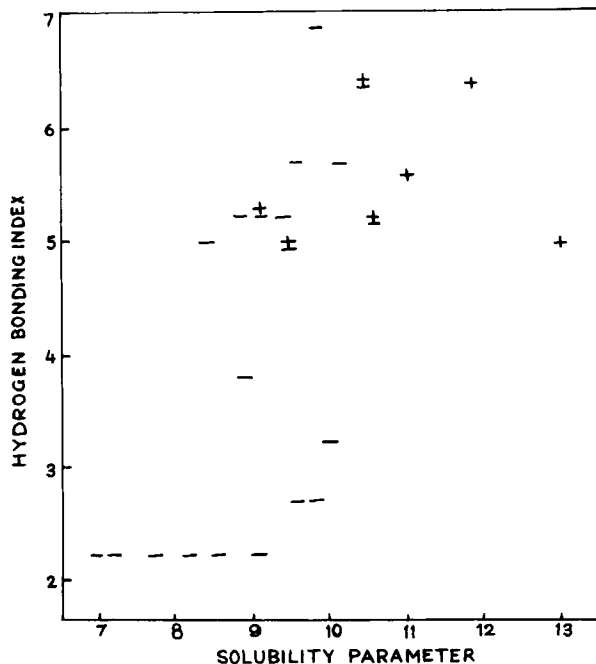
Fig. 4. Solubility map of the ortho polyamideimide.

Small's group contributions.[22] The molar attraction constant G values used here have been reported by Hoy.[23,24] The G values for various groups are shown in Table III. These are used to calculate the solubility parameter, δ, of the ortho-polymer using the relationship

$$\delta = \rho(\sum G/M)$$

TABLE III
Calculated Solubility Parameter of the Isomeric Polyamideimides

Functional groups	G value, $(cal \cdot cm^3)^{1/2}$	No. of functional groups/substitution in polymer repeat unit	Total G values for polymers		
			Ortho polymer	Meta polymer	Para polymer
—CH= (Aromatic)	117.12	11	1288.32	1288.32	1288.32
=C= (Aromatic)	98.12	7	686.84	686.84	686.84
>C=O	262.96	4	1051.84	1051.84	1051.84
—N—	61.08	1	61.08	61.08	61.08
—NH—	180.03	2	360.06	360.06	360.06
Six-membered ring	−23.44	3	−70.32	−70.32	−70.32
Five-membered ring	20.99	1	20.99	20.99	20.99
Ortho substitution	9.69	1	9.69		
Meta substitution	6.60	1	6.60		6.60
		2		13.20	
Para substitution	40.33	2	80.66	80.66	
		3			120.99
			$\sum G = 3495.76$	3492.67	3526.40
Solubility parameter δ			10.59	11.12	11.69

where ΣG is the sum of Small's group contribution, M is the formula weight of the polymer repeat unit, and ρ is the density of the polymer. The δ value of the ortho polymer at the midpoint of the solubility map (Fig. 4) is found to be 11.02 and is in fairly good agreement with the calculated δ value of 10.59 (Table III).

Solution Viscosity Behavior

The inherent viscosity of the isomeric polyamideimides follows the order para polymer > meta polymer > ortho polymer. The aging of the polymer solutions in DMF for 30 days of storage is shown in Figure 5. It is found that the inherent viscosity of the polymers initially decreases by about 3–5% within five days and then practically remains constant even after 30 days. On the other hand, the polyamic acid, a precursor of polyimide, does not form such stable solution.[25,26] It is interesting to note that the extent of decrease in inherent viscosity is 4.0, 4.4, and 6.2% in the para, meta, and ortho polymer, respectively, during the period of 30 days. The best storage characteristics of the para polymer compared with that of the other two isomeric polyamideimides is probably due to the higher molecular weight. The same behavior was also observed in other copolyimides.[27,28]

Density and Crystallinity

The relationship between polymer structure, crystallinity, and properties is best understood by examining the factors affecting crystallinity. The extent
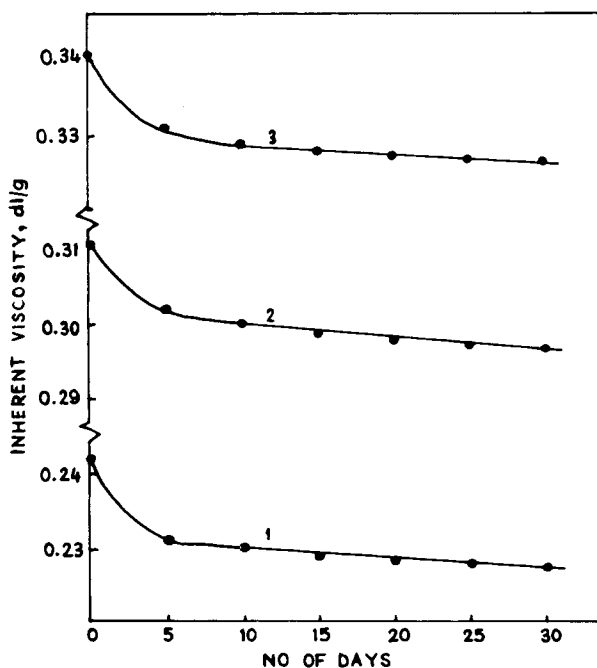

Fig. 5. Effect of aging of the isomeric polyamideimides (0.5%) in DMF at 30°C on inherent viscosity: 1, ortho polymer; 2, meta polymer; 3, para polymer.

to which a polymer will crystallize is determined first by the thermodynamic forces favoring maximum potential crystallinity at equilibrium and second by the kinetic forces determining the rate and extent to which the polymer may actually approach such a theoretical maximum degree of crystallinity.   When the polymer molecules crystallize, this high degree of organization becomes a major factor in the overall structure.   In particular, the forces holding the polymer molecule in the crystalline lattice greatly restrict its mobility and thus affect most of its properties which basically depend on the percent crystallinity and the size of the crystal lattice present in the polymer.

The X-ray diffraction diagrams of the polymers are shown in Figure 6.   The diagrams indicate that the para polymer possesses a relatively higher degree of crystallinity compared with the meta and ortho polymer.   The X-ray study therefore corroborates the highest density and poor solubility of the para polymer.   The greater chain symmetry leads to closer chain packing, which in turn results in a higher degree of crystallinity.   Similar behavior was also observed in copolyamides[12] and polyesterimides.[1]

Thermal Behavior

Thermogravimetric analysis (TGA) data for the three isomeric polyamideimides in air are shown in Figure 7.   The TGA data indicated that the order of thermal stability is para polymer > meta polymer > ortho polymer.   All three polymers undergo a weight loss of about 6–8% at 100–105°C, which is probably due to loss of moisture or entrapped solvent.   Subsequently, there is only weight loss of about 5% for para polymer, 8% for meta polymer, and 15% for ortho
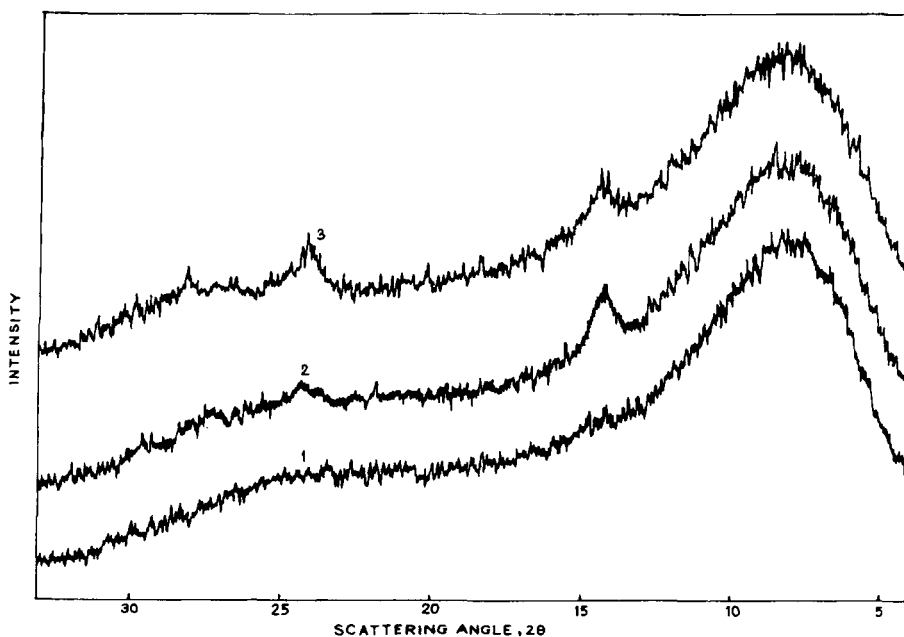

Fig. 6. X-Ray diffraction diagram showing intensity vs. scattering angle (2θ) for: 1, ortho polymer; 2, meta polymer; 3, para polymer.
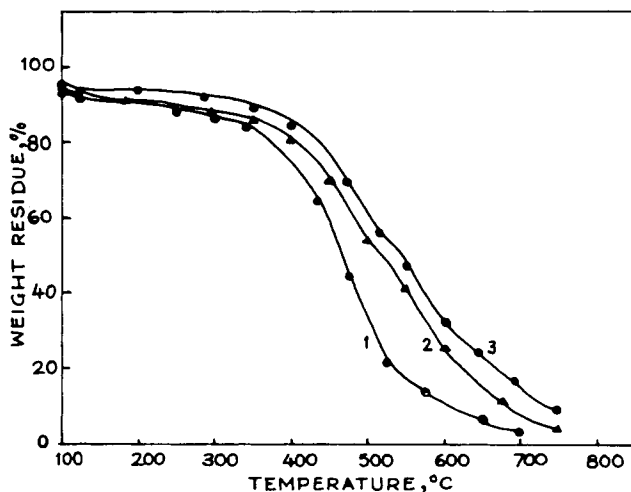
Fig. 7. Thermogravimetric analysis (TGA) of: 1, ortho polymer; 2, meta polymer; 3, para polymer.

polymer at 400°C. The higher symmetry and crystallinity of the para polymer is probably the reason for higher thermal stability.

Bower and Frost[11] reported that the orientation of the groups in the benzene ring did not generally have a great effect on the thermal stability but was a factor of flexibility and viscosity. Our observation in the present study indicates that although the thermal stability of the para and meta polymers are comparable, the ortho polymer possesses relatively inferior thermal stability. In our opinion, the question of thermal stability and/or oxidative stability, flexibility, and strength properties in polymers is very complex and should be considered from two general viewpoints: (1) interchain and (2) intrachain factors.[1] The slight asymmetric nature of the meta substitution prevents the close packing of the molecules that is possible in para substitution and thus strikes a balance between the highly ordered structure of para substitution and the completely amorphous structure of the ortho substitution. The temperature where maximum weight loss occurs is in the range 350–500°C for ortho polymer, 400–625°C for meta polymer, and 450–650°C for para polymer. Similar thermal behavior was observed in polyamides,[12,26] polyesterimides,[1] and other polyamide-imides.[5,13–15,29]

Isomer Effect on Glass Transition Temperature

The glass transition temperatures T_g of the ortho, meta, and para polymers are 215, 240, and 275°C, respectively, from the DTA curves shown in Figure 8(a). The results are consistent with the fact that meta and ortho substitution in polymer chains are more effective than para substitution in decreasing the glass transition temperature.[11,30] It may be noted that higher T_g values may also be due to the higher molecular weight of the para polymer as T_g increases with molecular weight.[31] From DTA data, it appears that the T_g of the ortho polymer is about 215°C. Although previous workers have utilized the DTA for the measurement of T_g,[32] we feel the additional support from DSC and/or TMA
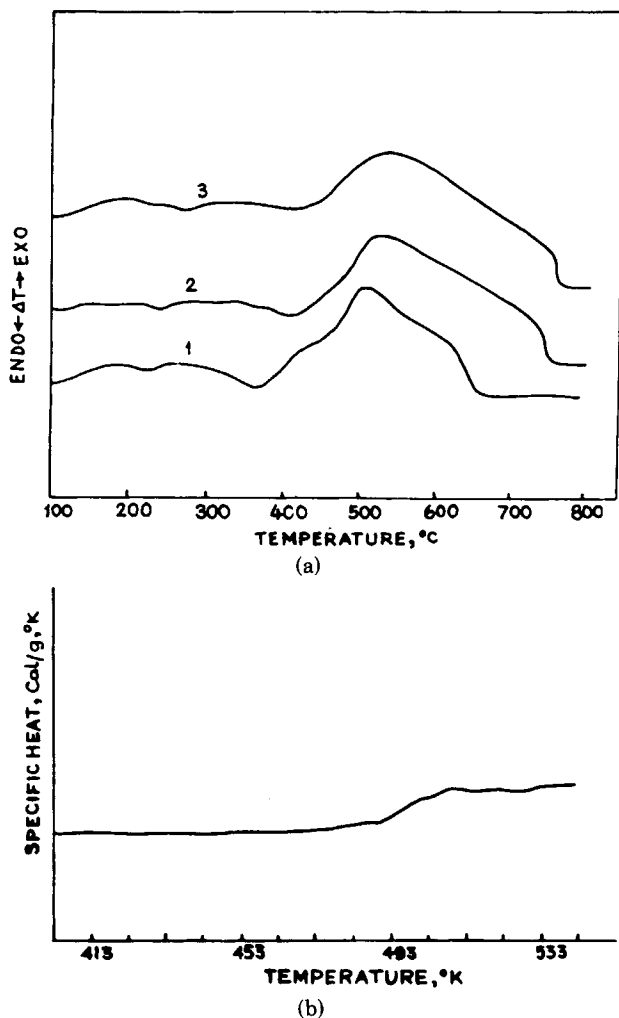
Fig. 8. (a) Differential thermal analysis (DTA) of: 1, ortho polymer; 2, meta polymer; 3, para polymer. (b) Differential scanning calorimetry (DSC) of the ortho polymer measured with Perkin–Elmer DSC-2 in N_2 at a heating rate of 10 K/min.

measurements may be required to come to a definite conclusion. The DSC measurement for the preheated ortho polymer was made in nitrogen atmosphere, and it was found that the T_g occurs at nearly 217°C [Fig. 8(b)]. The sharp endothermic peaks at 370, 405, and 425°C represent the melting temperature (T_m) for ortho, meta, and para polymer, respectively. The highest T_m value for the para polymer is consistent with the highest degree of crystallinity among these three isomers.[26] Similar observation was reported in other cases.[1,12]

Isothermal Aging of Isomeric Polyamideimides

The weight loss of the polymers heated at 200°C for 12 h in air is shown in Table IV. It has been observed that an initial weight loss of about 8.2, 7.1, and

TABLE IV
Isothermal Aging of the Isomeric Polyamideimides

Polymer	Cumulative % Weight loss at 200°C in air after						
	1 h	2 h	4 h	6 h	8 h	10 h	12 h
Ortho polymer	8.2	0.9	1.1	0.8	1.3	1.1	0.9
	—	9.1	10.2	11.0	12.3	13.4	14.3
Meta polymer	7.1	0.8	0.8	0.9	1.1	0.6	0.6
	—	7.9	8.7	9.6	10.7	11.3	11.9
Para polymer	6.1	0.7	0.6	0.7	0.5	0.5	0.5
	—	6.8	7.4	8.1	8.6	9.1	9.6

6.1% for ortho, meta, and para polymer, respectively, occurs at 1 h. This is probably due to loss of moisture or entrapped solvent. Subsequently, there was only 6.1, 4.8, and 3.5% weight loss for ortho, meta, and para polymer, respectively, after 12 h of heating. Similar thermal behavior was observed for related polymers.[1,5,12] It is interesting to note that the solubility of the aged polymer is reduced compared with that of the virgin polymer. This may be due to chain extension or to the removal of the solvents, where the intermolecular association between the polar groups in a macromolecule is maximum, which probably decreases the polymer solubility. Koton et al.[33] reported similar behavior for other polyamideimides.

Electrical Behavior

Variation of dielectric constant (ϵ') and dielectric loss (tan δ) with frequency (f) for polyamideimides at room temperature (~30°C) is presented in Figure 9. The dielectric constant of all polymers gradually decreases with increase in frequency (Fig. 9). A similar trend has been observed in other polyamideim-
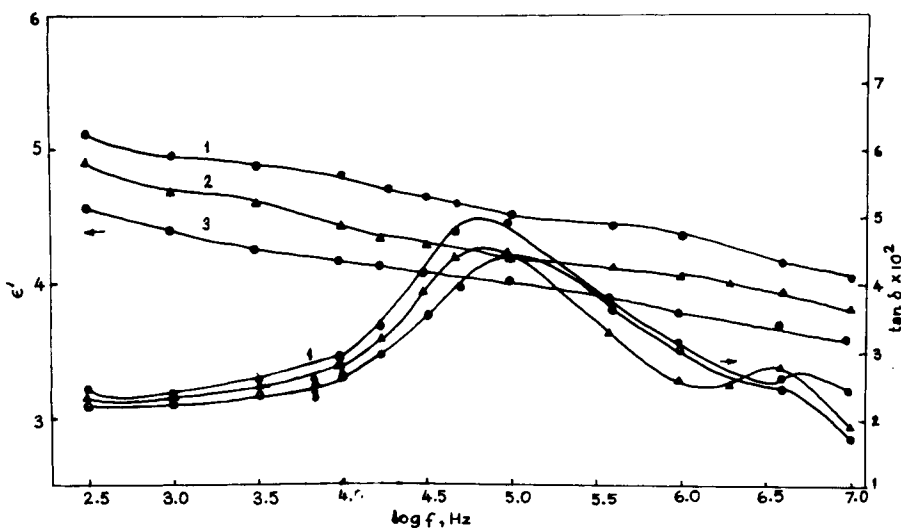

Fig. 9. Variation of dielectric constant (ϵ') and dielectric loss (tan δ) with frequency at room temperature (~30°C) of: 1, ortho polymer; 2, meta polymer; 3, para polymer.

ides.[13-15] This may be explained by the fact that when a polar polymer like polyamideimide is placed in an electric field, the polar groups will tend to orient in the direction of the applied field. If the polar groups are flexible, they will orient easily, whereas in a rigid polymer the orientation of polar groups in the direction of applied field takes place slowly and with great difficulty. In an alternating electric field, the polar groups in a polymer will orient to give a high dielectric constant only when the frequency of alternation is low enough to permit sufficient time for orientation. With increasing frequency, the polar groups will find little time to orient in the direction of applied field; and at very high frequency, they will hardly be able to orient at all and the polymer will exhibit a low dielectric constant. The higher dielectric constant of the ortho polymer compared with that of the meta and para polymers may be explained on the basis of the above fact. The plot of $\tan \delta$ vs. $\log f$ shows maxima at 7.94×10^4 and 6.31×10^6 Hz for the ortho polymer, at 9.33×10^4 and 3.98×10^6 Hz for the meta polymer, and at 1.17×10^5 Hz for the para polymer. The high dielectric loss of these polymers may be explained due to dipole group losses of the polar groups present in the polymer chain.[34] It may also be due to orientation polarization of the polar groups in the macromolecular chain in the direction of the applied field. The relaxation time (τ) calculated at these maxima was found to be 2.0×10^{-6} and 2.52×10^{-8} s for the ortho polymer, 1.70×10^{-6} and 4.0×10^{-8} s for the meta polymer, and 1.36×10^{-6} s for the para polymer. The relaxation time (τ) determined by following the equation $2\pi f_{max}\tau = 1$ is the average or most probable relaxation time that is determined by a set of structural units of different mobility.[35,36]

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