Processable Heat-Resistant Polymers. VII. Synthesis and Characterization of Polyamideimide from N-(p-Carboxyphenyl)trimellitimide and p,p'-Di(aminocyclohexyl)methane

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Synopsis

Polyamideimides were prepared either directly from N-(p-carboxyphenyl)trimellitimide and p,p'-di(aminocyclohexyl)methane (PACM-20) by low temperature ($<5°C$) polycondensation in presence of thionyl chloride or by reacting the diacid chloride of N-(p-carboxyphenyl)trimellitimide and PACM-20 at 30–70°C. The polymers were characterized by nitrogen analysis and IR spectra. The polymers are soluble in highly polar solvents such as DMF, DMAC, NMP, and m-cresol. The solubility parameter was calculated from the Small's group contribution, which agrees well with the experimental value. The solution viscosity of the polymer is fairly stable against ageing. The T_g of the polymer calculated from the DTA curve is 270°C or even higher. Thermal analyses indicated that the polymer is fairly stable and only 5–6% weight loss occurs up to 350°C or 380°C. Dielectric constant, dielectric loss, and electrical conductivity of the polymer were also studied.

INTRODUCTION

One of the major limitations of the versatile applications of synthetic polymers is their poor thermal stability compared with other materials, particularly metals, alloys, and refractories. To overcome this drawback, a large number of thermostable polymers have been developed during the last decade or so. Some of these newly developed polymers have successfully extended the working temperature limit beyond 250°C or even 300°C, but a new challenge has been faced. Thermostable polymers are in general either not processable or processable with great difficulty.[1–5]

The new challenge before the polymer scientists is, therefore, not merely the development of a thermally resistant polymer but of a processable heat-resistant polymer. The new thermostable polymer, unlike a conventional heat-resistant polymer, should be processed and fabricated by the existing techniques. These polymers should be soluble in commercial solvents and fusible with proper flow characteristics without decomposition and/or degradation. Polyamideimides with aliphatic amino acids and aliphatic or aromatic diamines have been reported by Abajo et al.,[6] Fontan,[7] and Lindberg et al.[8] Polyamideimides with p-aminobenzoic and aromatic diamines have also been reported in a recent patent.[9] However, no polyamideimides with cyclohexyl ring have yet been studied.

As a part of our program to synthesize and evaluate various copolyimides as processable heat-resistant polymers, we have recently reported the synthesis of polyamideimides[10–14] polyamide–sulfonamideimides[15] and polyesterimides.[16–19] In this present communication we wish to report the study of a new

polyamideimide prepared by low temperature polycondensation of a diacid or its diacid chloride containing preformed imido groups and an alicyclic diamine.

EXPERIMENTAL

Reagents

Trimellitic acid anhydride (Chemalog, U.S.A.) was used after recrystallization from acitic anhydride.[20]

p,p'-Di(aminocyclohexyl) methane (PACM-20) was obtained from DuPont Co. (U.S.A.) and was used without further purification. p-Aminobenzoic acid (E. Merck, India) was used after crystallization from ethanol. Thionyl chloride (SD, India) was freshly distilled before use.

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

Monomers

Preparation of N-(p-Carboxyphenyl)trimellitimide: N-(p-carboxy-phenyl)trimellitimide (IDCA) was prepared by condensing TMA and p-aminobenzoic acid in DMF by following the procedure of Maiti and Das.[17]

Preparation of Diacid Chloride Derivative of IDCA: The diacid chloride of N-(p-carboxyphenyl)trimellitimide (IDCA–DC) was prepared by reacting IDCA with excess thionyl chloride in a flask fitted with a condenser having a drying tube, a thermometer, and a stopcock at 70–80°C for 14 h. The unreacted thionyl chloride was distilled off under reduced pressure. The solid residue thus obtained was extracted with chloroform and purified by recrystallization. The details of the experimental procedure will be published shortly.[15]

Polymer Synthesis

The polyamideimide (PAI) was prepared by following two different methods.

Synthesis of PAI from IDCA by Low-Temperature Polycondensation (Method A): Polyamideimides were generally prepared by low-temperature polycondensation in thionyl chloride using polar solvents.[10–12] A typical run may be described as follows: 3.11 g (10 mmol) of IDCA were dissolved in 30 mL DMF and stirred in a 100-mL three-necked round bottom flask fitted with a thermometer and a calcium chloride drying tube. The solution was cooled to −10°C when 3.0 g (25 mmol) of thionyl chloride were added, and the solution was stirred for 1–2 min. 2.10 g (10 mmol) of PACM-20 and 1.97 g (25 mmol) of pyridine were added to the mixture. The mixture was vigorously stirred for 9 h at 0–5°C and finally 1 h at room temperature. At the end of the reaction the mixture was poured into ice/water and the precipitated polymer was isolated by filtration. It was washed with chloroform and finally purified by dissolving in DMF and precipitated by methanol.

Synthesis of Polyamideimide (PAI) from IDCA-DC (Method B): The

diacid chloride of N-(p-carboxyphenyl)trimellitimide was reacted with PACM-20 to form polyamideimide. A typical example is as follows: 3.48 g (10 mmol) of IDCA–DC were dissolved in 35 mL DMF in a three-necked flask fitted with a thermometer, a stirrer, and a nitrogen purge tube. 2.10 g (10 mmol) of PACM-20 and 1.58 g (20 mmol) of pyridine were added to the solution with stirring. The reaction mixture was stirred at room temperature for 2 h, at 40–50°C for 5 h and finally at 60–70°C for 3 h. At the end of the reaction the mixture was poured into ice/water and filtered immediately. It was dried, washed several times with chloroform, and finally purified by dissolving in DMF and precipitated by methanol.

Polymer Characterization

Viscosity Measurement: Viscosity measurements were carried out in 0.5% (g/mL) solutions in DMF at 30°C using a Ubbelhode suspended level viscometer.
Density Measurement: The density of the polymer samples were determined by means of a small pycnometer in dry benzene at 30°C.

Solubility Parameter

Polyamideimide samples (0.02 g) were placed in 2 mL of various solvents and allowed to stand for 2 weeks.[16,17,21] The polymer was then observed in order to judge solvent effect such as swelling or dissolution. A plot of the solubility parameter (δ) against the hydrogen bonding index (y) of the solvents used 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) were made simultaneously with a Hungarian Mom Derivatograph of the Paulik Paulik-Erdey system. The measurements were recorded in air at a heating rate of 5°C/min.

Electrical Properties

Dielectric properties and electrical conductivity of the polymer at room temperature ($\sim$30°C) were measured with a polymer pellet (diam. 1.253 cm and thickness 0.257 cm) using a General Radio Capacitance Bridge (Type-716C) and a Q-Meter (Mircony Circuit Magnification Meter Type-329G) at 10^3–10^7 Hz.
Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer on a KBr pellet.
X-ray diffraction diagrams were recorded with a Dron I (USSR) X-Ray Diffractometer using Ni-filtered CuK$_\alpha$ radiation.

RESULTS AND DISCUSSION

The polycondensation between IDCA or IDCA–DC and PACM-20 is, in effect, a polyamidization reaction involving a dicarboxylic acid or its diacid chloride derivative and a diamine. The polyamideimide obtained by low temperature polycondensation (method A) may be schematically represented as follows:
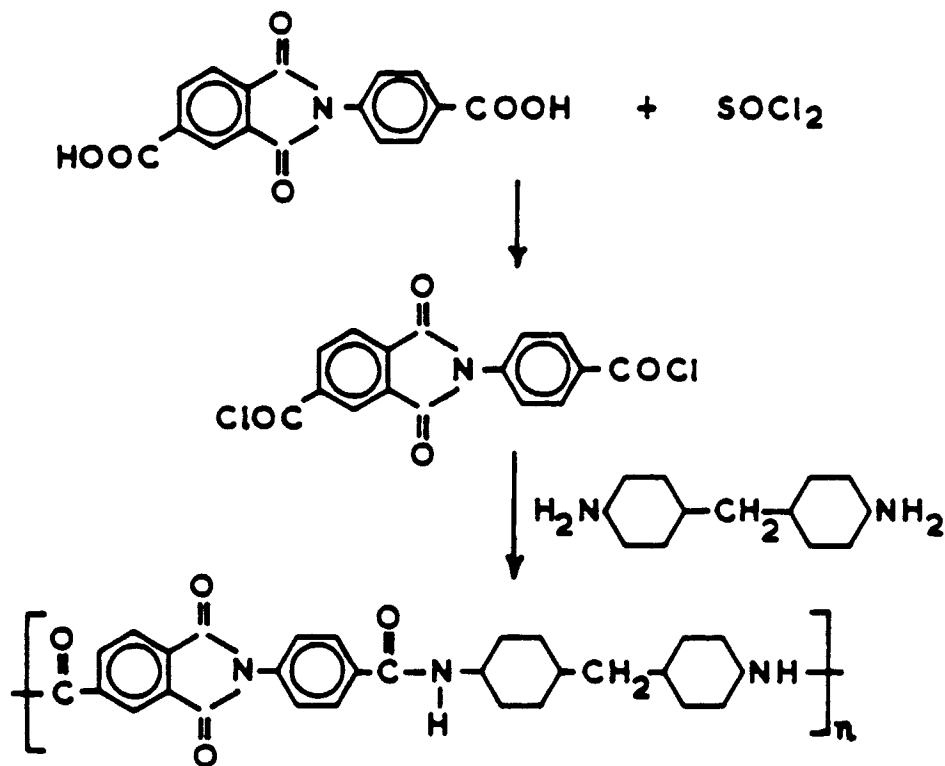
However, the intermediate acid chloride formation as shown in the above-mentioned scheme is evident from method B:
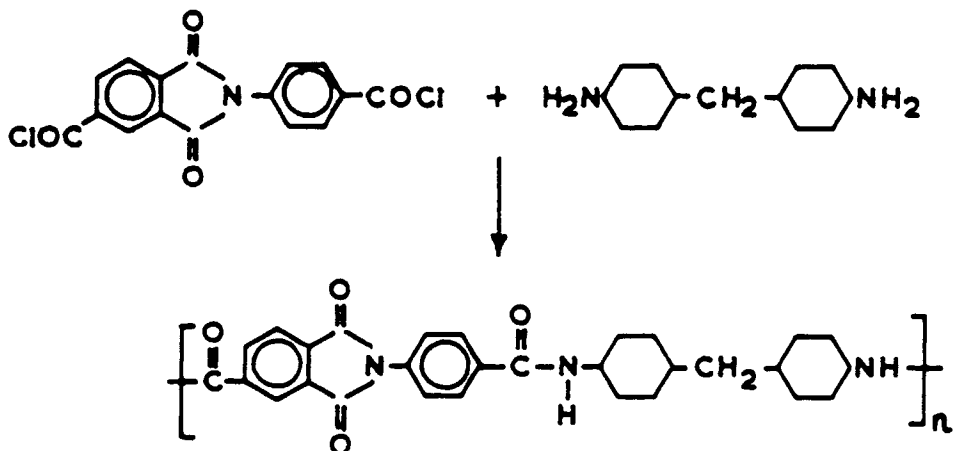
No catalyst was used in these polycondensations. Pyridine was used as an acid acceptor to facilitate the polymerization reaction. The reaction may be controlled by changing reaction time, temperature, solvents, and by the use of a suitable catalyst.

Polymer Characterization

The polyamideimide prepared was characterized by nitrogen analysis and IR spectroscopy. The general characteristics of the polyamideimide are shown in Table I. The characteristics IR bands of the polymer (Fig. 1) are observed near 1770 and 1715 cm^{-1} due to symmetrical and assymmetrical carbonyl stretching of imides and at 1640 and 1530 cm^{-1} due to amide groups. A broad band near 3300 cm^{-1} is due to >N—H stretching of secondary amine, a sharp band near 2930 and 2860 cm^{-1} is probably due to asymmetrical and symmetrical carbon hydrogen stretching of methylene group, and at 1450 cm^{-1} is probably due to carbon hydrogen bending vibration of the methylene group present in the polymer backbone.

Solution Viscosity Behavior

The inherent viscosity of the resulting polyamideimide is shown in Table I. The low inherent viscosity of the polymers corresponds to low molecular weight. However, the inherent viscosity of the polymer prepared by method A is lower than that of the polymer obtained by method B.

The conventional polyimide precursor, i.e., polyamic acid, does not form a stable solution. On standing, the inherent viscosity of the solution decreases.[1,22] However, this polymer forms a relatively stable solution in DMF. The decrease in the viscosity after 25 days at 30°C is of the order of 6.5% only (Fig. 2).

For high temperature coating applications such as cable insulation, low molecular weight amorphous polymers are desirable. X-ray diffraction data (Fig. 3) show that there are no sharp peak in the intensity vs. scattering angle (2θ), which indicates that the polymer is amorphous in nature.

TABLE I
Yields and Physical Properties of the Polyamideimide

Polymer- ization method	Solvent used	Yield (%)	Inherent viscosity[a] (dL/g)	Density (g/mL)	T_g^b (°C)	% Nitrogen	
						Calcd	Found
A	DMF	74–75	0.13 (0.17)[c]	1.19	270	8.66	8.49
	NMP	76–77	(0.18)[c]	1.20	—	8.66	8.36
B	DMF	80–82	0.23 (0.28)[d]	1.21	280	8.66	8.57
	NMP	82–85	(0.30)[d]	1.23	—	8.66	8.48

[a] Measured in 0.5% (w/v) solution in DMF at 30°C.
[b] Calculated from the DTA curve (Fig. 5).
[c] Maximum inherent viscosity observed after 16-h reaction.
[d] Maximum inherent viscosity observed after 15-h reaction.

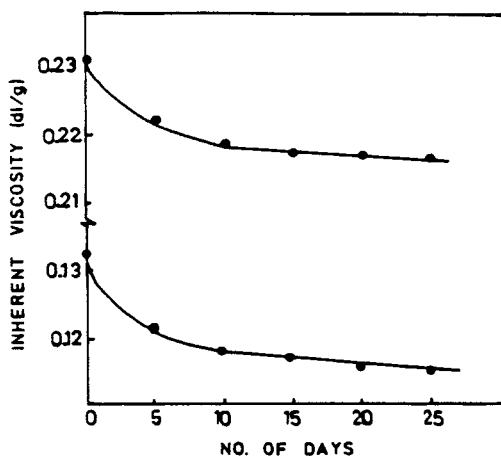Fig. 1. IR Spectrum of the polyamideimide.

Fig. 2. Aging of the polyamideimide solution in DMF at room temperature.

Solubility Characteristics

Solubility of the polyamideimide is listed in Table II. The polymer is found to be soluble in highly polar solvents. This solubility may be explained by the fact[23-25] 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.
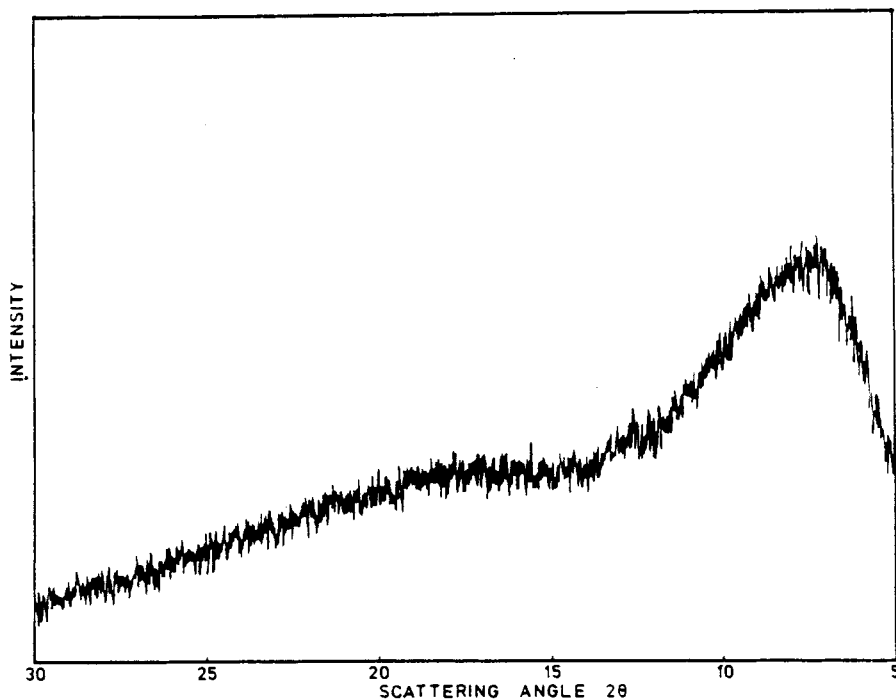

Fig. 3. X-ray diffraction diagram of the polyamideimide.

TABLE II
Solubility Characteristics of the Polyamideimide

Solvents	Solubility parameter (δ)	Hydrogen bonding index (γ)	Solubility[a]
Acetone	9.62	5.7	−
Benzene	9.16	2.2	−
Carbon tetrachloride	8.55	2.2	−
Chloroform	9.16	2.2	−
Cyclohexane	8.19	2.2	−
Chlorobenzene	9.67	2.7	−
Cyclohexanone	10.42	6.4	±
Cyclopentanone	10.53	5.2	±
Decane	7.74	2.2	−
Diacetone alcohol	9.77	6.9	−
N,N-Dimethyl formamide	11.79	6.4	+
Dimethyl sulfoxide	13.00	5.0	●
1,4-Dioxane	10.13	5.7	−
Ethyl acetate	8.91	5.2	−
Ethylene dichloride	9.86	2.7	−
Ethyl methyl ketone	9.45	5.0	−
n-Hexane	7.27	2.2	−
Methyl acetate	9.46	5.2	−
N-Methyl-2-pyrrolidone	11.00	5.6	+
Nitrobenzene	10.00	3.2	−
n-Pentane	7.02	2.2	−
Tetrahydrofuran	9.10	5.3	−
Toluene	8.93	3.8	−
m-cresol	10.20	—	+
Formic acid	12.10	—	±
N,N-Dimethyl acetamide	10.80	—	+
Concd H_2SO_4	—	—	+
Methylene dichloride	9.88	2.7	−
Methyl isobutyl ketone	8.40	5.0	−

[a] Solubility keys: (+) soluble; (±) partially soluble or swelling; (−) insoluble.

Solubility Parameter

A plot of solubility parameter (δ) vs. hydrogen bonding index (γ) for solvents shown in Table II is illustrated in Figure 4. The solubility parameter may be calculated from Small's group contributions.[26] The molar attraction constant G values used here have been reported by Hoy.[27-29] The G values for various groups are shown in Table III. These are used to calculate the solubility parameter (δ) of the polymer using the relationship

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

where ΣG is the sum of Small's group contribution, M the formula weight of the polymer repeat unit, and ρ the density of the polymer. The δ value obtained from the midpoint of the solubility map (Fig. 4) is found to be 11.40. This is in good agreement with the calculated value of δ, i.e., 11.27 (Table III).
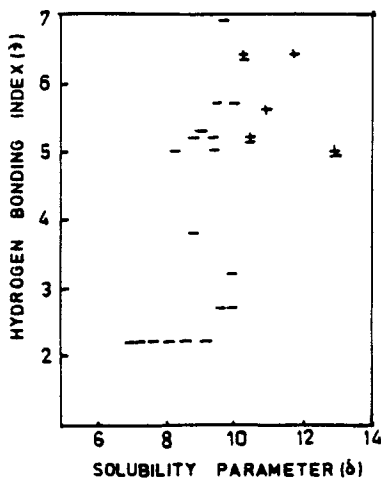
Fig. 4. Solubility map of the polyamideimide.

Thermal Behavior

Thermogravimetric analysis and differential thermal analysis data of the polyamideimide in air are presented in Figure 5. Thermogravimetric analysis indicates that an initial weight loss of about 10% occurs up to 100–110°C. This may be due to loss of moisture or entrapped solvent. Subsequently, there is only 5% weight loss up to 350°C or 380°C, depending on the method of polymerization. The degradation of the polymer is a single stage process, and maximum weight loss occurs around 400–500°C. From TGA data it is evident that the polymer obtained by method A is comparatively less thermostable than that obtained by method B. The glass transition temperature T_g of the polymer is found to be 270°C or 280°C, depending on the method of polymerization. The higher T_g and thermal stability of the polymer prepared by method B compared with the polymer obtained by method A may be due to the higher molecular weight of the former. The higher inherent viscosity value (Table I) of the former compared to the latter also corroborates the above fact.

TABLE III
Calculated Solubility Parameters of the Polyamideimide[a]

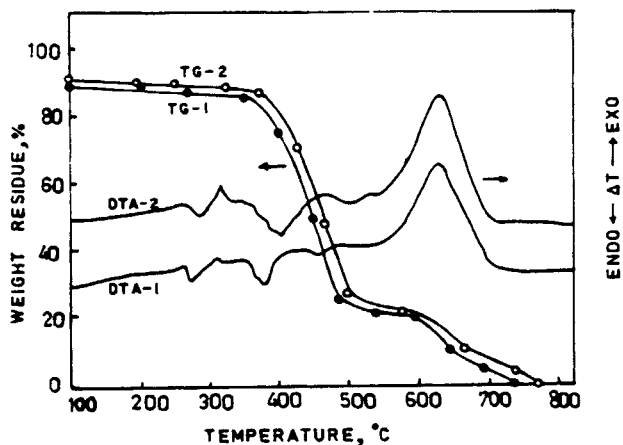| Functional group	G value $[(cal \cdot cm^3)^{1/2}]$	No. of functional groups/substitutions in the polymer unit	Total G values for polymers $[(cal \cdot cm^3)^{1/2}]$
—CH₂—	131.50	1	131.50
—CH= (aromatic)	117.12	7	819.84
=C= (aromatic)	98.12	5	490.60
>C=O	262.96	4	1051.84
—N<	61.08	1	61.08
—NH—	180.03	2	360.06
Five-membered ring	20.99	1	20.99
Six-membered ring	−23.44	2	−46.88
Cyclohexyl ring	718.68	2	1437.36
p-Substitution	40.33	4	161.32
m-Substitution	6.60	1	6.60
			ΣG = 4494.31

[a] Solubility parameter δ = 11.27

Fig. 5. Thermogravimetry (TG) and differential thermal analysis (DTA) of the polyamideimide. 1 and 2 refer to the polymers prepared by methods A and B, respectively.

Electrical Properties

The variation in dielectric constant (ϵ'), dielectric loss (tan δ), and electrical conductivity with frequency at room temperature ($\sim 30°C$) is presented in Figures 6 and 7.   The dielectric constant of the polymer decreases with the increase of frequency (Fig. 6) and the plot of tan δ with frequency shows two maxima at 4 $\times 10^3$ Hz and 10^6 Hz, respectively.   The higher dielectric loss at these two frequency ranges may be explained due to the dipole group loss of the polar substituents present in the polymer chain, and, consequently, the relaxation time
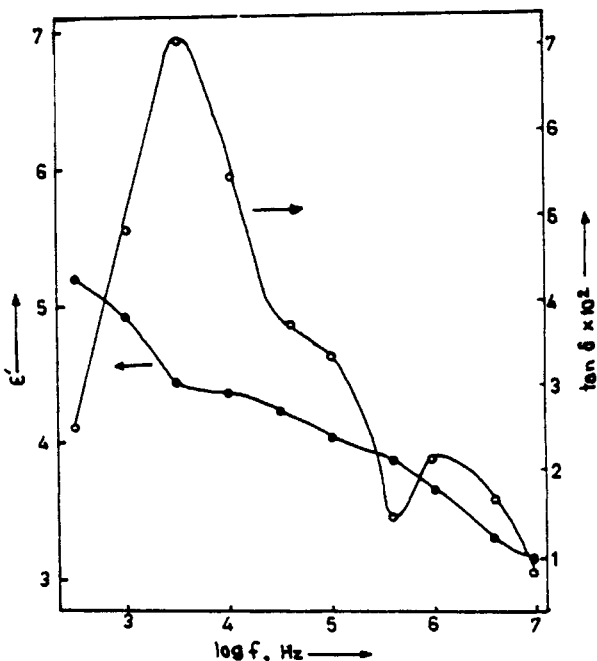

Fig. 6. Variation of dielectric constant (ϵ') and dielectric loss (tan δ) of the polyamideimide with frequency.
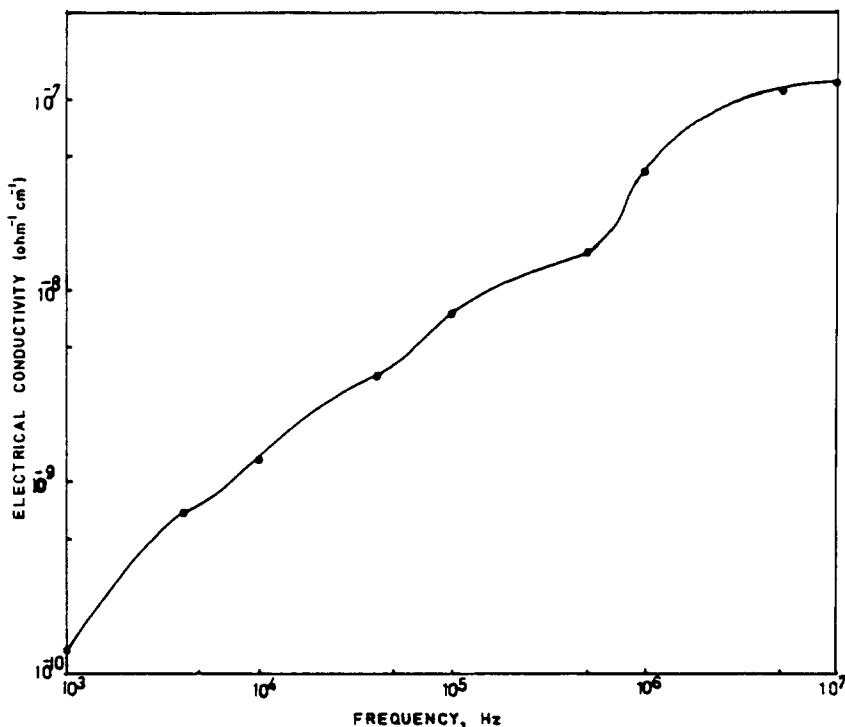
Fig. 7. Variation of electrical conductivity of the polyamideimide with frequency.

(τ) value at the maxima was found to be 3.98×10^{-5} s and 1.59×10^{-7} s, respectively. The relaxation time determined by following the equation $2 \pi f_{max} \tau = 1$ is the average, or the most probable, relaxation time, because actually every polymer has a set or spectrum of relaxation times that is determined by a set of structural units of different mobility.

The increase of electrical conductivity with frequency (Fig. 7) is probably due to the presence of low molecular weight impurities and free charges[30] present in the polymer chain. Generally, the free charges present in the polymer backbone is much less; thus the ac conductivity of this polymeric material is found to be very low at low frequency region.[30]

References

1. W. M. Alvino and L. W. Frost, *J. Polym. Sci., Part A-1*, 9, 2209 (1971).
2. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier, *J. Polym. Sci., Part A*, 3, 1373 (1965).
3. G. M. Bower and L. W. Frost, *J. Polym. Sci., Part A*, 1, 3135 (1963).
4. L. W. Frost and I. Kesse, *J. Appl. Polym. Sci.*, 8, 1039 (1964).
5. C. E. Sroog, in *Macromolecular Chemistry*, O. Wichterle and B. Sedlacek, Eds., Interscience, New York, 1967, p. 1191.
6. J. De Abajo, J. P. Gabarda, and J. Fontan, *Angew. Makromol. Chem.*, 71, 143 (1978).
7. J. Fontan, *Chem. Kunstst-Aktuell*, 32(5), 225 (1978).

8. S. E. Lindberg, K. A. Marchant, and R. E. Vanstrien, U.S. Pat. 041,065 (1977), Standard Oil Co.

9. I. Zugraveseu, M. Strul, E. Mantatuta, and G. Neamtu, Roum. Pat. 56995 (1974); *Chem. Abstr.*, **82**, 112430 (1975).

10. A. Ray, S. Das, and S. Maiti, *Makromol. Chem., Rapid Commun.*, **2**, 333 (1981).

11. S. Das and S. Maiti, *Makromol. Chem., Rapid Commun.*, **1**, 403 (1980).

12. S. Maiti and A. Ray, *Makromol. Chem., Rapid Commun.*, **2**, 649 (1981).

13. S. Maiti, S. Das, M. Maiti, and A. Ray, in *Use of Renewable Resources for Polymer Applications*, C. E. Carraher (Jr.) and L. H. Sperling, Eds., Plenum, New York, 1982, to appear.

14. S. Maiti, M. Maiti, A. Ray, and S. Das, *Org. Coatings Plastic Chem. Prepr.*, **45**, 449 (1981).

15. S. Maiti, A. Ray, and M. Maiti, *Angew. Makromol. Chem.*, 1982, to appear.

16. S. Maiti and S. Das, *Angew. Makromol. Chem.*, **86**, 181 (1980).

17. S. Maiti and S. Das, *J. Appl. Polym. Sci.*, **26**, 957 (1981).

18. S. Das, S. Maiti and M. Maiti, *J. Macromol. Sci.-Chem. A17* (8), 1177 (1982).

19. S. Maiti and S. Das, *Polym. Prepr.*, **21**(1), 190 (1980).

20. B. H. Nicolet and J. A. Bender, in *Organic Synthesis*, Coll. Vol. 1, 2nd ed., H. Gilman and A. H. Blatt, Eds., Wiley, New York, 1951, p. 410.

21. L. F. Charbonneau, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 197 (1978).

22. I. K. Varma, R. N. Goel, and D. S. Varma, *Angew. Makromol. Chem.*, **64**, 101 (1977).

23. S. V. Vinogradova, V. V. Korshak, and Y. S. Vygodskii, *Vysokomol. Soedin.*, **8**, 809 (1966).

24. V. V. Korshak, S. V. Vinogradova, Y. S. Vygodskii, S. A. Pavlova, and L. V. Bozhko, *Izv. Akad. Nauk. Ser. Khim.*, **50**, 2267 (1967).

25. V. V. Korshak, S. V. Vinogradova, G. L. Slonimskii, S. N. Salazkin, and A. A. Askadskii, *Vysokomol. Soedin.*, **8**, 548 (1966).

26. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).

27. S. Das, R. P. Singh and S. Maiti, *Polym. Bull.*, **2**, 403 (1980).

28. K. L. Hoy, *J. Paint Technol.*, **42**, 76 (1970).

29. H. Burrel, in *Polymer Handbook*, 2nd ed., J. Brandrup and E. H. Immergut, Eds., Interscience, New York, 1975, p. IV-337.

30. M. Kryszewski, XXIII IUPAC Symp., Boston, *Macromol. Prepr.*, **1**, 208 (1971).