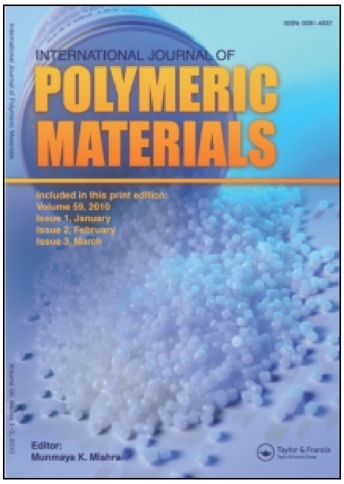

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# Structure Property Relationship in Unsaturated Polyamides

Atanu Ray[a]; Mrinal M. Maiti[a]; Sukumar Maiti[a]
[a] Polymer Division, Materials Science Centre, Indian Institute of Technology, Kharagpur, India

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# Structure Property Relationship in Unsaturated Polyamides

ATANU RAY, MRINAL M. MAITI and SUKUMAR MAITI

*Polymer Division, Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India*

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Unsaturated polyamides from fumaric acid and ortho-, meta- and para-phenylene diamine were prepared by thionyl chloride activated low temperature polycondensation in polar solvents. The polymers were found to be soluble in highly polar solvents. The solubility parameter of the polymers was calculated from Small's group contribution, which agreed well with the experimental values. X-ray diffraction study revealed that the polymers were amorphous. The isomeric effect on the thermal and electrical properties of polymers was discussed.

## INTRODUCTION

Polyamides are an important class of condensation polymers which find application in various areas of modern technology. Unsaturated polyamides have got the possibility of crosslinking reaction and are, therefore, of commercial interest. Different methods have been reported for the synthesis of unsaturated polyamides either by reacting an unsaturated aliphatic or aromatic dicarboxylic acid with various diamines or by reacting dicarboxylic acid with unsaturated diamines by melt or interfacial polycondensation method.[1–7] However, melt polycondensation technique in general results in a cross-linked product due to the activation of the unsaturated site in the polymer and/or monomers. The possibility of crosslinking reaction during melt polymerization in fumaric acid based copolyamides were reported by Tokarev, Korshak and their co-workers.[8,9] Low temperature polycondensation method reported by Imai *et al.*[10] is found to be satisfactory for the synthesis of unsaturated polyamides. We wish to report here the synthesis of unsaturated polyamides by reacting fumaric acid and ortho-, meta- and para-phenylene diamine at low temperature in the presence of thionyl chloride and the influence of isomeric effect on the properties of such copolyamides.

## EXPERIMENTAL

Fumaric acid (BDH, India) was used after crystallization from ethanol.

Ortho-phenylene diamine (VEB Lab, West Germany), meta- and para-phenylene diamine (BDH, England) were purified by following the usual procedure.[11]

Thionyl chloride (SD, India) was distilled before use.

N,N-Dimethyl formamide (DMF) (E. Merck, India) was dried over phosphorus pentoxide for 24 h and distilled under reduced pressure (~20 torr). All other solvents used were pure grade.

### Characterization of polyfumaramides

*Viscosity measurements* Viscosity measurements were made with 0.5% (w/v) solution in N-methyl-2-pyrrolidone (NMP) at 30°C using Ubbelhode suspended level viscometer.

*Density measurements* The density of the polymers was determined in dry benzene at 30°C by using a small pycnometer.

*IR spectroscopy* IR spectra of the polymers were recorded with a Perkin-Elmer 237B spectrophotometer using KBr pellets.

*X-ray* X-ray diffraction diagrams of the polymers were recorded with a Dorn I (U.S.S.R.) X-ray diffractometer using Ni-filtered CuK$\alpha$ radiation.

*Solubility characteristics* The polymer samples (0.02 g) were placed in various solvents and allowed to stand for two weeks[12–14] and observed thereafter for swelling or dissolution. A plot of solubility parameter ($\delta$) *vs.* hydrogen bonding index ($\gamma$) of the solvents used was prepared. The mid-point of the solubility parameter range was chosen as the solubility parameter of the polymer.

*Thermal behavior* Thermogravimetric and differential thermal analyses were made simultaneously with a Shimadzu, DTG system, 30-series, Japan. The measurements were recorded in air at a heating rate of 10°C/min.

*Isothermal ageing* The polymers were isothermally heated in a specially designed ageing oven (Thermogravimetric Analyser, Fertilizer Corporation of India) in air at 150°C to measure the weight loss at different time intervals.

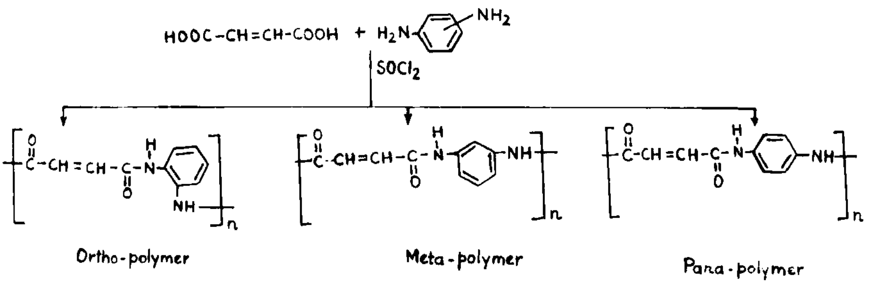
*Electrical behavior* The variation of dielectric properties of polymers with frequency and temperature was measured by using a polymer pellet of dia 1.253 cm and thickness 0.168 cm for ortho-polymer; 0.176 cm for meta-polymer and 0.156 cm for para-polymer using a Radio Capacitance Bridge (Type-716C).

*Polymer synthesis* The unsaturated polyamides from fumaric acid and meta- or para-phenylene diamine were prepared earlier by interfacial polycondensation technique.[7,8] The same polyfumaramides could be successfully synthesized from fumaric acid by following low temperature polycondensation method.[10] A typical run is as follows: 4.64 g (40 mmole) of fumaric acid were dissolved in 25 ml DMF in a three necked flask fitted with a stirrer, a thermometer and a nitrogen purge tube. The solution was cooled to −5°C when 9.52 g (80 mmole) of thionyl chloride were added so that the temperature should not rise more than 5°C. After 1–2 min 4.32 g (40 mmole) of diamine and 6.32 g (80 mmole) of pyridine were added to the mixture. The solution was stirred for 10 h at 0–5°C and was poured into ice/water. It was filtered immediately and washed several times with cold water and finally with chloroform. It was further purified by dissolving in DMF and precipitated by methanol.

*Amine addition reaction* 1.0 g of the polymer in 20 ml DMF was heated in a 100 ml flask together with 1.08 g (10 mmole) of phenylene diamines at 140–150°C for 10 h. The insoluble mass was filtered and dried. It was washed several times with hot DMF and finally with hot ethanol and dried in vacuum at 100°C.

## RESULTS AND DISCUSSION

The polycondensation of fumaric acid and ortho-, meta- and para-phenylene diamine is a direct polyamidization reaction involving an unsaturated dicarboxylic acid and a diamine. The polyfumaramides obtained from low temperature polycondensation may be schematically represented as follows:



In the above reaction pyridine was used as an acid acceptor to facilitate polymerization. However, triethyl amine may also be used as an acid acceptor in this polycondensation reaction. It has been observed that DMF, dimethyl sulfoxide (DMSO), dimethyl acetamide (DMAC) and NMP are suitable solvents for this polycondensation reaction. The molecular weight of the polymers may be controlled by changing reaction conditions, solvents and preferably by the use of a suitable catalyst.

## Polymer characterisation

The unsaturated polyamides thus prepared were characterized by nitrogen analyses and IR spectroscopy. The physical properties of the polymers are shown in Table I. The characteristic IR bands of the polymers (Figure 1) are observed near 1705–1710 and 1580–1590 $cm^{-1}$ for amides and a weak band near 1630 $cm^{-1}$ possibly due to the stretching band of CC-double bond of the fumaric acid moeity present in the polymer backbone. The -NH-stretching band for amides is observed near 3300–3400 $cm^{-1}$. There is practically no broad O—H stretching band for the carboxyl groups present in fumaric acid indicating the absence of free carboxyl group in the polymer chain.

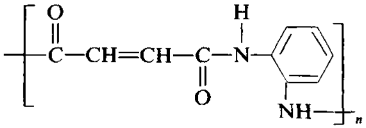
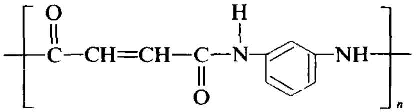
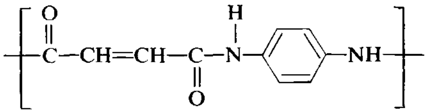
*Solution viscosity behavior* The inherent viscosities of the isomeric polyamides are shown in Table I. The inherent viscosity of the para-polymer is found to be the highest. The highest inherent viscosity of the para-polymer corresponds to the highest molecular weight among the three isomeric polyfumaramides. Similar viscosity behavior has also been observed for other isomeric polyimides,[14] polyesterimides[15] and polyamideimides.[16]

The role of different solvents on the polycondensation reaction i.e., on yield and inherent viscosity of polymers is shown in Table II. From Table II it is evident that the polymers obtained by using NMP as the solvent in the polycondensation reaction possess the highest yields and inherent viscosities. This may be explained by the fact that high polarity of NMP tends to dissolve the polymer to form a homogeneous solution at lower temperature as well as activates the monomers for further polymerization and hence increases the yield and inherent viscosity of the polymer. From the viscosity values it is found that the molecular weights of the resulting polyfumaramides follow the trend: para > meta > ortho.

The ageing characteristics of the polymers in NMP and conc. sulfuric acid are shown in Figure 2. The inherent viscosity of the ortho-polymer decreases more rapidly with time in both the solvents than that of meta- or para-polymer. The stability of the unsaturated polymers in both the solvents follows, therefore, the order: para > meta > ortho. It is to be noted, however, that the relative stability of all the isomeric polyfumaramides in sulfuric acid is

TABLE I

Physical properties of the polyfumaramides

| Polymer repeat unit | Yield % | Inherent[a] viscosity dl/g | Density g/cm$^3$ | $T_m$[b] °C | Nitrogen content, % | |
|---|---|---|---|---|---|---|
| | | | | | Calc. | Found |
| <br>Ortho-polymer | 74–76 | 0.18[c] | 1.14 | 230 | 14.89 | 14.62 |
| <br>Meta-polymer | 88–90 | 0.21[c] | 1.18 | 250 | 14.89 | 15.03 |
| <br>Para-polymer | 80–83 | 0.25[c] | 1.20 | 260 | 14.89 | 15.07 |

[a] Measured in NMP (0.5 weight—% solution) at 30°C.
[b] Calculated from DTA curves (Figure 5).
[c] Inherent viscosity observed using NMP solvent after 18 h reaction.

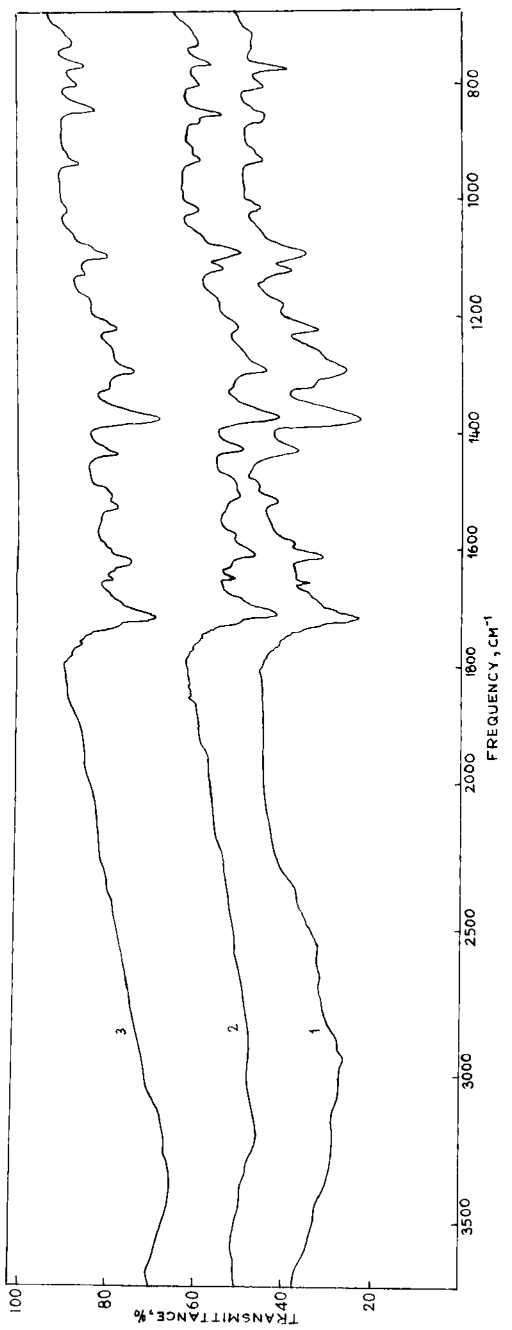


FIGURE 1 IR spectra of the polyfumaramides. 1: orthopolymer, 2: meta-polymer, 3: para-polymer.

TABLE II

Effect of solvent in polyamide synthesis[a]

| Solvent used | Ortho-polymer | | Meta-polymer | | Para-polymer | |
|---|---|---|---|---|---|---|
| | Yield % | inh[b] dl/g | Yield % | inh[b] dl/g | Yield % | inh[b] dl/g |
| DMF | 60–62 | 0.12 | 76–79 | 0.17 | 71–72 | 0.18 |
| DMSO | 63–65 | 0.11 | 75–78 | 0.14 | 70–72 | 0.16 |
| DMAC | 65–68 | 0.14 | 82–83 | 0.18 | 74–77 | 0.19 |
| NMP | 74–76 | 0.16 | 86–88 | 0.20 | 79–82 | 0.22 |

[a] Temp: 0–5°C; time: 10 h; solvent amount: 25 ml; reactant concentration: acid (0.04 mole); and amine (0.04 mole).

[b] Measured in NMP (0.5 weight—% solution) at 30°C.

much less than that in the organic solvents (Figure 2). This may be due to the hydrolysis of the amide groups of the polymer chain in sulfuric acid medium. Inherent viscosity of all the polymers decreases by about 11–19% in NMP and 16–36% in sulfuric acid after 35 days at room temperature (~30°C).

*X-ray characteristics* X-ray diffraction data of the polymers show that there is no sharp peak in the plot of intensity *vs.* scattering angle ($2\theta$). This indicates that the polymers are amorphous in nature (Figure 3).

*Solubility behavior* The solubilities of the polymers are listed in Table III. The solubility of the para-polymer was found to be the lowest followed by meta- and ortho-polymer. The higher solubility of the ortho-polymer may be explained by the fact[17,18] that the decrease in the chain symmetry reduces the degree of crystallinity, which in turn increases the solubility of the polymer.

*Solubility parameter* A plot of solubility parameter ($\delta$) *vs.* hydrogen bonding index ($\gamma$) for solvents is illustrated in Figure 4. The solubility parameter may be calculated from Small's group contributions.[19] The molar attraction constant, $G$, values for various groups used here have been reported by Hoy [20,21] and are presented in Table IV. These values are used to calculate the solubility parameter ($\delta$) of the polymers using the relationship

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

where $\Sigma G$ is the sum of Small's group contribution, $M$, the formula weight of the polymer repeat unit and $\rho$ is the density of the polymer. The $\delta$ value obtained from the midpoint of the solubility map for ortho-polymer (Figure 4) is found to be 10.55. This is in excellent agreement with the calculated value of $\delta$ i.e., 10.79 (Table IV).

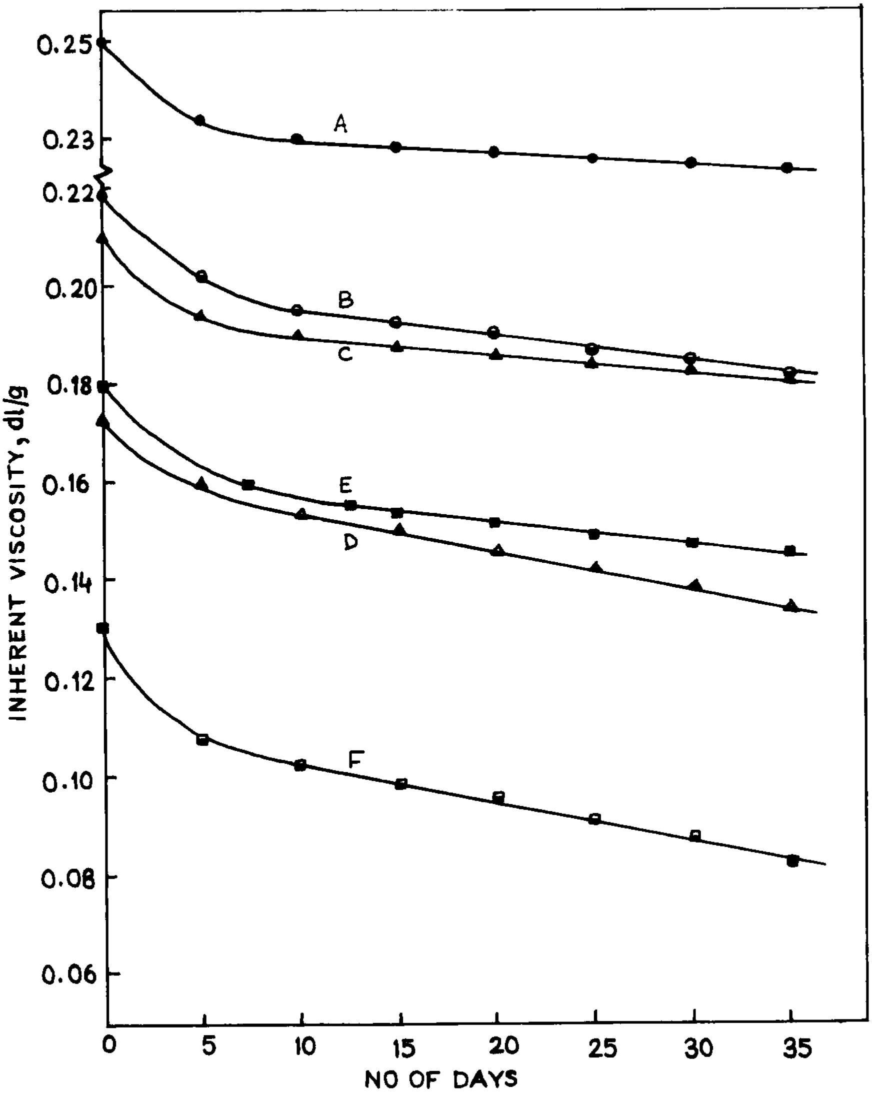


FIGURE 2 Ageing of the isomeric polyfumaramide solutions at room temperature (~30°C). A: para-polymers in NMP; B: para-polymer in $H_2SO_4$; C: meta-polymer in NMP; D: meta-polymer in $H_2SO_4$; E: ortho-polymer in NMP; F: ortho-polymer in $H_2SO_4$.

*Thermal behavior* The results of the thermogravimetric and differential thermal analysis of the isomeric polyfumaramides in air are shown in Figure 5. It has been observed that the thermal stability of the para- and meta-polymer is comparable, but the ortho-polymer possesses somewhat lower stability. The melting points of the polymers obtained from DTA curves (Figure 5) are found

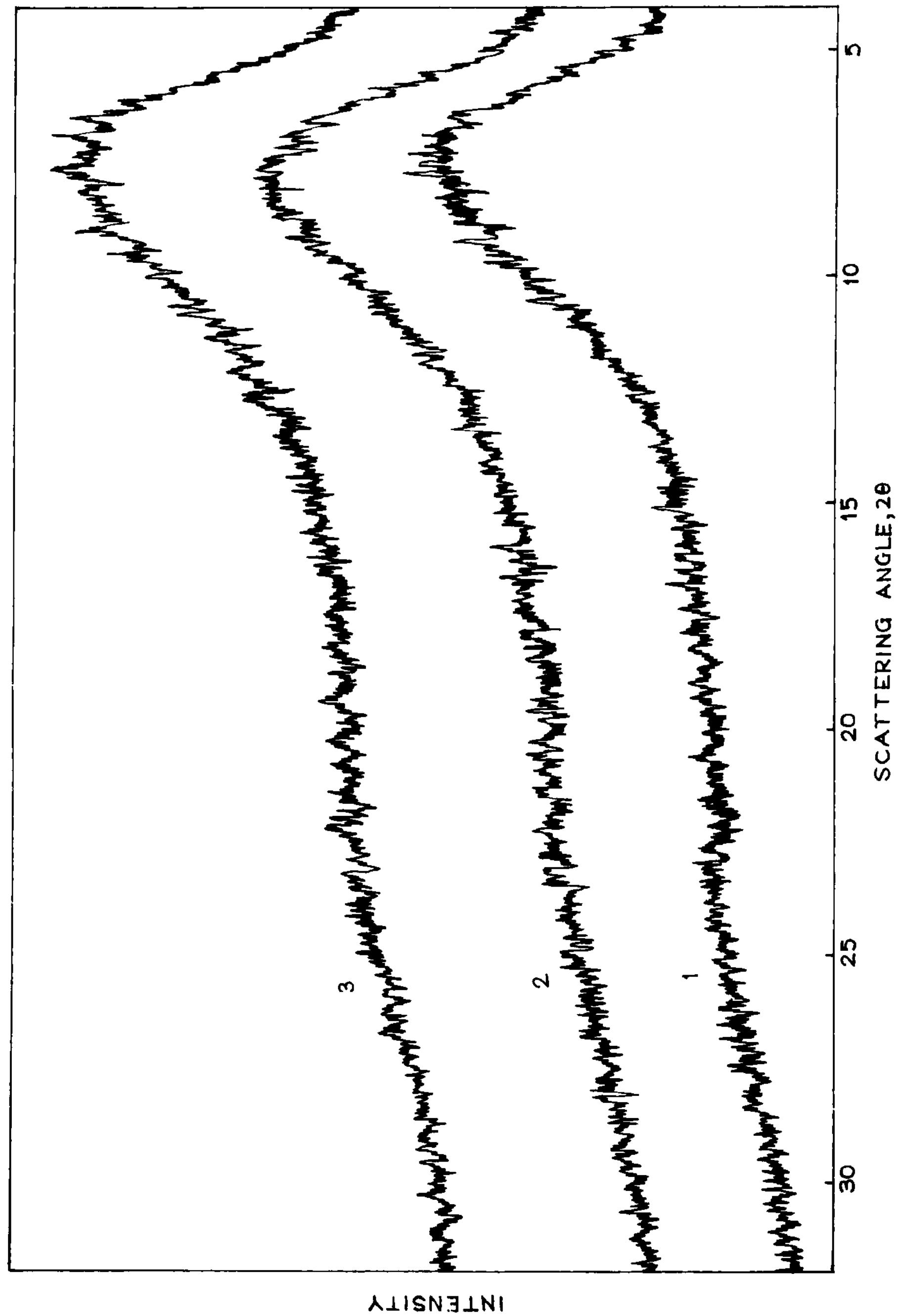


FIGURE 3 X-ray diffraction diagram of 1 : ortho-polymer; 2 : meta-polymer; 3 : para-polymer.

TABLE III

Solubility behavior of the polyfumaramides

| Solvent | Solubility parameter ($\delta$) | Hydrogen bonding index ($\gamma$) | Solubility[a] Ortho-polymer | Meta-polymer | Para-polymer |
|---|---|---|---|---|---|
| Benzene | 9.16 | 2.2 | − | − | − |
| Carbon tetrachloride | 8.55 | 2.2 | − | − | − |
| Nitrobenzene | 10.00 | 3.2 | ± | − | − |
| Chloroform | 9.16 | 2.2 | − | − | − |
| Cyclohexanone | 10.42 | 6.4 | + | + | + |
| Cyclopentanone | 10.53 | 5.2 | + | + | + |
| Dioxan | 10.13 | 5.7 | ± | − | − |
| Tetrahydrofuran | 9.10 | 5.3 | + | ± | ± |
| Ethyl methyl ketone | 9.45 | 5.0 | ± | ± | ± |
| N,N-dimethyl formamide | 11.79 | 6.4 | + | + | + |
| N,N-dimethyl acetamide | 10.80 | — | + | + | + |
| N-methyl-2-pyrrolidone | 11.00 | 5.6 | + | + | + |
| Dimethyl sulfoxide | 13.00 | 5.0 | + | + | + |
| Formic acid | 12.10 | — | + | + | + |
| Cyclohexane | 8.19 | 2.2 | − | − | − |
| Chlorobenzene | 9.67 | 2.7 | − | − | − |
| m-Cresol | 10.20 | — | + | + | + |
| Methylene dichloride | 9.88 | 2.7 | ± | − | − |
| Methyl acetate | 9.46 | 5.2 | − | − | − |
| Acetone | 9.62 | 5.7 | − | − | − |
| n-Hexane | 7.27 | 2.2 | − | − | − |
| n-Pentane | 7.02 | 2.2 | − | − | − |
| Decane | 7.74 | 2.2 | − | − | − |
| Methyl isobutyl ketone | 8.40 | 5.0 | − | − | − |
| Diacetone alcohol | 9.77 | 6.9 | − | − | − |
| Ethyl acetate | 8.91 | 5.2 | − | − | − |
| Ethylene dichloride | 9.86 | 2.7 | ± | − | − |
| Conc. $H_2SO_4$ | — | — | + | + | + |
| Toluene | 8.93 | 3.8 | − | − | − |

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

to be 230, 250 and 260°C for ortho-, meta- and para-polymer respectively. The maximum decomposition temperatures of these polymers were observed near 530–540°C and maximum weight loss occurs at 300–550°C. It was reported by Bower and Frost[14] that the orientation of groups on the benzene ring does not generally have a great effect on the thermal stability but is a factor of flexibility and viscosity of the polymer. However, it is important to mention here that the flexibility, thermal stability as well as strength properties of polymers are very complex and generally considered to be due to intra-chain and inter-chain interactions.[15] Chain symmetry is responsible for flexibility which contributes to close packing and hence crystallinity of the material. In ortho substitution the benzene ring is highly unsymmetric about the macromolecular chain axis, whereas in para-substitution the benzene ring is perfectly symmetric and therefore responsible for higher thermal stability and poor solubility compared to ortho-polymer. Moreover, slight unsymmetric nature of the meta-

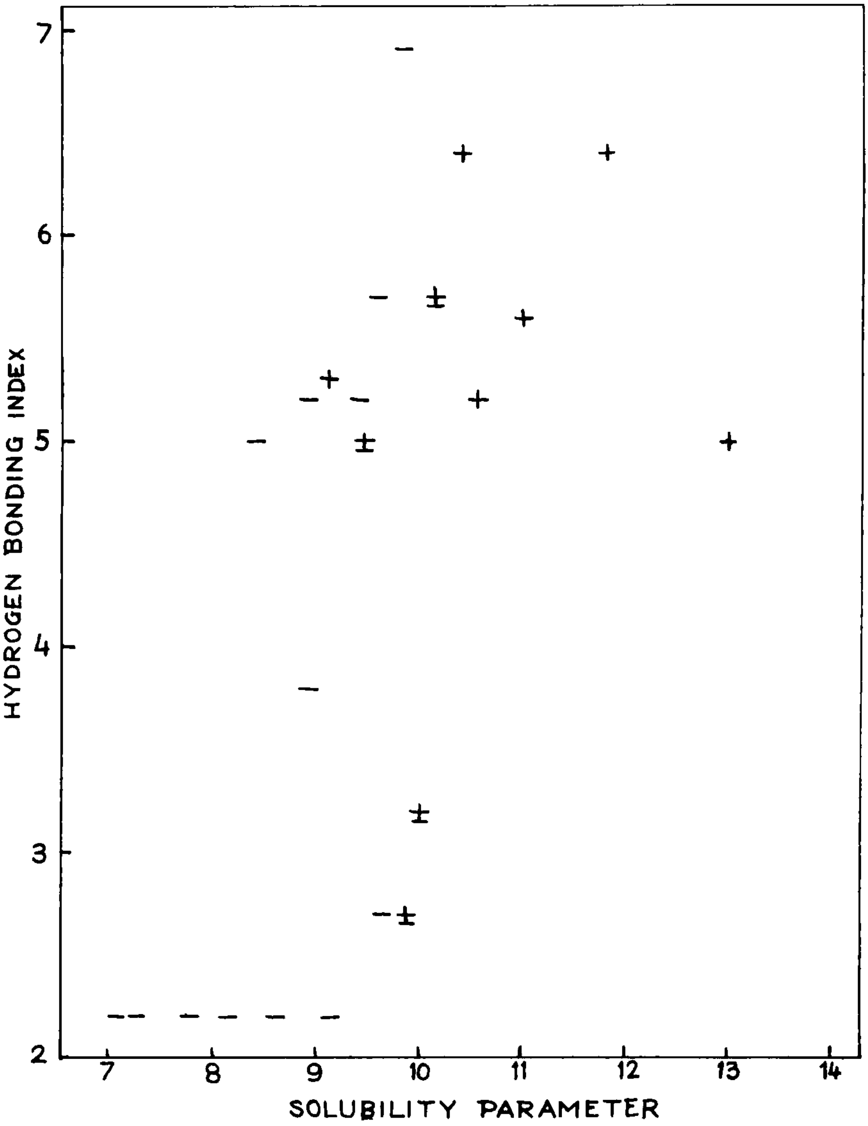


FIGURE 4 Solubility map of ortho polyfumaramide.

substitution prevents the close packing of the molecules as closely as in the para-substituted polymer. Metapolymer thus strikes a balance between highly ordered structure of para-polymer and the complete random structure of ortho-polymer. This may be a probable reason for greater success of meta-

TABLE IV

Calculated solubility parameter of the polyfumaramides

| Functional groups | $G$ value $(\text{Cal-cm}^3)^{1/2}$ | No. of functional groups/ substitution in the polymer repeat unit | Total $G$ values for polymers $(\text{Cal-cm}^3)^{1/2}$ Ortho-polymer | Meta-polymer | Para-polymer |
|---|---|---|---|---|---|
| —CH= (Aromatic) | 117.12 | 4 | 468.48 | 468.48 | 468.48 |
| =C= (Aromatic) | 98.12 | 2 | 196.24 | 196.24 | 196.24 |
| —CH= (Aliphatic) | 121.53 | 2 | 243.06 | 243.06 | 243.06 |
| >C=O | 262.96 | 2 | 525.92 | 525.92 | 525.92 |
| —NH— | 180.03 | 2 | 360.06 | 360.06 | 360.06 |
| Six membered ring | −23.44 | 1 | −23.44 | −23.44 | −23.44 |
| Ortho-substitution | 9.69 | 1 | 9.69 | | |
| Meta-substitution | 6.60 | 1 | | 6.60 | |
| Para-substitution | 40.33 | 1 | | | 40.33 |
| | | $\Sigma G =$ | 1780.01 | 1776.92 | 1810.65 |
| Solubility parameter, $\delta =$ | | | 10.79 | 11.15 | 11.56 |

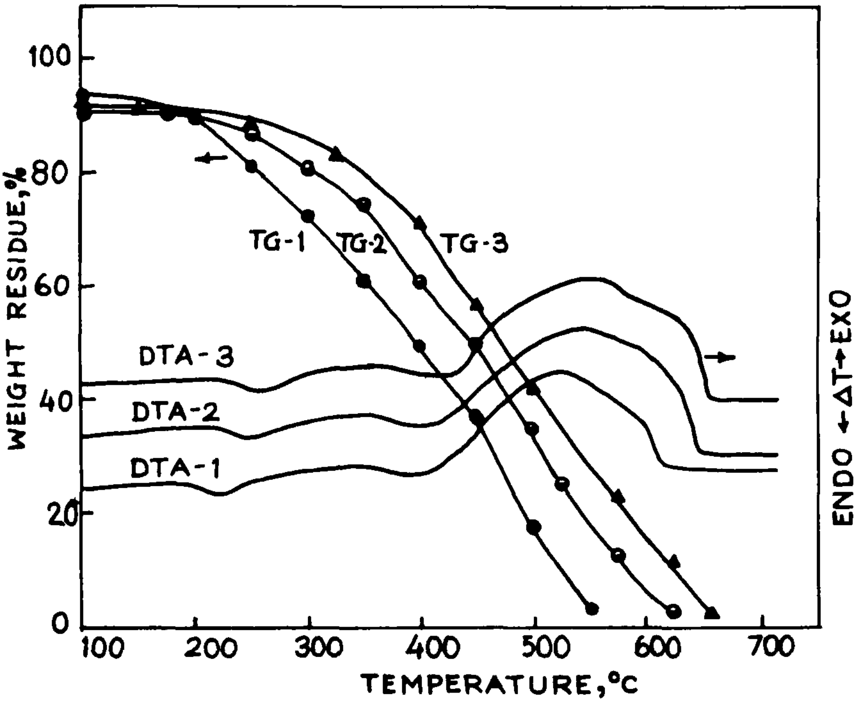


FIGURE 5 Thermogravimetric and differential thermal analysis of ortho-polymer (DTA-1, TG-1); meta-polymer (DTA-2, TG-2); para-polymer (DTA-3, TG-3).

substituted polymers in applications requiring thermal stability and chain flexibility.[15]

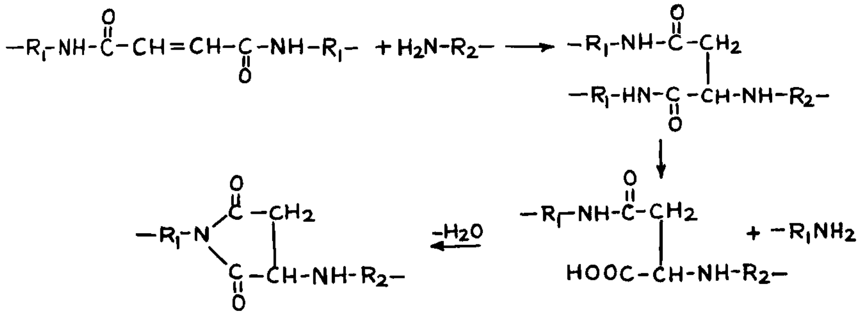
*Isothermal ageing* The weight loss at 150°C in air for the isomeric polyfumaramides at different time intervals is shown in Table V. It has been observed that an initial weight loss of about 6.4% for ortho-, 9.1% for meta- and 7.3% for para-polymer respectively occurs within 1 h which is probably due to loss of moisture or entrapped solvent present (Table V). Subsequently there occur only 9.3%, 6.1% and 4.8% weight losses for ortho-, meta- and para-polymer respectively after 14 h heating. This indicates that para-polymer possesses the highest thermal stability and ortho-polymer the lowest. Similar behavior was also observed from thermal analyses (DTA and TGA) (Figure 5) of the polymers.

TABLE V

Isothermal ageing of the polyfumaramides

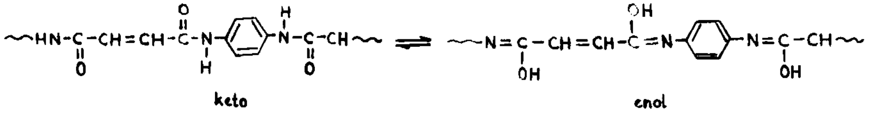
| | | %-weight loss at 150°C in air at different time intervals | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Polymer | 1 h | 2 h | 4 h | 6 h | 8 h | 10 h | 12 h | 14 h |
| | Ortho- | 6.4 | 0.9 | 0.9 | 1.4 | 0.7 | 1.1 | 1.4 | 1.9 |
| Cumulative weight loss | | — | 7.3 | 9.2 | 10.6 | 11.3 | 12.4 | 13.8 | 15.7 |
| | Meta- | 9.1 | 1.1 | 0.7 | 0.8 | 1.1 | 0.7 | 1.1 | 0.6 |
| Cumulative weight loss | | — | 10.2 | 10.9 | 11.7 | 12.8 | 13.5 | 14.6 | 15.2 |
| | Para- | 7.3 | 0.6 | 0.6 | 0.8 | 0.8 | 0.5 | 0.7 | 0.8 |
| Cumulative weight loss | | — | 7.9 | 8.5 | 9.3 | 10.1 | 10.6 | 11.3 | 12.1 |

*Amine addition reaction* Copolyfumaramides readily form cross-linked products under suitable conditions.[5,8] To explain the crosslinking reaction Tokarev *et al.*[8] first predicted that amine addition to the double bond of fumaric acid moiety in the polymer was responsible. They showed that amines do add to the CC-double bond at 110°C and above. The mechanism of this reaction was established by Fedotova *et al.*[9] who found that succinic acid derivatives were obtained from fumaric acid moieties by addition of amines:



In the isomeric polyfumaramides, the above amine addition to the double bond was found to be satisfactory in case of para- and meta-polymer with the formation of corresponding imide structure which was characterized by strong IR bands near 1780 and 1710 cm$^{-1}$. However, for ortho-polymer, the imide formation did not take place by the addition of excess amine under the same condition. This is probably due to the inherent structure of ortho-phenylene diamine which makes the —NH— groups less available for imide formation and also to steric effect of the macromolecular chain.

*Effect of frequency on dielectric behavior of polyfumaramides* The variation of dielectric constant or permitivity ($\varepsilon'$) and dielectric loss (tan $\delta$) with frequency, $f$, at room temperature (~30°C) of isomeric polyfumaramides is shown in Figure 6. The dielectric constant of the polymers gradually decreases with the increase of frequency. This may be explained by the fact that the polar groups in the macromolecule tend to orient in the direction of the applied field. In an alternating electric field, a particular polar group will be flexible enough to respond at low frequency but not flexible enough to respond at high frequency and consequently the dielectric constant decreases as frequency increases.[22] The dielectric constant of the para-polymer was found to be the least among the isomeric polyamides. However, the internal conjugation of the para-polymer does not have remarkable effect on the dielectric poroperties as expected. The conjugation of the para-polymer is likely to arise due to the formation of enolate structure:



The lowest permitivity of the para-polymer may be explained on the basis of the fact that the conjugation is not favourable due to the presence of strong hydrogen bonding in polyamides and thus the keto$\rightleftharpoons$enol tautomerism is less favourable at room temperature (~30°C).

The plot of tan $\delta$ *vs.* log$f$ shows maxima at $1.58 \times 10^3$, $2.24 \times 10^3$ and $3.98 \times 10^3$ Hz respectively for ortho-, meta- and para-polymer. From Figure 6, it is evident that the dielectric loss of the parapolymer is the lowest followed by meta- and ortho-polymer. It is interesting to note that the loss maximum is gradually shifted to the higher frequency region from ortho- to para-polymer. It is probably due to higher molecular weight as well as the rigidity and close packing of the chain of the parapolymer. The highest thermal stability and density of the parapolymer are also due to the above fact. The relaxation time ($\tau$) value calculated at this maximum have been found to be $1.01 \times 10^{-4}$, 7.11

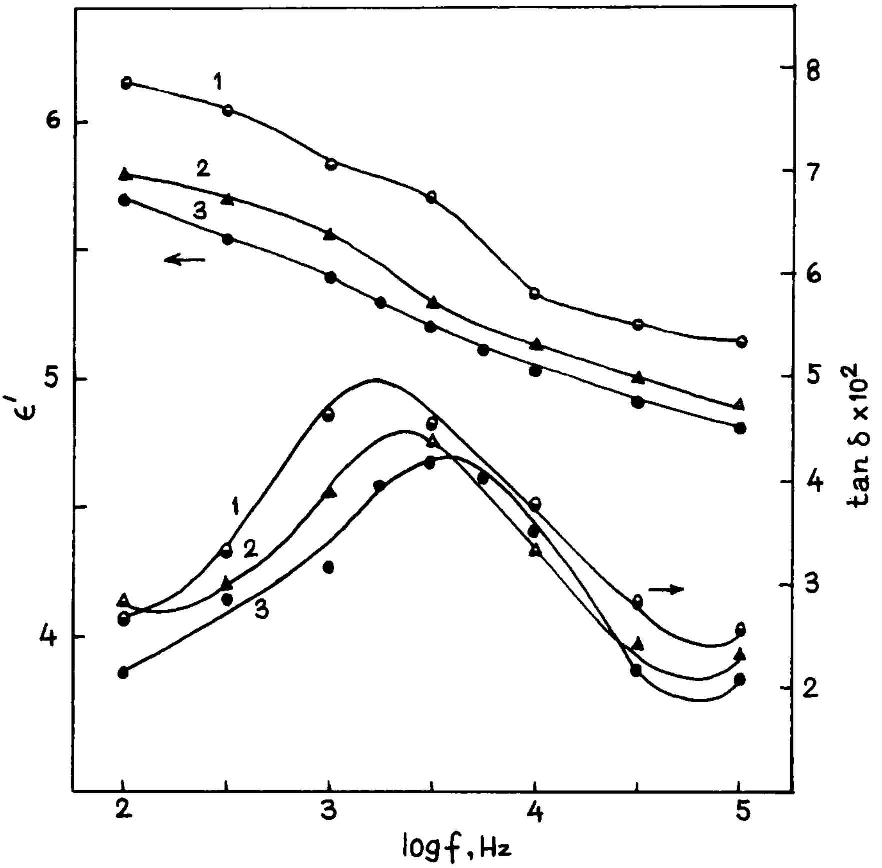


FIGURE 6 Variation of dielectric constant (ε′) and dielectric loss (tan δ) with frequency of 1: ortho-polymer; 2: meta-polymer; 3: para-polymer.

× $10^{-5}$ and 4.0 × $10^{-5}$ sec for ortho-, meta- and para-polymer respectively. Relaxation time ($\tau$) obtained by following the equation $2\pi f_{\max}\tau = 1$ is an average or most probable relaxation time that is determined by a set of structural units of different mobility.[23]

*Effect of temperature on dielectric behavior* Variation of dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) of para-polyfumaramide with temperature at $10^3$ and $10^4$ Hz was shown in Figure 7. The dielectric constant of the para-polymer gradually rises with the increase of temperature up to 90° and 120°C at $10^3$ and $10^4$ Hz respectively and then decreases with further rise of temperature as observed in other copolyamides.[24] The dielectric loss gradually increases with

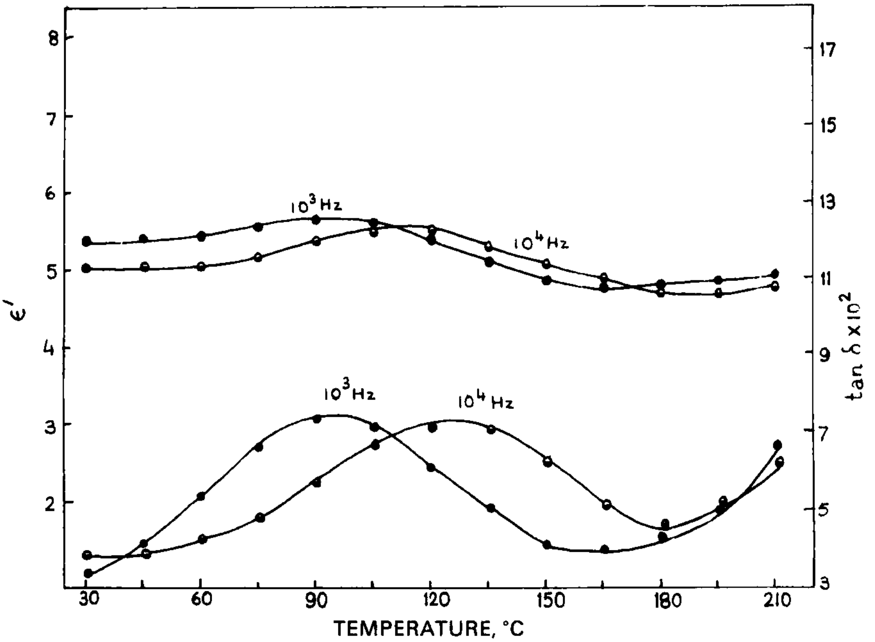


FIGURE 7 Variation of dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) of para-polyfumaramide with temperature.

temperature and attains maxima at 95° and 125°C at $10^3$ and $10^4$ Hz respectively. The high loss at these temperatures are probably due to the dipole group loss of the polar substituents present in the polymer backbone. The low frequency polarization may be due to intermolecular hydrogen bonding responsible for segmental rigidity which is also observed in tan $\delta$ *vs.* log $f$ curve (Figure 6).

## Acknowledgements

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