

Polyimine, a C=N Double Bond Containing Polymers: Synthesis and Properties

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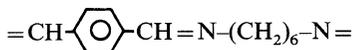
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ABSTRACT: The polymerization of terephthalaldehyde and hexamethylenediamine to obtain a film-forming high molecular weight polyimine solution was considerably facilitated through the use of *m*-cresol as a solvent under mild conditions. The reaction was reversible, though the equilibrium favored a high product concentration. A crystalline but partially cross-linked powder and film were obtained from the solution.

KEY WORDS Polyimine / Terephthalaldehyde / Hexamethylenediamine / Polycondensation / Film-Forming / Equilibrium / Cross-Linking /

In this paper we report the results of various studies on the synthesis of a compound containing C=N double bonds. The substance studied is a polyimine having the formula,¹



(I)

Various methods for preparing polyimines by the condensation of dialdehydes with diamines have been proposed.^{2,8} Polymer (I) was first prepared by Krässig and Greber³ in benzene using an azeotropic method; these authors were unable to use colligative properties for molecular weight determination but estimated a molecular weight of 2161 from analysis.

Dyer and Anderson⁴ reported the preparation of polymer (I) by solution polymerization in dimethyl sulfoxide or *N*-methyl-2-pyrrolidone. However the resulting white product was found to have a low molecular weight of 3000.

D'Allelio and coworkers⁵ prepared (I) in benzene, but the end group analysis showed this polymer to have a degree of polymerization (DP) of 8. These authors allowed that they produced high molecular weight polyimine (I) by a Schiff base exchange reaction using molten reagents at high temperature. However, Hodgkin and Heller showed that this claim could not be validated.⁶

As mentioned above, the characterization and

film formation of high molecular weight polyimine (I) apparently have not been studied up until now. Thus, it seemed worthwhile to prepare the polymer and film and examine their properties.

EXPERIMENTAL

Terephthalaldehyde and hexamethylenediamine were obtained from Tokyo Kasei Co., Japan and used without further purification. Purification of *m*-cresol was carried out by distillation in a N₂ atmosphere.

Viscosity was measured in *m*-cresol or 98% sulfuric acid at a 1% concentration at 27°C ± 0.1°C using an Ubbelohde viscometer.

X-ray diffraction spectra were obtained from powders using Ni-filtered Cu-K_α radiation at 35 kV-100 mA and a 4°C min⁻¹ scanning speed.

Dynamic viscoelasticity was measured with a Rheovibron DDV-II (Toyo Baldwin, Japan) at 1°C min⁻¹ and 110 Hz.

Infrared spectra were recorded on a Hitachi Model 285 and DSC with a Perkin-Elmer DSC-1B.

Films were prepared by evaporating the reaction solution under reduced pressure at 100°C.

Solubility tests were carried out as follows: 1 g of polymer was added to 30 ml of *m*-cresol and shaken at 20°C with a Tokyo Rikakikai SS-8 Shaker. After 24 hours, the insoluble portion was filtered off,

washed with chloroform, dried for 10 hours at 60°C (1 mmHg) and weighed.

POLYMERIZATION

In 200 ml of freshly distilled *m*-cresol were dissolved hexamethylenediamine (0.2 mol) and terephthalaldehyde (0.2 mol) at 20°C with stirring. The viscosity of the solution increased rapidly to give a viscous polymer solution. After stirring at 20°C for 2 h, the polymer solution was poured into methanol to precipitate a fibrillar polymer which was then filtered and dried at 80°C for 2 hours to give a white material (33 g). This polymer had a high crystallinity, a high glass transition temperature (T_g) at 80°C and a melting point (T_m) at 174°C. The polymer solution was uniformly cast on a glass plate and dried under a pressure of 0.1 mmHg at 100°C for 4 hours. The film thus obtained had a thickness of 26 microns, as measured with a micrometer, and the following mechanical properties:

No	Thickness	Tensile strength	Elongation	Young's modulus
	μm	kg cm^{-2}	%	kg cm^{-2}
1	23	386	9.1	13,520
2	24	406	12.4	14,320
3	35	394	18.3	10,872

RESULTS AND DISCUSSION

Equivalent quantities of hexamethylenediamine and terephthalaldehyde rapidly condensed at room temperature in *m*-cresol to give a solution containing 10 to 30% polymer. Contrary to other organic

solvent, *m*-cresol did not separate the resultant polymer from solution. A white fibrillar polymer was obtained when poured into methanol. A tough, flexible and white opaque film could be cast from the solution. Polymerization results are summarized in Table I.

The polyimine was stable in air and resistant to water, alkali solution (10% KOH) and polar solvents such as amides and alcohols but was easily decomposed by dilute acids such as 5% H_2SO_4 and 5% HCl. The polyimine was soluble in *m*-cresol and partially soluble in tetrachloroethane, chloroform and 98% H_2SO_4 . However, when the sulfuric acid solution was poured into water, the raw material could not be recovered owing to hydrolysis.

Infrared spectroscopy showed strong absorption bands at 1650 cm^{-1} , 2900 cm^{-1} and 1580 cm^{-1} characteristic of the C=N bond, methylene units of the aliphatic chain and benzene moiety, respectively. Peaks for the terminal group CHO (1700 cm^{-1}) were small and became smaller with increasing reaction time. ^1H NMR showed imino protons and aromatic protons at 8.24 and 7.72 ppm, respectively. Thus, the spectrum was consistent with the imino structure for a polymer having a high molecular weight (Figures 1 and 2).

It was found that the polyimine prepared in *m*-cresol was not easily redissolved in the same solvent once isolated. The insoluble part increased with increasing reaction time (Table II), while the C=N band absorption at 1650 cm^{-1} decreased and became broader (Figure 1).

Figure 3 shows the DSC curve of the polyimine. An endotherm point at 82°C corresponds to a T_g and a peak at 170°C to a T_m which lowered and broadened with polymerization time (Figure 4). Figure 5 shows X-ray diffraction patterns by the

Table I. The polymerization of terephthalaldehyde and hexamethylenediamine at 20°C

No.	Solvent	Monomer concentration	Reaction time	Yield	$\eta_{\text{inh}}/\text{dl g}^{-1}$	
		mol l^{-1}	hours	%	98% H_2SO_4	<i>m</i> -Cresol
1	<i>m</i> -Cresol	1.0	2.0	100	Insoluble	0.22 ^a
2	<i>m</i> -Cresol	1.0	24.0	100	Insoluble	0.18 ^a
3	HMPA ^b	0.5	2.0	92	1.19	0.19

^a η_{inh} of soluble portion.

^b Hexamethylphosphoramide.

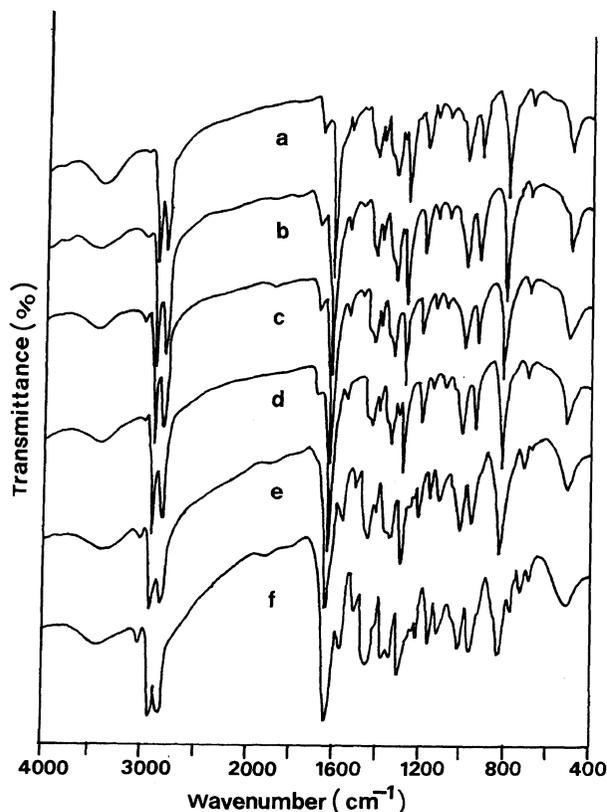
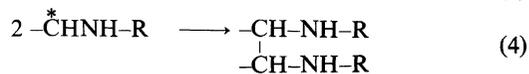
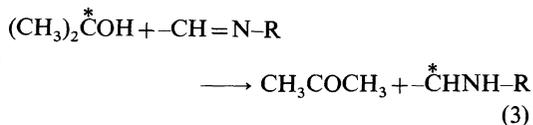
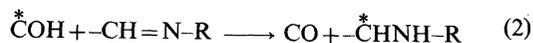
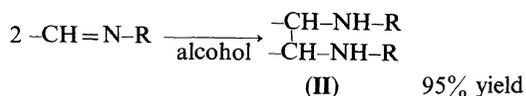


Figure 1. Infrared spectra of the polyimines obtained after a) 0.5, b) 1.0, c) 2.0, d) 5.0, e) 8.5, and f) 27 hours reactions (KBr disc).

powder method. Crystallinity decreased with increasing polymerization time. The longest polymerization time produced a typical amorphous pattern (Figure 5f). Some changes including decreasing solubility, a lowering and broadening T_m on the DSC curves, decreasing and broadening C=N absorption on the IR spectra and decreasing crystallinity suggest that cross-linking reactions must gradually proceed in *m*-cresol with the lapse of time, particularly at C=N sites. Though the reaction was not studied in detail, one possible reaction mechanism is given in Figure 6, on the basis of some photochemical reactions of imines. Padwa and Bergmerk⁷ reported the synthesis of *N,N*-1,2-diphenyl-1,2-diaminoethane (II) in high yield by the irradiation of benzaldehyde *N*-alkylimine in an alcohol. Their observation suggests that the photochemical reduction is sensitized by a small amount of a ketone and represented by the sequence of

reactions (1)–(4).



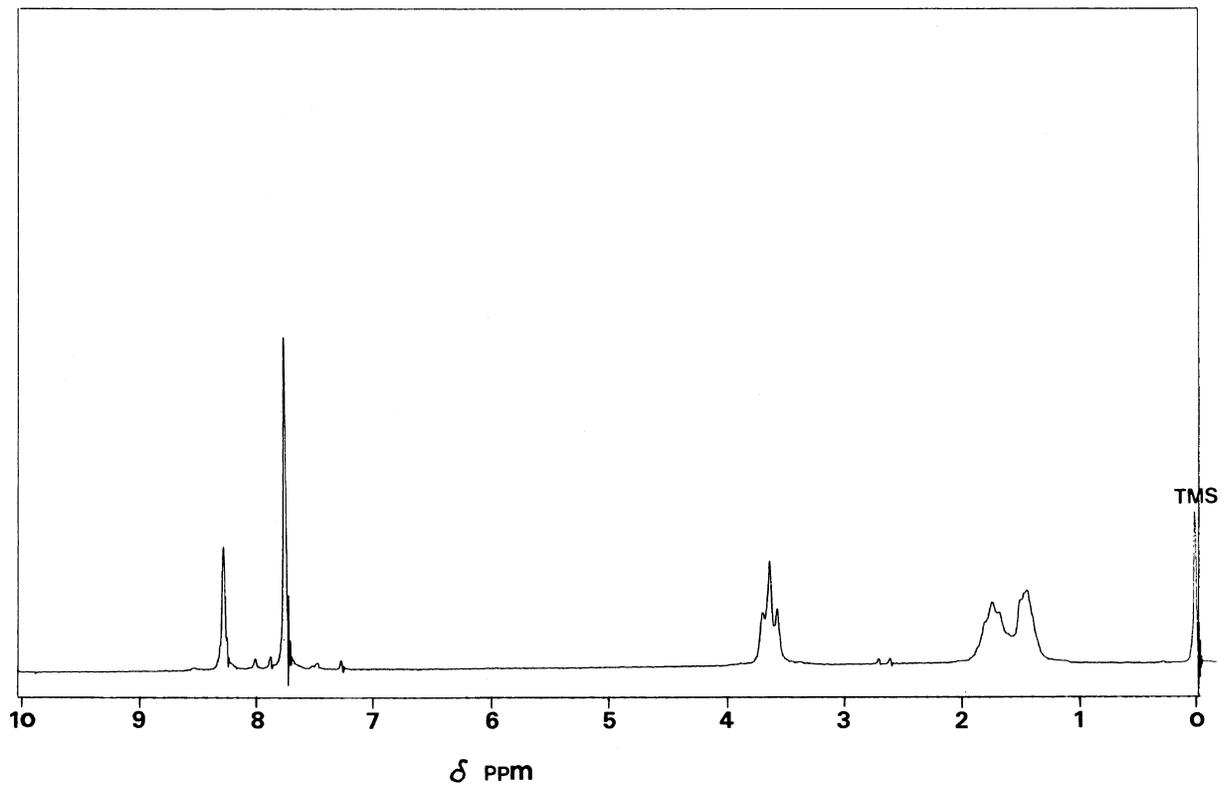


Figure 2. ¹H NMR spectrum of the polyimine obtained after 0.5 hours reactions (in CDCl₃ at 100 MHz).

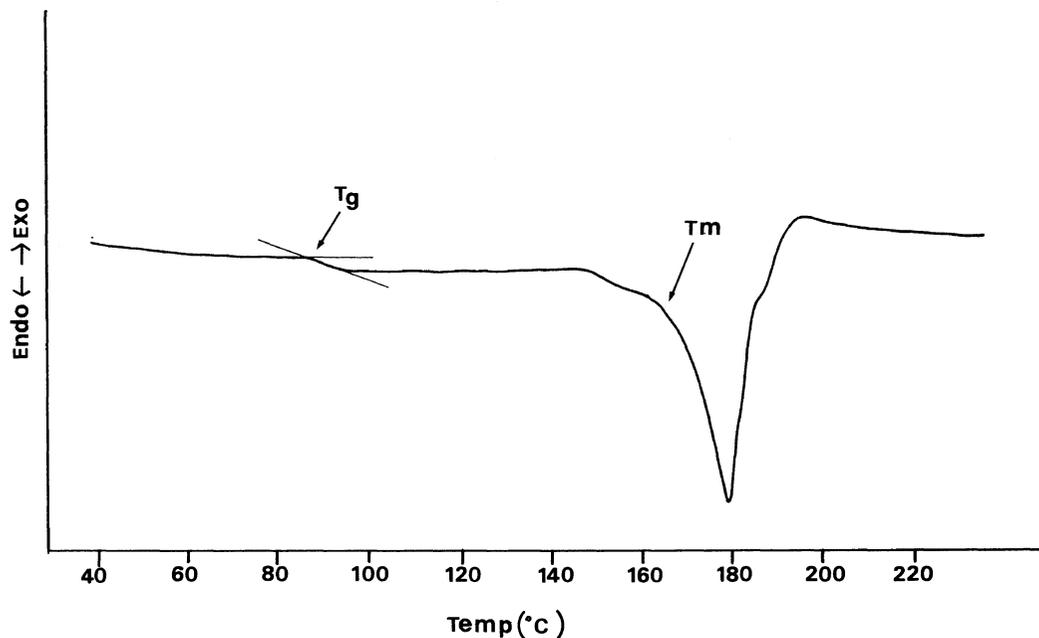


Figure 3. DSC curve of the polyimines obtained after 2.0 hours reactions (powder) $20^{\circ}\text{C min}^{-1}$ in N_2 .

Table II. Solubility test of the polyimine

Reaction time	Soluble portion
hours ^a	%
0.5	100
2.0	25
5.0	20
27.0	15

^a Following the termination of a definite period of time, each part of the reaction solution was poured into methanol to precipitate the polymer which was used for this test.

Table III. Elemental analysis of polyimine

Reaction time	C	H	N
hours	%	%	%
0.5	78.09	8.43	12.55
1.0	78.32	8.48	12.66
2.0	77.93	8.33	12.47
5.0	78.14	8.38	12.60
8.5	78.58	8.40	12.50
27.0	77.37	8.48	14.00
Calculated for $\text{C}_{14}\text{H}_{18}\text{N}_2$	78.51	8.41	13.08

The polyimine solution contained a small amount of aldehyde end groups and *m*-cresol as hydrogen sources which offer possible conditions for the same reaction. If C–C bonding is produced intermolecularly according to the reaction mentioned above, cross-linking continues, but since the solution never gels, the efficiency of the reaction is probably low.

The η_{inh} values in *m*-cresol was found to become smaller on addition of H_2O (Table IV). Further, the η_{inh} approached zero with the dilution of the polyimine solution (Figure 7). This viscosity-concentration relationship is at variance with Huggins' law. Thus, polyimine is hydrolyzed in a

Table IV. The influence of H_2O upon viscosity

Added H_2O	η_{inh}^a in <i>m</i> -cresol
%	dl g^{-1}
0.00	0.33
0.02	0.30
0.04	0.28
0.10	0.24

^a The viscosity of *m*-cresol itself does not change on addition of H_2O .

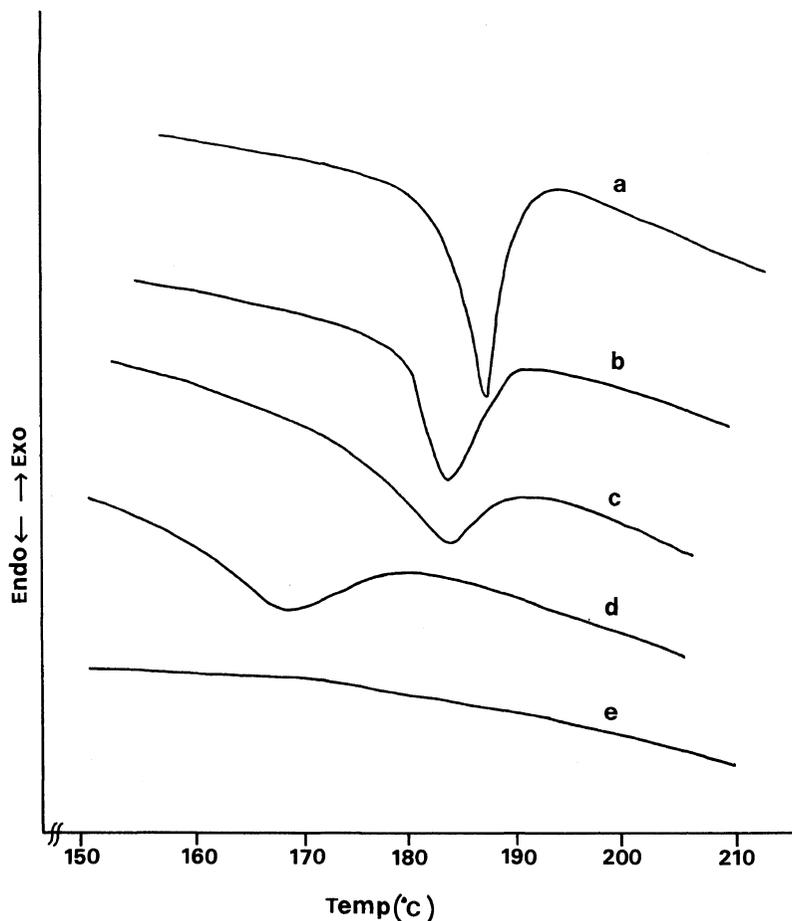


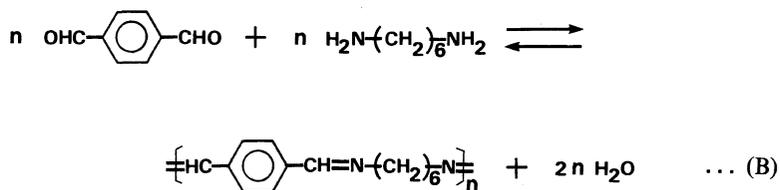
Figure 4. DSC curves of the polyimines obtained after a) 0.5, b) 1.0, c) 2.0, d) 5.0, and e) 27 hours reactions (powder) at $4^{\circ}\text{C min}^{-1}$ in N_2 .

dilute solution. Accordingly, the reaction of an aldehyde and a primary amine in *m*-cresol is reversible, though the reaction is highly inclined toward a high product concentration and a low monomer concentration.

On the basis of the findings above, it may be concluded that the η_{inh} value in *m*-cresol is smaller

than the real value because of hydrolysis of the polymer by a small amount of water.

Krässig and Greber reported^{3,9} reversibility between a linear polyimine and a cyclic dimer prepared from terephthalaldehyde and a heteroatom-containing aliphatic diamine. The cyclic dimer was converted to linear polyimine by heating in a 4%



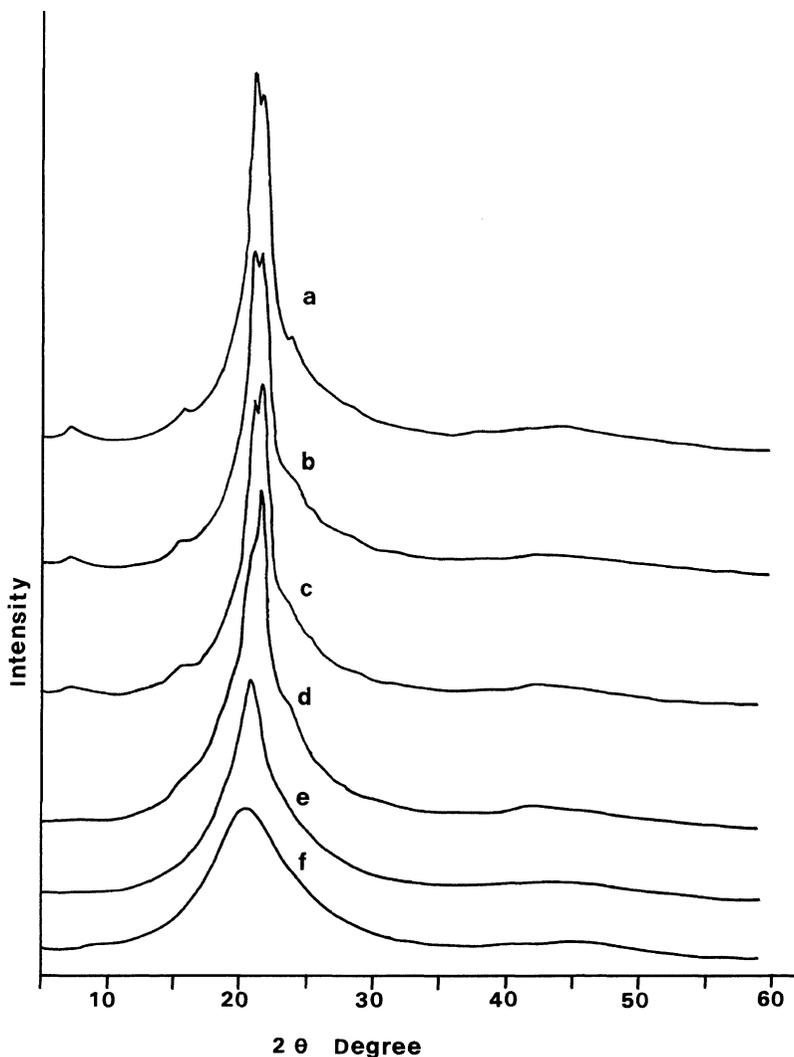


Figure 5. X-ray diffraction pattern of the polyimines obtained after a) 0.5, b) 1.0, c) 2.0, d) 5.0, e) 8.5, and f) 27 hours reactions.

benzene solution. When the same solution was cooled and diluted, the viscosity gradually decreased and the equilibrium shifted in the opposite direction over a period from 10 to 24 hours. In contrast to Krässig and coworkers' findings, our equilibrium depended only upon the concentration of the solute and required the presence of H_2O . η_{inh} became a constant value within about 2 minutes. No gradual lowering of viscosity was observed. It is therefore concluded that the above reversible reaction (B) is very rapid.

The polyimine could also be synthesized in HMPA in the same manner, though the polymer precipitated from the reaction medium. The polymer exhibited the same infrared spectrum as that prepared in *m*-cresol but had a higher and sharper T_m at 200°C and higher crystallinity. It was significantly soluble in *m*-cresol and even as in 98% H_2SO_4 . The reason for these differences is that cross-linking does not occur in HMPA because of a lack of hydrogen sources and polymer separation from the system.

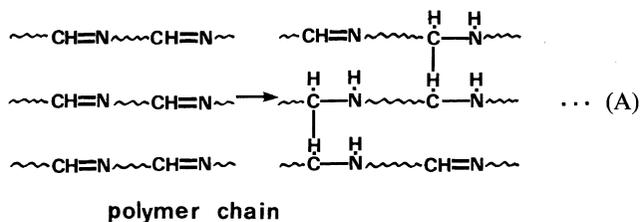


Figure 6. Postulated cross-linking reaction.

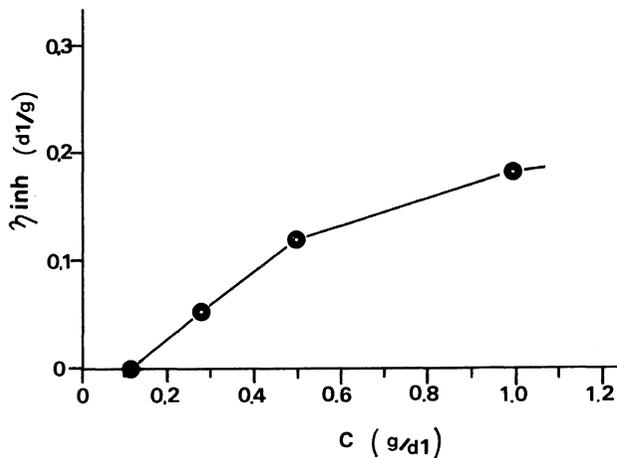


Figure 7. A viscosity-concentration curve in *m*-cresol.

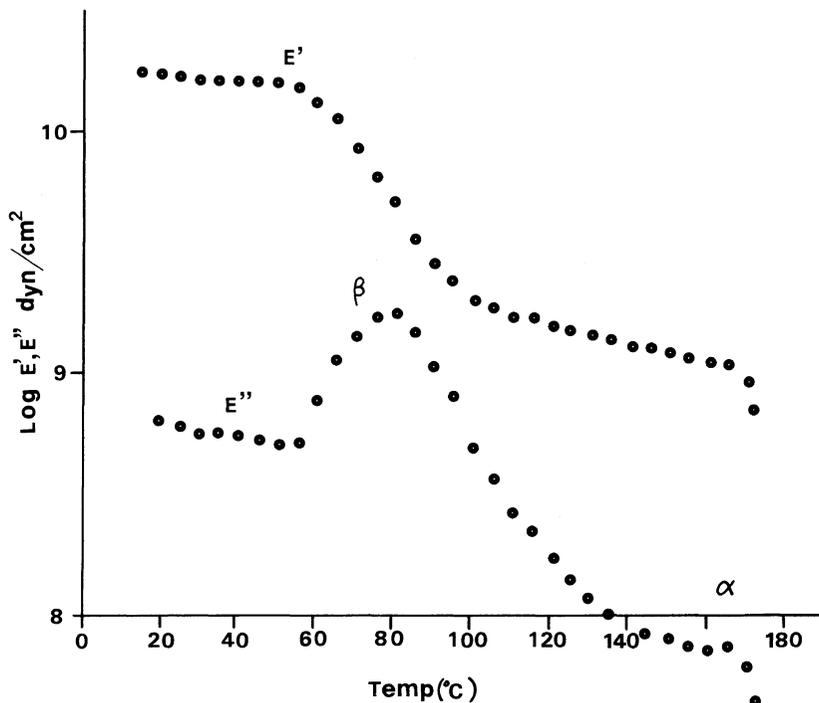


Figure 8. Dynamic storage and loss modulus vs. temperature (film) in air.

Figure 8 shows dynamic storage (E') and loss modulus (E'') curves of a polyimine film. This polymer has two dynamic mechanical relaxation peaks at 110 Hz from 20°C to 180°C. In order of decreasing temperature, these peaks are labeled α and β , respectively. The α peak at about 165°C corresponds to the T_m . The β peak at about 80°C is due to the T_g .

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