

Addition Polyimides. II. Synthesis and Characterization of Bisitaconimide Prepolymers

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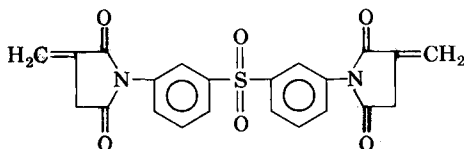
Synopsis

N,N'-bis(3,3'-itaconimidophenyl) sulfone has been synthesized by reacting itaconic anhydride with 3,3'-diamino diphenyl sulfone. The bisitaconimides and the intermediates were characterized by chemical analysis, IR, NMR, TG, and GPC. The degree of polymerization (DP) of the prepolymers of the bisitaconimide was followed by GPC and from the NMR data on vinylidene and aromatic proton ratios. The correlation between DP and intrinsic viscosity of the prepolymers was made use of to determine the Mark-Houwink constants (K and α). The thermal stability and the decomposition kinetics of the prepolymers were evaluated from TG data. The kinetic parameters, viz. energy of activation, E , and preexponential factor A , were computed using four nonisothermal integral equations, and their values are not appreciably affected by the degree of polymerization, within the range studied.

INTRODUCTION

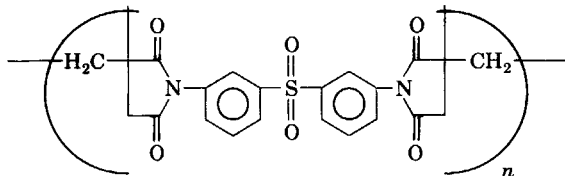
Aromatic polyimides are widely used as high temperature polymers in adhesives, laminates, coatings, electrical insulations, etc.¹⁻⁴ There are two types of polyimides, viz., condensation and addition polyimides. The latter, though marginally lower in thermal properties, has the great advantage of giving void-free structures, since the polymerization process does not evolve any gaseous byproducts.⁵ Bismaleimides are the ones commonly used in this category, and some aspects of the kinetics of their cure reaction and thermal decomposition have been reported by us recently.⁶ However, the polymers made from bismaleimides are generally brittle in character,⁷ while the ones from bisitaconimides have better flexibility. Bisitaconimides also homopolymerize faster than bismaleimides.⁸⁻¹⁰

In this communication we present our studies on the synthesis and characterization of *N,N'*-bis(3,3'-itaconimidophenyl) sulfone (I):



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It can undergo addition polymerization to give polymers of the following structure:



A similar structure has been proposed for the addition polymer obtained from bismaleimides.¹¹

The processing of the bisimides for making laminates generally involves the preparation of prepolymer intermediates.¹² The characterization of the prepolymer intermediate is, therefore, of considerable importance in order to obtain products with reproducible properties. In the present work, the molecular weight buildup of the prepolymer has been followed through gel-permeation chromatography, intrinsic viscosity measurements, and ¹H-NMR. The Mark-Houwink constants have been evaluated using the prepolymers. Their thermal stability and decomposition kinetics have also been studied using the TG data.

EXPERIMENTAL

Starting Materials

3,3'-Diaminodiphenyl sulfone was obtained from Hindustan Organic Chemicals, Ltd. (India), itaconic acid from Sigma Chemical Co. (U.S.), and dimethyl formamide from SD Fine Chemicals (India). Dimethyl formamide was distilled before use. Sodium acetate (anhydrous) and acetic anhydride were obtained from BDH. Acetic anhydride was also distilled before use.

Preparation of *N,N'*-Bis(3,3'-Itaconimidophenyl) Sulfone

N,N'-bis(3,3'-itaconimidophenyl) sulfone was prepared by the method similar to the one reported by Hartford et al.¹¹ It involves the formation of bisitaconamic acid by the addition reaction of 3,3'-diaminodiphenyl sulfone and itaconic anhydride, followed by chemical dehydration using acetic anhydride and sodium acetate.

Itaconic Anhydride

The dehydration of itaconic acid (1 mol) to itaconic anhydride was brought about by using phosphorous pentoxide (0.4 mol) in toluene as the solvent, in a round-bottomed flask, heated at 65–70°C for 2.5 h with constant stirring. Itaconic anhydride was obtained after distilling off the toluene at 55–60°C under reduced pressure. It was finally dried in a vacuum oven at 50–55°C. The product had a melting point of 67–69°C and the yield was 80–85%.

Bisitaconamic Acid Intermediate

3,3'-Diaminodiphenyl sulfone (0.2 mol) was dissolved in purified acetone in a 2-L three-necked flask. Itaconic anhydride (0.4 mol), dissolved in acetone,

was added with constant stirring to the amine solution. The temperature was maintained at 50–55°C for 3 h for the complete formation of bisitaconamic acid.

Imidization of Bisitaconamic Acid

Catalytic quantity of anhydrous sodium acetate was added to the above reaction mixture. This was followed by the dropwise addition of 1 mol of acetic anhydride. The reaction was continued for 6–7 h. The solution was cooled to room temperature and added slowly to distilled water, stirred continuously. The precipitated imide was filtered and washed free of acid impurities, using distilled water. 93–98% of *N,N'*-bis-(3,3'-itaconimidophenyl) sulfone was obtained.

Preparation of the Prepolymer of *N,N'*-Bis(3,3'-Itaconimidophenyl) Sulfone

The prepolymers of *N,N'*-bis(3,3'-itaconimidophenyl) sulfone were prepared by heating *N,N'*-bis(3,3'-itaconimidophenyl) sulfone in dimethyl formamide. *N,N'*-bis(3,3'-itaconimidophenyl) sulfone (200 g) was dissolved in 300 g of dimethyl formamide taken in a three-necked round bottomed flask, which was then placed on a water bath maintained at 92–95°C. The reaction mixture (10 mL) was withdrawn from the reaction flask at regular intervals of 1 h for 6 h, and added immediately in drops into 300 mL cold water. The precipitated prepolymers (P_1, P_2, \dots, P_6 obtained after 1, 2, ..., 6 h, respectively) were filtered through a sintered funnel. The precipitate was washed several times with distilled water, and dried in a vacuum oven at 45–50°C.

Instrumental

The IR spectra of the samples were recorded in KBr pellets, using a Perkin-Elmer Model 283 infrared spectrophotometer. $^1\text{H-NMR}$ spectra were recorded in DMSO-d_6 with JEOL MH-100 NMR spectrometer, using tetramethyl silane as the internal standard.

Carbon-hydrogen estimations were done with a Hermann-Moritz Model-10 semimicro semiautomatic elemental analyzer. The nitrogen estimation was done using the Kjeldahl method.

Gel permeation chromatograms of the samples were recorded on a Waters Associates Model 244 GPC equipped with a RI detector and data module M 730. Styragel (100 and 500 Å) columns were used with THF as the mobile phase (flow rate of 1 mL min⁻¹). The intrinsic viscosity of the samples was determined at 30°C, using Cannon-Ubbelohde dilution viscometer fitted with Wescan model 221 viscosity timer (precision 0.01 s). The solvent used was cyclohexanone.

Thermogravimetric analysis was done using a Dupont 990 Modular Thermal Analyzer in conjunction with a 951 Thermogravimetric Analyzer. The furnace atmosphere was dry nitrogen, purged at a rate of 50 cm³ min⁻¹. The heating rate was 10°C min⁻¹ and a constant sample mass of 5.0 ± 0.1 mg was used for the entire study. The computational work was done with CDC computer, using a FORTRAN IV program.

RESULTS AND DISCUSSION

The IR spectrum of the bisitaconamic acid is shown in Figure 1. The broad absorption region from 1600 to 1700 cm^{-1} is due to the overlap of the amide carbonyl and acid carbonyl stretching absorption. The broad absorption in the region 2500–3500 cm^{-1} is due to the O—H and N—H stretching. The peaks due to $-\text{SO}_2$ groups are observed at 1155 and 1330 cm^{-1} .

The $^1\text{H-NMR}$ spectrum of bisitaconamic acid (Fig. 2) showed the peaks caused by the vinylidene protons at 5.8 and 6.2 δ and those caused by aromatic protons between 7.8 and 8.2 δ . The $-\text{COOH}$ protons are observed at 11.0 δ . The integrated intensities of these protons are in the ratio 2:4:1, which agrees with the acid structure.

The acid value of the bisitaconamic acid, determined by titration against potassium hydroxide in DMSO as solvent and cresol red as indicator was found to be 237.0 mg KOH g^{-1} (theoretical: 237.7 mg KOH g^{-1}), corresponding to a purity of 99.7%. The melting point of bisitaconamic acid was found to be 190–192°C.

Bisitaconimide was characterized by IR (Fig. 3) and $^1\text{H-NMR}$ spectra (Fig. 4). In the IR spectrum, characteristic bands resulting from the imide group were observed at 1720 and 1780 cm^{-1} . The other prominent peaks at 1150 and 1380 cm^{-1} were caused by the $-\text{SO}_2$ group. In the $^1\text{H-NMR}$ spectrum the peaks caused by vinylidene and the aromatic protons were observed, and they were in the ratio 1:2, which agrees with the imide structure.

The TG curve of the bisitaconimide is shown in Figure 5, which shows that the imide is thermally stable up to about 380°C. There is an initial rapid weight loss, and the char residue at 600°C is around 45%.

The purity of the imide from GPC analysis is around 99% (Fig. 6). The percentages of carbon, hydrogen, and nitrogen were found to be 59.5% (theoretical: 60.5%), 3.4% (theoretical: 3.7%), and 6.2% (theoretical: 6.4%), respectively.

Determination of the Degree of Polymerization by Gel Permeation Chromatography

The degree of polymerization of the prepolymers was determined using GPC. A typical GPC curve of the prepolymer is shown in Figure 7. It was observed that the percentage of monomer (represented as A) was decreasing, while the percentage of the high molecular weight fraction (represented as B), was increasing from P_1 to P_6 . The results from GPC analysis are given in Table I. With an increase in reaction time, the percentage of A was found to decrease from 83.6% for P_1 to 33.9% for P_6 , while the percentage of B increased from 15.9% for P_1 to 66.1% for P_6 . There is a gradual increase in the mean molecular weight of B from 1200 to 1700, while that of A remains steady within the scatter observed in usual GPC experiments. The degree of polymerization of the product isolated at different time intervals was calculated from percentages of A and B and their respective molecular weights obtained from GPC. The average molecular weights of the samples P_1 – P_6 were calculated from the DP values.

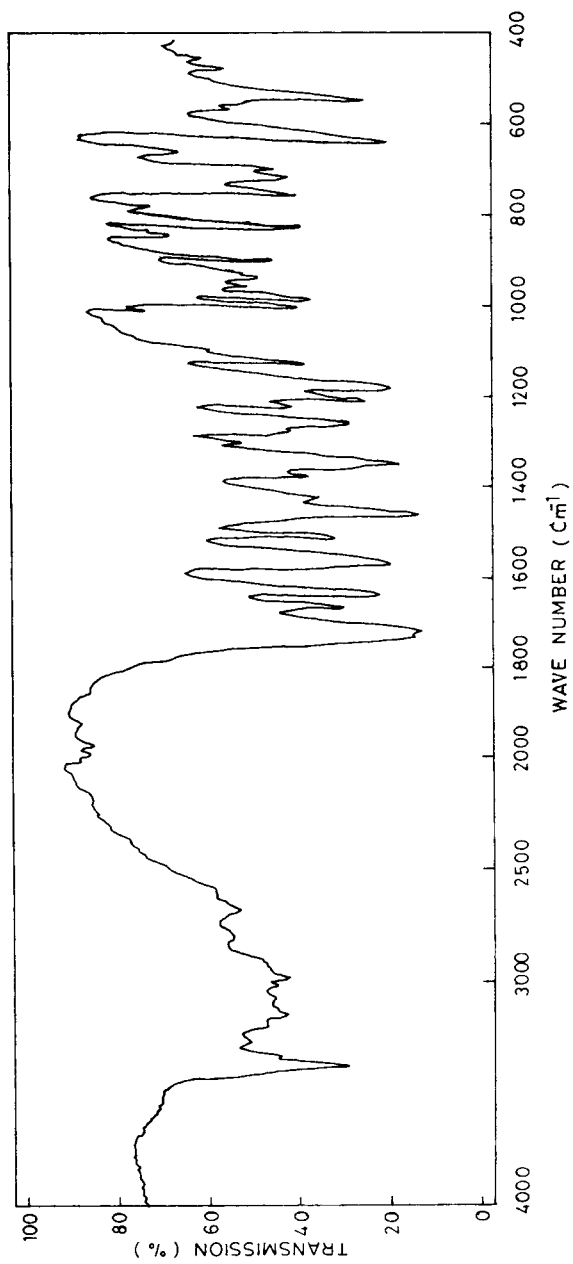


Fig. 1. IR spectrum of bisitaconamic acid.

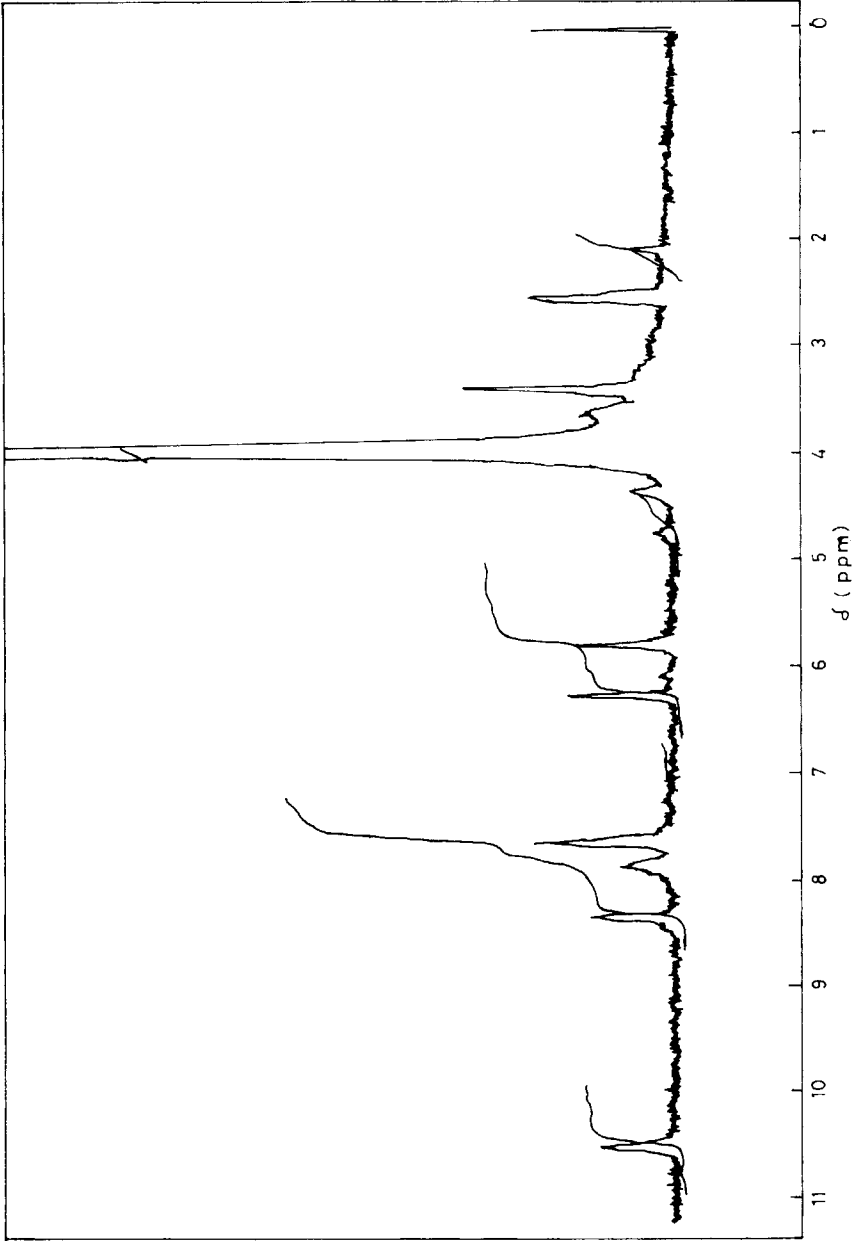


Fig. 2. ¹H-NMR spectrum of bisitaconamic acid.

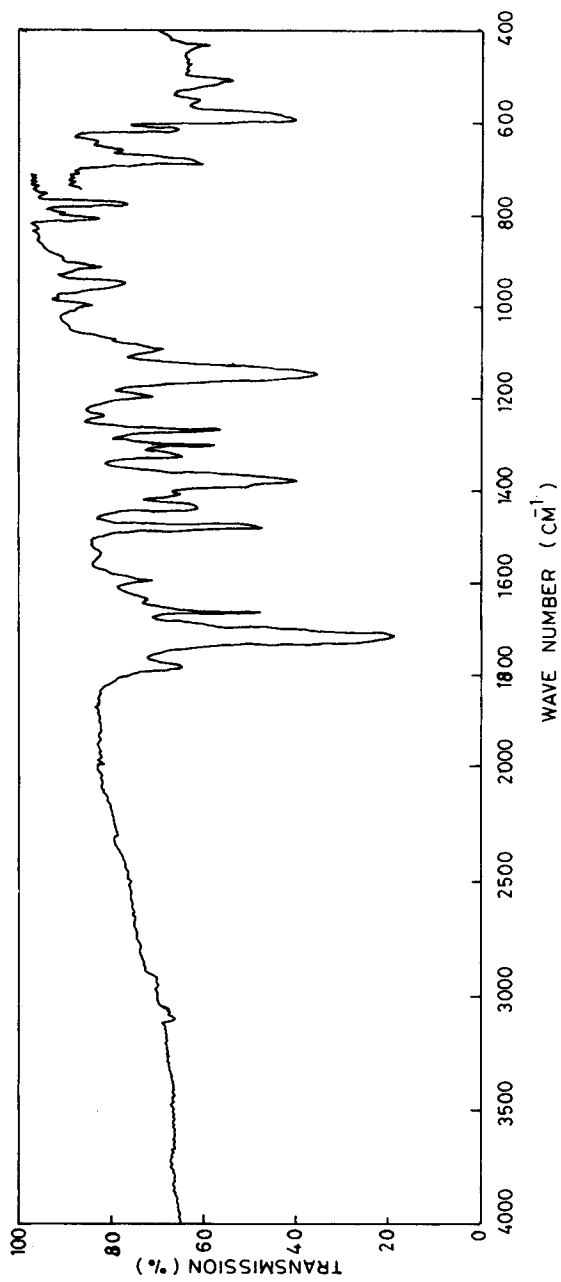


Fig. 3. IR spectrum of *N,N'*-bis(3,3'-itaconimidophenyl) sulfone.

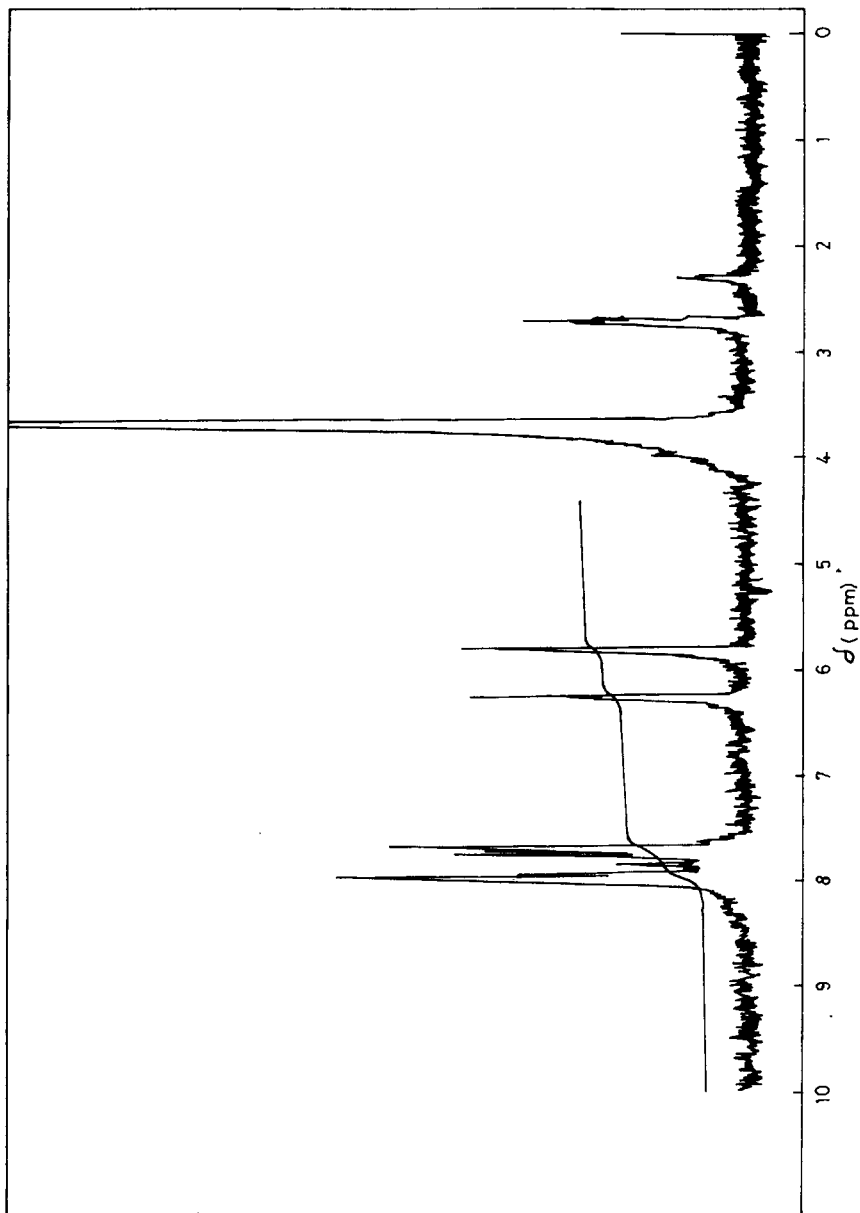


Fig. 4. ¹H-NMR spectrum of N,N'-bis(3,3'-itaconimidophenyl) sulfone.

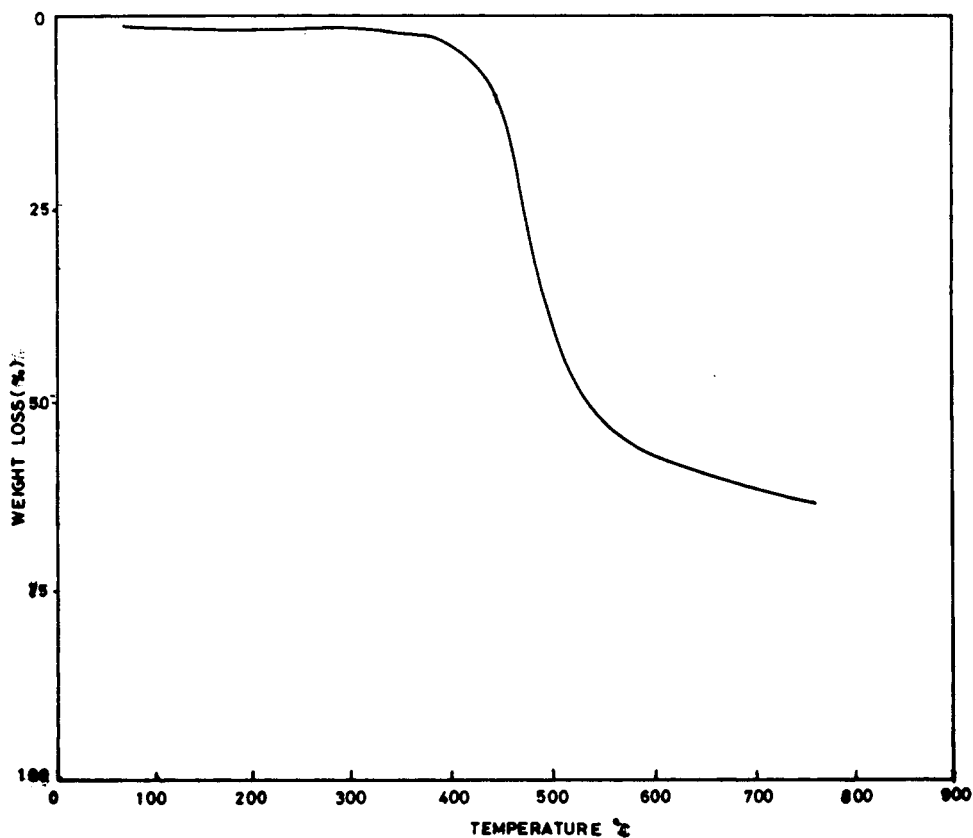


Fig. 5. TG curve of *N,N'*-bis(3,3'-itaconimidophenyl) sulfone.

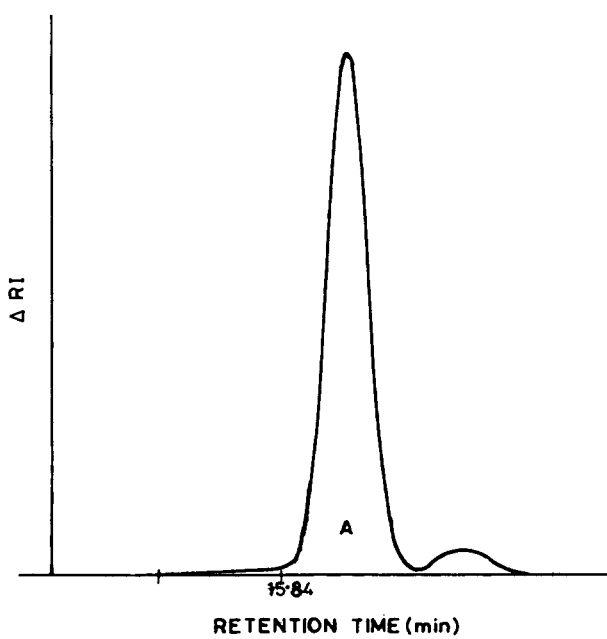


Fig. 6. GPC curve of *N,N'*-bis(3,3'-itaconimidophenyl) sulfone.

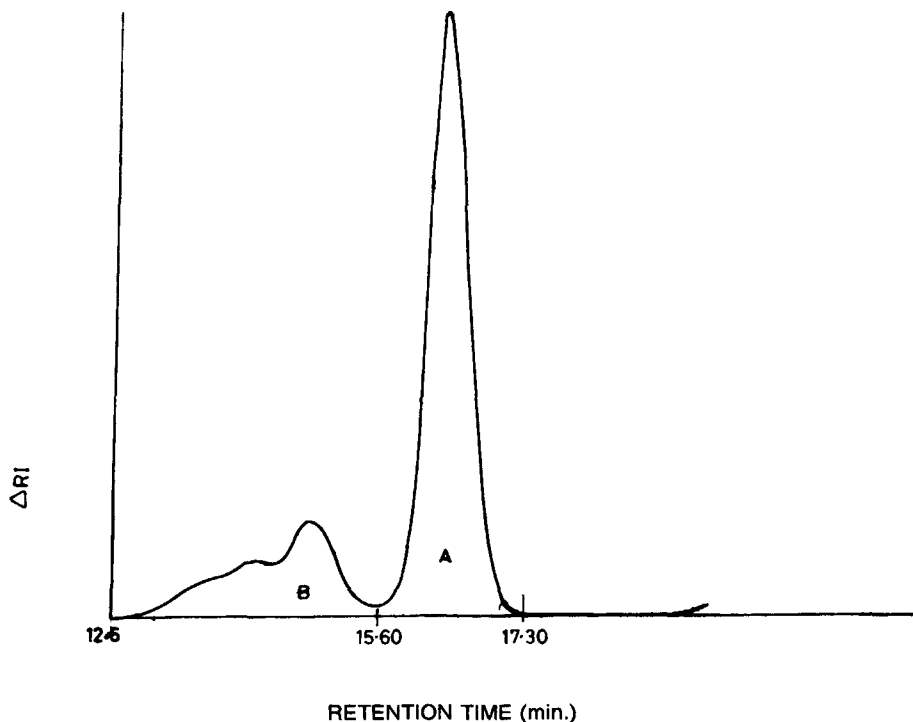


Fig. 7. GPC curve of prepolymer of bisitaconimide.

TABLE I
Results from GPC Analysis

Sample	% A	% B	Molecular weight of A	Molecular weight of B	Degree of polymerization	Average molecular weight (M_n)	Intrinsic viscosity $[\eta]$
P ₁	83.6	15.9	416	1242	1.31	570	0.031
P ₂	73.0	27.0	440	1367	1.57	684	0.032
P ₃	73.1	27.5	444	1388	1.59	693	0.034
P ₄	60.4	39.5	417	1411	1.94	847	0.040
P ₅	37.5	62.5	441	1750	2.86	1247	0.048
P ₆	33.9	66.1	410	1680	3.04	1326	0.059

Determination of the Degree of Polymerization by ¹H-NMR

The degree of polymerization was also calculated from the NMR data. The bisitaconimide monomer has two terminal vinylidene groups (i.e., four vinylidene protons) per molecule, and they are the sites for polymerization. The oligomers also have the same number of vinylidene protons per molecule. However, the number of aromatic protons in them increase as multiples of the DP. The number of aromatic and vinylidene protons for the monomer and oligomers are given in Table II.

If x is the integrated intensity of vinylidene protons and y that of the aromatic protons, in the NMR spectrum of a given sample, it can be shown that the DP of the sample is related to x and y by the equation

$$DP = y/2x$$

TABLE II
Aromatic:Vinylidene Proton in Oligomers (Theoretical)

DP	Vinylidene protons (X)	Aromatic protons (Y)	Ratio (Y/X)
1 (monomer)	4	8	2
2	4	16	4
3	4	24	6
4	4	32	8
⋮	⋮	⋮	⋮
<i>n</i>	4	8 <i>n</i>	2 <i>n</i>

The samples (P₁—P₆) were analyzed by ¹H-NMR, using DMSO-d₆ as solvent. For calculations of DP, the peaks other than those of the vinylidene (at 5.8 δ and 6.2 δ) and the aromatic protons (7.8 δ—8.2 δ) were not taken into account. It was observed that the intensities of the peaks, due to the vinylidene protons diminished with the increase in reaction time. The NMR spectra of the samples P₁ and P₆ are shown in Figures 4 and 8, respectively. DP was calculated from the above equation by substituting the values of *x* and *y* obtained for the samples. DP was found to increase from 1 for P₁ to 9.75 for P₆. From the values of DP, the molecular weight was calculated, and the values are given in Table III.

The values of DP obtained from GPC and ¹H-NMR data were found to be fairly close, except for P₆. For higher DP, as the number of vinylidene protons decreases, the values calculated from NMR data are less reliable.

The experimental conditions employed in this study (92–95°C) result in the formation of prepolymers of low molecular weight. To obtain high molecular weight polymer, higher temperature and pressure are required.¹¹

Determination of Mark-Houwink Constants

The relationship between intrinsic viscosity and molecular weight is given by the Mark-Houwink equation

$$[\eta] = KM^\alpha$$

where $[\eta]$ is the intrinsic viscosity, *M*, the molecular weight, *K* and α the Mark-Houwink constants. The above relation can also be written as:

$$\ln[\eta] = \ln K + \alpha \ln M$$

The intrinsic viscosities were found to increase from samples P₁–P₆ and these results are shown in Table I.

To determine *K* and α values using the GPC data, a linear plot of $\ln M$ vs. $\ln[\eta]$ was made, and it is shown in Figure 9. The values of *K* and α were evaluated from the slope and intercept of this plot, and were found to be 3.05×10^{-4} and 0.721, respectively. The correlation coefficient was calculated to be 0.972.

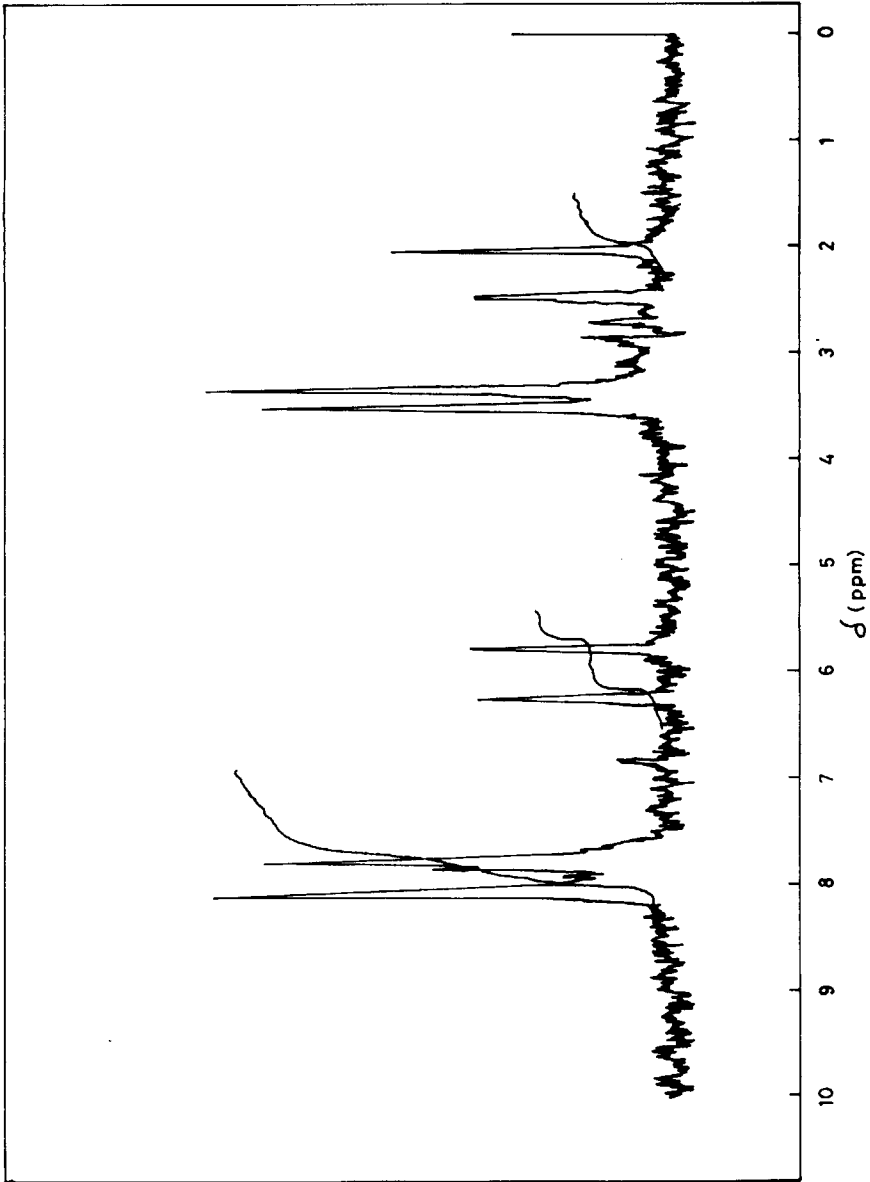


Fig. 8. $^1\text{H-NMR}$ spectrum of prepolymer of bisitaconimide (P_6).

TABLE III
DP and Molecular Weight from NMR Data

Sample	Degree of polymerization	Molecular weight (M_n')
P ₁	1.05	458
P ₂	1.12	488
P ₃	1.24	540
P ₄	2.48	1081
P ₅	2.61	1138
P ₆	9.75	4251

In a similar way, K and α values were evaluated using the M_n' values obtained from NMR data. $\ln M_n'$ was plotted against $\ln[\eta]$ (fig. 10). The values of K and α were evaluated from the slope and intercept of this plot, and were found to be 5.76×10^{-3} and 0.283, respectively. The correlation coefficient was calculated to be 0.968. The higher value of correlation coefficient and a more reasonable value of α (falling between 0.5 and 1.0) show that the GPC data is more reliable.

Thermal Stability and Thermal Decomposition Kinetics

Thermogravimetry has been extensively used for the evaluation of thermal stability and thermal decomposition kinetics of polymers.¹³ These studies have also been extended to oligomers of low molecular weight.¹⁴ Hence, it is attempted to evaluate the thermal decomposition parameters of the bisitaconimide prepolymers using TG experiments. Figure 11 shows the TG curves of the prepolymer samples P₁-P₆. The temperature of inception of the major decomposition reaction, T_i , and the temperature of completion of the reaction, T_f , were determined from TG curves. The values of T_i and T_f along with the percentage char residue obtained at 650°C are given in Table IV. These values are not appreciably affected by the degree of polymerization.

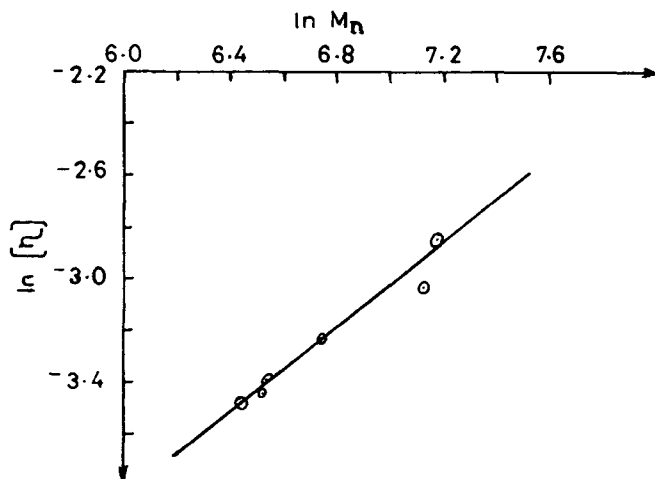
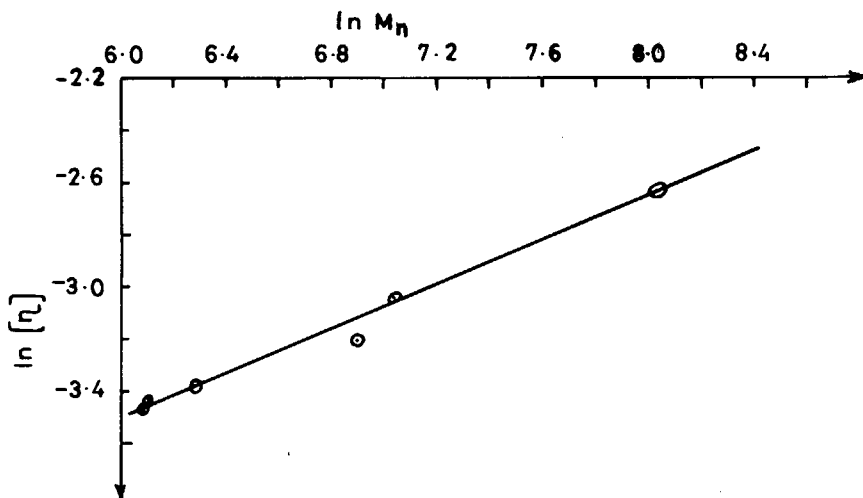


Fig. 9. $\ln M_n$ vs. $\ln[\eta]$.

Fig. 10. $\ln M_n'$ vs. $\ln[\eta]$.

The kinetic parameters, viz., energy of activation, E , preexponential factor A , and order parameter n , for the thermal decomposition of the bisitaconimide prepolymers were computed using four integral equations. In the equations given below, a term $g(\alpha)$ is used for convenience and is defined as

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n}$$

(1) Madhusudanan-Krishnan-Ninan (MKN) equation¹⁵

$$\ln \frac{g(\alpha)}{T^{1.9215}} = \ln \frac{AE}{\phi R} + 3.77205 + 1.9215 \ln E - 0.120394(E/T)$$

(2) Coats-Redfern (CR) equation¹⁶

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AR}{\phi E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT}$$

TABLE IV
TG Results of Bisitaconimide Prepolymers

Sample	Volatile matter (%)	T_i (°C)	T_f (°C)	% Residue at 650°C
P ₁	1.5	388	612	39
P ₂	2.0	390	617	40
P ₃	1.5	387	612	39
P ₄	2.0	390	617	40
P ₅	2.0	393	617	40
P ₆	2.5	382	612	38

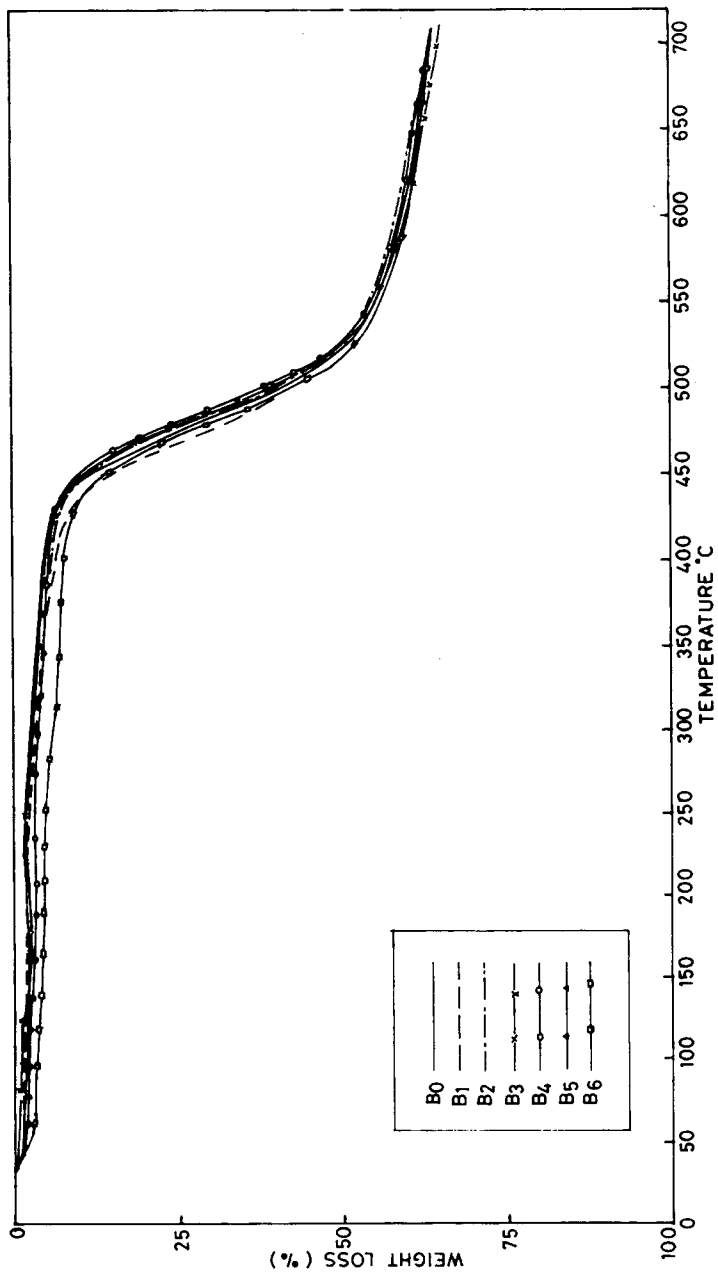


Fig. 11. TG curves of prepolymers of bisitaconimide: (—) B₀; (---) B₁; (-·-·) B₂; (-x-x-) B₃; (-o-o-) B₄; (-▲-) B₅; (-□-) B₆.

(3) MacCallum–Tanner (MT) equation¹⁷

$$\log g(\alpha) = \log \frac{AE}{\phi R} - 0.483E^{0.435} - \frac{(0.449 + 0.217E)10^3}{T}$$

(4) Horowitz–Metzger (HM) equation¹⁸

$$\ln g(\alpha) = \ln \frac{ART_s^2}{\phi E} - \frac{E}{RT_s} + \frac{E\Theta}{RT_s^2}$$

where α = fraction decomposed, T = temperature (K), ϕ = heating rate in K s^{-1} , R = gas constant, T_s = DTG peak temperature, and $\Theta = T - T_s$.

A computational method was used for the determination of the order parameter, and the MKN equation was used for this purpose. Linear plots of $\ln g(\alpha)/T^{1.9215}$ vs. $1/T$ were drawn by the method of least squares, by taking α and T values from the TG experiments. Curves were drawn for different values of n ranging from 0 to 3 in the increment of 0.05 and the best fit value of n was found to be 2. Using this value of n , the values of E and A were computed with the four kinetic equations, and they are given in Table V. The correlation coefficients are near unity (above 0.99), in all the cases indicating nearly perfect linear fits.

From Table V it can be seen that the energy of activation for the thermal decomposition of the bisitaconimide prepolymers is in the range of 52–57 kcal mol^{-1} and the preexponential factor in the range of 10^{12} – 10^{14} . The E and A values obtained from the four equations are nearly the same. The kinetic parameters are not significantly affected by DP; the minor variations are irregular, well within the scatter usually observed in TG experiments.¹⁹ Compared to the corresponding bismaleimide,⁶ the values of E and A are lower here, which agrees with the relative lower thermal stability of bisitaconimides.

CONCLUSIONS

The present study's important conclusions are given below:

- i. *N,N'*bis(3,3'-Itaconimidophenyl) sulfone (*I*) has been synthesized and its structure confirmed by IR, NMR, and chemical analysis.
- ii. The DP computed from NMR data on the ratio of vinylidene and aromatic protons in the prepolymers of bisitaconimide shows good agreement with the values from GPC for lower DP. However, as the DP increases and the number of vinylidene protons decreases, the values calculated from the NMR data are less reliable, and they deviate from the GPC results.
- iii. The intrinsic viscosities of the prepolymers increased from 0.031 to 0.059 with increase in DP. The computed values of the Mark–Houwinks constants determined from GPC and NMR are $K = 30.5 \times 10^{-4}$, 5.76×10^{-3} , and $\alpha = 0.721$, 0.283, respectively. A better correlation is obtained in the case of the GPC results.

TABLE V
Kinetic Parameters for the Thermal Decomposition of Bisitaconimide Prepolymers

Sample	Madhusudan-Krishnan-Ninan		Coats-Redfern		MacCallum-Tanner		Horowitz-Metzger	
	E	r	E	r	E	r	E	r
P ₁	52.05	8.356×10^{12}	51.92	7.718×10^{12}	53.29	2.297×10^{13}	53.67	2.396×10^{13}
P ₂	54.42	3.671×10^{13}	54.35	2.531×10^{13}	55.73	1.136×10^{14}	57.04	1.966×10^{14}
P ₃	54.42	3.671×10^{13}	55.39	7.267×10^{13}	56.79	2.387×10^{14}	57.56	2.833×10^{14}
P ₄	52.70	1.084×10^{13}	55.63	1.042×10^{13}	54.00	3.275×10^{13}	54.99	4.657×10^{13}
P ₅	52.02	7.427×10^{12}	51.95	7.138×10^{12}	53.32	2.223×10^{13}	54.19	2.938×10^{13}
P ₆	57.05	2.126×10^{14}	56.98	2.048×10^{14}	58.40	6.892×10^{14}	59.26	8.604×10^{14}

iv. The kinetic parameters are not appreciably affected by DP. The activation energy for decomposition of the prepolymers is in the range of 52–57 kcal mol⁻¹ and the *A* values are in the range of 10¹²–10¹⁴ s⁻¹. These values are lower to those of the corresponding bismaleimide, which also has higher thermal stability.

We thank Mr. T. M. Vijayan for help in the synthetic work and Dr. M. Kanakavel and Miss Bina Korah for help in NMR and GPC analyses. We also thank SSD, SPPC, and the Director, VSSC for the permission to publish this paper.

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Received December 18, 1986

Accepted May 14, 1987