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Synthesis of *N*-Substituted Bisitaconimide Monomers for Use as Thermosetting Polyimide Resins

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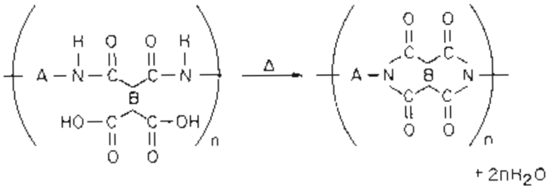
Synopsis

Two monomeric *N*-substituted bisitaconimides, *N,N'*-bisitaconimido-*p,p'*-diphenylmethane and *N,N'*-bis(itaconimido-*p,p'*-diphenyl ether), were synthesized from the corresponding diamines. The synthesis was accomplished by reaction of the diamine with itaconic anhydride and cyclocondensation of the resultant bisitaconamic acid. Attempts to use *p,p'*-diaminodiphenylsulfone as the diamine gave *N,N'*-biscitraconimido-*p,p'*-diphenylsulfone and *N*-citraconimido-*N'*-itaconimido-*p,p'*-diphenylsulfone instead of the bisitaconimide. The two bisitaconimides polymerize thermally at 180°C and 225°C, respectively, and yield tough polymers with very high thermal stability.

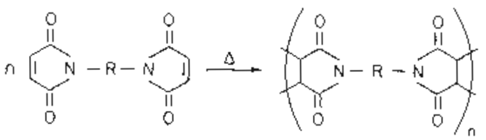
INTRODUCTION

Polyimides are one of a growing number of classes of thermosetting resins which offer very high thermal stability and high-temperature mechanical strength. The most common synthesis of polyimides takes place by the cyclocondensation of the corresponding polyamic acid.[1,2] Unfortunately, volatile by-products are evolved which interfere with the curing of the polymer [eq. (1)].



(1)

Here A and B can be a wide variety of organic moieties, usually aromatic for higher thermal stability. In recent years, the use of *N*-substituted bismaleimide monomers has eliminated the problem of volatiles from polyimide synthesis.[3] With the bismaleimides, the imide bonds are preformed in the monomer, and the polymer is subsequently formed by an addition type reaction [eq. (2)].



(2)

Here R is generally an aromatic structure to enhance the thermal stability of the polymer. However, it is a rather general rule that 1,2-disubstituted ethylenes, such as maleimides, do not readily homopolymerize,[4,5] and it would be advantageous to use a more reactive species. It has been shown that itaconic deriva-

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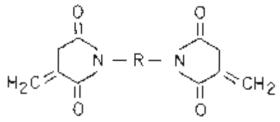
tives homopolymerize by an addition type reaction more readily than maleic derivatives.[6–9] Therefore, it is reasonable to speculate that itaconimides may be more suitable than maleimides as precursors for polyimides. There has been very little discussion of itaconimides in the literature,[10–14] and we wish to report the synthesis of several *N*-substituted bisitaconimides, which yield polyimides upon thermal curing. These *N*-substituted bisitaconimides have the general structure:



EXPERIMENTAL

Materials and Instrumentation

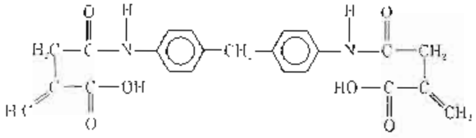
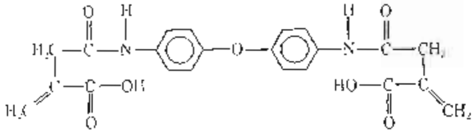
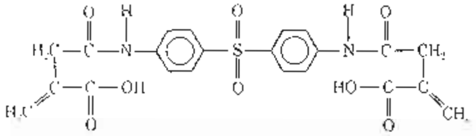
The *N*-substituted bisitaconimides were prepared by the method of Searle.[15] First, the bisitaconamic acid was formed from a diamine and itaconic anhydride. Then the amic acid was dehydrated by using acetic anhydride and sodium acetate to give the bisitaconimide. All chemicals were reagent grade and were used directly as obtained from the supplier. Diamines and chloroform were obtained from Aldrich Chemical Company, itaconic acid from Pfizer Chemicals Division, acetic anhydride, silica gel, and phosphorus pentoxide from Baker Chemical Company, sodium acetate from Eastman Chemicals Division, and acetone from Mallinckrodt Chemical Company.

Melting-point determinations were performed by using a Thomas Hoover uni-melt apparatus and are uncorrected. Melting points were also determined by differential thermal analysis (DTA) with a DuPont 990 differential thermal analyzer. Infrared spectra were taken on a Perkin-Elmer Model 180 infrared spectrometer. NMR spectra were obtained with a 100-MHz Varian HA 100 spectrometer. The liquid chromatographs were run on a Waters Associates Model 202/401 high-pressure liquid chromatograph equipped with a differential ultraviolet detector and an M6000 pumping unit. Thermogravimetric analysis (TGA) was performed by using a DuPont 950 thermogravimetric analyzer. Elemental analysis was done by I. J. Wilk Associates, Stanford, Calif.

Synthesis of Itaconic Anhydride

Itaconic anhydride was prepared in the laboratory from itaconic acid by use of phosphorus pentoxide as the dehydrating agent.[16] The reaction is carried out by mixing 2.0 moles of itaconic acid and 1.5 moles (excess) of phosphorus pentoxide in a 3-liter reaction flask containing 2 liters of chloroform. The mixture is allowed to reflux with stirring for 24 hr. After refluxing, the chloroform solution is decanted from the viscous brown residue at the bottom of the flask, and the volume of solution is reduced to 1 liter by rotary evaporation. The remaining chloroform solution is cooled to −10°C, resulting in crystallization of itaconic anhydride from the solution. Three crops of white crystals, mp 68°C, can be obtained in this manner. The average yield is about 85%.

TABLE I
Characteristics of Monomeric Bisitaconamic Acid Compounds

Bisitaconamic acid	Melting point, °C		Elemental analysis					Physical description	Yield, %
			C, %	H, %	N, %	O, %	S, %		
 I	211–212	Calcd Found	65.40 64.96	5.21 5.25	6.64 6.51	22.75 22.29		Slightly yellow powder	94
 II	195–196	Calcd Found	62.26 61.97	4.72 4.76	6.60 6.46	26.42 26.42		Slightly grey powder	91
 III	201–202	Calcd Found	55.93 55.78	4.24 4.39	5.93 5.50	27.12 27.03	6.78 6.30	White powder	61

General Synthesis of Bisitaconamic Acids

The synthesis of the bisitaconamic acids is similar to the synthesis of the monoitaconamic acids.[11] A 0.5-mole portion of the appropriate primary diamine is dissolved in 2 liters of acetone in a 3-liter round-bottomed flask, and 1.1 mole (10% excess) of itaconic anhydride is added slowly. A slight excess of the anhydride is used to assure complete reaction of the diamine so that no monoamic acid is present. After addition of the itaconic anhydride, the mixture is refluxed with stirring for 24 hr. The bisitaconamic acid that precipitates from the acetone is collected by suction filtration and washed with fresh acetone. After air drying at room temperature for 24 hr, the product is vacuum-dried at 75°C to remove any remaining solvent. The yields of the different bisitaconamic acids are given in Table I.

General Synthesis of Bisitaconimides

The bisitaconimides are made by the cyclocondensation of the bisitaconamic acids. First, 0.06 mole of the bisitaconamic acid is suspended in 700 ml of acetone in a 1-liter round-bottomed flask. Next, 0.18 mole (excess) of acetic anhydride, the dehydrating agent, and 1.0 g of sodium acetate, as catalyst, are added to the suspension. The mixture is refluxed with stirring until the solution just becomes clear and no solid remains. Then the reaction mixture is poured into 8 liters of distilled water with vigorous stirring, causing the imide to precipitate. The imide is filtered and washed with copious quantities of distilled water. After air-drying at room temperature for 24–48 hr, the imide is vacuum-dried at 75°C to remove any remaining solvent. The product, a mixture of bisimides, is obtained in 80–90% yield.

Isolation of Pure Bisimides

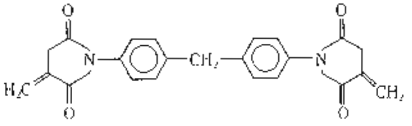
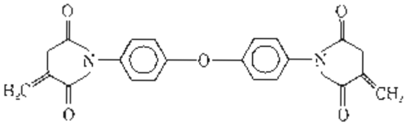
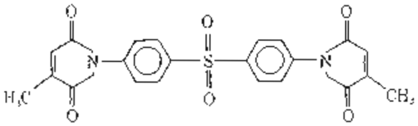
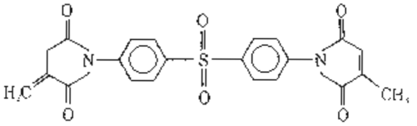
The mixtures resulting from the cyclocondensation of the different bis(itaconamic acids) were fractionated by using a 4.9 cm (i.d.) × 100 cm chromatographic column filled with 60–200 mesh silica gel. For each mixture, 50 g of material was fractionated at a time, chloroform being used as the eluting solvent. Fractions were collected in 250 ml volumes and examined by high-pressure liquid chromatography (HPLC) to determine which fractions contained only one species and which fractions contained more than one. Pure compounds were obtained by rotary evaporation of the solvent from the pure fractions. The yields of the different bisimides which were obtained by this process are given in Table II.

RESULTS AND DISCUSSION

Characterization of Bisitaconamic Acids

Three different diamines were used in the synthesis of the bisitaconamic acids: *p,p′*-diaminodiphenylmethane; *p,p′*-diaminodiphenyl ether; and *p,p′*-diaminodiphenylsulfone. The resulting amic acids were *N,N′*-bisitaconamic acid-*p,p′*-diphenylmethane (I), *N,N′*-bisitaconamic acid-*p,p′*-diphenyl ether (II), and *N,N′*-bisitaconamic acid-*p,p′*-diphenylsulfone (III), respectively. There are two structural isomers possible for the itaconamic acids:

TABLE II
Characteristics of Monomeric Bisimide Compounds

Bisimide	Melting point, °C		Elemental analysis					Physical description	Yield, %
			C, %	H, %	N, %	O, %	S, %		
 IV	160–161	Calcd Found	71.51 71.09	4.66 4.67	7.25 7.09	16.58 16.65		White powder	32
 V	210–211[a]	Calcd Found	68.04 67.98	4.12 4.15	7.22 7.07	20.62 20.59		White powder	44
 VIa	214–215	Calcd Found	60.55 60.35	3.67 3.67	6.42 6.18	22.02 22.00	7.34 7.25	White powder	10
 VIb	240–241	Calcd Found	60.55 60.46	3.67 3.74	6.42 6.20	22.02 22.19	7.34 7.10	White powder	26

[a] See discussion in text.

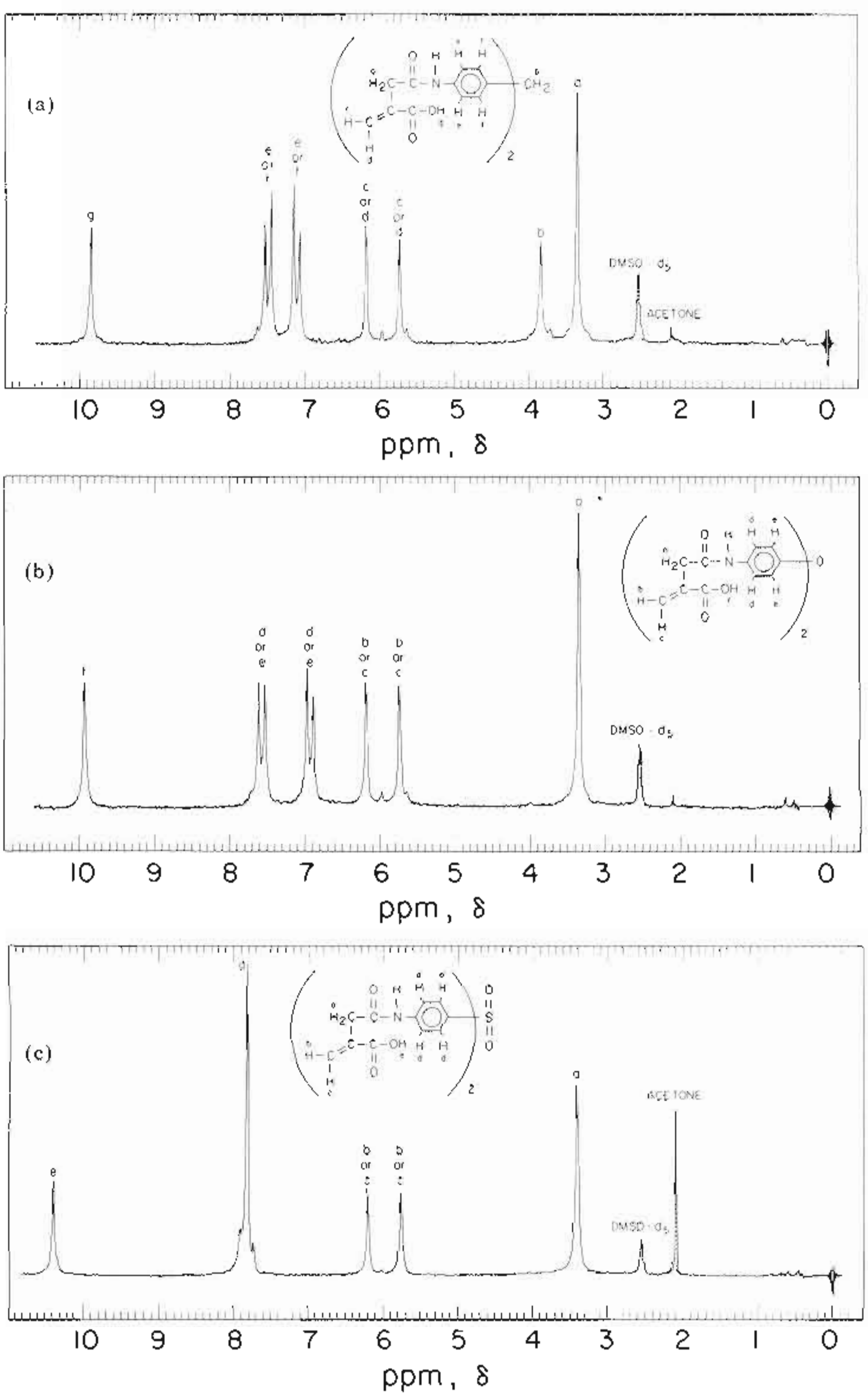
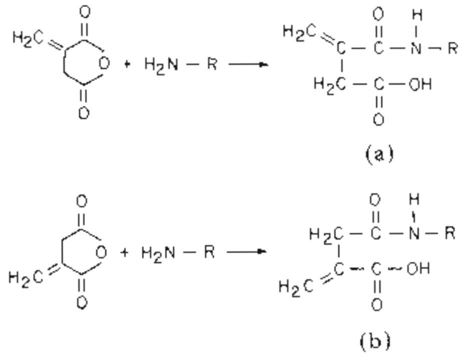
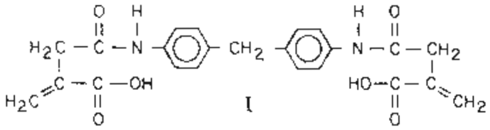


Fig. 1. 100-MHz ^1H-NMR spectra of (*a*) *N,N'*-bisitaconamic acid-*p,p'*-diphenylmethane, (*b*) *N,N'*-bisitaconamic acid-*p,p'*-diphenyl ether, and (*c*) *N,N'*-bisitaconamic acid-*p,p'*-diphenylsulfone in DMSO-d_6.

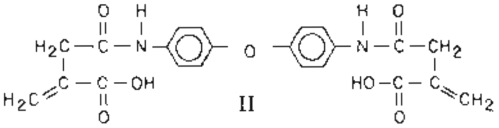


(3)

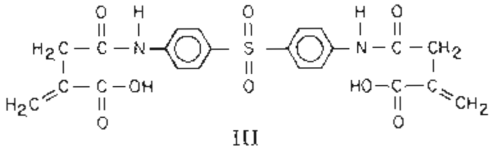
It has been demonstrated[17] that only one product, (b), is obtained. Therefore, the bisitaconamic acids have the structures I–III.



I



II



III

Figure 1 shows the 100-MHz ^{1}H-NMR spectra of the bisitaconamic acids I, II, and III. The different resonances in the spectra are assigned, but the absence of a resonance for the amide hydrogen indicates a very rapid equilibrium between amide-bound hydrogen and solvated hydrogen ion. This rapid equilibrium broadens the peak to the point where it is unobservable. Also, there are two small peaks at 5.64 and 5.96 ppm. These small peaks may be due to the presence of small amounts of the isomer in which the amine has attached to the conjugated carbonyl. The small peaks do occur in the same region of the spectrum as the larger itaconic methylene hydrogen peaks.

Figure 2 shows the infrared spectra of the bisitaconamic acids I, II, and III. In each spectrum there is a broad absorption region from approximately 1600 to 1700 cm^{-1}. This broad absorption is due to overlap of the amide carbonyl and acid carbonyl stretching absorptions of the amic acid. It should be pointed out that even though there is a very broad absorption in the region 2500–3500 cm^{-1} due to the OH stretch of the amic acid, there is also a significant contribution in this region due to the OH stretch of H_2O. The H_2O could not be completely eliminated from the KBr pellets.

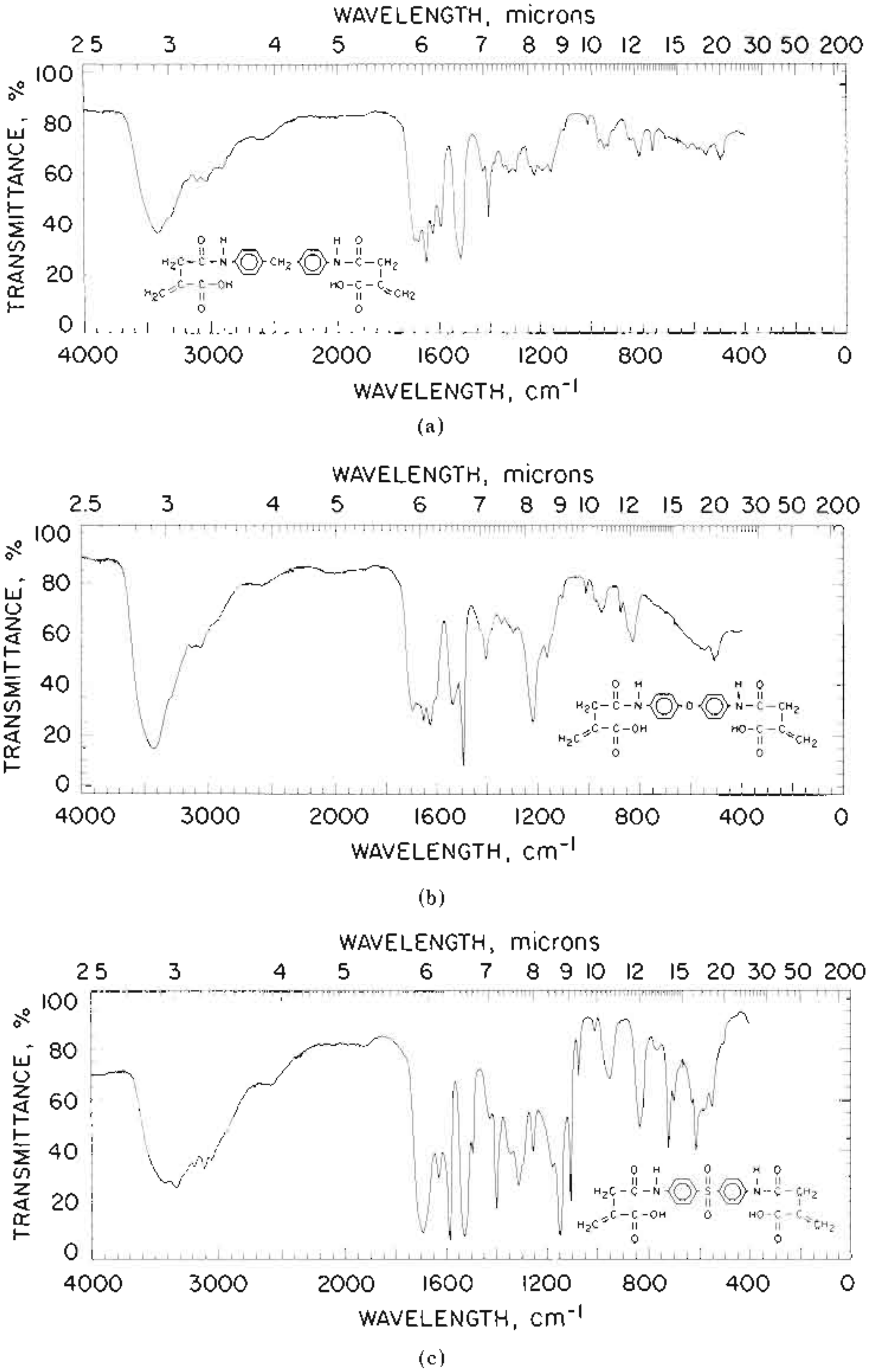


Fig. 2. Infrared spectra of (*a*) *N,N′*-bisitaconamic acid-*p,p′*-diphenylmethane, (*b*) *N,N′*-bisitaconamic acid-*p,p′*-diphenyl ether, and (*c*) *N,N′*-bisitaconamic acid-*p,p′*-diphenylsulfone in KBr pellet form.

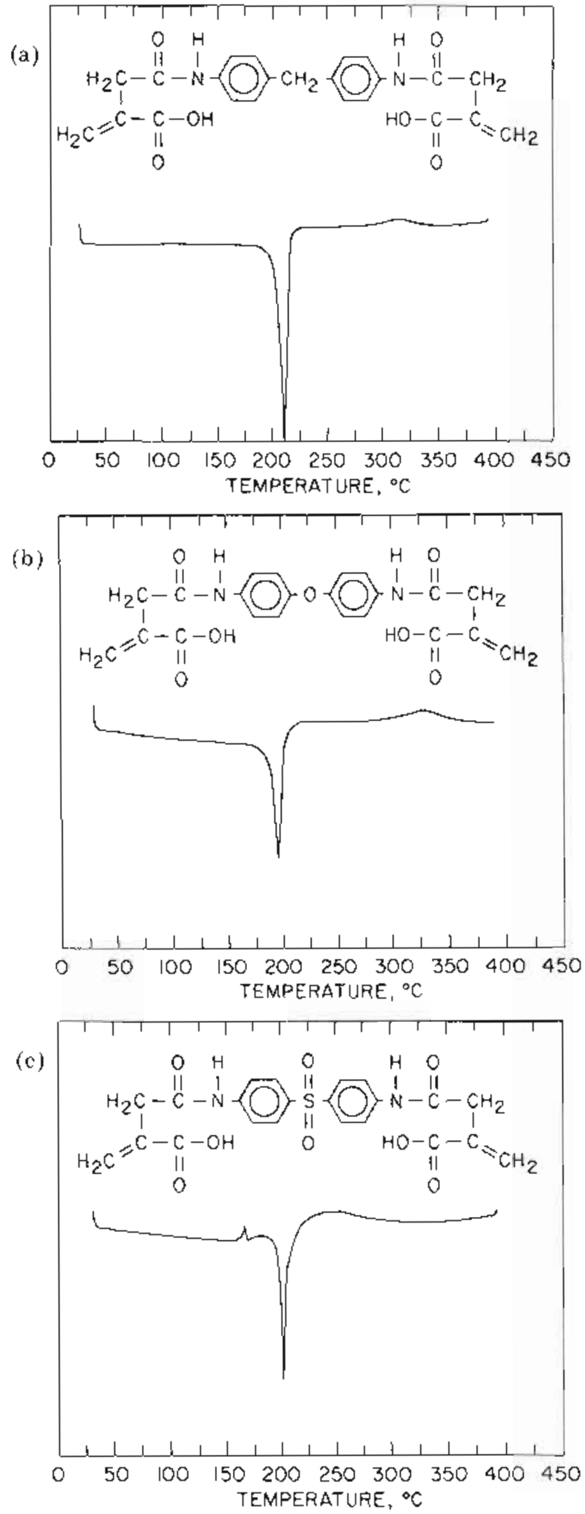


Fig. 3. Differential thermal analysis plots of (*a*) *N*,*N*′-bisitaconamic acid-*p*,*p*′-diphenylmethane, (*b*) *N*,*N*′-bisitaconamic acid-*p*,*p*′-diphenyl ether, and (*c*) *N*,*N*′-bisitaconamic acid-*p*,*p*′-diphenylsulfone with alumina as the reference and a heating rate of 10°C/min.

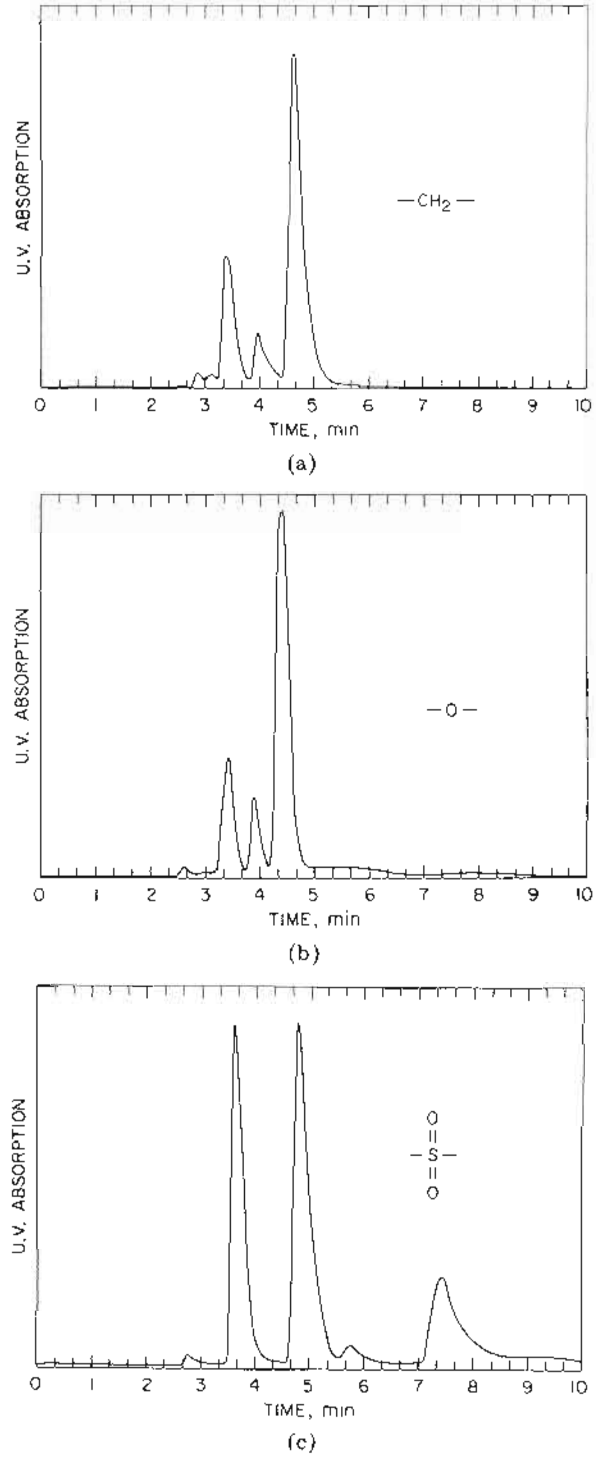


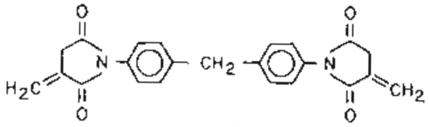
Fig. 4. High-pressure liquid chromatographs of the reaction products of the cyclodehydration reactions of (*a*) *N,N'*-bisitaconamic acid-*p,p'*-diphenylmethane, (*b*) *N,N'*-bisitaconamic acid-*p,p'*-diphenyl ether, and (*c*) *N,N'*-bisitaconamic acid-*p,p'*-diphenylsulfone by use of a Microporasil (Waters Associates) column.

Figure 3 contains the DTA data for the bisitaconamic acids I, II, and III. These compounds exhibit normal melting behavior which was substantiated by using a standard melting point apparatus. The melting point data, elemental analysis, physical description, and yield of each compound are given in Table I. The slight coloration in compounds I and II could be due to slight amounts of impurity. The low yield of compound III is reproducible and cannot be accounted for.

Characterization of Bisitaconimides

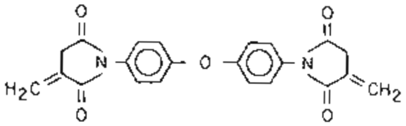
Figures 4*a*, 4*b*, and 4*c* show the high-pressure liquid chromatographs (HPLC) of the reaction products which resulted from the cyclocondensation of the bis(itaconamic acids) I, II and III, respectively. Only the major component, IV, was isolated in the pure form from the cyclocondensation products of bis(itaconamic acid) I. Compound IV corresponds to the peak appearing at 4.6 min in Figure 4*a*. Only the major component, V, was isolated in the pure form from the cyclocondensation products of bis(itaconamic acid) II. Compound V corresponds to the peak appearing at 4.4 min in Figure 4*b*. Compounds VIa and VIb were both isolated in the pure form from the cyclocondensation products of bis(itaconamic acid) III. Compounds VIa and VIb correspond to the peaks at 3.6 min and 4.8 min, respectively, in Figure 4*c*.

Figure 5 shows the 100-MHz ^{1}H-NMR spectra of compounds IV, V, VIa, and VIb. Figure 5*a* is the NMR spectrum of IV, which was identified as *N,N'*-bisitaconimido-*p,p'*-diphenylmethane.



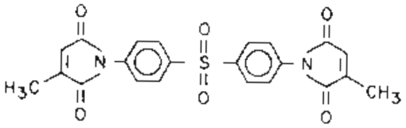
IV

Figure 5*b* is the NMR spectrum of V, which was identified as *N,N'*-bisitaconimido-*p,p'*-diphenyl ether.



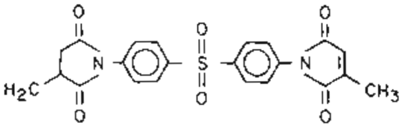
V

Figure 5*c* is the NMR spectrum of VIa, which was identified as *N,N'*-biscitraconimido-*p,p'*-diphenylsulfone.



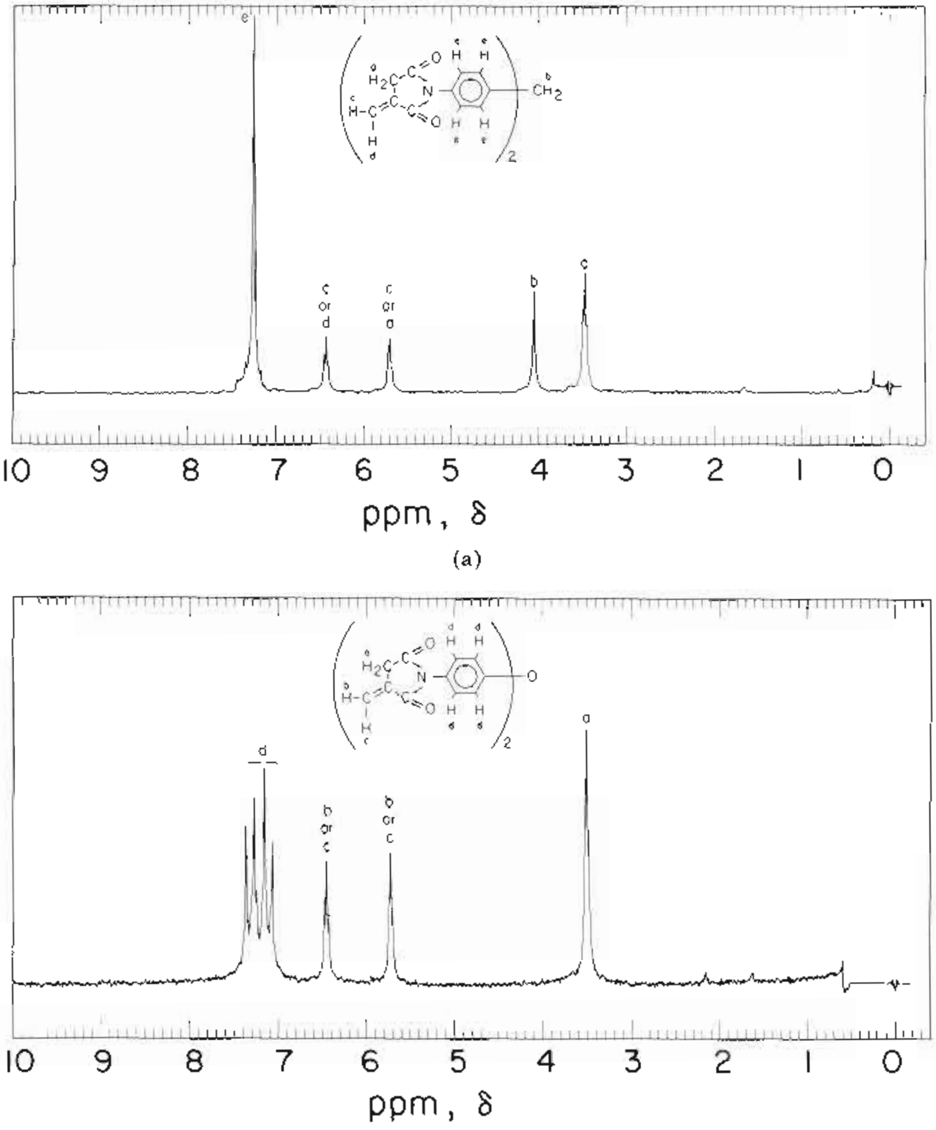
VI a

Figure 5*d* is the NMR spectrum of VIb, which was identified as *N*-citraconimido-*N'*-itaconimido-*p,p'*-diphenylsulfone.



VI b

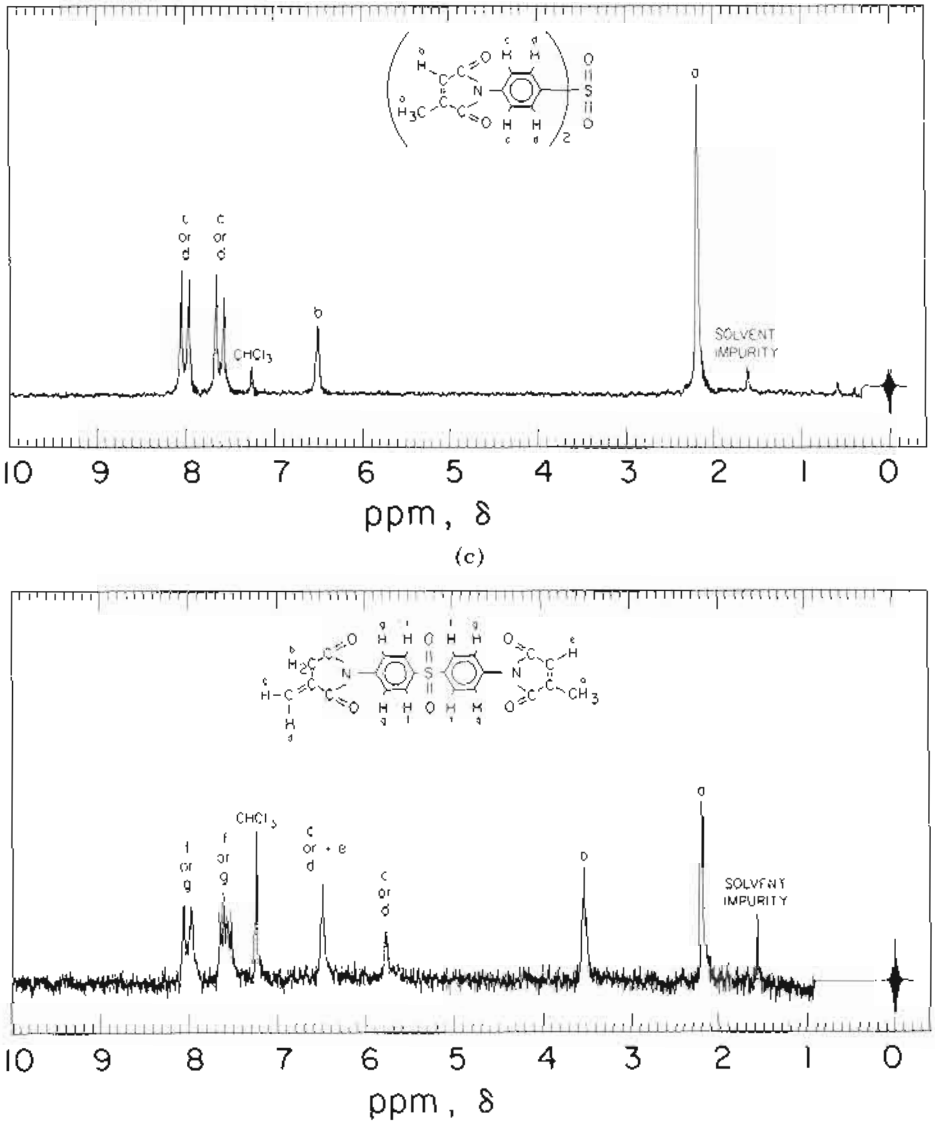
The low signal/noise level in Figure 5*d* is a result of the low solubility of the bisimide, VIb, in $CDCl_3$. Attempts to dissolve this compound in other solvents



(a)

(b)

Fig. 5. 100-MHz ^{1}H-NMR spectra of the products that were isolated pure from the cyclocondensation reaction of the bisitaconamic acids I, II, and III: (*a*) *N,N'*-bisitaconimido-*p,p'*-diphenylmethane, (*b*) *N,N'*-bisitaconimido-*p,p'*-diphenyl ether, (*c*) *N,N'*-biscitraconimido-*p,p'*-diphenylsulfone, and (*d*) *N*-citraconimido-*N'*-itaconimido-*p,p'*-diphenylsulfone in $CDCl_3$.



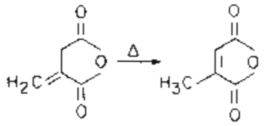
(c)

(d)

Fig. 5 (*continued from the previous page*)

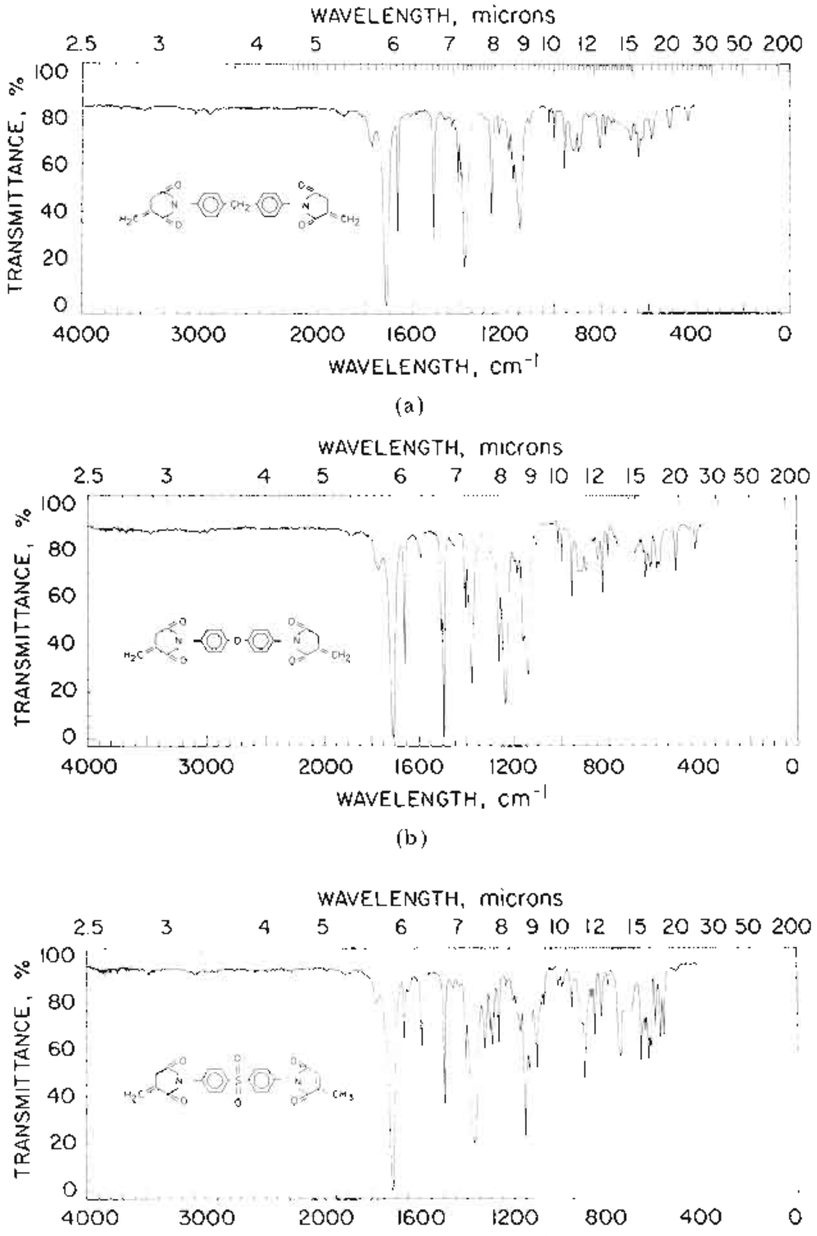
such as acetone-d_6, acetonitrile-d_3, and DMSO-d_6 produced a pink solution which gave an altered NMR spectrum.

The presence of citraconimide as a by-product of itaconimide synthesis is not unexpected, since the isomerization of itaconic anhydride to citraconic anhydride [eq. (4)] is known to take place readily.[18] The citraconimide is distinguished in the NMR spectra by a peak at 6.44 ppm and another, approximately three times as large, at 2.15 ppm.



(4)

Figure 6 shows the infrared spectra of the bisimides IV, V, VIa, and VIb. All of the spectra show the large absorption at 1710 cm^{-1} which is characteristic of imides. The spectral region from approximately 700–800 cm^{-1} is obscured by the absorption of the C—Cl stretch of the solvent.

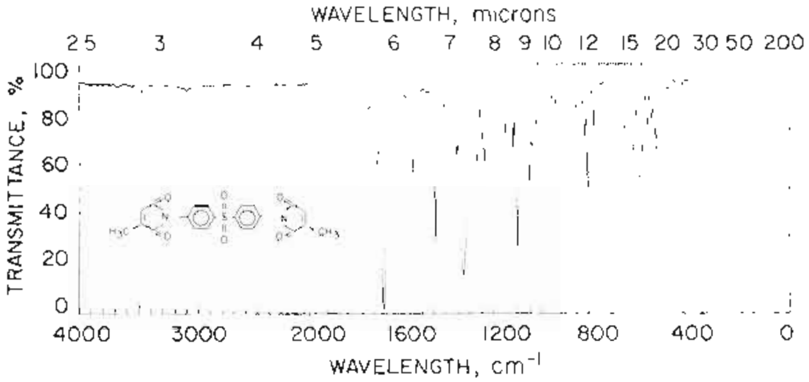


(a)

(b)

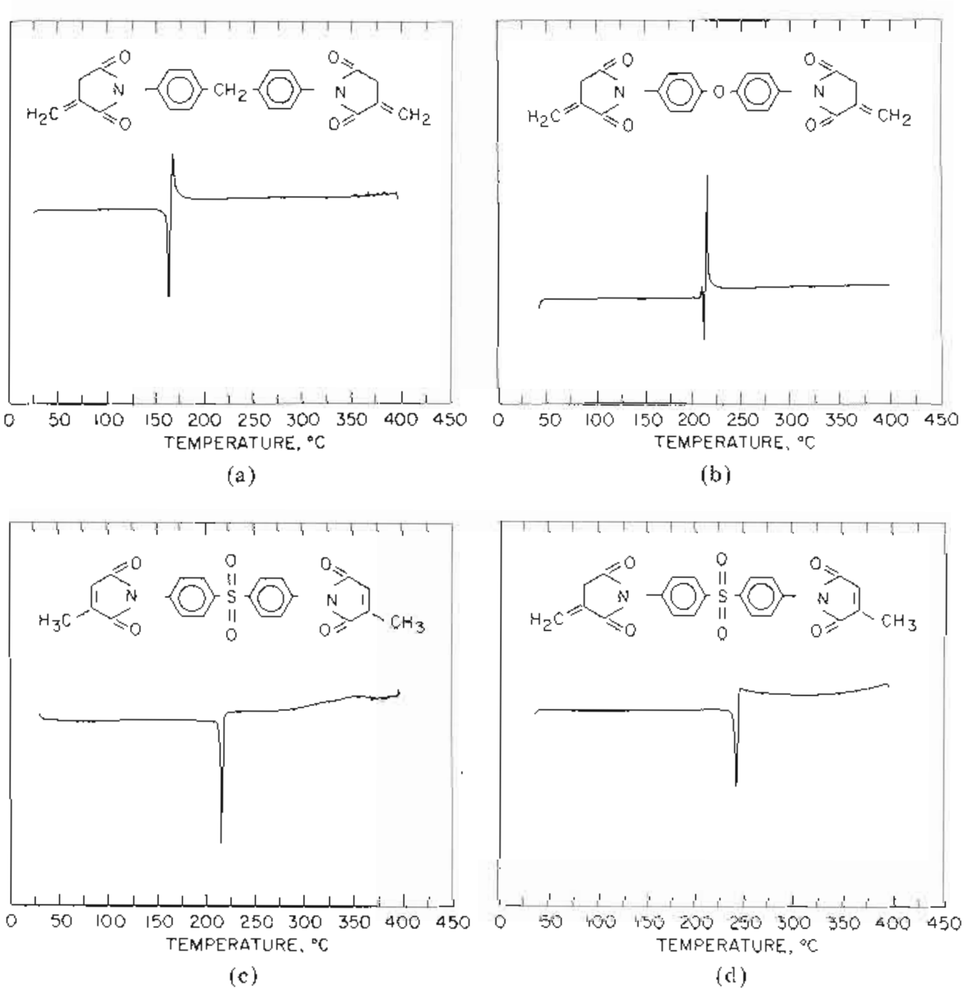
(c)

Fig. 6. Infrared spectra of (*a*) *N,N'*-bisitaconimido-*p,p'*-diphenylmethane, (*b*) *N,N'*-bisitaconimido-*p,p'*-diphenyl ether, (*c*) *N,N'*-biscitraconimido-*p,p'*-diphenylsulfone, and (*d*) *N*-citraconimido-*N'*-itaconimido-*p,p'*-diphenylsulfone in $CDCl_3$ with the use of a matched 0.1-mm reference cell.



(d)

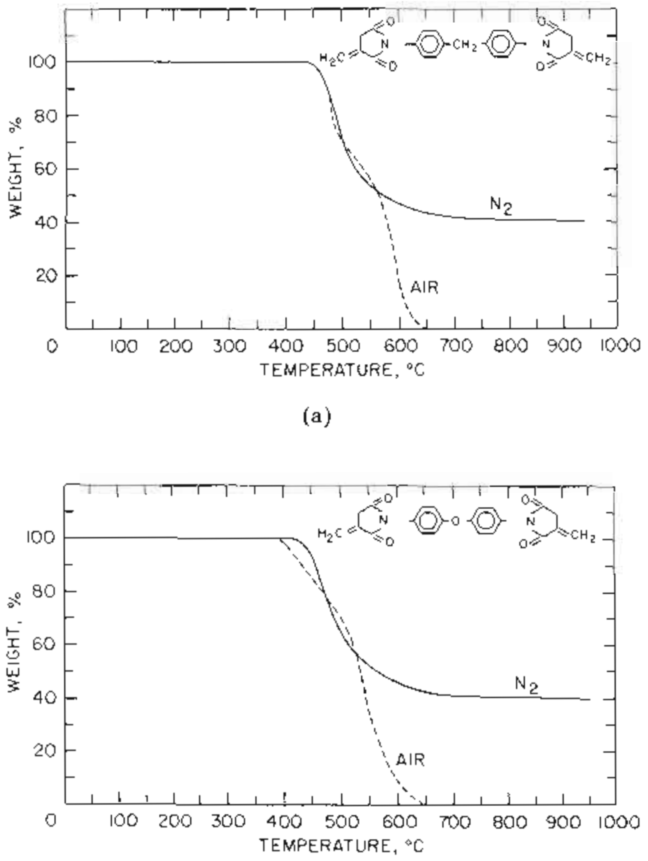
Fig. 6 (*continued from the previous page*)



(a) (b)

(c) (d)

Fig. 7. Differential thermal analysis plots of (*a*) *N,N'*-bisitaconimido-*p,p'*-diphenylmethane, (*b*) *N,N'*-bisitaconimido-*p,p'*-diphenyl ether, (*c*) *N,N'*-biscitraconimido-*p,p'*-diphenylsulfone, and (*d*) *N*-citraconimido-*N'*-itaconimido-*p,p'*-diphenylsulfone with alumina as the reference and a heating rate of 10°C/min.



(a)

(b)

Fig. 8. Thermogravimetric analsis of (*a*) poly(*N*,*N*′-bisitaconimido-*p*,*p*′-diphenylmethane) and (*b*) poly(*N*,*N*′-bisitaconimido-*p*,*p*′-diphenyl ether) with a heating rate of 10°C/min.

The DTA data for the bisimides IV, V, VIa, and VIb are shown in Figure 7. It is interesting to note that the bisitaconimides IV and V show a strong exotherm just after the endotherm of melting. It is believed that this exotherm is caused by the thermally induced polymerization of double bonds in the bisitaconimides. In correlating the DTA data with standard melting point tests, it was observed that the bisitaconimide V did not melt when heated from room temperature to the 210–211°C melting point shown in Figure 7*b*. However, the compound did melt when immersed directly into an oil bath at 211°C, but not less than that temperature. Apparently, if the compound is heated gradually, sufficient crosslinking occurs at lower temperatures so that melting does not occur at the normal melting temperature. The observation that the bisitaconimide IV shows normal melting behavior when heated gradually is attributed to the fact that it has a lower melting point, and sufficient thermal crosslinking to prevent melting does not occur. Table II summarizes the melting point data of the bisimides, IV, V, VIa, and VIb as determined by DTA and standard techniques, as well as elemental analysis, physical description, and yields of these compounds.

Thermal Polymerization of the Monomeric Bisitaconimides

The two bisitaconimides, IV and V, were thermally polymerized by heating in a cylindrical press of 1.25 in. diameter at 2500 psi for 24 hr. Bisitaconimide IV was heated to 180°C and bisitaconimide V was heated to 225°C. Both compounds yielded tough, light yellow, transparent disks with a density of approximately 1.3 g/cm^3. Figure 8 shows the TGA data for the two polymers. These curves show that the bisitaconimide polymers have very high thermal stability, which is comparable to that of the bismaleimide polymers. Further physical tests are currently being conducted on the bisitaconimide polymers.

References

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