

# Synthesis, Characterization, and Polymerization of Bismaleimides and Bisnadimides Chain-Extended by *N,N'*-Substituted Ureas

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## Synopsis

A series of new polymer precursors such as bismaleimides, bisnadimides, and bismethylnadimides chain-extended by *N,N'*-substituted ureas was synthesized and characterized. They were prepared by reacting a diamine containing ureylene linkages with maleic/nadic/methylnadic anhydride. Another alternative method for preparing these monomers included reaction of a diamine (1 mol) with an equimolar amount of maleic/nadic/methylnadic anhydride, subsequent reaction with a diisocyanate (0.5 mol) followed by cyclodehydration of the intermediate diamic acid. The monomers were characterized by infrared (IR) and proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy. Their thermal polymerization was investigated by differential thermal analysis (DTA). The thermal stability of the polymers was evaluated by dynamic thermogravimetric analysis (TGA) and isothermal gravimetric analysis (IGA). No weight loss was observed when the polymers containing arylureas in their backbone were heated up to 324–334°C in nitrogen or air atmospheres. Their anaerobic char yield at 800°C fluctuated between 41 and 61%.

## INTRODUCTION

Maleimide or nadimide end-capped monomers and oligomers are prime candidates as matrix resins for fiber-reinforced composites. This is primarily because of their stability at elevated temperatures and hot-wet environment.<sup>1</sup>

The major disadvantage of maleimide and nadimide resins is their brittleness due to the extensive crosslinking attained during polymerization through the olefinic bonds. To overcome this problem, several bismaleimides or bisnadimides chain-extended by various imide<sup>2,3</sup> or amide<sup>4</sup> structures have been prepared and characterized recently.

We now report the synthesis and characterization of a new class of bismaleimides and bisnadimides containing ureylene linkages in their backbone. These chain-extended polymer precursors should afford less brittle cured resins due to the presence of the flexible ureylene groups. However, these resins are expected to show a lower thermal stability than those obtained from bismaleimides or bisnadimides containing imide or amide bridging groups because the ureylene linkages are less thermally stable.<sup>5–7</sup> The effect of urea structure on thermal stability is of interest because of increasing demands for

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urea-urethane polymers which retain good mechanical properties at high temperatures.<sup>8,9</sup>

## EXPERIMENTAL

### Reagents and Solvents

Maleic anhydride and 5-norbornene-2,3-dicarboxylic anhydride (nadic anhydride) (Merck) were purified by recrystallization from acetic anhydride and chloroform, respectively. *p*-Phenylenediamine (Aldrich) was sublimed at about 110°C under vacuum (2–3 mm). Hexamethylene-1,6-diisocyanate (Aldrich) and methylenebis(4-phenylenediisocyanate) (Merck) were purified by distillation under reduced pressure (bp 120–125°C/10 mm and 185–188°C/4 mm, respectively). Toluene diisocyanate (Merck) utilized a mixture of the 2,4- and 2,6-isomer of 65 and 35%, respectively, was also distilled under reduced pressure (bp 126°C/11 mm). 1,4-Phenylene diisocyanate, 4-nitrophenyl isocyanate, 4-nitroaniline, and methyl-5-norbornene-2,3-dicarboxylic anhydride (methyl nadic anhydride) (Aldrich) were used as supplied. *N,N*-dimethyl formamide (DMF) (Aldrich) were refluxed in the presence of calcium hydride and then distilled under reduced pressure.

### Preparation of Monomers

#### *Preparation of Bismaleimide 1*

Granular 4-nitroaniline (2.8317 g, 20.50 mmol) was added portionwise to a stirred solution of 4-nitrophenyl isocyanate (3.2224 g, 20.00 mmol) in acetone (40 mL) under nitrogen atmosphere. The reaction solution was stirred at ambient temperature for about 2 h and subsequently refluxed for another 2 h. The pale yellow solid precipitated was filtered, washed with a dilute solution of hydrochloric acid, next with a solution of sodium carbonate, and finally with water. It was dried to yield *N,N'*-bis(4-nitrophenyl)urea (4.35 g, 72%) having mp 312–314°C.

*N,N'*-bis(4-nitrophenyl)urea (3.8203 g, 12.64 mmol), DMF (20 mL) and a small quantity of catalyst, 10% palladium on carbon, were introduced in a hydrogenation flask of a Parr apparatus. The hydrogenation was carried out under a pressure of 3.5 atm at room temperature for 2 h and subsequently at about 50°C for 3 h. The initially heterogenous reaction mixture became a homogenous solution at the end of hydrogenation. After filtration of the catalyst, the filtrate was concentrated under reduced pressure and moderate heating to remove about one-half of the solvent. The concentrate was subsequently poured into water. The pale brown solid thus obtained was filtered, washed with water, and dried to afford *N,N'*-bis(4-aminophenyl)urea (2.71 g, 88%), which did not melt up to 350°C. It was recrystallized from DMF–MeOH (2 : 1 vol/vol).

Maleic anhydride (1.9612 g, 20.00 mmol) dissolved in DMF (7 mL) was added dropwise to a stirred solution of *N,N'*-bis(4-aminophenyl)urea (2.4227 g, 10.00 mmol) in DMF (15 mL) under nitrogen atmosphere. A slightly exothermic reaction was observed and the reaction solution was stirred at

room temperature for 4 h. Bismaleamic acid precipitated as a pale brown solid which could be dissolved in the reaction mixture by moderate heating. A part of the solid precipitated was collected by filtration, washed with water, and dried to yield the required for characterization bismaleamic acid. Cyclodehydration was accomplished by adding acetic anhydride and fused sodium acetate (300 mL and 27 g, respectively, per mol of water condensed) to the reaction mixture and heating at 90°C for 2.5 h. The reaction mixture was poured over crushed ice to yield bismaleimide 1 as a brown solid. This was filtered, washed with a dilute solution of sodium bicarbonate, next with water, and finally with methanol and dried (3.66 g, 91%).

*Preparation of Bismaleimide 5 by Reacting Toluene-2,4- and -2,6-bis(N,N'-4-Aminophenylurea) with Maleic Anhydride*

A mixture of toluene diisocyanate (1.7416 g, 10.00 mmol), 4-nitroaniline (2.8317 g, 20.50 mmol), and DMF (25 mL) was stirred and heated at 90°C for 5 h in a stream of N<sub>2</sub>. The reaction mixture was subsequently poured into water. The yellow solid thus obtained was filtered, washed with a dilute solution of hydrochloric acid, next with a solution of sodium carbonate, and finally with water. It was dried to yield toluene-2,4- and -2,6-bis(N,N'-4-nitrophenylurea) (3.33 g, 74%). Recrystallizations from DMF-methanol (3:1 vol/vol) gave a sample having mp 306–308°C (decomposition) which was spectroscopically characterized as follows: IR (KBr) cm<sup>-1</sup>: 3340 (NH stretching); 2880 (CH<sub>3</sub>); 1690 (C=O); 1590, 1485 (aromatic); 1545, 1330 (NO<sub>2</sub>). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ: 8.90 (bs, 4H, NHCONH, exchangeable to D<sub>2</sub>O); 8.20 (m, 4H, aromatic ortho to NO<sub>2</sub>); 7.90–7.20 (m, 7H, aromatic ortho to NH and aromatic of toluene ring); 2.25 (s, 3H, CH<sub>3</sub>).

A solution of recrystallized toluene-2,4- and -2,6-bis(N,N'-4-nitrophenylurea) (3.6032 g, 8.00 mmol) in DMF (25 mL) and a small quantity of catalyst, 10% palladium on carbon, were introduced in a hydrogenation flask of a Parr apparatus. The hydrogenation was carried out under a pressure of 3.5 atm at room temperature until no more hydrogen was taken up. After removal of the catalyst by filtration, the solution was poured into water to afford toluene-2,4- and -2,6-bis(N,N'-4-aminophenylurea) as a brown solid. The product was filtered, washed with water, and dried (2.62 g, 84%). Recrystallizations from DMF-acetonitrile (1:1 vol/vol) gave a sample which did not melt up to 340°C. It was spectroscopically characterized as follows: IR (KBr) cm<sup>-1</sup>: 3370–3210 (NH stretching); 2900 (CH<sub>3</sub>); 1645 (C=O); 1605, 1510 (aromatic); 1550 (NH deformation and C—N stretching). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ: 8.40 (bs, 4H, NHCONH, exchangeable to D<sub>2</sub>O); 7.80–7.20 (m, 7H, aromatic ortho to NH and aromatic of toluene ring); 6.80 (m, 4H, aromatic ortho to NH<sub>2</sub>); 4.60 (s, 4H, NH<sub>2</sub>, exchangeable to D<sub>2</sub>O); 2.10 (s, 3H, CH<sub>3</sub>).

Maleic anhydride (1.9612 g, 20.00 mmol) dissolved in DMF (8 mL) was added portionwise to a stirred solution of recrystallized toluene-2,4- and -2,6-bis(N,N'-4-aminophenylurea) (3.9043 g, 10.00 mmol) in DMF (15 mL) under nitrogen atmosphere. A slightly exothermic reaction was observed, and the reaction solution was stirred for 4 h. Cyclodehydration was carried out by adding acetic anhydride (6 mL) and sodium acetate (0.55 g) to the reaction solution and heating at 90°C for 2.5 h. The solid obtained was filtered, washed

with a dilute solution of sodium bicarbonate, then with water, and dried to yield bismaleimide 5 (4.87 g, 88%).

#### *General Procedure for the Preparation of Monomers 2-7*

To a vigorously stirred solution of *p*-phenylenediamine (1 mol) in DMF an equimolar amount of maleic or nadic or methylnadic anhydride dissolved in DMF was added dropwise under nitrogen atmosphere. Stirring of the solution was continued for 4 h in a stream of nitrogen. Diisocyanate (0.5 mol) dissolved in DMF was added portionwise to this stirred solution under nitrogen atmosphere at room temperature. The mixture was subsequently heated at 60°C for 3 h in a stream of nitrogen. An aliquot of the reaction solution was poured over crushed ice in order to isolate the diamic acid formed. The yellow solid thus obtained was filtered, washed with water, and dried. Acetic anhydride and sodium acetate (300 mL and 27 g, respectively, per mol of water condensed) were added to the remaining solution in order to cyclodehydrate the diamic acid. The mixture was heated at 90°C for 2.5 h. During this period the color of the reaction mixture became dark brown. Next, it was poured over crushed ice. The brown solid obtained was filtered, washed with a dilute solution of sodium bicarbonate, then with water, and dried to afford the monomer. The yields of monomers thus prepared were 84-93%.

#### **Polymer Preparation**

About 8 mL of a 20-25% solution of diamic acid in DMF were introduced in a shallow dish. The dish was placed into a circulated air oven heated at 160°C for 30 min. At this stage evaporation of the solvent occurred. The temperature of the oven was subsequently raised to 230°C for 2 h. Postcuring was accomplished by heating at 250°C for 40 min.

#### **Characterization Methods**

Infrared (IR) spectra were recorded on a Perkin-Elmer 710B spectrometer with KBr pellets. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were obtained using a Varian T-60A spectrometer at 60 MHz with DMSO-d<sub>6</sub> as solvent. Chemical shifts ( $\delta$ ) are given in parts per million with tetramethylsilane as an internal standard.

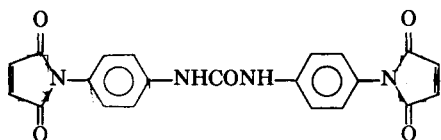
Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a Du Pont 990 thermal analyzer system. DTA measurements were made using a high temperature (1200°C) cell in N<sub>2</sub> atmosphere at a flow rate of 60 cm<sup>3</sup>/min. TGA measurements were made at a heating rate of 20°C/min in atmospheres of N<sub>2</sub> or air at a flow rate of 60 cm<sup>3</sup>/min.

Melting points were determined on an electrothermal melting point apparatus IA6304 and are uncorrected.

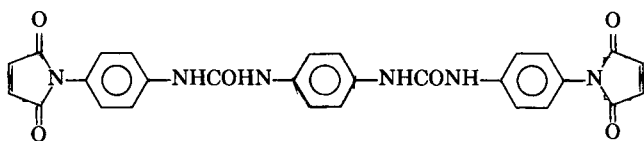
### **RESULTS AND DISCUSSION**

#### **Synthesis of Monomers**

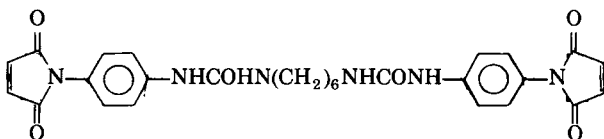
A series of new bismaleimides and bisnadimides containing ureylene linkages were synthesized, and these are numbered as follows:



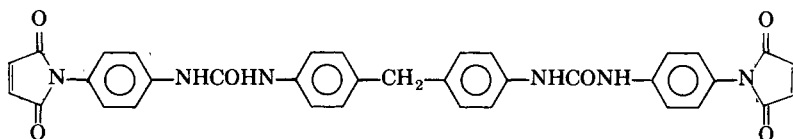
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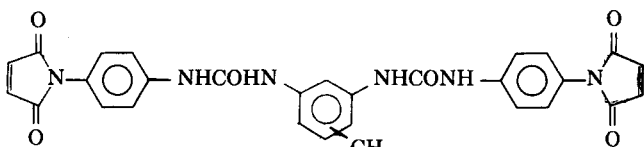
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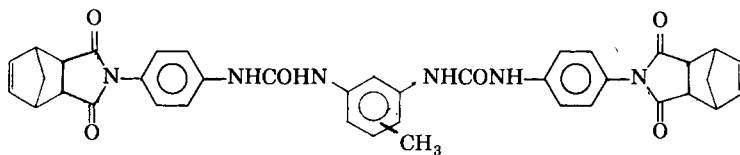
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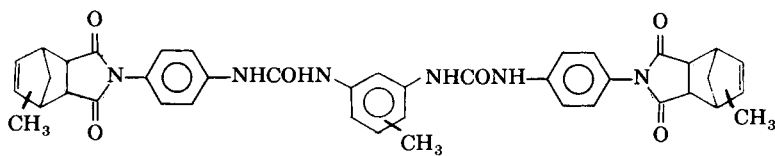
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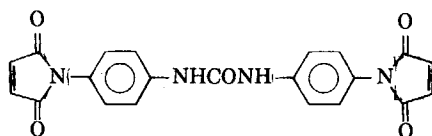
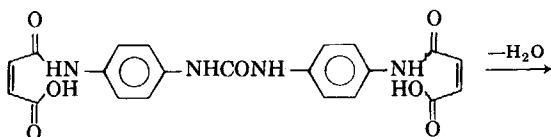
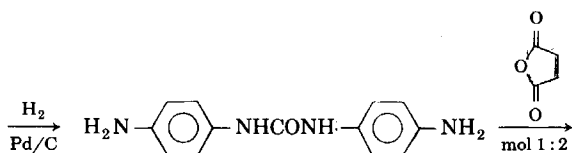
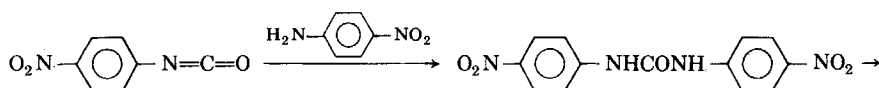
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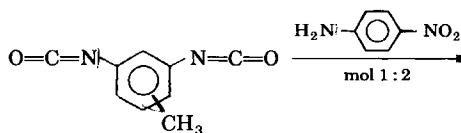
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From observing the structure of the monomers synthesized, it is seen that the polymerizable groups were maleimido or nadimido or methylnadimido. Therefore, the influence of these three types of polymerizable groups on the curing temperature as well as on the thermal stability of the cured resins could be studied in a systematic way. The length of the bridge connecting the two polymerizable groups varied by incorporating one or two ureylene linkages. In addition, the bridge between the two ureylene groups had various chemical structures in bismaleimides 2-5.

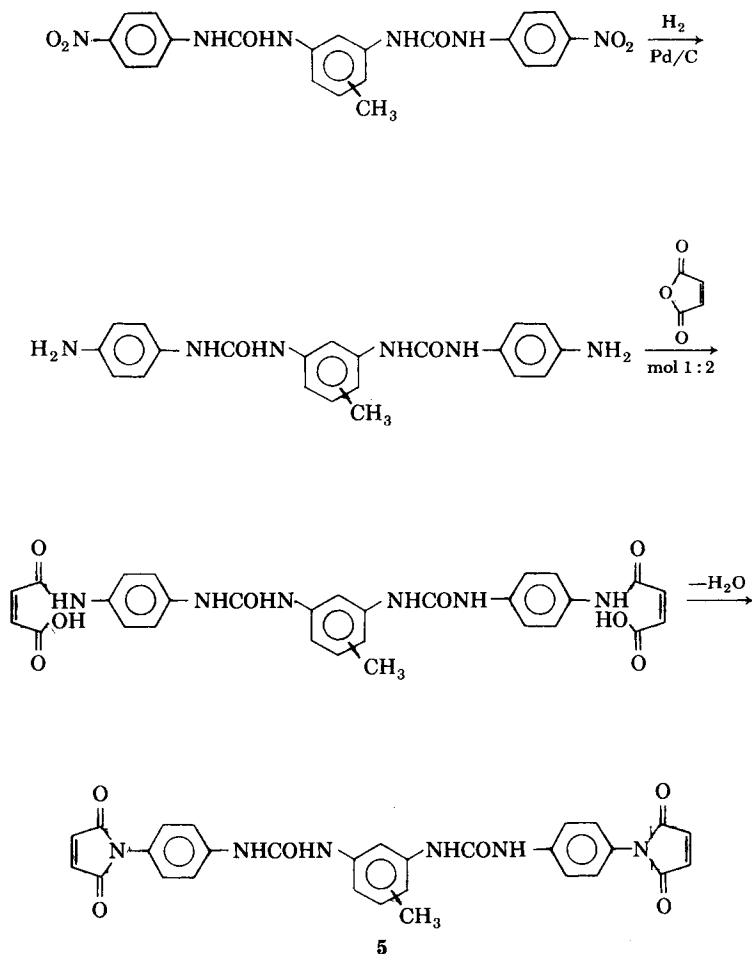
The reaction sequences of Scheme I outline the method utilized for preparing bismaleimides 1 and 5:



1



Scheme I

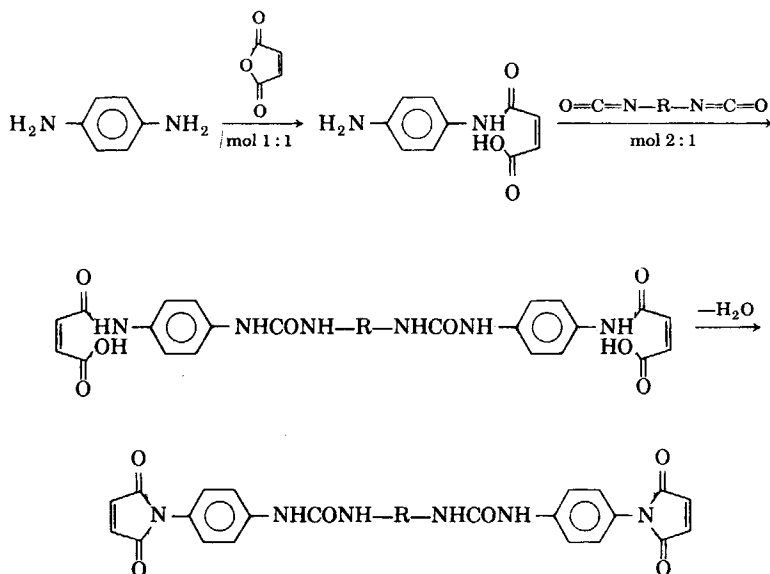


Scheme I. (Continued from the previous page.)

More particularly, 4-nitrophenyl isocyanate reacted with 4-nitroaniline to yield *N,N'*-bis(4-nitrophenyl)urea.<sup>10</sup> The latter has been also prepared by a different synthetic route.<sup>11</sup> Catalytic hydrogenation of this compound afforded the corresponding diamine. A literature survey revealed that the latter has been prepared by hydrogenation of the dinitro compound utilizing concentrated HCl and Fe.<sup>12</sup> In addition, this compound has been prepared from aminoazobenzene and COCl<sub>2</sub>.<sup>13</sup> Bismaleimide 1 was prepared by reacting this diamine with maleic anhydride followed by cyclodehydration of the intermediate bismaleamic acid. Similarly, the synthesis of bismaleimide 5 was achieved by reacting maleic anhydride with tolylene-2,4- and -2,6-bis(*N,N'*-4-aminophenylurea). The latter was prepared by reacting tolylene diisocyanate with 4-nitroaniline under a mol ratio 1:2 and subsequent hydrogenation of the dinitro compound.

Monomers 2-7 were prepared by a new method which is analogous to that utilized for the preparation of bismaleimides or bisnadimides containing

amide linkages.<sup>4</sup> Scheme II shows this method for preparing bismaleimides 2-5:



More particularly, *p*-phenylenediamine reacted with an equimolar amount of maleic anhydride at ambient temperature to yield the monomaleamic acid. The bismaleamic acid derived from diamine was not produced to a detectable amount under the experimental conditions utilized.<sup>2</sup> The monomaleamic acid reacted subsequently *in situ* with a diisocyanate under a mol ratio 2 : 1. The latter reaction was monitored by IR measurements of the reaction solution. Particularly, the reaction was completed when the absorption band around  $2270\text{ cm}^{-1}$  associated with the  $\text{O}=\text{C}=\text{N}-$  group disappeared. The reactions of Scheme II were carried out in DMF although several other polar aprotic solvents such as *N,N*-dimethylacetamide (DMAc) and *N*-methylpyrrolidinone (NMP) could be also used.

The urea forming reaction between diisocyanate and the monomaleamic acid derived from *p*-phenylenediamine proceeded via a nucleophilic attack of the amine nitrogen on the unsaturated carbon of isocyanate followed by a proton transfer which stabilized the adduct. The carboxylic group of the monomaleamic acid might also react with isocyanate via a nucleophilic attack of the carboxylic OH on the isocyanate carbon thus forming an anhydride. Since the amine nitrogen exhibits a considerably higher nucleophilicity than that of the carboxylic OH, the urea forming reaction was more favoured. It should be noted that this reaction was catalyzed<sup>14</sup> by DMF, the reaction medium, which behaves as a weak base.

The required monomers were obtained by cyclodehydration of the corresponding diamic acids (Scheme II). Cyclodehydration was carried out by thermal or chemical means. Thermal cyclodehydration was achieved by refluxing the diamic acid solution for about 2.5 h. The cyclodehydrated product remained soluble in DMF and this solution might be used for composite



fabrication. Chemical cyclodehydration was accomplished by moderate heating of the diamic acid solution in the presence of acetic anhydride and sodium acetate.

The synthetic route outlined in Scheme II was used not only for preparing bismaleimides 2–5 but also for preparing bisnadimide 6 and bismethylnadimide 7. Apparently, this method is applicable for preparing other monomers in the backbone of which various diisocyanates and diamines can be incorporated.

The polymer precursors prepared by the new synthetic route outlined in Scheme II had almost the same purity as those derived from the corresponding diamines containing ureylene linkages. This was shown for bismaleimide 5 which was prepared both by the synthetic route outlined in Scheme I and by that of Scheme II. The IR and <sup>1</sup>H-NMR spectra not only of bismaleimides but also of bismaleamic acids obtained from these methods were identical. In addition, the polymers obtained from these bismaleimides exhibited the same thermal- and thermooxidative stability.

The new synthetic route outlined in Scheme II which can be applied for preparing polymer precursors containing ureylene linkages, is of interest because it makes isolation of the intermediate products dispensable, afforded polymer precursors in relatively high yields, and overcame the hydrogenation followed by the regular route of synthesis. Since hydrogenation is carried out in high pressure reactors in the presence of expensive catalysts, the new preparation method reduces significantly the production cost of these monomers.

### Characterization of Monomers

All monomers as well as their diamic acids were characterized by IR spectroscopy. The characteristic absorptions and their assignments of all monomers are tabulated in Table I. Figure 1 presents typical IR spectra of bismaleimide 3 and the corresponding bismaleamic acid. It is known<sup>15,16</sup> that amic acids absorb around 3270, 1560, and 1270 cm<sup>-1</sup>. These absorptions were somewhat broad in the IR spectra of the diamic acids isolated due to their overlapping with several characteristic absorption bands of the ureylene

TABLE I  
IR Absorption Bands (cm<sup>-1</sup>) of Monomers

Monomer	<i>N,N'</i> -Substituted Urea Structure			Imide structure	Aromatic		Other structures
	I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>		ring	C=C	
1	3370–3275	1542	1665	1785, 1723, 688	1595, 1505	1602	
2	3340–3245	1550	1660	1782, 1717, 692	1598, 1512	1613	
3	3355–3280	1542	1675	1785, 1732, 730	1575, 1500	1620	2940, 1430 (—(CH <sub>2</sub> ) <sub>6</sub> —)
4	3360–3245	1560	1680	1790, 1725, 707	1595, 1525	1615	2910, 1445 (—CH <sub>2</sub> —)
5	3320–3240	1545	1630	1785, 1719, 695	1590, 1510	1610	2885, 1455 (—CH <sub>3</sub> )
6	3380–3240	1547	1645	1787, 1725, 715	1585, 1520	1610	
7	3410–3270	1555	1665	1785, 1730, 695	1580, 1525	1615	2890, 1440 (—CH <sub>3</sub> )

<sup>a</sup> NH stretching.

<sup>b</sup> NH deformation and C–N stretching.

<sup>c</sup> C=O stretching.

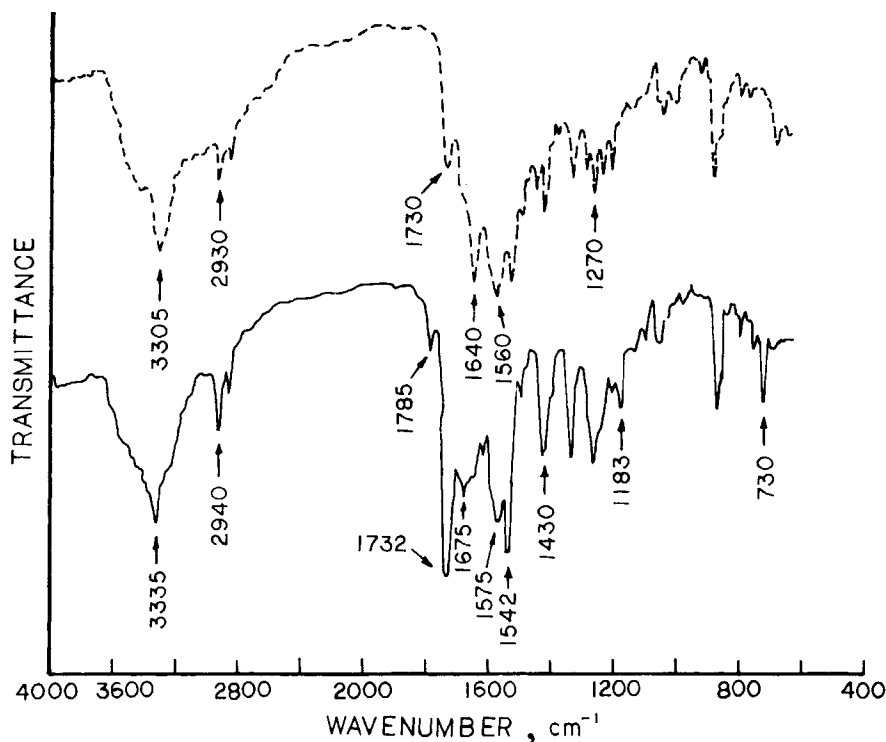


Fig. 1. IR spectra of bismaleimide 3 (—) and the corresponding bismaleamic acid (---).

group. More particularly, the substituted derivatives  $\text{—NHCONH—}$  exhibited absorption bands at  $3410\text{--}3240\text{ cm}^{-1}$  (NH stretching vibration),  $1565\text{--}1542\text{ cm}^{-1}$  (amide II) and near  $1270\text{ cm}^{-1}$  (amide III). The urea carbonyl absorbed at about  $1640\text{ cm}^{-1}$  whereas the carboxylic carbonyl of the amic acids showed an absorption band around  $1730\text{ cm}^{-1}$ .

The IR spectra of bismaleimide 3 and the corresponding bismaleamic acid exhibited several distinctive differences (Fig. 1). More particularly, bismaleimide showed a strong absorption at  $1732\text{ cm}^{-1}$  (imide carbonyl) and weak absorptions at  $1785\text{ cm}^{-1}$  (imide I),  $1183\text{ cm}^{-1}$  (imide III), and  $730\text{ cm}^{-1}$  (imide IV). In addition, it lacked the broad absorption at  $3100\text{--}2600\text{ cm}^{-1}$  associated with the carboxylic OH stretching vibration. Consequently, imidization could be monitored by means of these absorptions.

The monomers containing ureylene linkages showed a higher solubility than that of the corresponding monomers bearing imido<sup>2,3</sup> or amido<sup>4</sup> linkages. However, due to the limited solubility of the monomers containing ureylene linkages even in polar aprotic solvents their  $^1\text{H-NMR}$  spectra could not be recorded clearly. In contrast, intermediate diamic acids exhibited a relatively higher solubility, and therefore their  $^1\text{H-NMR}$  spectra were recorded from  $\text{DMSO-d}_6$  solution. The results are listed in Table II. Protons exchangeable to deuterous by treatment with  $\text{D}_2\text{O}$  appeared at the regions of  $10.90\text{--}10.45$ ,  $9.00\text{--}8.20$ , and  $8.30\text{--}7.70\text{ }\delta$  assigned to the  $\text{—COOH}$ ,  $\text{—CH=CHCONH—}$  or  $\text{>CHCONH—}$  and  $\text{—NHCONH—}$  protons, respectively. All diamic acids showed a peak at  $6.50\text{--}6.00\text{ }\delta$  associated with the olefinic protons which

TABLE II  
<sup>1</sup>H-NMR Spectral Data of Diamic Acids

Diamic acid	Chemical shifts ( $\delta^a$ , ppm) and assignments
1	10.90 (bs, <sup>b</sup> 2H, —COOH); 9.10–8.80 (bs, 2H, —CH=CHCONH—); 8.00–7.40 (m, <sup>c</sup> 2H, —NHCONH— and 8H, aromatic); 6.50 (m, 4H, olefinic)
2	10.70 (bs, 2H, —COOH); 9.00 (bs, 2H, —CH=CHCONH—); 8.25 (bs, 4H, —NHCONH—); 7.60–7.20 (m, 12H, aromatic); 6.40 (m, 4H, olefinic)
3	10.50 (bs, 2H, —COOH); 8.20 (bs, 2H, —CH=CHCONH—); 7.60–7.20 (bm, <sup>d</sup> 4H, —NHCONH— and 8H, aromatic); 6.20 (m, 4H, olefinic); 3.25 (m, 4H, —NHCH <sub>2</sub> —); 1.70–1.10 (m, 8H, —CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> —)
4	10.60 (bs, 2H, —COOH); 8.70 (bs, 2H, —CH=CHCONH—); 8.10 (bs, 4H, —NHCONH—); 7.45 (m, 12H, aromatic ortho to —NH—); 6.90 (m, 4H, aromatic ortho to —CH <sub>2</sub> —); 6.25 (m, 4H, olefinic); 3.60 (s, <sup>e</sup> 2H, —C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> —)
5	10.80 (bs, 2H, —COOH); 8.90 (bs, 2H, —CH=CHCONH—); 8.20 (bs, 4H, —NHCONH—); 7.50–7.20 (m, 11H, aromatic); 6.50 (m, 4H, olefinic); 2.20 (s, 3H, methyl of tolylene ring)
6	10.55 (bs, 2H, —COOH); 8.70 (bs, 2H, >CHCONH—); 8.10 (bs, 4H, —NHCONH—); 7.55–7.15 (m, 11H, aromatic); 6.20 (m, 4H, olefinic); 3.50–3.10 (m, 8H, aliphatic of nadimide ring); 2.20–1.50 (m, 4H, methylene of nadimide bridge and 3H, methyl of tolylene ring)
7	10.45 (bs, 2H, —COOH); 8.60–8.25 (bs, 2H, >CHCONH— and 4H, —NHCONH—); 7.60–7.20 (m, 11H, aromatic); 6.00 (m, 4H, olefinic); 3.40–3.00 (m, 6H, aliphatic of nadimide ring); 2.30–1.35 (m, 3H, methyl of tolylene ring, 4H, methylene of nadimide bridge and 6H, methyl of nadimide ring)

<sup>a</sup>In DMSO-d<sub>6</sub> solution.

<sup>b</sup>Broad singlet.

<sup>c</sup>Multiplet.

<sup>d</sup>Broad multiplet.

<sup>e</sup>Singlet.

clearly indicated the incorporation of the polymerizable groups. From Table II it can be seen that the olefinic protons of bismaleimide 5 showed a downfield shift than that of the olefinic protons of the corresponding bisnadimide 6 due to the deshielding effect of the electron-withdrawing carbonyl group of  $\alpha$ -position. On the other hand, the olefinic protons of bismethylnadimide 7 exhibited an upfield shift than that of the olefinic protons of the corresponding bisnadimide 6 due to the shielding effect of the electron-donating methyl group.

Melting temperatures of the monomers isolated could not be determined by standard test methods because they did not show a clear melting point when heated into a capillary tube. The formation of crosslinks during their gradual heating is considered to be responsible for this behavior.

### Polymerization of Monomers

Bismaleimides or bisnadimides are thermally polymerized through their olefinic bonds to afford crosslinked structures. Thermal polymerization is

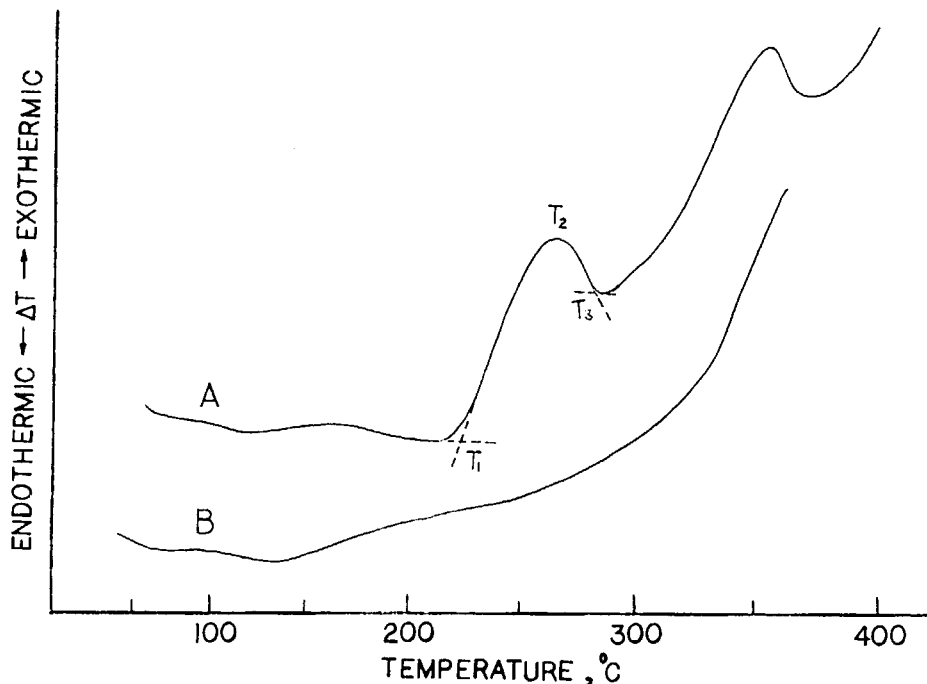


Fig. 2. DTA thermograms of bismaleimide 5 (trace A) and the corresponding cured resin (trace B).

believed to proceed via a free radical mechanism. On the other hand, cyclopentadiene is evolved by retrograde Diels-Alder reaction upon heating of bisnadimides at about 300–400°C, but most of this is captured by copolymerization.<sup>17</sup>

Thermal polymerization of monomers was investigated by DTA in nitrogen atmosphere. Figure 2 presents typical DTA thermograms of bismaleimide 5 (trace A) and its cured resin (trace B). It is seen that monomer exhibited an exotherm at 229–289°C whereas its polymer did not show exotherm at this temperature range. Consequently, this exotherm was attributed to the thermally induced polymerization reaction. The exotherm that appeared above 340°C in both traces was assigned to thermal degradation because the corresponding TGA thermogram showed a larger rate of weight loss above this temperature.

The relative reactivity of the olefinic bonds could be assessed by comparing some characteristic temperatures. Particularly, the onset temperature ( $T_1$ ) for polymerization reaction, the exothermic peak temperature ( $T_2$ ), and the temperature for completion of polymerization ( $T_3$ ) were determined from the DTA traces of monomers and are listed in Table III. The  $T_1$  and  $T_3$  were obtained by extrapolating the front side and the back side of the exothermic peak, respectively, to the base line (Fig. 2).  $T_2$  may be obtained as a criterion of the relative reactivity of the olefinic bonds. On this basis, bisnadimide 6 was the most reactive monomer synthesized because it showed the lowest  $T_2$ . This is probably due to the strained bicyclic ring system. On the other hand, bismaleimide 1 containing one ureylene group was more reactive than the

TABLE III  
 Curing Temperatures of Monomers

Monomer	$T_1^a$ (°C)	$T_2^b$ (°C)	$T_3^c$ (°C)
1	228	255	281
2	242	270	294
3	244	276	297
4	249	272	288
5	229	266	289
6	203	223	256
7	206	228	265

<sup>a</sup>The onset temperature for polymerization reaction.

<sup>b</sup>The exothermic peak temperature.

<sup>c</sup>The temperature for completion of polymerization.

other bismaleimides bearing two ureylene groups. Thus, chain extension of polymer precursors might improve flexibility but reduce their reactivity. In bismaleimides 2, 3, 4, and 5 the  $T_2$  varied from 266 to 276°C, thus indicating a comparable reactivity of the olefinic bonds.

Throughout the text the cured resins obtained from monomers 1–7 according to the procedure described in the experimental section, are referred to by the numbers 1'–7', respectively.

#### Thermal- and Thermooxidative Stability of Polymers

Polymers were thermally characterized by dynamic TGA. Figure 3 presents typical TGA thermograms in  $N_2$  atmosphere. The temperature of initial weight loss (TIWL), the maximum polymer decomposition temperature ( $PDT_{max}$ ) both in  $N_2$  and air atmospheres as well as the temperature of complete pyrolysis (TCP) and the char yield ( $Y_c$ ) at 800°C under anaerobic conditions were determined from the TGA traces and are listed in Table IV. It can be seen that all polymers, except of 3', were thermally stable up to 324–334°C in  $N_2$  and air. Polymer 3' derived from the aliphatic hexamethylene-1,6-diisocyanate started losing weight at a lower temperature (297°C). The chemical structure of diisocyanates utilized for preparing monomers did not remarkably influence the TIWL. This supports that thermal degradation of polymers proceeded rather by scission of the ureylene linkages than of the aromatic structures. An analogous behavior has been observed in the cured resins derived from monomers containing amide linkages.<sup>4</sup> The relatively lower TIWL of 3' indicated that the aliphatic segments of its backbone were less thermally stable than the ureylene groups. Polymers 1' and 2' containing one and two ureylene groups, respectively, had almost the same TIWL but the former exhibited a considerably higher  $PDT_{max}$  both in  $N_2$  and air. Interestingly, as Table IV points out, the polymers derived from bismaleimide 5, bisnadimide 6, and bismethylnadimide 7 showed almost the same thermal- and thermooxidative stability since their TGA data were equal approximately. The anaerobic char yield at 800°C varied from 41 to 61%.

The ratio of the temperature of initial weight loss in air to that in  $N_2$  atmosphere ( $TIWL_{air}/TIWL_{N_2}$ ) fluctuated between 0.97 and 1.00. This sug-

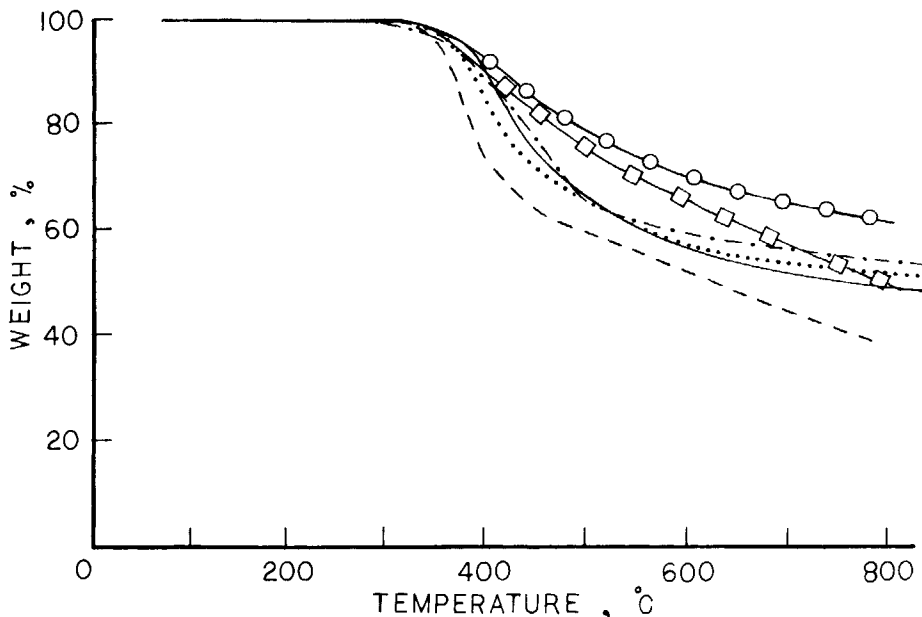


Fig. 3. Typical TGA curves of polymers in  $N_2$  atmosphere: (—) 1'; (---) 2'; (- - -) 3'; (···) 4'; (○-○) 5'; (□-□) 6'.

gests that thermal degradation was not seriously affected by the presence of oxygen. However, all polymers were almost completely pyrolyzed upon heating beyond 650°C in air.

Figure 4 presents typical IGA traces of cured resins 1', 2', 5', and 6' at 300°C in air atmosphere (static) which showed a weight loss 46.5, 52.8, 30.3, and 38.0%, respectively, after 12 h. The lower weight loss of 1' in comparison to that of 2' is in agreement with its relatively higher values of TIWL and  $PDT_{max}$  in air. Similarly, polymer 5' derived from a bismaleimide showed lower weight loss than that of polymer 6' obtained from the corresponding bisnadimide.

TABLE IV  
TGA Data of Polymers

Polymer	In $N_2$				In air		$TIWL_{air}/TIWL_{N_2}$
	TIWL <sup>a</sup> (°C)	$PDT_{max}^b$ (°C)	TCP <sup>c</sup> (°C)	$Y_c^d$ (%)	TIWL (°C)	$PDT_{max}$ (°C)	
1'	332	426	548	49	333	420, 548	1.00
2'	334	401	430	41	324	363, 482	0.97
3'	297	402, 466	490	54	297	384, 446	1.00
4'	324	416	483	52	326	385, 490	1.00
5'	334	432	537	61	334	429, 534	1.00
6'	331	431	516	49	329	387, 530	0.99
7'	328	430	520	50	325	456	0.99

<sup>a</sup> Temperature of initial weight loss.

<sup>b</sup> Maximum polymer decomposition temperature.

<sup>c</sup> Temperature of complete pyrolysis.

<sup>d</sup> Char yield at 800°C.

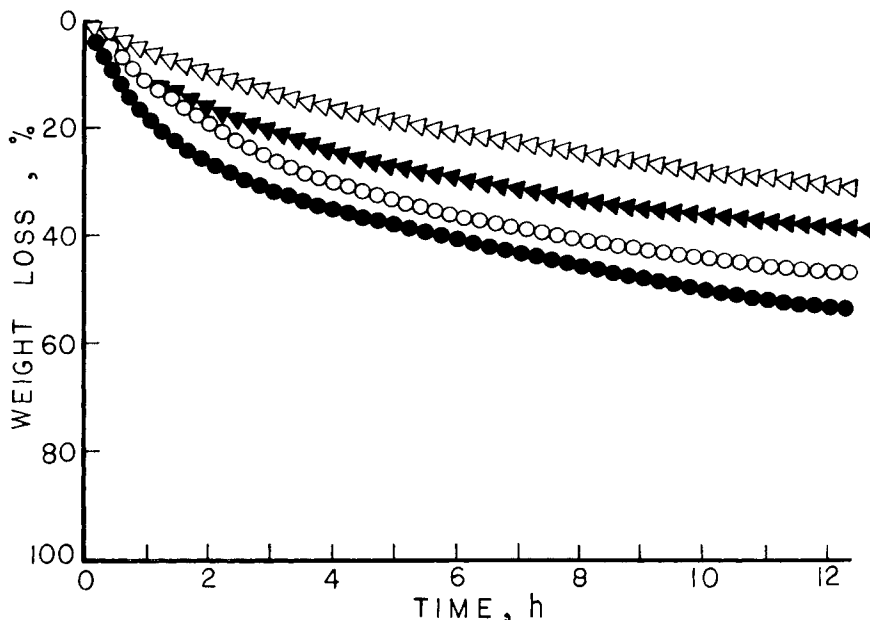


Fig. 4. TGA traces of polymers 1' (○), 2' (●), 5' (△) and 6' (◐) at 300°C in air atmosphere (static).

## CONCLUSIONS

Several new polymer precursors such as bismaleimides, bisnadimides, and bismethylnadimides were prepared by two different synthetic routes. The new synthetic route developed is of interest because it proceeded without isolation of the intermediate products, afforded polymer precursors in relatively high yields (84–93%), and circumvented the hydrogenation necessary in the regular route of synthesis. The DTA thermograms of monomers showed that they were thermally polymerized at 203–297°C. The TGA data revealed that all polymers containing substituted arylureas in their backbone were stable up to 324–334°C in N<sub>2</sub> or air. Their temperature of initial weight loss was not remarkably influenced by the chemical structure of the diisocyanates utilized for monomer preparation. The monomer derived from the aliphatic hexamethylene-1,6-diisocyanate afforded polymer having a relatively lower temperature of initial weight loss. The polymers obtained from a bismaleimide and the corresponding bisnadimide and bismethylnadimide showed a comparable thermal- and thermooxydative stability. The anaerobic char yield of all polymers at 800°C varied from 41 to 61%.

A grant from the Greek Ministry of Industry, Energy, and Technology (General Secretariat of Research and Technology) is gratefully acknowledged.

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Received January 7, 1987

Accepted April 7, 1987