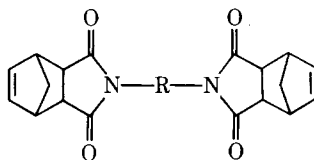# Synthesis and Polymerization of Aliphatic Bisnadimides*

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## Synopsis

A series of linear aliphatic and cycloaliphatic bisnadimides of structure



has been prepared and polymerized thermally to give highly crosslinked moisture-resistant laminating resins. Cyclopentadiene is evolved by retrograde Diels–Alder reaction during processing, but most is captured by copolymerization. Moisture resistance increases as chain length increases for the homologous series of straight-chain polybisnadimides.

## INTRODUCTION

In response to the needs of the aerospace industry, a variety of graphite and glass fiber-reinforced composite formulations have been developed in recent years, in particular the epoxy and polyimide type. While much of the emphasis has been directed toward high thermal stability, the importance of good moisture resistance has not been overlooked. Loss of mechanical properties upon prolonged exposure to moisture may arise from either a weakening of the fiber–resin bond or from moisture-induced degradation of the resin itself.[1–3]

The goal of this research was to develop easily processable moisture-resistant polyimide resins by thermal polymerization of a series of aliphatic bisnadimides (1):
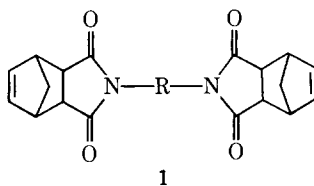


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(The term nadimide is in common use for the more unwieldy *endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide or *endo*-5-norbornene-2,3-dicarboximide.) Thus, it was hoped that a balance would be achieved between the polar imide groups necessary for good adhesion to the fiber and the aliphatic character required for good moisture resistance. The nadimide functional group was chosen (1) because the monomers are easily synthesized from commercially available materials; (2) the strained bicyclic ring system undergoes thermal polymerization at relatively low temperatures; and (3) composites are simple to manufacture in that only a single compound is involved and the addition of accelerators or initiators is unnecessary.

Prior to this research, there has been commercial development of nadimide-capped prepolymers for high temperature-resistant laminates[4-6] as well as the structurally related polybismaleimides.[7-9] A preliminary report of some more complex long-chain bisnadimides has also appeared.[10]

## EXPERIMENTAL

Melting points were measured on a Thomas Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer model 457 grating spectrophotometer. Mass spectra were recorded on a JEOL model JMS-D100 mass spectrometer coupled with a Dohrmann Envirotech gas chromatograph. Carbon, hydrogen, and nitrogen analyses were determined on a Perkin–Elmer model 240 elemental analyzer. Differential thermal analyses were recorded under nitrogen with a Stone DTA apparatus model SH-12CR2-SS2 at an up-heat rate of 39°C/min.
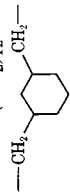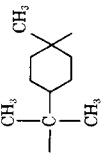
### Bisnadimide Synthesis

All bisnadimides (1) were prepared in essentially the same way by reacting a 2:1 molar ratio of nadic anhydride and diamine in refluxing *N,N*-dimethylformamide (DMF). The numbering system and structure of each monomer are given in Table I. The following procedure is representative.

In a four-necked flask equipped with stirrer, reflux condenser, and thermometer are placed 0.4 mole diamine and about 150 ml DMF. The temperature is raised to about 65°C and nadic anhydride (0.8 mole) is added over 30 min to 1 hr, depending on the reaction exotherm which heats the mixture to about 100°C. When addition is complete, the mixture is refluxed for 1 to 2 hr. The initially formed precipitate of intermediate amic acid undergoes imidization rapidly to give clear solution.

Upon cooling, bisnadimide usually precipitates. In some instances, particularly with longer-chain linear monomers, the solution was first concentrated on a rotary evaporator and cooled in a refrigerator to induce crystallization. The most difficult to isolate was the bisnadimide 1-9 which required trituration with methanol to obtain crystals. In the case of 1-MBCA, slower addition of nadic anhydride was necessary to prevent the intermediate precipitate from stopping the stirrer. With 1-DAM, considerable amounts of amic acid remained after 2 hr of refluxing, and washing with base was required to effect crystallization.

Melting points, yields, recrystallization conditions, and C, H, and N analyses are given in Table I.

TABLE I
Aliphatic Bisnadimides

| Sample No. | R | Yield, % | Recryst. solvent[a] | mp, °C[b] | Elemental analysis,% | | | | | |
| | | | | | Found | | | Calculated | | |
| | | | | | C | H | N | C | H | N |
|---|---|---|---|---|---|---|---|---|---|---|
| 1-2 | $-(CH_2)_2-$ | 80 | EtOH/DMF | 252–253.5 | 68.13 | 5.74 | 8.12 | 68.16 | 5.72 | 7.95 |
| 1-3 | $-(CH_2)_3-$ | 76 | EtOH/DMF | 173.5–175 | 68.94 | 6.07 | 7.74 | 68.83 | 6.05 | 7.65 |
| 1-4 | $-(CH_2)_4-$ | 78 | EtOH/DMF | 210.5–212[c] | 70.07 | 6.44 | 7.44 | 69.45 | 6.36 | 7.37 |
| 1-5 | $-(CH_2)_5-$ | 34 | EtOH | 124.5–125 | 70.02 | 6.68 | 7.13 | 70.03 | 6.64 | 7.10 |
| 1-6 | $-(CH_2)_6-$ | 46 | EtOH | 134.5–135.5[d] | 70.66 | 6.90 | 6.87 | 70.56 | 6.91 | 6.86 |
| 1-7 | $-(CH_2)_7-$ | 41 | EtOH | 93–94.5 | 71.42 | 7.21 | 6.66 | 71.06 | 7.16 | 6.63 |
| 1-8 | $-(CH_2)_8-$ | 50 | EtOH | 109–109.5 | 71.81 | 7.51 | 6.21 | 71.53 | 7.39 | 6.42 |
| 1-9 | $-(CH_2)_9-$ | 39 | EtOH | 64–64.5 | 71.83 | 7.43 | 6.32 | 71.97 | 7.61 | 6.22 |
| 1-10 | $-(CH_2)_{10}-$ | 47 | EtOH | 89.5–90.5 | 72.36 | 7.76 | 5.95 | 72.38 | 7.81 | 6.03 |
| 1-12 | $-(CH_2)_{12}-$ | 60 | EtOH | 80–82 | 73.34 | 8.26 | 5.60 | 73.14 | 8.18 | 5.69 |
| 1-CBMA | (cyclohexane-bis(methylene) structure) | 85 | EtOH/DMF | 195–197 | 71.76 | 7.15 | 6.38 | 71.86 | 6.96 | 6.45 |
| 1-MBCA | (methyl-substituted bicyclohexyl methylene structure) | 38 | EtOH | 205–217 | 74.12 | 7.68 | 5.61 | 74.07 | 7.62 | 5.57 |
| 1-DAM | (dimethyl cyclohexyl isopropyl structure) | 22 | MeOH | 189–193 | 72.85 | 7.48 | 5.99 | 72.70 | 7.41 | 6.06 |

[a] EtOH = Ethanol; DMF = $N,N$-dimethylformamide; MeOH = methanol.
[b] All samples sintered before melting.
[c] Lit.[11] mp = 213–214°C.
[d] Lit.[12] mp = 133–134°C.

### Trimethylene-$N,N'$-bistetrahydrophthalimide (2)

Diimide 2 was prepared in 58% yield in the same manner as the bisnadimides using tetrahydrophthalic anhydride in place of nadic anhydride. The product was crystallized from ethanol, mp 108.5–109.5°C (with sintering at 106°C).

ANAL. Calcd for $C_{19}H_{22}N_2O_4$: C, 66.66; H, 6.48; N, 8.19%. Found: C, 66.82; H, 6.56; N, 8.18%.

## Bisnadimide Polymerization

### B-Staging

Samples of bisnadimide were heated at 250°C until molten, at which point a nitrogen bubbling tube was inserted. The temperature was maintained at 250°C for 1 hr, then increased slowly to a maximum of 300°C. The sample was cooled rapidly when it appeared close to the gel point which frequently occurred between 280 and 290°C.

Resins prepared from bisnadimides 1-2 through 1-8, 1-MBCA, and 1-CBMA were ground in a mortar to a coarse powder. Resins from 1-9, 1-10, and 1-12 were not hard enough for grinding at room temperature, although they could be cooled in a freezer and ground prior to making disks.

### Preparation of Disk Test Specimens

Because cyclopentadiene is evolved during processing, good press control is essential to prepare void-free specimens. Approximately 4 g of B-staged resin was placed in a Teflon-sprayed mold cavity 1 in. in diameter. The mold plunger was set in position, and the mold was placed in a preheated press at 293°C. Pressure was applied immediately to consolidate the sample, then it was released. The sample softened at 250°C and was allowed to remain at that temperature until it could support a load, as indicated by application of pressure. Pressure was then applied (500 psi, 3.44 MPa) and held for 10 min. The temperature was allowed to rise to 293°C, and the sample was held at this temperature and 500 psi (3.44 MPa) for 1 hr. Pressure was released, and the sample was removed from the press and allowed to cool to room temperature unrestrained. By this procedure, solid resin disks 1 in. (25.4 mm) in diameter by 0.25 in. (6.35 mm) thick were produced for each bisnadimide sample, with the exception of 1-DAM. The disks were cut into quarters for characterization.

### Determination of Weight Loss during Polymerization

Accurately weighed samples of approximately 3 g of each of the bisnadimides in test tubes were heated together in a Thermodyne type 2000 furnace at 250°C for 45 min and 1 hr at 300°C. Weight % and mole % loss of cyclopentadiene are recorded in Table II.

TABLE II
Cyclopentadiene Loss during Polymerization of Bisnadimides[a]

| Sample No. | DCP[b] | Initial Weight, g | Weight loss, % | Mole % loss[c] | Mole C=C per mg monomer |
|---|---|---|---|---|---|
| 1-2 | − | 3.005 | 0.80 | 2.13 | 5.68 |
| 1-2 | + | 3.086 | 1.68 | 4.47 | 5.68 |
| 1-3 | − | 2.895 | 1.23 | 3.39 | 5.46 |
| 1-3 | + | 3.014 | 0.79 | 2.19 | 5.46 |
| 1-4 | − | 2.903 | 1.79 | 5.16 | 5.26 |
| 1-4 | + | 3.042 | 1.28 | 3.69 | 5.26 |
| 1-5 | − | 2.075 | 1.83 | 5.44 | 5.08 |
| 1-6 | − | 3.127 | 1.53 | 4.87 | 4.90 |
| 1-6 | + | 3.002 | 1.05 | 3.23 | 4.90 |
| 1-7 | − | 2.981 | 1.74 | 5.55 | 4.73 |
| 1-8 | − | 2.919 | 2.35 | 7.78 | 4.58 |
| 1-8 | + | 3.031 | 1.99 | 6.57 | 4.58 |
| 1-9 | − | 2.776 | 4.44 | 15.14 | 4.43 |
| 1-10 | − | 3.077 | 3.51 | 12.35 | 4.30 |
| 1-12 | − | 2.912 | 8.49 | 31.65 | 4.06 |
| 1-12 | + | 2.930 | 8.14 | 30.37 | 4.06 |
| 1-CBMA | − | 3.119 | 5.33 | 17.50 | 4.60 |
| 1-CBMA | + | 2.966 | 4.84 | 15.89 | 4.60 |
| 1-MBCA | − | 2.566 | 2.23 | 8.48 | 3.90 |

[a] Heating cycle: 250 up to 300°C during 3/4 hr, 1 hr at 300°C. Samples in open test tubes in air.

[b] DCP = Dicumyl peroxide; + = 1 mole % based on moles of C=C in monomer; − = no DCP added.

[c] Percent of theoretical number of moles of cyclopentadiene.

## Vacuum Line Experiments

Samples were measured into cylindrical tubes having a thermocouple port in the base extending approximately one third of the way into the tube. The system was evacuated to about 0.02 torr and pumped for 1 hr to remove all volatile material. The pump was then sealed off from the system, and the oven was raised around the sample tube by means of a lab jack. Material balances were maintained throughout.

## Preparation of Tensile Lap Shear Specimens

Single lap shear specimens were prepared from two pieces 2.54 cm wide × 7.62 cm long × 0.31 cm thick aluminum (previously surface treated by the FPL etch process) bounded together in a 1/2 in. (12.7 mm) overlap area. The specimens were prepared by coating a 3/4 in. (19.05 mm) section with a 10% solution of B-staged resin in chloroform. The coated aluminum sections were treated in a vacuum at room temperature for 1/2 hr. The two coated sections were placed together to form a 1/2 in. (12.7 mm) overlap. Stainless steel spacers (thickness 0.15 mm, 6 mil) were positioned in the fixture holding the lap shear specimens to maintain 0.015 cm (6 mil) cured bond line. For specimens containing scrim cloth within the bond line, glass scrim cloth (0.05 mm thick, 2 mil) was also coated with the same resin solution as the aluminum specimen. The scrim cloth was treated in a vacuum for 1/2 hr at room temperature, and a small piece of the

coated scrim cloth was positioned within the 1/2-in. overlap section of the resin-coated aluminum specimens. As with the specimens without scrim cloth, spacers (0.015 mm, 6 mil) were positioned in the fixture to maintain a bond line of 6 mil in the cured lap shear specimen.

The specimens were placed in a preheated press at 316°C. When the specimens reached a temperature of 275°C, a pressure of 0.414 MPa (60 psi) was applied. The specimens were allowed to reach 316°C and were maintained at 316°C, 60 psi, for 1 hr.

## Determination of Resin Properties

### Moisture Absorption

One quarter-inch sections of each resin disk were exposed to room temperature distilled water for 24 hr and to boiling distilled water for 168 hr (seven days). The quantity of water absorbed as a result of these exposures was determined by weight differences before and after exposures. Before each weight measurement, the samples were dried to remove surface water and weighed immediately. The results of these tests are plotted graphically for each resin system in Figures 6–8.

### Density

The density of each resin material was determined by the liquid displacement technique, using water as the displacement liquid.

### Glass Transition Temperature

The glass transition temperature ($T_g$) of each resin was determined by the thermal mechanical analysis (TMA) method using a du Pont 943 TMA unit attached to a du Pont 990 thermal analyzer.

### Isothermal Weight Loss

One quarter-inch sections of each resin disk were placed in an aluminum dish and subjected to a temperature of 204°C in an air circulating oven for 240 hr. Weight changes occurring as a result of this exposure were determined.

### Tensile Lap Shear Strength Measurements

Tensile lap shear strength measurements were made on a Tinius–Olsen Universal testing machine at a crosshead speed of 0.127 cm/min (0.05 in./min). Room temperature measurements were made at ambient conditions, while the 204°C measurements were made by treating the specimens at 204°C in an air oven for 20 min and then making the measurement.
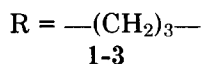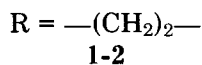
## RESULTS AND DISCUSSION

### Bisnadimide Synthesis

Bisnadimides (1) were prepared by the two-step, one-pot reaction by refluxing a 2:1 molar ratio of nadic anhydride with diamine in DMF, reaction (1) (only one of the amic acid structures is shown):



(1)
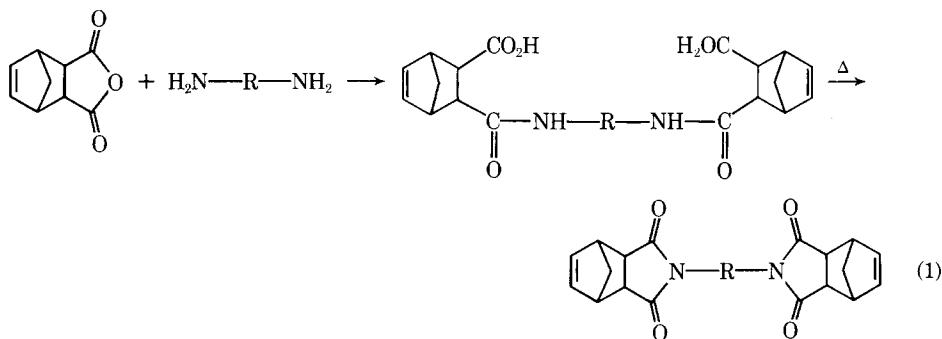
A series of straight-chain aliphatic bisnadimides were synthesized, and these are numbered as follows:

$$R = —(CH_2)_2—$$
**1-2**

$$R = —(CH_2)_3—$$
**1-3**

etc.

In addition, three cycloaliphatic bisnadimides were synthesized using the commercially available diamines cyclohexanebis(methylamine) (CBMA), 4,4'-methylenebis(cyclohexylamine) (MBCA), and 1,8-diamino-$p$-menthane (DAM). These are numbered accordingly:



1-CBMA



1-MBCA



1-DAM
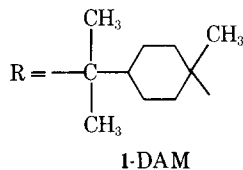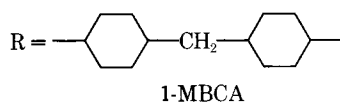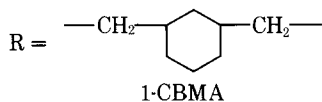
Yields were not uniformly high, ranging from 22 to 85%; however, no attempt was made to determine optimum conditions. Compounds **1-2** through **1-6** have been reported previously.[11–13] Results are given in Table I. The broad melting

ranges of 1-MBCA and 1-DAM are probably due to mixtures of stereoisomers.

The only bisnadimides difficult to obtain in crystalline form were 1-9 and 1-DAM. In the case of 1-DAM, the difficulty appears to be one of steric blocking hindering the imidization reaction. This is suggested by infrared studies which show considerable unreacted amic acid prior to purification. For monomer 1-9, the low melting point resulting from the long chain length and odd number of carbon atoms inhibits crystallization. This odd–even relationship, which is typical of homologous series, is shown graphically in Figure 1.

Infrared spectra of bisnadimides exhibit characteristic carbonyl doublets at 1680 and 1760 cm$^{-1}$ and the olefinic carbon–hydrogen stretch at 3040 cm$^{-1}$. The carbon–carbon double-bond stretch shows up as a very weak band at 1565 cm$^{-1}$. Other peaks probably arising from the olefinic function appear at 1050 cm$^{-1}$ and at 710 to 735 cm$^{-1}$. These peaks diminish in size or disappear upon polymerization. The spectra of two of the bisnadimides (1-3 and 1-12) are shown in Figures 2 and 3.

For purposes of comparing polymerization characteristics, the trimethylene bisimide (2) of tetrahydrophthalic anhydride was prepared.
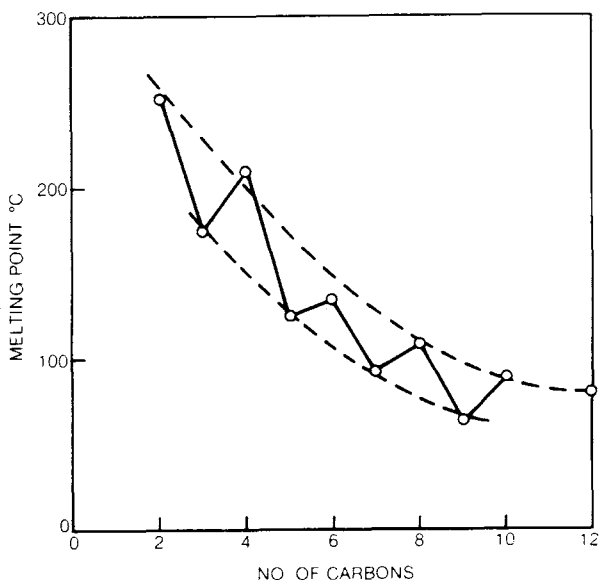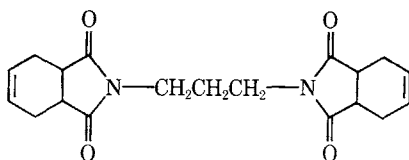


2



Fig. 1. Melting point as function of number of carbon atoms for a homologous series of aliphatic straight-chain bisnadimides.
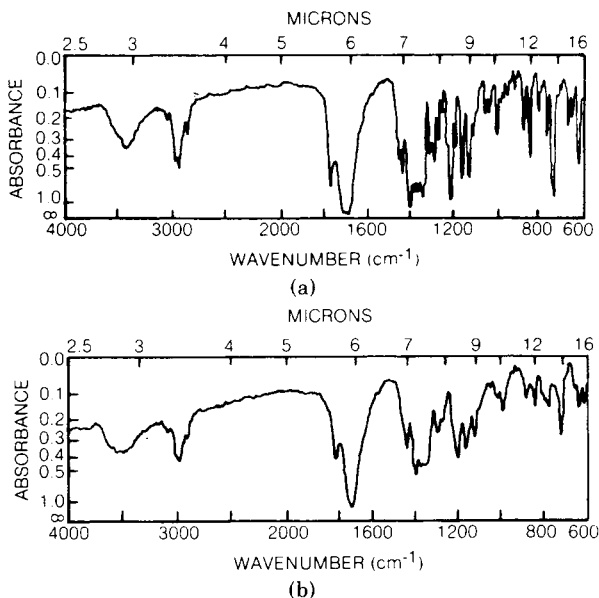
Fig. 2. Infrared spectra (KBr): (a) bisnadimide 1-3; (b) polymer formed by heating 1-3 at 250°C for 2 hr.

The infrared spectrum of **2** was simpler than those of the bisnadimides but exhibited the same characteristic imide and olefinic absorptions.

Differential thermal analysis (DTA) thermograms were recorded for all the bisnadimides. A representative example (**1-10**) is given in Figure 4. All exhibit endothermic peaks at temperatures corresponding quite well to the melting points, and all have strong endothermic transitions between about 300 and 400°C, probably corresponding to the retrograde Diels–Alder reaction, reaction (2), and loss of cyclopentadiene:



(2)
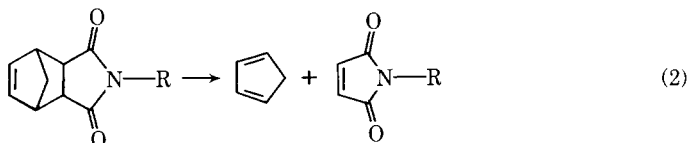
This is a very important reaction from the standpoint of polymer processing and will be discussed more fully later. Exothermic transitions occurring at temperatures above 400°C no doubt correspond to the polymerization reaction. All thermograms show decomposition and loss of volatiles at about 500°C, and a tarry residue results from each sample. As expected, **2** did not exhibit the strong endothermic transition between 300 and 400°C but did undergo decomposition above 450°C.

## Polymerization of Bisnadimides

Bisnadimides undergo thermal polymerization above 250°C to form tough, crosslinked resins. The reaction occurs in air or nitrogen and does not appear to be appreciably affected by either free-radical or cationic initiators apart from some decrease in gel time with the former. Polymerization occurs readily for
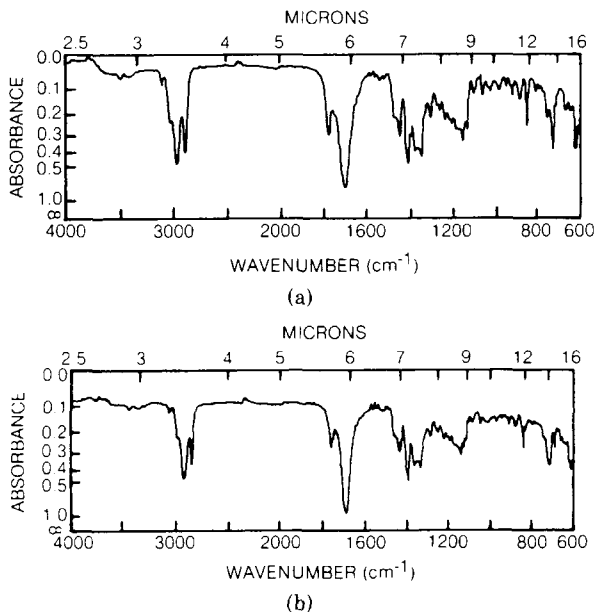
Fig. 3. Infrared spectra (film):   (a) bisnadimide 1-12 (molten film); (b) polymer formed by heating
1-12 at 300°C for 1 hr.

all bisnadimides, with the exception of 1-DAM which reacts very slowly (pre-
sumably because of steric hindrance) to form very dark polymer even under ni-
trogen.

Resins vary from clear amber-colored, hard glassy solids where monomer chain
length is short to dark, rubbery solids in the case of the longer chain monomers.
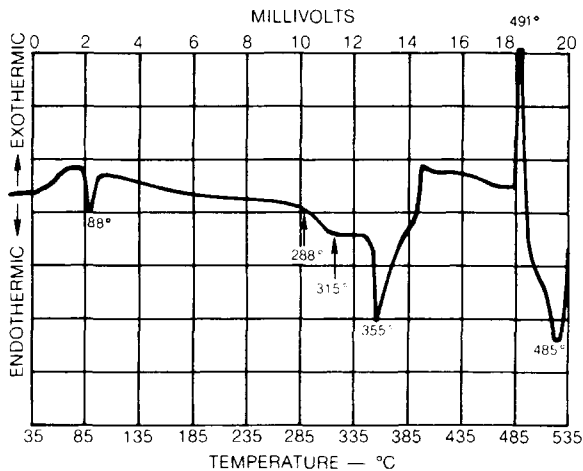Resin color is generally lighter for samples prepared under nitrogen.   All have



Fig. 4.  DTA thermogram of bisnadimide 1-10.

excellent adhesion to glass as shown by the fact that it is very difficult to separate resin from the reaction tubes, and in many instances contraction of the resin upon cooling causes the reaction tube to fracture.

The ability of the nadimide system to undergo thermal addition polymerization so readily is probably due to a combination of ring strain and the formation of two other reactive species, maleimide and cyclopentadiene, upon retrograde Diels–Alder reaction. Unstrained olefins are quite reluctant to polymerize in the absence of initiators. Bisimide 2, for example, polymerized extremely slowly under the same conditions to give low-molecular-weight material; furthermore, 2 showed little, if any, tendency to copolymerize with cyclopentadiene. Bismaleimides, also possessing a strained ring, are the only other type known to undergo such ready thermal polymerization.[7-9] Thus, the bisnadimides and bismaleimides are unusual in their ease of processing and are by no means representative of the usual type of addition polymerization monomers.

The structure of the crosslinked polymers is undoubtedly complex, with three major structural units (3, 4, and 5)
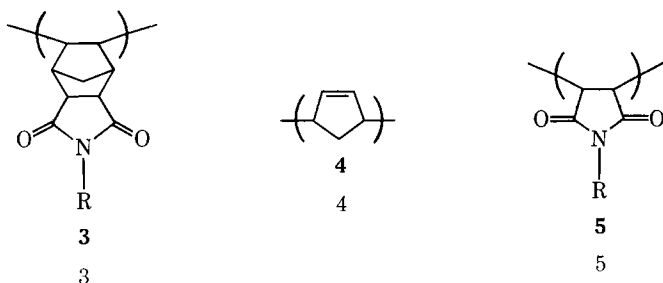


predominating arising, respectively, from homopolymerization of bisnadimide, and polymerization (or copolymerization) of cyclopentadiene and maleimide from the retrograde Diels–Alder reaction. Other possible structures could arise from 1,2-polymerization of cyclopentadiene[14] or bond migration,[15] known reactions in diene polymerization.

How much of each repeating unit is present depends in large measure on the degree of retrograde Diels–Alder reaction. However, it appears from infrared stuides that 3 predominates since the spectra do not change appreciably upon polymerization. Figures 2 and 3 show representative spectra (KBr and film, respectively) of two monomers and their corresponding resins prepared under different conditions of polymerization.

To test the effect of initiators on polymerization rate, three samples of 1-3 (approximately 2 g each), one containing 2 wt % dicumyl peroxide (DCP), another 0.5 wt % anhydrous stannic chloride, and the third no initiator, were heated uniformly in air at 250–280°C. The sample containing peroxide gelled in 33/4 hr, whereas the remaining two were still molten after 4 1/2 hr. The stannic chloride-containing resin was dark brown in color.

Cyclopentadiene was evolved from all resins during polymerization, but in no instance was the theoretical amount lost, even under high vacuum or from films in aluminum dishes. Percent weight loss for 1-3 resins ranged from about 11% under vacuum to as low as 1% for samples polymerized in bulk at atmospheric pressure. Maximum weight loss for 1-3 would be 36% if the theoretical

amount of cyclopentadiene were evolved. Thus, copolymerization of cyclopentadiene with bisnadimide or bismaleimide occurs rapidly, although some loss is unavoidable under normal processing conditions. Only in sealed tubes was all the cyclopentadiene captured. Vacuum line experiments using a liquid nitrogen cold trap showed that cyclopentadiene (and its dimer) were the only compounds trapped in measurable quantities.

Loss of cyclopentadiene was determined for approximately 3-g samples of each of the bisnadimides (with the exception of 1-DAM), both with and without added dicumyl peroxide. Results are given in Table II. The amount lost depends on several factors, including rate of polymerization, sample size, and viscosity. As the molecular weight of the bisnadimide increases, polymerization rate should decrease due to the decreasing concentration of double bonds. This is shown graphically in Figure 5. Despite the considerable scattering, it is apparent that cyclopentadiene loss is more of a problem at higher monomer molecular weights, and peroxide has no appreciable effect in reducing loss.

Decomposition occurs more readily for the higher molecular weight bisnadimides as evidenced by the darker color. With samples 1-9, 1-10, 1-12, and 1-CBMA, the resins exhibit a slight fluorescence suggesting formation of some aromatic groups during polymerization. Small peaks at 700 and 830 cm$^{-1}$ in the infrared spectrum of the resin from 1-12 (Fig. 3) may result from aromatic C—H deformation.

## Copolymerization

Bisnadimide 1-3 was copolymerized in evacuated, sealed tubes with three comonomers—norbornadiene, styrene, and divinylbenzene—at concentrations such that monomer and comonomer had equal amounts of unsaturation. Results are given in Table III. With norbornadiene, polymerization was incomplete after 1 hr at 300°C, and residual liquid, consisting mainly of norbornadiene and cy-
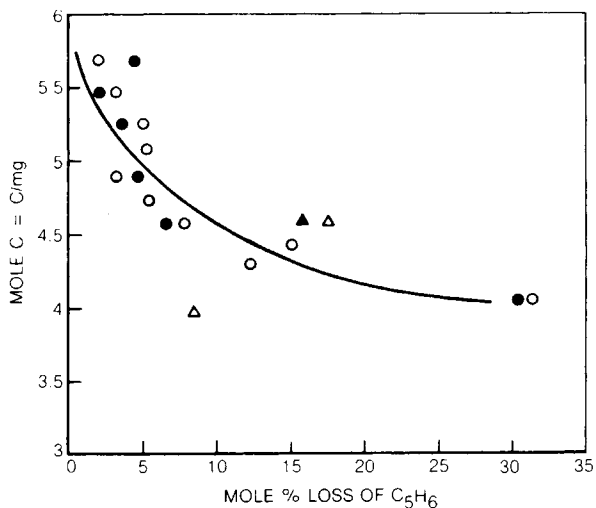


Fig. 5. Mole C═C per mg bisnadimide as function of mole % loss of cyclopentadiene: (O) straight-chain aliphatic bisnadimides; (△) cyclic aliphatic bisnadimides; (●, ▲) DCP added (1 mole % based on moles of C═C).

clopentadiene, was still visible. When azobisisobutyronitrile (AIBN) was added, no liquid was evident, although the odor of monomer was very strong.

Styrene and divinylbenzene appeared to homopolymerize since the products exhibited phases of different color (yellow and brown). Only in the case of styrene with AIBN added was the resin completely homogeneous.

## Processing and Properties of Polybisnadimides

Evolution of cyclopentadiene causes difficulties in preparing test specimens of bisnadimide polymers because voids are formed in the crosslinked product. Voids can provide regions in a sample for penetration of moisture into the polymer matrix.

Another problem arising during thermal polymerization in air is surface skinning, leading to gel particles dispersed in the specimen. Skinning probably results from formation of hydroperoxide at the allylic positions of cyclopentadiene upon contact with oxygen leading to free radical polymerization of monomers near the surface, a reaction analogous to the skinning of drying oils. Molten polymer does not, however, form a surface skin in air at 150–170°C, which is below the temperature of the retrograde Diels–Alder reaction. Thus, the allylic position of the nadimide group, which is at the bridgehead of a strained tricyclic ring system, may resist free radical formation. Skinning does not occur when samples are processed under nitrogen.

Careful control of the pressure to allow gas to escape and to press out bubbles before the resin becomes highly crosslinked is essential to mold void-free test samples. To avoid gel particles on the surface, bisnadimides can be polymerized to a B-stage under nitrogen, thus keeping press time to a minimum. B-staged resins are also soluble in methylene chloride, and solutions can be used to coat fibers for preparing composites.

Samples of all bisnadimides, with the exception of 1-DAM which reacts extremely slowly, were polymerized to a B-stage under nitrogen, then ground, where possible, to coarse powder in a mortar. Resins prepared from **1-9**, **1-10**, and **1-11** were too rubbery to grind, and those from **1-7** and **1-8** formed sticky powder upon grinding. The ground or rubbery samples were used for preparing disks for determining physical properties and moisture resistance.

TABLE III
Copolymerization of Bisnadimide 1-3[a]

| Conditions | Weight,[b] g | Mole[b] | Mole C=C[b] | Results |
|---|---|---|---|---|
| 1-3 Alone | 3.66 | 0.01 | 0.02 | clear resin |
| 1-3 + Comonomer | | | | |
| Norbornadiene | 0.92 | 0.01 | 0.02 | residual monomer |
| Norbornadiene + AIBN[c] | 0.92 | 0.01 | 0.02 | monomer odor |
| Styrene | 2.08 | 0.02 | 0.02 | phase separation |
| Styrene + AIBN[c] | 2.08 | 0.02 | 0.02 | homogeneous |
| Divinylbenzene | 1.30 | 0.01 | 0.02 | partial separation |
| Divinylbenzene + AIBN[c] | 1.30 | 0.01 | 0.02 | phase separation |

[a] Sealed, evacuated reaction tubes.

[b] Refers to comonomer amounts only with the exception of **1-3** alone; all copolymerizations contain 3.66 g (0.1 mole) of **1-3**.

[c] 0.04 g AIBN.

TABLE IV
Moisture Absorption Properties of Polybisnadimides

| Resin prepared from | Moisture absorption, wt % | | | | |
|---|---|---|---|---|---|
| | Room temp. 24 hr | Boiling water | | | |
| | | 24 hr | 72 hr | 144 hr | 168 hr |
| 1-2 | 1.08 | 4.62 | 5.59 | 5.86 | 6.00 |
| 1-3 | 0.69 | 3.21 | 4.59 | 5.66 | 5.84 |
| 1-4 | 0.90 | 3.65 | 5.44 | 5.88 | 6.04 |
| 1-5 | 0.51 | 3.04 | 4.23 | — | 4.73 |
| 1-6 | 0.92 | 3.57 | 4.55 | — | 4.89 |
| 1-7 | 0.78 | 3.00 | 3.97 | 4.17 | 4.22 |
| 1-8 | 0.45 | 2.33 | — | 3.29 | 3.42 |
| 1-10 | 0.54 | 2.15 | 2.65 | 2.82 | 2.69 |
| 1-12 | 0.26 | 1.92 | 1.98 | — | 2.16 |
| 1-CBMA | 0.83 | 2.87 | 4.01 | — | 4.65 |
| 1-MBCA | 0.75 | 2.36 | 2.82 | — | 3.08 |
| PMR-11[a] | 0.37 | — | — | — | 1.70 |
| PMR-15[a] | 0.38 | — | — | — | 2.00 |

[a] Nadimide-capped oligomers prepared from 5-bicyclo[2.2.1]heptene-2,3-dicarboxylic acid mo-nomethyl ester, 4,4'-methylenebis(cyclohexylamine), and tetramethyl 3,3',4,4'-benzophenone te-tracarboxylate in mole ratios, respectively, of 1.00:1.00:0.50 (PMR-11) and 1.00:1.54:1.04 (PMR-15).

Polymer samples (with the exception of those prepared from 1-9 and 1-DAM) were subjected to distilled water at room temperature and at the boiling point. Moisture absorption characteristics are given in Table IV and Figures 6–8. For comparison, samples of nadimide-capped aromatic polyimide resins under the same conditions of exposure are included in Table IV. The concept of increasing the nonpolar character of the polymer to reduce moisture absorption is clearly shown by these data. Moreover, an odd–even relationship of the homologous series of aliphatic polybisnadimides is apparent for resins prepared from 1-2 through 1-7, at which point moisture absorption begins to drop more precipitously. This is illustrated particularly in Figure 6 for the room temperature water-exposed polymers.

It is clear from these results that, as expected, one must introduce a considerable amount of aliphatic character in order to obtain moisture-resistant resins. Only the resin from 1-12 has moisture resistance comparable to that of the PMR polyimides.
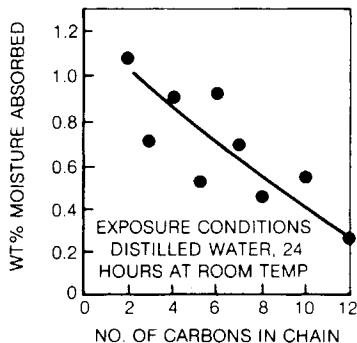


Fig. 6. Moisture absorption as function of carbon chain length for the homologous series of straight-chain aliphatic polybisnadimides (room-temperature water exposure).
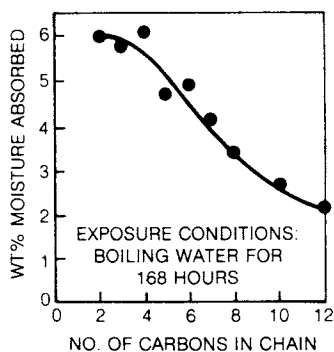
Fig. 7. Moisture absorption as function of carbon chain length for the homologous series of straight-chain aliphatic polybisnadimides (boiling water exposure).

Table V lists some physical and heat-resistance properties of polybisnadimides prepared from the straight-chain homologous series of monomers. Densities are comparable to those of the PMR polyimides, indicating that the aliphatic resins are highly crosslinked. This is further supported by the glass transition temperature of the resin from 1-3. All of the polybisnadimides tested exhibit excellent heat stability at 204°C in air.

The adhesive characteristics of the aliphatic polybisnadimides are listed in Table VI. The adhesive properties of PMR-15 polyimide, two high-temperature-cured epoxies (177°C), and a room temperature-cured epoxy adhesive are shown for comparison. Several points are worthy of mention with regard to these adhesive properties:

(1)   Specimens containing scrim cloth in the adhesive bond line exhibit higher tensile lap shear strength than specimens without scrim cloth in the bond line.

(2)   There is a correlation between adhesive strength and chain length of the aliphatic group between nadimide groups, namely, that the adhesive strength is low for polymers 1-2 through 1-7 and increases dramatically for 1-8 through 1-12. This is unexpected in that the lower bisnadimides have a shorter distance between imide polar groups than the higher bisnadimides. Therefore, the polarity of the higher polybisnadimides should be lower than the polarity of the lower polybisnadimides thereby resulting in decreased surface adhesion.
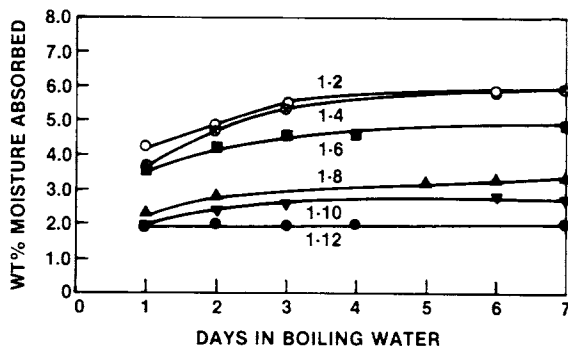


Fig. 8. Moisture absorption as function of time in boiling water for the homologous series of straight-chain polybisnadimides.

TABLE V
Physical and Heat-Resistance Properties of Polybisnadimides

| Resin prepared from | Appearance | Density g/cm³ | $T_g$,°C | Isothermal weight loss,[b] % |
|---|---|---|---|---|
| 1-2 | transparent, amber | 1.31 | | 0.39 |
| 1-3 | transparent, dark amber | 1.30 | 329 | 0.22 |
| 1-4 | transparent, yellow | 1.28 | | 0.25 |
| 1-5 | transparent, orange | 1.27 | | 0.18 |
| 1-6 | transparent, orange | 1.24 | | 0.31 |
| 1-7 | transparent, orange | 1.23 | | 0.19 |
| 1-8 | transparent, orange | 1.25 | | −0.02 |
| 1-10 | dark orange, green fluorescence | 1.21 | | 0.03 |
| 1-12 | orange-brown, green fluorescence | 1.17 | | 0.14 |
| PMR-11[a] | dark brown | 1.28 | 330 | — |
| PMR-15[a] | dark brown | 1.29 | 322 | — |

[a] See footnote a, Table IV.
[b] 204°C for 240 hr in air.

However, the short distance between nadimide groups for the $n = 2$ through 7 series causes a higher crosslink density than the polymers for the $n = 8$ through 12 series. The higher densities of the lower polybisnadimides is evidence for the higher crosslink density. The higher crosslink density generates a more brittle polymer system which appears to have a greater influence in controlling the adhesive properties than the polarity of the polymer system. The failure mode of the specimens containing 1-2 through 1-7 resins was cohesive in nature, while specimens 1-8 through 1-12 failed in an adhesive mode. This is further evidence for the brittle nature of the lower series polymers.

TABLE VI
Adhesive Properties of Aliphatic Bisnadimide Polymers[a]

| Polymer System | Specimens with scrim cloth, at RT | | Specimens without scrim cloth | | | |
|---|---|---|---|---|---|---|
| | | | RT | | 200°C | |
| | psi | MPa | psi | MPa | psi | MPa |
| 1-2 | | | 1190 | 8.20 | 735 | 5.06 |
| 1-3 | 1360 | 9.37 | 1085 | 7.48 | | |
| 1-4 | | | 1190 | 8.20 | 850 | 5.87 |
| 1-5 | 1209 | 8.33 | 808 | 5.57 | | |
| 1-6 | 1000 | 6.89 | 1015 | 6.99 | 838 | 5.77 |
| 1-7 | | | 905 | 6.24 | | |
| 1-8 | 1990 | 13.72 | 1200 | 8.27 | 1420 | 9.78 |
| 1-9 | | | 1610 | 11.09 | | |
| 1-10 | | | 1410 | 9.71 | 1400 | 9.65 |
| 1-12 | 2127 | 14.69 | 1840 | 12.68 | | |
| PMR-15[a] | 2183 | 15.05 | 1515 | 10.43 | 1390 | 9.58 |
| Epoxy Hysol 9649[b] | 2500 | 17.24 | — | | | |
| Shell Epon 907 RT epoxy[c] | 2200 | 15.17 | — | | | |

[a] Cured at 316°C for 1 hr, 0.414 MPa (60 psi).
[b] Cured at 150°C (2 hr) and 177°C (1 hr), 0.414 MPa (60 psi).
[c] Cured at room temperature for seven days, contact pressure.

(3)    The adhesive strengths of the 1-8 through 1-12 polymers are comparable to the adhesive strengths of the PMR-15 polyimide and room temperature-cured epoxy adhesives and approximately 400 psi lower than that of the Hysol 9649 epoxy adhesive.

## References

1.  J. D. Forest, *Advanced Composite Applications for Spacecraft and Missiles,* Progress Report No. 3, General Dynamics, Convair Aerospace Div., 1970, Report No. GDC-CHB70-001, Contract F33615-70-C-1442, WPAFB.

2.  J. Hertz, *Investigation into the High-Temperature Strength Degradation of Fiber-Reinforced Resin Composite During Ambient Aging,* Report No. GDCA-DBG73-005, Contract NAS8-27435, General Dynamics, Convair Aerospace Div., 1973.

3.  H. L. Young and W. L. Greever, *High-Temperature Strength Degradation of Composites During Aging in Ambient Atmosphere,* 6th St. Louis Symposium on Composites Materials in Engineering Design, May 12, 1972.

4.  T. T. Serafini and P. Delvigs, *J. Appl. Polym. Sci. Appl. Polym. Symp.,* No. 22, 89 (1973).

5.  T. T. Serafini, P. Delvigs, and G. R. Lightsey, *J. Appl. Polym. Sci.,* 16, 905 (1972).

6.  A. K. St. Clair and T. L. St. Clair, *Polym. Eng. Sci.,* 16, 314 (1976).

7.  F. Grundschober and J. Sambeth (to Societé Rhodiaceta), U.S. Pat. 3,533,996 (Oct. 13, 1970); (to Societé Rhodiaceta), U.S. Pat. 3,380,964 (April 30, 1968).

8.  D. O. Hummel, K.-U. Heinen, H. Stenzenberger, and H. Siesler, *J. Appl Polym. Sci.,* 18, 2015 (1974).

9.  H. Stenzenberger, *Appl. Polym. Symp.,* 22, 77 (1973).

10.  D. A. Scola and R. H. Pater, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* 20(2), 564 (1979).

11.  A. Furdik and V. Sutoris, *Chem. Zvesti,* 17(1), 31 (1963); Chem. Abstr., 60, 7930a (1964).

12.  J. K. Stille and L. Plummer, *J. Org. Chem.,* 26, 4026 (1961).

13.  C. Y. Lee (to Cities Service Co.), Ger. Offen. 2,730,316 (Jan. 26, 1978); U.S. Pat. Appl. 706,665 (July 19, 1976); *Chem. Abstr.,* 88, P136453Z (1978).

14.  C. Aso, T. Kunitake, and Y. Ishimoto, *J. Polym. Sci. Part A-1,* 6, 1163 (1968).

15.  J. Upadhyay, P. Gaston, A. A. Levy, and A. Wassermann, *J. Chem. Soc.,* 3252 (1965).