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A New Heat-Resistant Polymer From Dimer Diamine Bismaleimide

Part 1. Preparation and Free Radical Cure of Dimer Diamine Bismaleimide

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FOREWORD

A new thermally stable polymer is described and methods for synthesis and free radical cure of its "monomer" are presented. The bismaleimide of dimer diamine can be prepared in 35 to 56% yield by a mild method involving cyclodehydration of the precursor bismaleamic acid. Free radical cure can be accomplished with hydroperoxides promoted with a vanadium trineodecanoate/N,N-dimethyl-p-toluidine mixture to form a hard polymer. Thermal properties and tensile strengths of the polymerized material are also presented and discussed.

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(U) The preparation and free radical cure of the bismaleimide of dimer diamine is described where the polymer shows excellent thermal stability comparable to the aromatic substituted bismaleimide counterparts. An improved process for making the "monomeric" bismaleimide of dimer diamine provides good yields of highly pure material. Contamination by polymer or other by-products commonly encountered is eliminated by a process that uses N,N'-dicyclohexylcarbodiimide/1-hydroxybenzotriazole co-reagents for cyclodehydration of the precursor bismaleamic acid of dimer diamine. Purification of the crude product can be accomplished by chromatography which also fractionates the "monomer" from higher molecular weight materials thereby giving a prepolymer with a polydispersity of 1.02 as shown by gel permeation chromatography. The bismaleimide of dimer diamine is a free flowing oil at room temperature and should facilitate processing and curing in adhesive, sealant and composite applications since solvent would not be necessary as compared to currently used solid aromatic bismaleimides that require fabrication with solvent. Storage of the bismaleimide of dimer diamine in the cold can be indefinite without evidence of thermal polymerization. Free radical cure of the bismaleimide of dimer diamine at a moderate temperature and time by the use of hydroperoxide initiators promoted with a vanadium trineodecanoate/N,N-dimethyl-p-toluidine solution results in polymers that are very hard. Analysis by DSC and TGA shows that these materials can withstand temperatures greater than 300°C without significant degradation. Proton and carbon NMR as well as infrared (IR) spectroscopy greatly aid in analysis of the "monomer" and polymers of the bismaleimide of dimer diamine. IR spectroscopy serves to complement Differential Scanning Calorimetry (DSC) thermograms where the extent of free radical cure is concerned.

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INTRODUCTION

Polymers with improved heat-resistance over those currently used in composites for structural repair of aircraft and bonding in weapons systems as well as in materials for protection of electrical components from the environment are needed for advanced aircraft and armament. A guideline requirement for polymers with these intended uses is typically prolonged exposure to 450°F (230°C) without significant degradation. Other requirements such as moderate cure temperatures and times as well as storage, handling, and fabrication convenience are also important considerations when selecting or modifying materials for potential use.

Aromatic substituted bismaleimide prepolymers have received much attention because of their exceptional thermal stability after cure (References 1-4). Prepared from parent aromatic diamines and maleic anhydride, these prepolymers are usually solids at room temperature and commonly can be cured above their melting points at temperatures >200°C. Radical initiators (References 5-8), Lewis acid catalysts (References 7 and 9) and gamma radiation (References 10 and 11) are also known to polymerize similar materials in solution or as thin films.

However, for processing and fabrication purposes it would be advantageous to cure bismaleimides without solvent and at lower temperatures. Application with solvents can be detrimental to the properties of the cured polymers since solvent molecules may remain trapped in the interstitial volume of the polymeric network. Attaining lower cure temperatures would result in less costly processes with decreased energy demands and possibly new field repair kits for various applications.

Aliphatic substituted bismaleimide "monomers" or prepolymers would be a superior substitute for the aromatic systems since selected moderate molecular weight liquid diamines would lead to liquid bismaleimides. Thermal cure of these materials might be accomplished at lower temperatures since solid aliphatic maleimides are known to polymerize slightly above their melting points (Reference 12). Furthermore, the need for a solvent to facilitate processing these materials can be eliminated so that structural integrity of the polymers can be maintained along with lower processing costs.

We describe the preparation and techniques for curing a new aliphatic bismaleimide. Dimer diamine (Reference 13) is chosen as the parent amine to be modified and proves to maintain its liquidity at room temperature after transformation to its bismaleimide. It is noteworthy that the latter material can be stored in the cold for an indefinite length of time without evidence of thermal polymerization.

RESULTS AND DISCUSSION

PREPARATION OF DIMER DIAMINE BISMALEIMIDE

Several methods for the synthesis of aliphatic (References 12, 14-20, and 29) and aromatic (References 4, 10, 11, 17, and 21-37) substituted maleimides from the parent maleamic acids are known and have proven to be effective with dimer diamine (Reference 13) as shown in Table 1 although the yields of the product are generally low. Materials that are contaminated with polymer and acetamide by-product(s), which are difficult to remove, are continually encountered when the method described by Searle (Reference 23) is used. Reactions that use acetic anhydride as a dehydrating agent give >65% unreacted maleamic acid if the reaction temperature is maintained below 60°C. Acetic acid alone at 120°C gives the bismaleimide of dimer diamine, 2, in variable yields.

Although a variation of the method of Searle (Reference 23) in which nickelous acetate is used leads to the desired product, isomaleimide formation can be troublesome (References 33, and 38-44). Also, when triethylamine (TEA)/acetyl chloride (AcCl) is used at ambient temperature exclusive formation of isomaleimide results whereas some maleimide forms when the reaction is run at 35°C. Unfortunately, isomaleimide is difficult or impossible to remove and although it can be isomerized to maleimide (References 33 and 34), temperatures necessary for that transformation frequently cause thermal polymerization of the maleimide product.

A more recently developed method for the synthesis of aromatic maleimides involves the cyclodehydration of the precursor maleamic acids with N,N'-dicyclohexylcarbodiimide (DCCD) and 1-hydroxybenzotriazole (HOBT) co-reagents (Reference 46). Yields from 80 to 100% are reported from reactions that occur at 0°C in 2 hours where the products can be purified easily. No contamination by polymer or other by-products is observed during the synthesis of low molecular weight aromatic substituted maleimides.

TABLE 1. Cyclodehydration Reactions of 1 to Form 2.

Reagents	Conditions temp (°C)/time (H)	Yield of 2 (%)	Comments
Ac_2O/NaOAc	100/3	32	...
Ac_2O/NaOAc	95/1	36	...
Ac_2O/NaOAc	55/2.5	~0	Recovered unreacted bismaleamic acid
AcOH/NaOAc	122/6.5	34	...
AcOH	120/6.5	27-41	...
Ac_2O/TEA	60/7.5	35	...
Ac_2O/TEA/EDC[a]	25/1 then 67/2	9	Recovered unreacted bismaleamic acid
$Ac_2O/Ni(OAc)_2 \cdot 4H_2O$/TEA	86/4	37	...
$Ac_2O/Ni(OAc)_2 \cdot 4H_2O$/TEA	87/3	33	...
$Ac_2O/Ni(OAc)_2 \cdot 4H_2O$/TEA	60/4	18	Remainder of product is isomaleimide
TEA/AcCl	25/72	0	Produced isomaleimide
TEA/AcCl	35/1.75	36	Remainder of product is isomaleimide

[a] Ethylene dichloride.

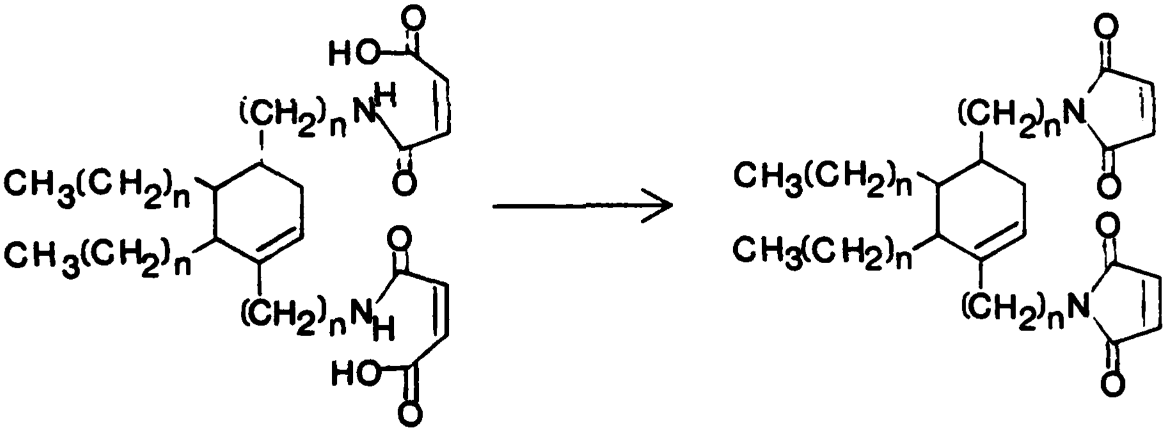
We find that the DCCD/HOBT co-reagents are particularly useful for the mild synthesis of dimer diamine bismaleimide from the parent diamine and maleic anhydride (Table 2). Yields on moderate-scale repetitive runs are in the range of 38 to 56% of exceptionally pure material. We also find that 80% of crude HOBT is recoverable and reusable after recrystallization from water followed by drying. This latter process makes the synthetic transformations very inexpensive and amenable to larger scale reactions. Note that tetrahydrofuran (THF) is preferred over ethylene dichloride (EDC) as a solvent (Table 2).

TABLE 2. Cyclodehydrations of 1 with DCCD and HOBT in THF.

Conditions; temperature (°C)/time (H)	Yield of 2 (%)
3-5/5 then 25/16	50
5-10/4 then 25/16	42
5/7 then 25/16	38
0/4 then 25/16	56
0/4 then[a] 25/16	0

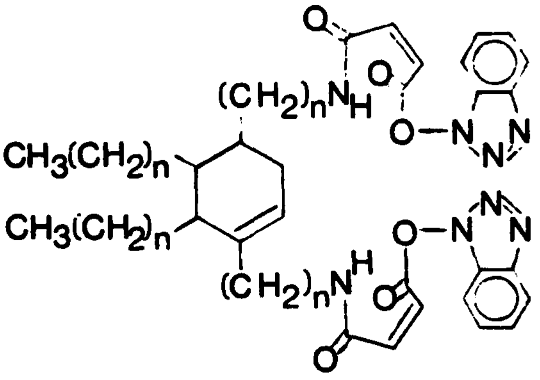
[a] EDC was used as solvent instead of THF.

Reaction of dimer diamine with maleic anhydride gives the bismaleamic aid, 1, which is used directly from its reaction mixture. Adding twofold molar amounts of DCCD and HOBT to 1 in THF affords crude bismaleimide 2, precipitated N,N'-dicyclohexylurea (DCU), and HOBT. Maleimide formation presumably occurs via the activated ester 3 which is generated in the presence of DCCD and 1 (References 47 and 48).



1 2

From a thorough investigation concerned with the production of 2, we find that improved yields over those listed in Table 2 cannot be expected by this procedure. Considerable amounts of "monomer" appear to be lost during isolation and purification even though monitoring the reaction mixture by proton nuclear magnetic resonance (NMR) shows



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complete conversion of 1 to 2. Alterations in the isolation and purification processes described in the experimental section result in even lower yields of impure 2. Insight into the reason for maximum yields being limited as such can be gained through gel permeation chromatography (GPC) and carbon NMR spectroscopy.

Dimer diamine is manufactured from dimer acid which is known as a mixture of mono, di, and trifunctional oligomeric, aliphatic, carboxylic acids (Reference 13). In turn, dimer acid is produced commercially from thermal cyclization of unsaturated fatty acids via a Diels-Alder process (Reference 13). The nature of these materials reflects the reasons why yields of 2 are limited and cannot be improved without sacrificing the quality of the final product.

Figure 1a shows a GPC trace of dimer diamine where the molecular weight ranges from 825 to 210 g/mole. Figure 1b displays a GPC trace of pure dimer diamine bismaleimide, 2, and the fact that this material is nearly "monomeric" with a polydispersity ($\bar{M}_W/\bar{M}_N$) of 1.02. Differences in these two GPC traces are results of product fractionation during isolation and purification. The molecular weight distribution plots shown in Figure 2 for dimer diamine (a) and its bismaleimide (b) further elaborate the results of fractionation.

Support for fractionation is also given through carbon NMR spectroscopy where the olefinic region of dimer diamine (Figure 3a) shows many peaks whereas 2 (Figure 3b) shows only two olefinic carbons for the polymer chain as well as the maleimide olefin (Reference 49). Isolated as a single "monomeric" molecule, the product 2 has a well defined molecular weight of 707 g/mole (from proton NMR peak integration, see Figure 4) instead of a broad distribution of molecular

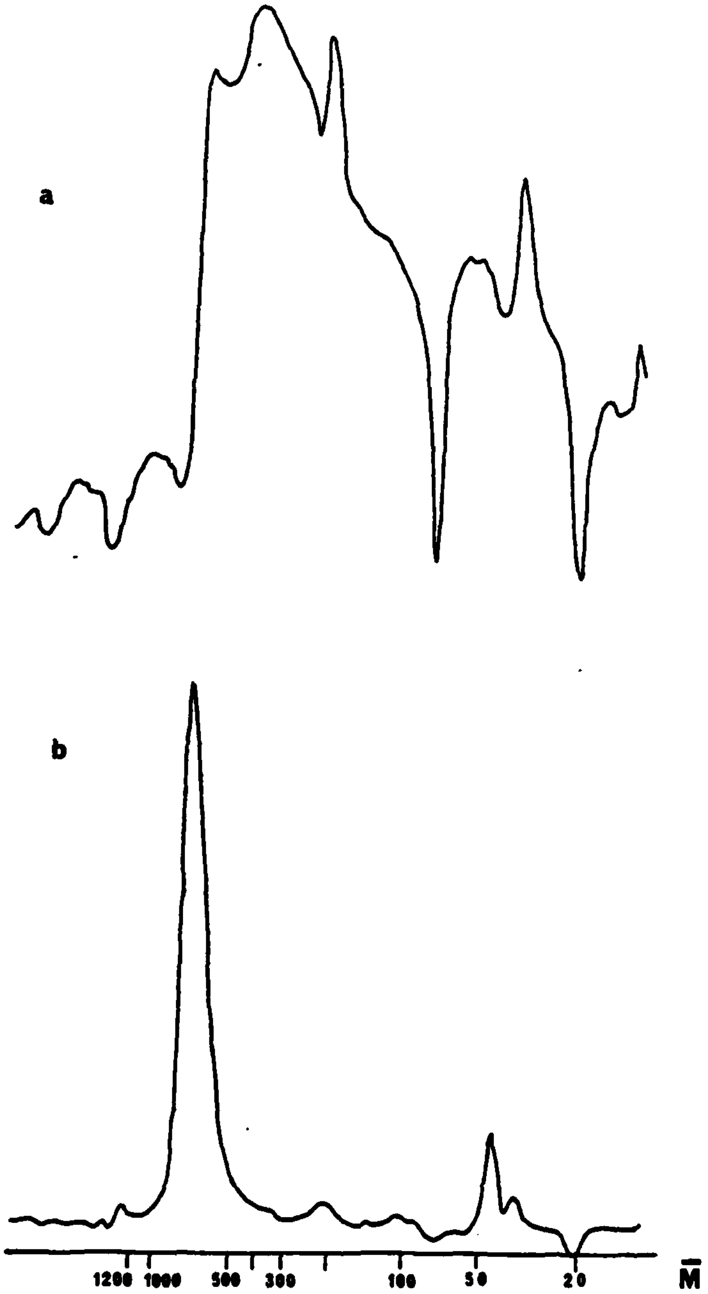

FIGURE 1. GPC Traces of Dimer Diamine (a) and its Bismaleimide (b).

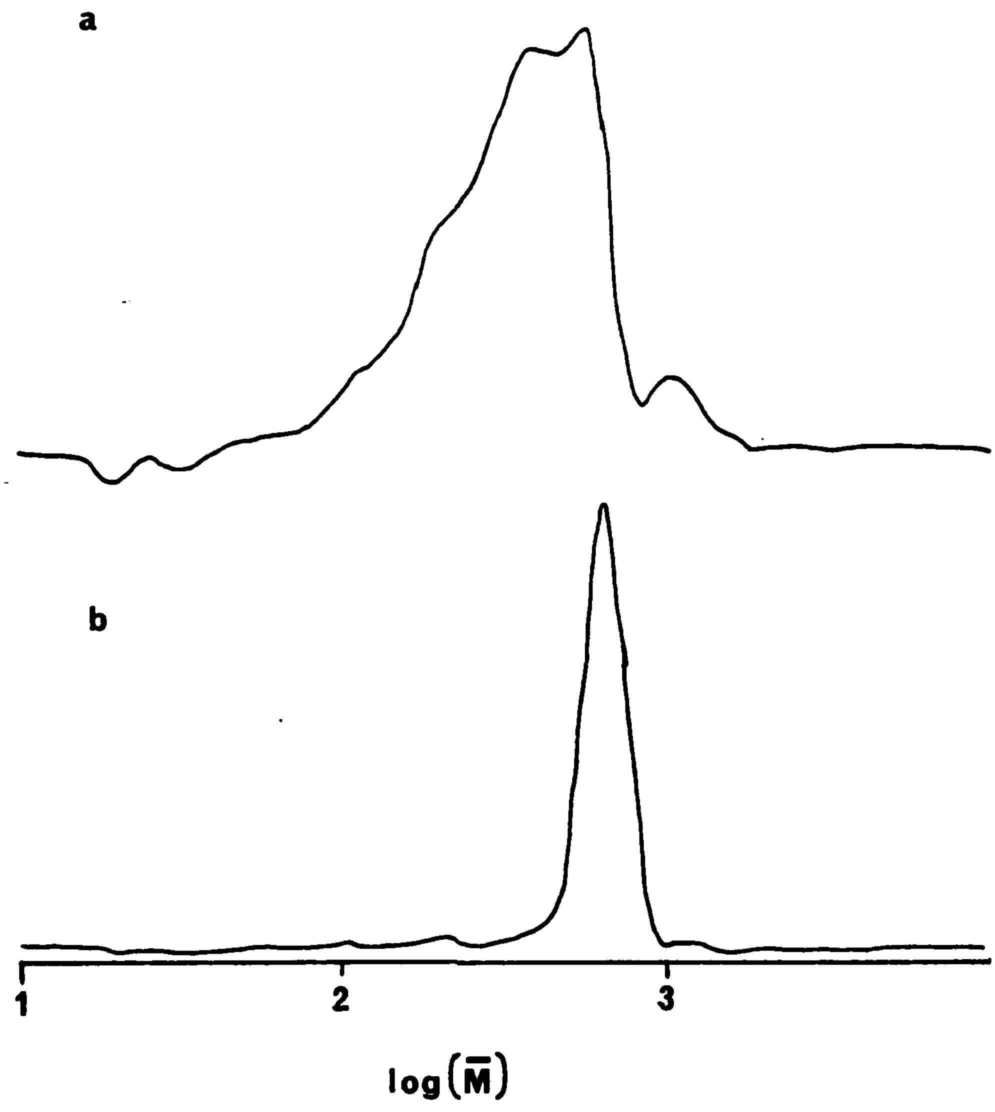

FIGURE 2. Molecular Weight Distribution of Dimer Diamine (a) and its Bismaleimide (b).

weights resulting from an agglomeration of many different molecular weight fractions as in dimer diamine. Since the purification of crude 2 presumably involves extraction of one molecular weight fraction of the cyclodehydration products from 1, it is very unlikely then that higher yields of pure 2 can be obtained. High and mostly low molecular weight materials are undoubtedly removed from 2 during purification.

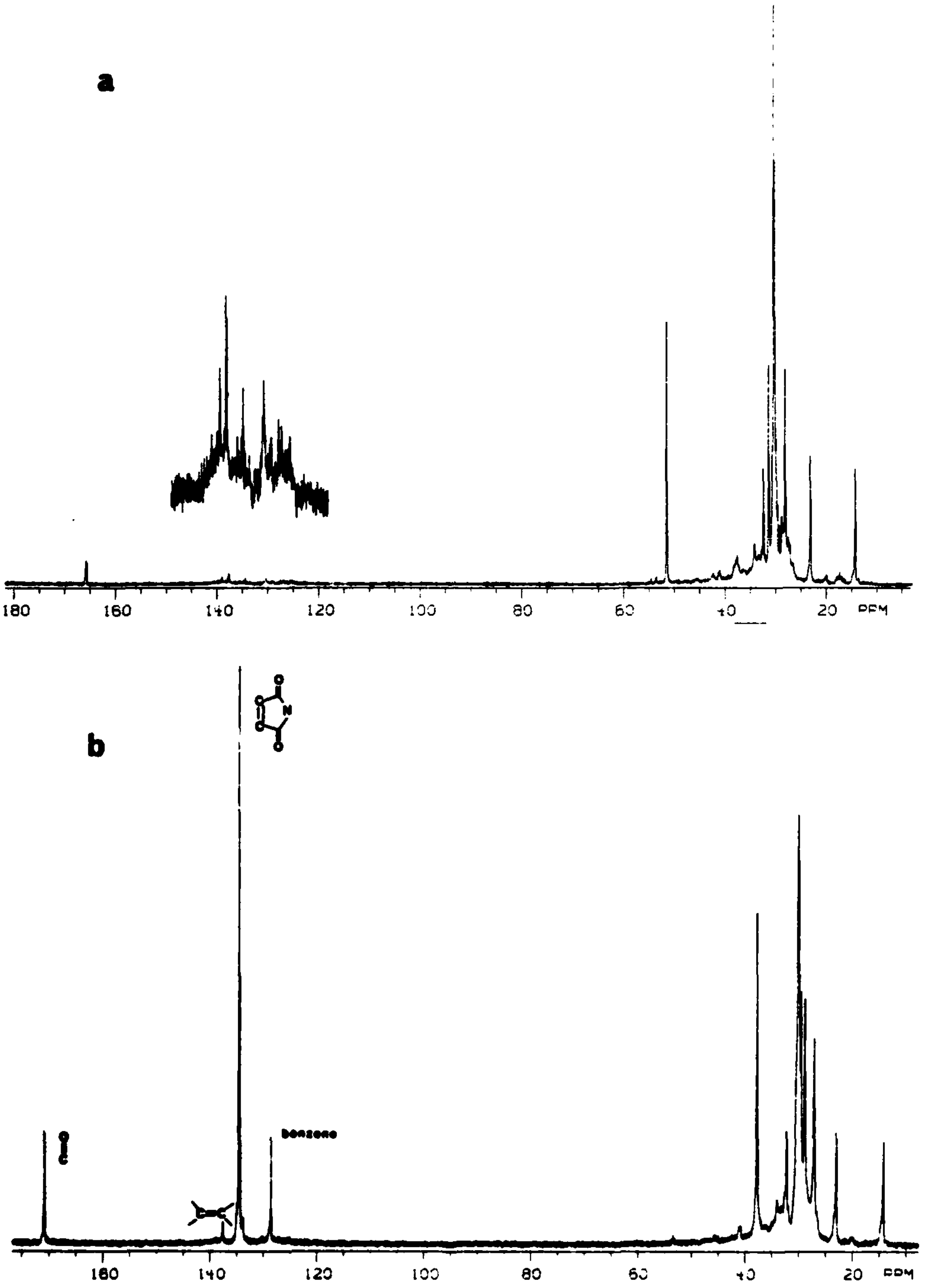

FIGURE 3. ^{13}C NMR (Acetone-d_6) of Dimer Diamine (a) and its Bismaleimide (b).

It must be noted that fractionation of dimer diamine before use is not feasible since several methods for this purpose have been studied and found ineffective (Reference 13).

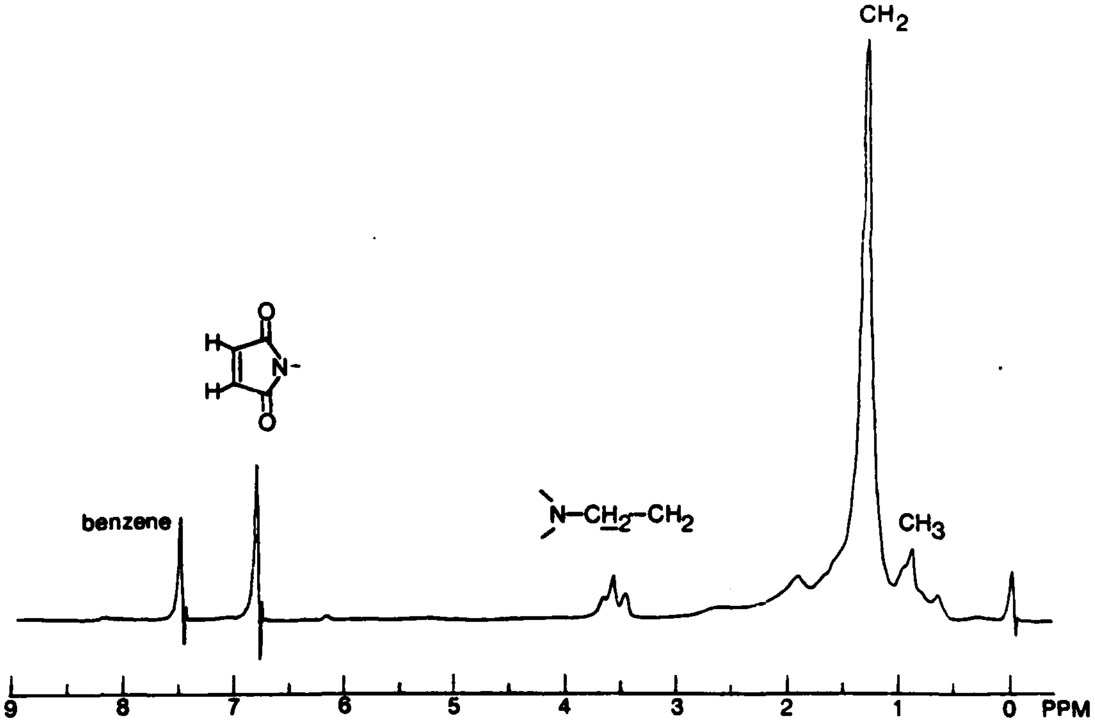

FIGURE 4. Proton NMR of Dimer Diamine Bismaleimide.

FREE RADICAL POLYMERIZATION OF DIMER DIAMINE BISMALEIMIDE, 2

Olefin polymerization is well known and can be accomplished efficiently with free radical initiators such as peroxides (Reference 50). Knowledge of peroxide half-life temperatures aids in selecting the appropriate initiator such that optimum temperature ranges and cure times can be obtained in order to provide useful materials. Furthermore, adequate processing times can be achieved where, for example, liquid resins can be cast into preshaped molds before gel formation occurs.

We find that 2 can be cured with a variety of peroxide initiators at various temperatures. t-Butylperbenzoic acid, Lupersol 231, and di-t-butylperoxide promoted with N,N-dimethyl-p-toluidine (DMT) require 100°C or more and 1.5 to 2.5 days to cure liquid resin samples of 2. Benzoyl peroxide promoted with Component C at 100°C after 4 days with 2 gives a very soft polymer. More efficient systems are those that use t-butylhydroperoxide or cumene hydroperoxide with a vanadium trineodecanoate/DMT co-promoter solution (Reference 51). Cure of 2 can then take place at 80 to 100°C in no more than 16 hours.

In general, curing under vacuum or in an inert atmosphere provides materials that are very hard and have tack-free surfaces. Since oxygen is known to inhibit free radical formation, curing in air results in polymers with uncured surfaces presumably from free radical quenching of the peroxide or propagating radical. Use of a one-piece mold provides the necessary apparatus to cure the liquid resin of 2 into minidogbone samples in an inert atmosphere after evacuation/purge cycles are performed.* Dissolved air can be removed from the samples by this process.

Table 3 shows the amount of reagents as well as the temperature used to cure 2 to a hard polymer. For our purposes, only those samples cured with t-butylhydroperoxide or cumene hydroperoxide have satisfactory cure times and temperatures. The resulting materials are used in further evaluations.

TABLE 3. Free Radical Cure of 2 with Peroxide and a Vanadium Trineodecanoate/DMT Promoter Solution.[a]

Sample	Peroxide (g/g resin)	Promoter g/g resin	Temp (°C)/time (H)
4-17	Cumene hydroperoxide (0.011)	0.0028	80/18
5-31	t-Butylhydroperoxide (0.011)	0.0028	100/16
5-32	Cumene hydroperoxide (0.011)	0.0014	100/16
5-35	t-Butylhydroperoxide (0.022)	0.0050	100/18

[a] The resin of 2 can be cured to ca. 33% (IR analysis) by heating at 100°C for 18 hours under N_2 and results in a very soft polymer. A DSC thermogram of that polymer does not show an exotherm at 140°C as the free radical cured polymers thus indicating different cure mechanisms for thermal and free radical polymerizations.

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[*] This mold is made of Sylgard 184 (Dow Corning) with the shape of minidog bones (1 inch long by 1/8 inch thick) imbedded.

In all cases, the time to gel formation is >1.5 hours. It is interesting to note that if more than 0.0028 g of promoter solution per gram of resin is used with cumene hydroperoxide, gel formation occurs too rapidly to allow satisfactory mixing, casting, and degassing time. This problem is not evident with t-butylhydroperoxide where 0.005 g of promoter solution per gram of resin can be used. A thorough description of the cure procedure can be found in the experimental section.

In order to characterize the polymerization process, infrared (IR) spectroscopy proves to be a useful tool for evaluating these polymers since differences between a maleimide resin and its cured material can be easily identified (Reference 7). An IR spectrum from 2000 to 400 cm ^{1} of "monomer" 2 is shown in Figure 5 along with the polymer of 2 from free radical cure. The absorption for the maleimide carbonyls at 1709 cm ^{1} (Figure 5a) changes drastically after polymerization where two peaks at 1774 and 1703 cm ^{1} (Figure 5b) are evident and due to unsymmetrical stretching vibrations between the two carbonyls of the polymerized maleimide group. A peak at 1354 cm ^{1} is also present in the polymer, but absent in the "monomer," and indicates a methyne C-H deformation arising from polymerization of the maleimide double bond. Significant changes in the 800 to 400 cm ^{1} region are particularly noteworthy. Nearly all of the absorption intensity for the maleimide olefin at 696 cm ^{1} is absent in the polymer. Furthermore, the doublet at 741 and 722 cm ^{1} in the polymer is due to crystal field splitting of polymethylene rocking motions in the dimer diamine backbone.

THERMAL PROPERTIES OF DIMER DIAMINE BISMALEIMIDE POLYMERS

Differential Scanning Calorimetry (DSC) of a typical sample of this material (Figure 6, Run 1) shows exotherms at ca. 140 and 350°C in air. Cooling the sample back to ambient temperature followed by heating past 350°C (Figure 6, Run 2) shows disappearance of the exotherms. Small amounts of unreacted olefins presumably remain in the otherwise cured material such that annealing past 350°C for even very short times causes their thermal polymerization. However, in N_2 atmosphere (Figure 7) the sample does not show an exotherm at 350°C. This result indicates that the latter exotherm at 350°C (Figure 6) is due to oxidative decomposition of the polymer. Samples of polymers that are post-cured at 180°C for 2 to 3 hours also show exotherms at 140 and 350°C in their DSC curves (not shown) indicating that a higher temperature or prolonged exposure may be required for complete post-cure.

Comparison of IR spectra of 2 and its polymer product (Figure 5) can provide information on the approximate extent of cure and complement DSC thermograms. The peak at 696 cm ^{1} in the "monomer" 2 (Figure 5a) can be used to evaluate the extent of cure by determining the

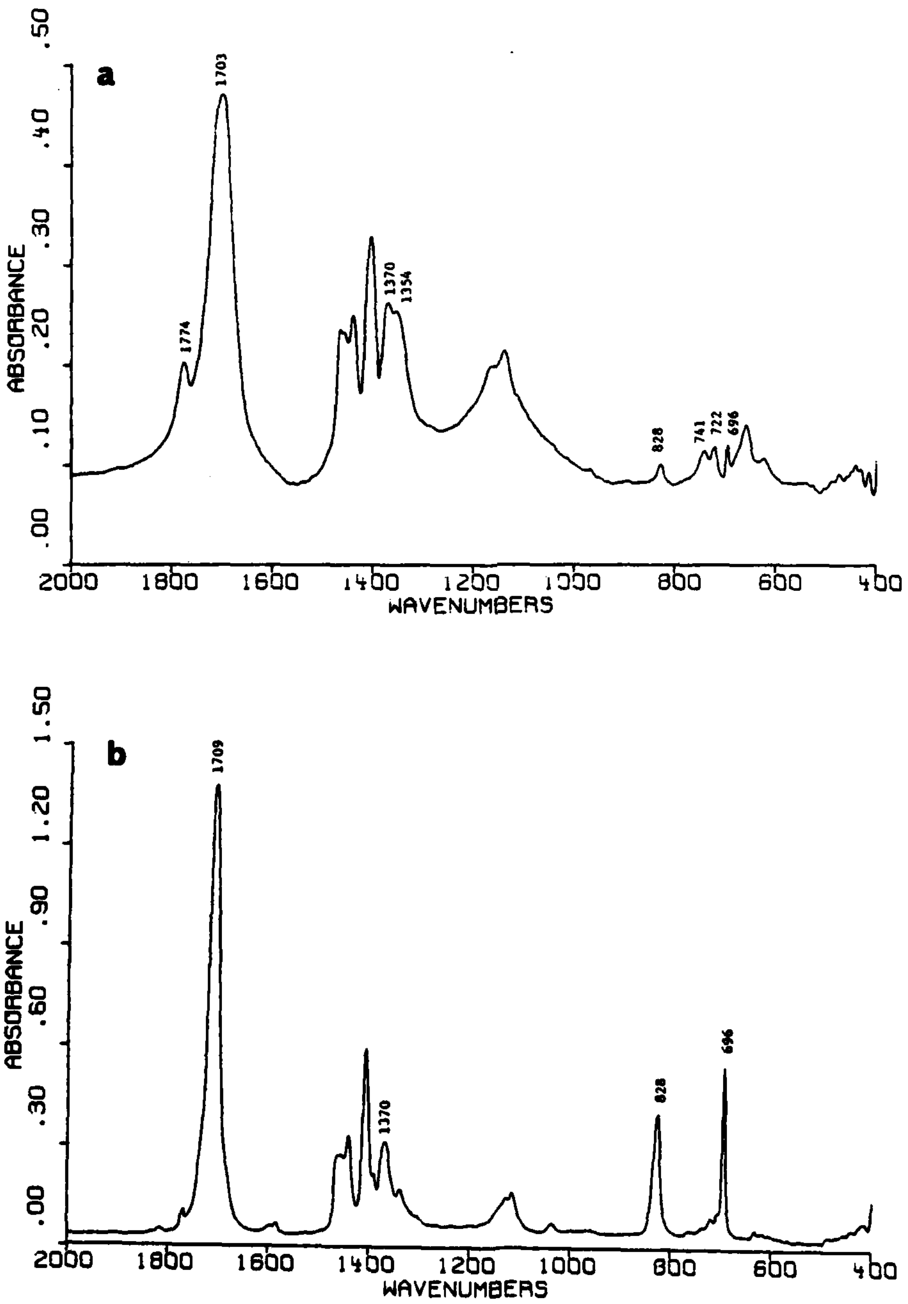

FIGURE 5. IR Spectra of the Bismaleimide of Dimer Diamine (a) and its Polymer (b).

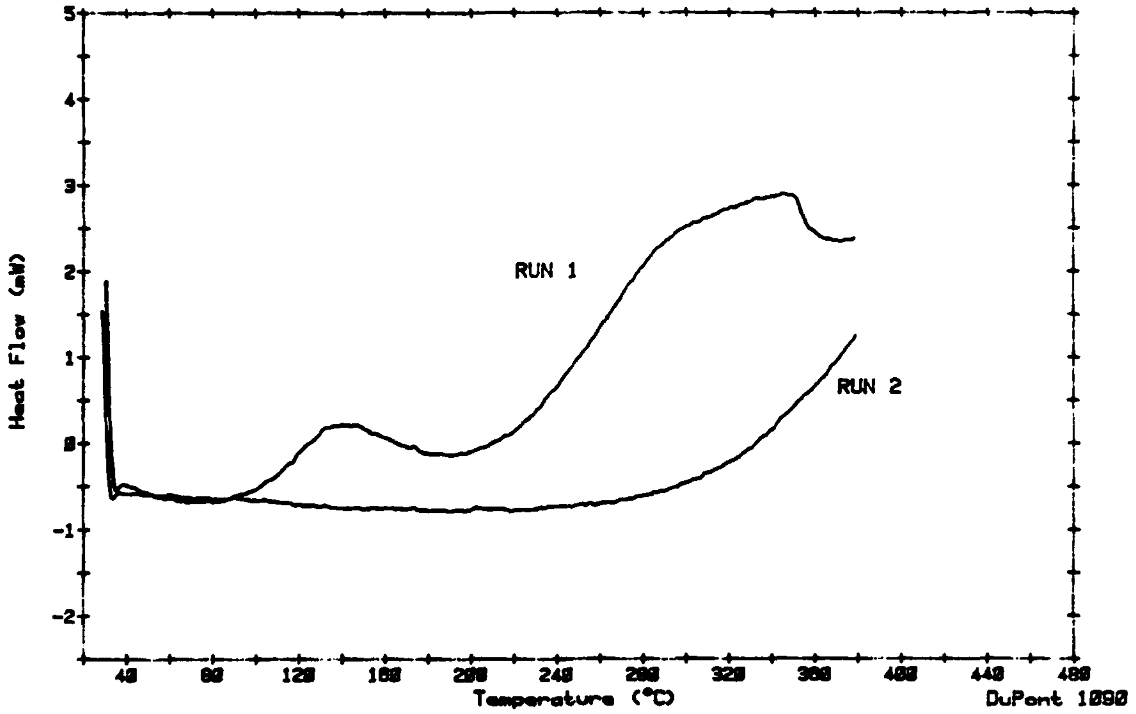

FIGURE 6. DSC Trace of Dimer Diamine Bismaleimide Polymer.

residual amount of unreacted maleimide groups through peak integration after cure (Figure 5b). Unreacted maleimide remaining in the polymer amounts to approximately 15%. This result is typical of all the samples (Table 4) evaluated by IR spectroscopy (not shown) even after post-cure and reflects a situation where post-curing at 180°C does not aid in polymerizing residual maleimide olefins. Support for this latter result is given by DSC where the exotherms at 140°C (Figure 6) can be integrated and related to sample size. However, the samples which are post-cured (Table 4) do not show smaller peak areas than samples that are not post-cured thereby indicating that a temperature greater than 180°C may be required for complete post-cure of the bulk samples (ca. 1 g of mass). Oddly enough, a DSC thermogram on sample 5-32 indicates that the exotherm at 140°C is removed if a small sample (ca. 5 mg) is heated to 180°C, cooled back to ambient temperature and reheated to 180°C. A reason for these ambiguous results is not obvious.

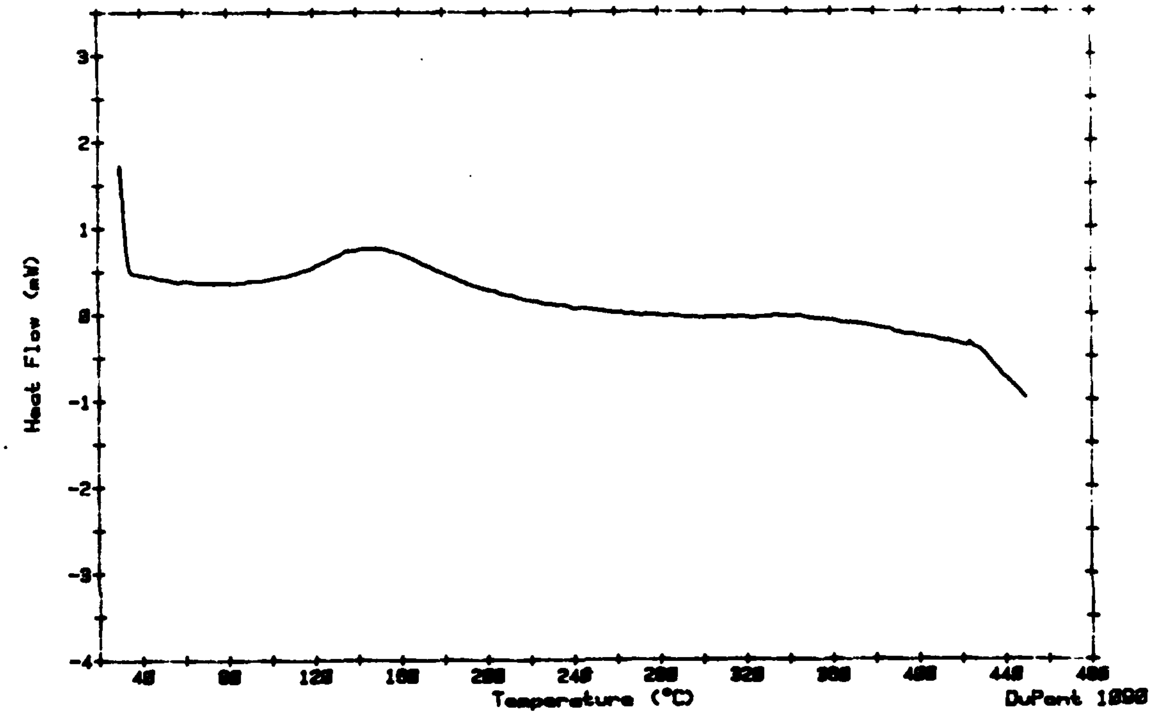

FIGURE 7. DSC Trace of Dimer Diamine Bismaleimide Polymer, N_2.

TABLE 4. Relative energies of DSC exotherms at 140°C[a].

Sample	Energy (J/g)	
5-31	12.4	(19.9)
5-32	38.3	(50.6)
5-35	20.2	(11.5)

[a] The numbers in parenthesis are those for post-cured samples.

Thermogravimetric analysis (TGA) of a typical sample (Figure 8) shows that the cured material is very stable to heating in air since only 1% of the polymer mass is lost through decomposition at 270°C. Rapid decomposition then follows at ca. 445°C. Post-cured samples also display this same type of decomposition in air indicating that they do retain thermal stability even when heated at 180°C for 2 to 3 hours. Under a N_2 atmosphere, the samples lose 1% of their weight at 320°C (Figure 9) and also decompose at a higher temperature than in air. It is worthwhile to note that because of this latter effect, the prepolymer 2 might be amenable to processing in an inert atmosphere or under vacuum at temperatures <320°C if necessary without significant decomposition of the resulting polymer.

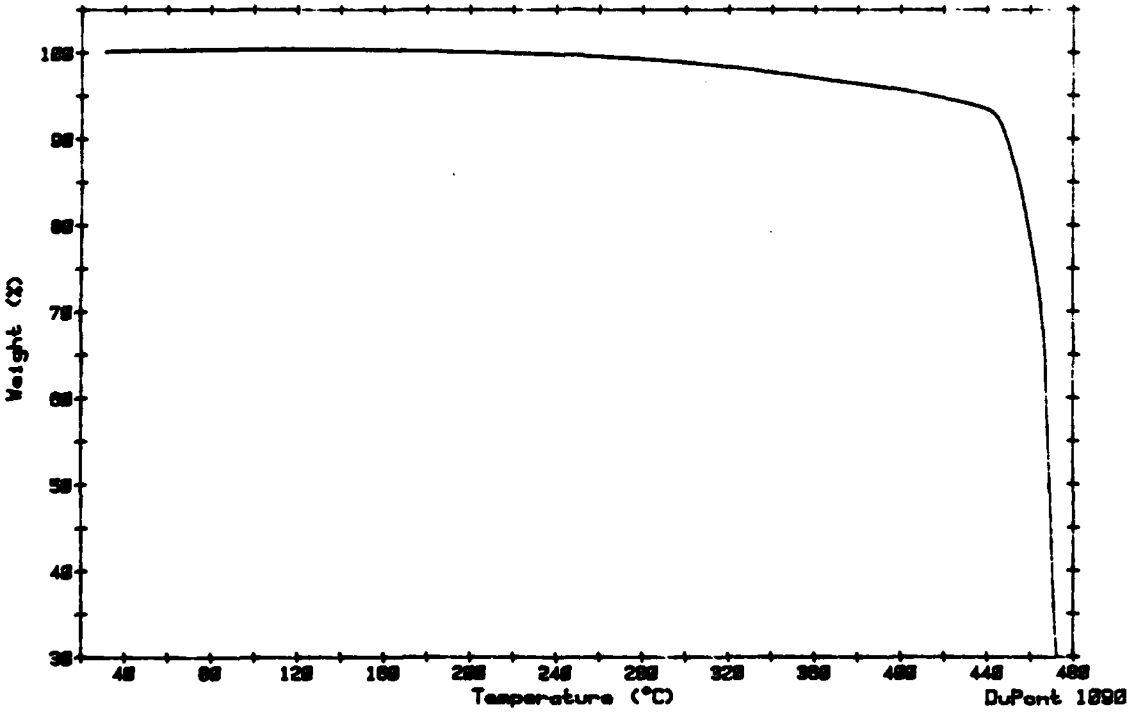

FIGURE 8. TGA of Dimer Diamine Bismaleimide Polymer.

TENSILE PROPERTIES OF DIMER DIAMINE BISMALEIMIDE POLYMER

Results of tensile tests for sample 5-31, 5-32, and 5-35 are given in Table 5. It can be seen that the polymers produced from using larger amounts of peroxide and promoter (e.g., sample 5-35 versus 5-31, Table 3) possess greater tensile strength at break (σ) and tensile modulus (E_0) presumably due to more efficient polymerization during cure. After annealing, the polymers generally have even greater strength except for sample 5-35. In that case, the prolonged annealing time probably causes slight degradation of the material such that the tensile strength is partially lost. A concomitant increase in elongation can also be observed for sample 5-35 after annealing.

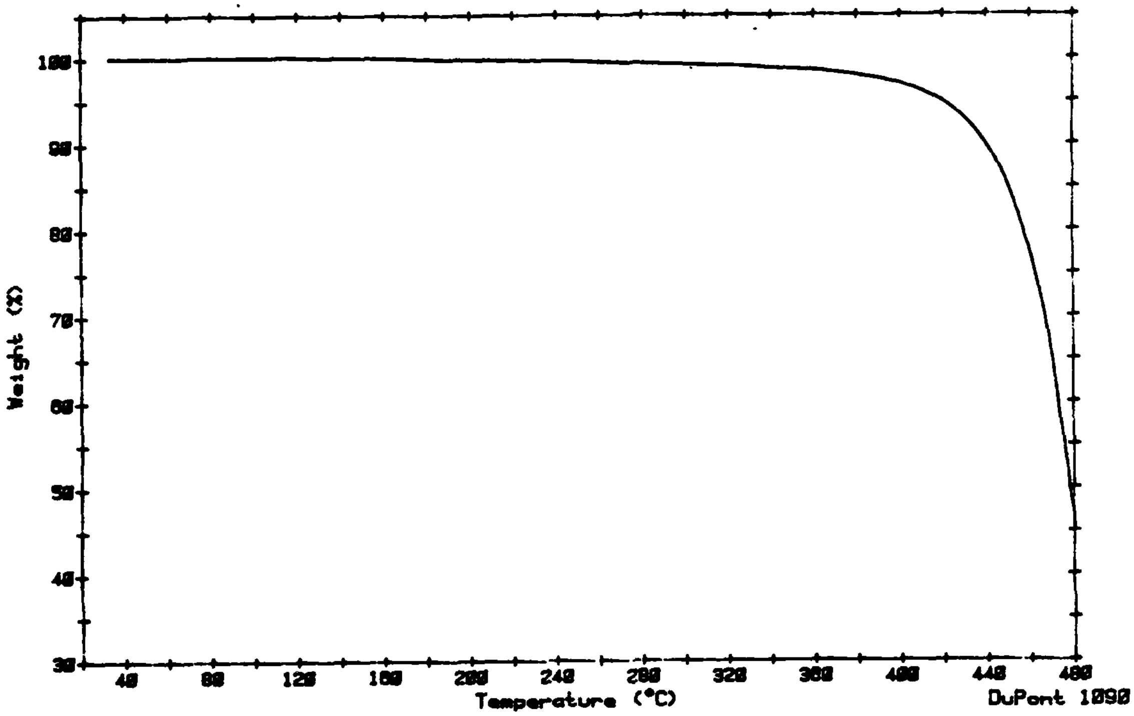

FIGURE 9. TGA Trace of Dimer Diamine Bismaleimide Polymer, N_2.

TABLE 5. Tensile Strengths of Dimer Diamine Bismaleimide Polymer.[a]

Samples	Strength at break (σ, psi)	Initial modulus (E_0, psi)	% Elongation (stress)
5-31[b]	1,488 (1,435)	14,387 (18,214)	15.2 (9.5)
5-32[b]	955 (1,210)	6,293 (16,436)	18.0 (10.0)
5-35[c]	1,046 (1,548)	22,443 (21,045)	7.6 (10.9)

[a] The numbers in parenthesis represent the samples after annealing.

[b] Annealed at 180°C for 2 hours.

[c] Annealed at 180°C for 3 hours.

CONCLUSIONS

An efficient process is now available for the synthesis of exceptionally pure dimer diamine bismaleimide which can be polymerized to a very hard material. Polymers from this aliphatic bismaleimide are also very thermally stable and may be useful as a heat-resistant polymer in adhesive, sealant, or composite applications. Further experimentation on the thermal cure of the bismaleimide of dimer diamine and its prereaction with diamines and dithiols in various amounts followed by thermal cure is presently in progress and will be reported at a later date. Analysis of the effects of storage of 2 at room temperature are also in progress and are concerned with the possible tendency for thermal polymerization over long periods of time.

EXPERIMENTAL

Dimer diamine was purchased from General Mills and heated to 80°C in vacuum (27 in Hg) for 18 hours before use. Maleic anhydride was purified as follows. The crude material (180 g) is diluted to 400 mL with chloroform while warming followed by filtration and addition of 40 mL of heptane. Cooling followed by filtration affords 169.2 g pure material (mp 47 to 51°C, lit.: 54°C (Reference 52)). THF was purchased from Burdick and Jackson Laboratories, Inc. and was distilled under N_2 from potassium in the presence of napthalene while a green color remained. DCCD was purchased from Aldrich Chemical Co. and used without further purification. HOBT-H_2O was purchased from Aldrich Chemical Co. and dried by heating at 100°C under vacuum (27 in Hg) to a constant weight. All peroxide catalysts were furnished by Lucidol Division, Pennwalt Corp. The promoter solution was prepared according to the procedure as described (Reference 51) and an equal volume of DMT was added to it.

Minidogbone casts were tested on an Instron universal tester at a rate of 1 inch per minute. Thermal analyses were performed on a DuPont 1090 Thermal Analyzer at a heating rate of 10°C per minute for both DSC and TGA. GPC were run with a Beckman 112 Solvent Delivery Module and an Altex 156 Refractive Index Detector along with a column set consisting of a 1000, two 500 and two 100 Å Altex, Inc. columns calibrated with polypropylene glycol standards having molecular weights of 4000, 2000 and 800. A flow rate of 1 mL/min was used along with a sample size of ca. 5 mg/mL and a sample loop size of 100 µL. Proton NMR spectra were recorded on a Varian EM360 Spectrometer. Carbon NMR spectra were recorded on a Nicolet NT200WB Spectrometer. IR spectra were recorded on a Perkin-Elmer 137 and Nicolet 7000 Spectrometer.

PREPARATION OF DIMER DIAMINE BISMALEIMIDE

Maleic anhydride (17.7 g, 0.1805 moles) was weighed into a 1 L, 4-neck, reaction flask equipped with a mechanical stirrer, a 250 ml dropping funnel, and a N_2 inlet/outlet. After the flask was purged with N_2 for a short while, 100 ml of dry THF was added under positive N_2 flow. The dropping funnel was charged with a solution of 50.4 g (0.0894 moles) of dimer diamine and 125 mL dry THF under positive N_2 flow. The dimer diamine solution was added drop-wise at ambient temperature over a 2-hour period. After stirring for an additional 2 hours, the mixture was cooled to 0°C and 24.4 g (0.1806 moles) of HOBT along with 100 mL of dry THF was added in one portion under positive N_2 flow. A solution of 37.3 g (0.1808 moles) of DCCD in 100 mL of dry THF was then added drop-wise over a 15-minute period. At the end of the addition period, the reaction mixture was a light yellow solution which began to precipitate a solid (DCU) after stirring for 10 minutes at 0°C.

After 2 hours of stirring, a 1 mL aliquot was extracted, filtered and the THF was evaporated. The residue was analyzed by proton NMR ($CDCl_3$) and showed the presence of unreacted bismaleamic acid (δ6.60, 2 H, CH = CH). At that time, the reaction mixture was allowed to come to room temperature without stirring. After standing at room temperature overnight, stirring was continued again and another 1 mL aliquot was extracted. Proton NMR ($CDCl_3$) showed only the presence of the bismaleimide and no bismaleamic acid.

The reaction mixture was filtered and the filtrate was evaporated to give an oil/solid mixture which was taken up in 300 mL of cyclohexane and stored at -5°C overnight. The cyclohexane mixture was centrifuged at 3500 rpm for 20 minutes. The resulting cloudy cyclohexane supernatant liquid was decanted, filtered, and evaporated to give a cloudy oil. The remaining solid from centrifugation was air dried and amounted to ca. 80% of the original amount of HOBT.

The cloudy oil product was dissolved in a minimum amount of benzene and chromatographed on 125 g of silica gel. Table 6 outlines the procedure for chromatography along with the fraction identities and their amounts after evaporation of solvent. The purity of the fractions from chromatography was determined by IR spectroscopy. Fractions 2, 3 and 4 were pooled and amounted to 28.7 g (44.4%) of pure dimer diamine bismaleimide, 2. The proton NMR ($CDCl_3$) spectrum of 2 is shown in Figure 3. The carbon NMR (acetone-d_6) spectrum of 2 is shown in Figure 2. An IR spectrum shows peaks at 3000 (maleimide CH), 2850, 2780, 1680 (maleimide CO), 1450, 1425, 1390, 1350, 1110, 825 and 692 cm^{-1} and is displayed partially in Figure 5a.

TABLE 6. Silica Gel Chromatography of Crude 2.

Fraction	Solvent	Product
1 (200 mL)	benzene	4.4 g of thick syrup
2 (200 mL)	benzene	13.8 g of pure 2
3 (250 mL)	3% ethyl acetate/ benzene	12.5 g of pure 2
4 (250 mL)	5% ethyl acetate/ benzene	2.4 g of pure 2
5 (300 mL)	7% ethyl acetate/ benzene	0.7 g of cloudy oil
6 (300 mL)	10% ethyl acetate/ benzene	0.4 g of cloudy oil

FREE RADICAL CURE OF DIMER DIAMINE BISMALEIMIDE, 2

Approximately 3 g of 2 were weighed accurately into a polypropylene cup. The promoter solution (see Table 3) was then added and the mixture was folded manually with a spatula for a few minutes. The peroxide (see Table 3) was then added and the mixture again folded well for a few minutes followed by quickly casting into the minidogbone shapes in a Sylgard mold previously treated with a Teflon mold-release spray. The mold was then placed in a vacuum oven at room temperature and evacuated to degas the samples. After several minutes under vacuum (27 in Hg), N_2 gas was bled into the vacuum oven until a positive pressure was obtained. This degas/purge process was repeated twice and usually required 0.5 hours to complete. Once the degas/purge cycles were completed, the specimens were heated to the desired temperature for a length of time (see Table 3) under a blanket of N_2. At the end of the heating period, the specimens were allowed to cool slowly under N_2 and then removed from the mold for testing. Post-curing was accomplished by placing the specimens on a glass plate previously treated with a Teflon mold-release spray and then placed in a preheated oven (180°C) in air.

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