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HIGH-TEMPERATURE THERMOSETS DERIVED FROM THE
DIELS-ALDER POLYMERIZATION OF BISBENZOCYCLO-
BUTENES AND BIMALEIMIDES

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Nonmetallic Materials Division

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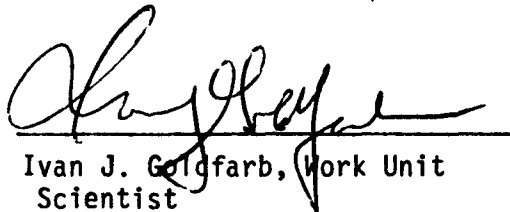
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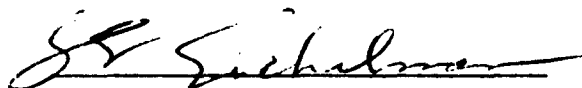


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polymerization is indeed the predominant curing process in the BCB/BMI system. Two important implications emerge from this study: (1) in a non-stoichiometric fashion, i.e., using various amounts of BCB which are less than 1 equivalent, BCB can not only help to elevate the thermo-oxidative stability of BMI, but also serve to control its cross-linking density; (2) more toughness is expected in the BCB/BMI system than BMI alone because of the linear character of the Diels-Alder product.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 230303, Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. I. J. Goldfarb as the ML Project Scientist. Co-authors were Loon-Seng Tan, Edward J. Soloski and Dr. F. E. Arnold, Materials laboratory, (AFWAL/MLBP).

This report covers research conducted from January 1986 to January 1987.

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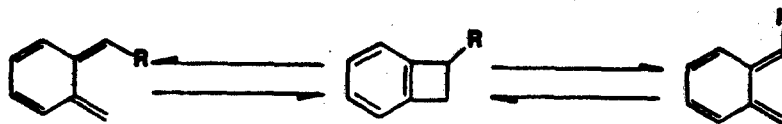
SECTION I

INTRODUCTION

Historically, benzocyclobutene* and its derivatives are laboratory curiosities because of their highly strained molecular structure and chemical reactivities. Despite a tremendous amount of strain energy embodied in these molecules, they are stable enough to permit isolation under room conditions, and many of them have indefinite shelf-lives. As such, this class of compounds has sustained a great interest in the areas of synthetic and physical organic chemistry since the preparation of the parent molecule was reported about 30 years ago^{2,3}. In recent years, their accessibility has been improved by the new synthetic technique, flash vacuum pyrolysis^{4,5}.

However, the utilization of benzocyclobutene functionality in polymer synthesis has appeared in open and patent literature only in the last few years. Aalbersberg and Vollhardt⁶ briefly mentioned their inadvertent preparation of the first polymer derived from a bisbenzocyclobutene monomer, albeit the polymer was brittle and not well-characterized. Kirchhoff and his coworkers⁷ described a more detailed effort in synthesizing the polymeric materials based on bisbenzocyclobutene-terminated monomers. Independently, we had also prepared a series of bisbenzocyclobutene-terminated monomers and oligomers, and a series of AB aromatic benzocyclobutene-alkyne monomers, as well as the thermosetting systems derived from them^{8,9}.

The cure chemistry of these systems is primarily based upon the fact that under appropriate thermal conditions, the strained four-membered ring of benzocyclobutene undergoes an electrocyclic ring opening. The temperature at which such a concerted process occurs depends principally on the substituents at the alicyclic, rather than the aromatic, positions.



*Although the correct name, as recommended by IUPAC, is 1,2-dihydrobenzocyclobutene, we use the trivial name benzocyclobutene for our convenience.

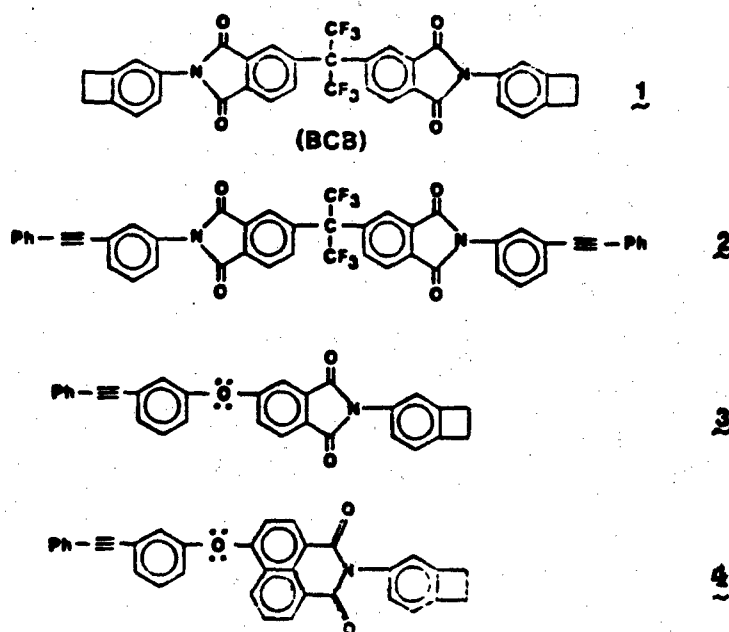
In the presence of a suitable dienophile, the more reactive valence-isomer, namely o-xylylene (or o-quindodimethane will be engaged in a Diels-Alder reaction ^{4d}, otherwise, it will dimerize and polymerize^{10,11}. The fact that the benzo-cyclobutene-based thermosetting resins have displayed remarkable thermo-oxidative stability prompts us to explore further different dienophile/benzocyclobutene combinations in addition to the alkyne/benzocyclobutene system. As a result, maleimide stands out as an ideal candidate for the dienophilic component, from both chemical and commercial standpoints. Although two main chemical reactivities, namely Diels-Alder cyclo-addition and Michael addition reactions, of maleimide are well-known in organic chemistry, only the latter, particularly with sulfur or nitrogen nucleophiles¹², have received much attention in polymer synthesis. However, Diels-Alder polymerization of bismaleimides and phenylated biscyclopentadienones has been reported to form linear polydihydrophthalimides¹³.

This paper will discuss research in our laboratory on the melt state Diels-Alder polymerization of a bisbenzocyclobutene (BCB) with a commercial bismaleimide (BMI).

SECTION II

RESULTS AND DISCUSSION

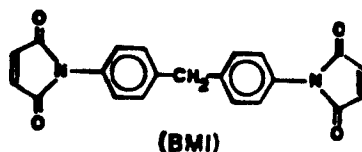
Although the diene form of benzocyclobutene is known to react with a variety of dienophiles, including unactivated terminal olefins in an intramolecular Diels-Alder reaction^{4d}, our previous studies⁹ show that alkynes are moderate dienophiles in the solid phase Diels-Alder polymerization. Their dienophilic reactivity with an in situ generated o-xylylene from a benzocyclobutenyl precursor is further restricted by the nature of their terminal substituents. Thus, a 1:1 stoichiometric mixture of bis(benzocyclobutene) terminated monomer 1, and bis(phenylacetylene) terminated monomer 2, when subjected to a differential scanning calorimetric (DSC) study, exhibited residual polymerization exotherm (maximum at ca. 366°C), attributable to the homopolymerization of the phenylacetylene groups. A similar characteristic polymerization exotherm was also observed for the AB aromatic benzocyclobutene/alkyne monomers 3 and 4 which are deactivated toward Diels-Alder reaction by the terminal electron-donating phenoxy group.



In order to counter the problem of incomplete Diels-Alder polymerization between a bifunctional benzocyclobutene and a less powerful bisdienophile, a more reactive system was selected. Maleimide is well-known to possess a dienophilicity greatly exceeding that of an alkyne. Furthermore, the dienophilic site, that is, the carbon-carbon double bond, is not subjected to the substituent effect imposed by the rest of the structure. As a consequence, we anticipate that Diels-Alder curing of maleimide/benzocyclobutene combination should occur to its fullest extent.

Compatible Mixtures of BCB/BMI

A number of compatible blends of the bisbenzocyclobutene (BCB) monomer 1, and 1,1'-(methylene di-4,1-phenylene)-bismaleimide (BMI) monomer 5, were prepared according to the molar ratios (BCB/BMI): 1:1; 1:1.5; 1:3; 1.5:1. These samples were examined by DSC and thermogravimetric analysis (TGA), and their thermal characteristics are tabulated in Table 1. Comparative data on BCB and BMI are also included in the same table. A representative DSC thermogram is depicted in Figure 1 showing complete compatibility as evidenced by a single initial glass-transition temperature (T_g).



5

In brevity, all mixtures show relatively low initial T_g 's (61-70°C) and the characteristic polymerization exotherms of benzocyclobutene-based systems (onset: 221-225°C; maximum: 257-259°C), providing an excellent processing window (ca. 155°C).

The samples of mixtures and pure BCB and BMI were cured at about 250°C under N_2 atmosphere for 8 hours. Cured samples were subsequently subjected to isothermal gravimetric analysis (ITGA). The ITGA results indicate that after an extended period (200 h) at 650°F (343°C) in circulating air, the cured BMI sample was almost completely vaporized, whereas all the mixtures of BCB and BMI exhibited similar thermo-oxidative stabilities to pure BCB (13-15% weight loss). A 0.5 molar excess of BMI in the 1:1.5 mixture did not at all affect its thermo-oxidative resistance (Figure 2). Such observation definitely provides positive evidence to support the conviction that Diels-Alder polymerization is the predominant, if not the only,

TABLE 1

THERMAL CHARACTERISTICS OF COMPATIBLE MIXTURES
OF BCB AND BMI

BCB	BMI	$T_{g(i)}^{(ini)}$	T_m	T_{poly}		T_g (cure)	$T_{10\%}$ (Air)
		°C	°C	Onset	Max.	°C	°C ^a
1	0	116	219	232	258	281 ^b	496
0	1	-	162	185	239	- ^c	492
1	1	61	-	224	259	293	500
1	1.5	68	-	221	257	298	520
1	3	70	-	225	257	- ^c	492
1.5	1	68	-	222	257	298	515

NOTE:

(a) Temperature at which 10% weight loss is observed by TGA.

(b) Measured by TMA.

(c) Not observed by DSC.

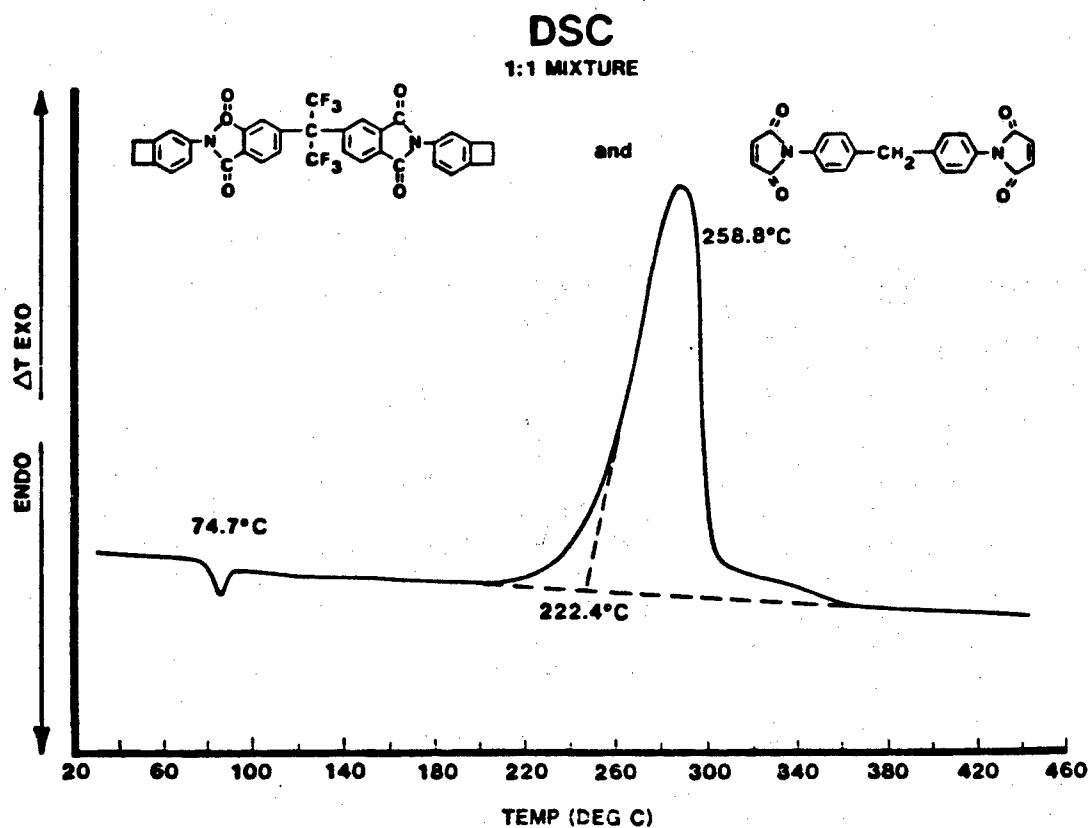


Figure 1. DSC thermogram of 1:1 molar mixture of 2,2-bis 4-(N-4-benzocyclobutenyl phthalimido) hexafluoropropane (BCB) and 1,1'-(methylene di-4,1-phenylene)bismaleimide (BMI)

ISOTHERMAL AGEING (AIR, 650°F, 200 HRS)

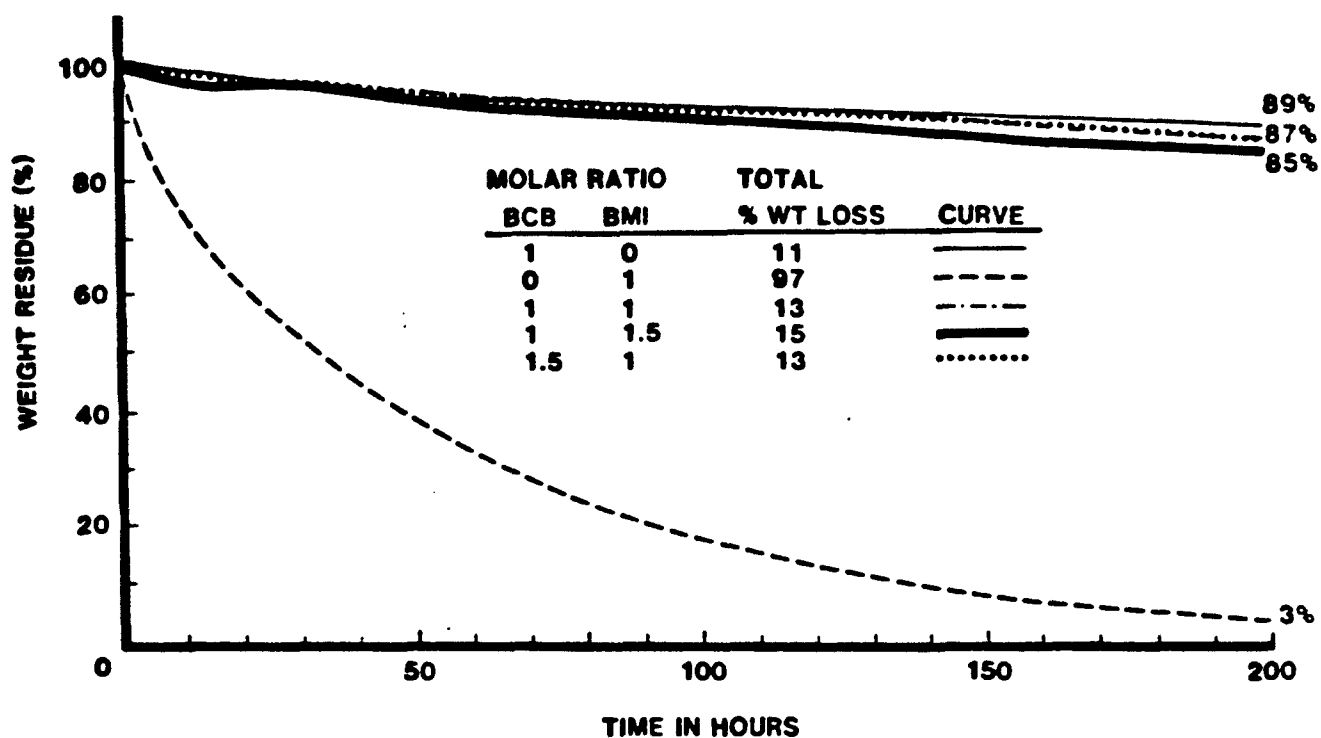
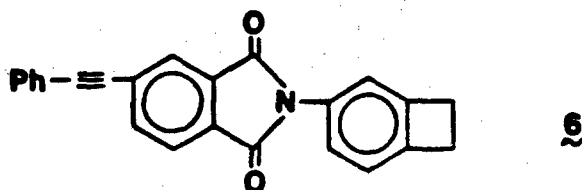


Figure 2. Isothermal ageing studies of the thermosetting resins derived from the compatible mixtures of BCB and BMI in comparison with those derived from pure BCB and BMI, at 650°F, under circulating air for 200 hours. All samples were previously cured at ca. 250°C under N₂ atmosphere for 8 hours.

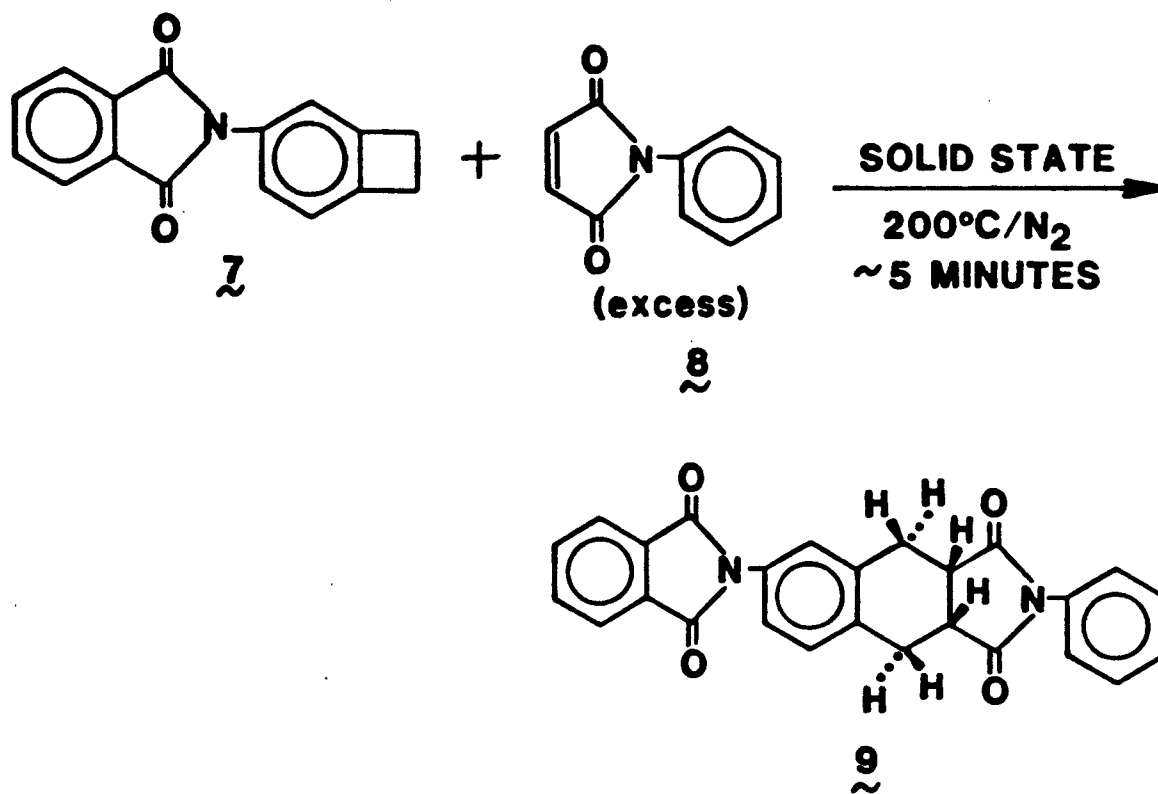
curing process in the BCB/BMI system. Similarly, we note that for the benzocyclobutene/alkyne system, the most thermo-oxidatively stable thermoset is the one that is derived from the benzocyclobutene/alkyne monomer 6, which has (by DSC study) the greatest extent of Diels-Alder polymerization (i.e., the least amount of residual polymerization exotherm ascribable to the homopolymerization of the phenylacetylene groups).



Model Compound

Since both the benzocyclobutene and maleimide can homopolymerize at the temperature range that benzocyclobutene was transformed into the reactive o-xylylene, it was paramount to demonstrate that under similar conditions, the Diels-Alder reaction of the in situ-generated o-xylylene and maleimide was the principal cure-pathway for the BCB/BMI system.

Indeed, when an intimate mixture of N-phenyl maleimide 8 (in 30-percent excess to compensate for material loss due to its facile sublimation near the reaction temperature) and N-benzocyclobutenyl phthalimide 7 was heated neat at 200-220°C under N₂ for about 5 minutes, the adduct 9 was obtained in 63-percent recrystallized yield. Its identity was confirmed by elemental analysis, proton and carbon-13 NMR, IR and MS spectroscopic techniques.



For comparison purposes, the proton NMR spectra of the starting materials and the adduct 9 are shown in Figure 3 and carbon-13 NMR spectrum of 9 is depicted in Figure 4. The assignments of the characteristic carbon-13 chemical shifts of compounds 7, 8 and 9 are shown in Table 2¹⁴. For complete tabulation of carbon-13 chemical shifts, see Experimental section.

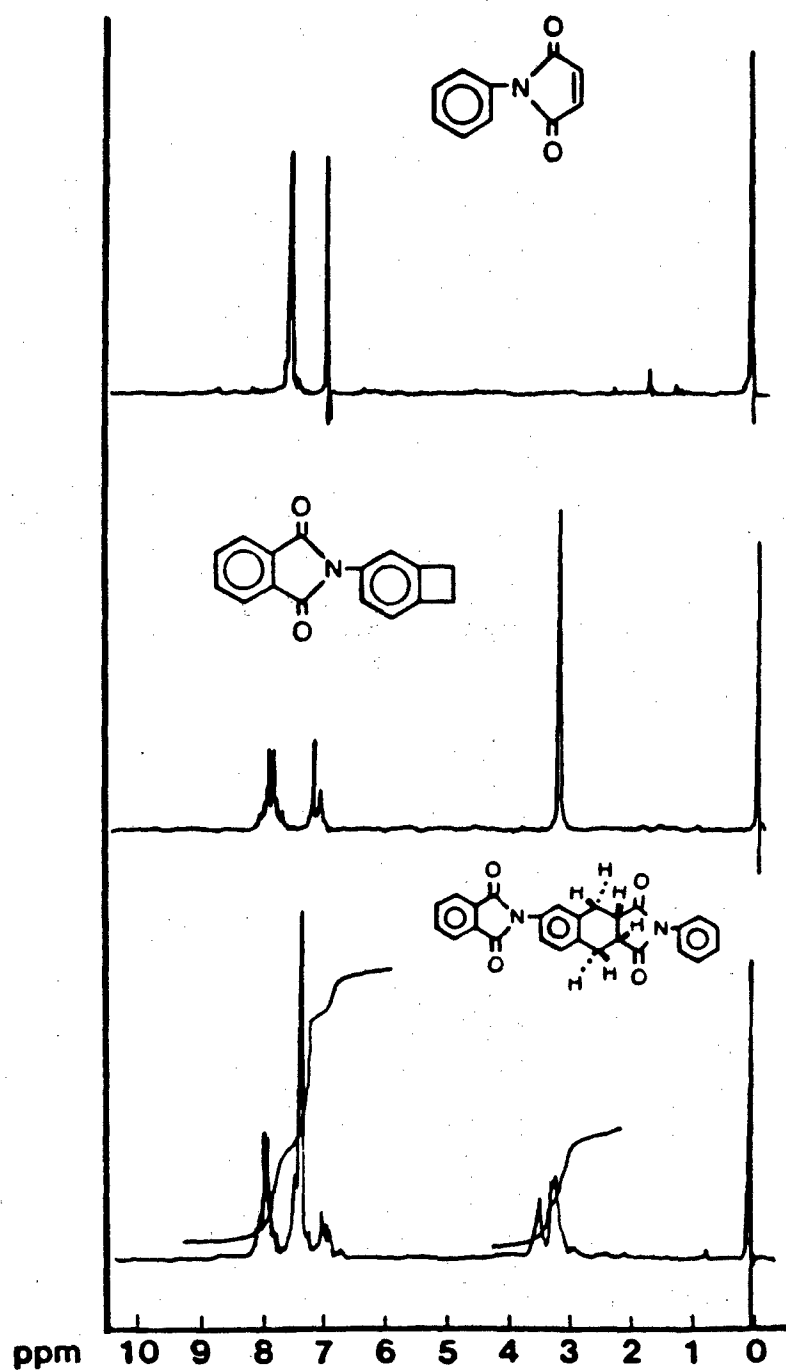


Figure 3. Proton NMR (60 MHz) spectra of (a) N-phenylmaleimide; (b) N-benzocyclobutenyl phthalimide; (c) the Diels-Alder adduct from N-phenylmaleimide and N-benzocyclobutenyl phthalimide.

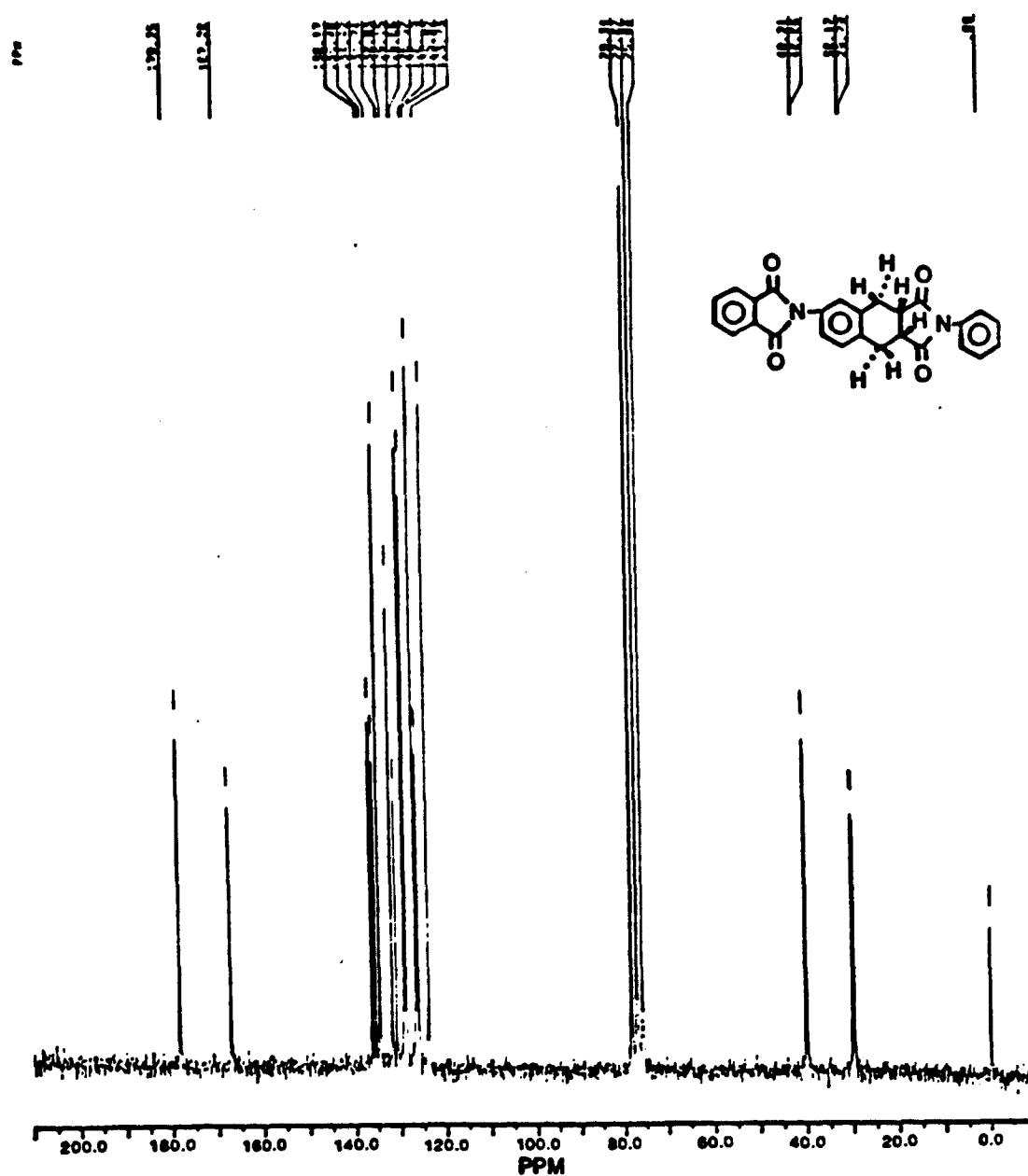
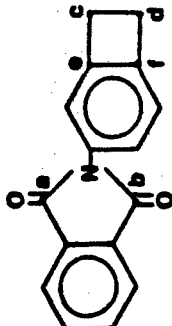
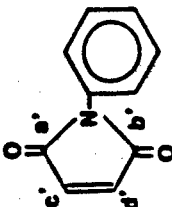
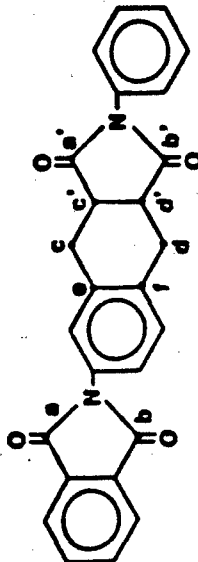


Figure 4. Carbon-13 NMR (25.2 MHz, noise-decoupled) spectrum of the Diels-Alder adduct from N-phenylmaleimide and N-benzocyclobutenyl phthalimide. Solvent: CDCl₃. Internal standard: TMS.

**TABLE 2: COMPARISON OF SOME CHARACTERISTIC
CARBON-13 CHEMICAL SHIFTS**

		
C(a) C(b)	C(a') C(b')	C(a) C(b)
C(c) C(d)	C(c') C(d')	C(c') C(d')
C(e) C(f)		C(e) C(f)
167.54 29.43 29.33 146.34 146.08	169.55 127.83*	167.20 29.79 30.17 136.17 135.40
		178.25 40.06 40.21

ALL VALUES ARE EXPRESSED IN PPM. SOLVENT: CDCl_3 .
INTERNAL STANDARD: TMS

*ASSIGNMENT WAS MADE BASED ON THE FACT THAT THE CARBON-13
SPECTRA OF N-BENZOCYCLOBUTENYL PHTHALIMIDE AND THE
DIELS-ALDER ADDUCT DID NOT CONTAIN THIS PEAK.

In conjunction with the ITGA results (*Vida Supra*), the isolation of the model compounds provides strong evidence for the Diels-Alder polymerization as the predominant cure mechanism for the BCB/BMI systems. (Figure 5 depicts schematically such Diels-Alder polymerization.) The cure-site structure, which can be represented by 1,4-dihydro-2,3-naphthalimide, can be conceivably converted quite easily to a more thermodynamically stable structure via either aromatization or formation of para-benzoquinone because of the ease of the alicyclic hydrogens toward oxidation at high temperature in the presence of oxygen (see Figures 6 and 7). Such rationale may be used to explain the remarkable resistance of the BCB/BMI systems toward thermo-oxidative degradation.

SOLID-STATE DIELS-ALDER POLYMERIZATION OF BCB/BMI

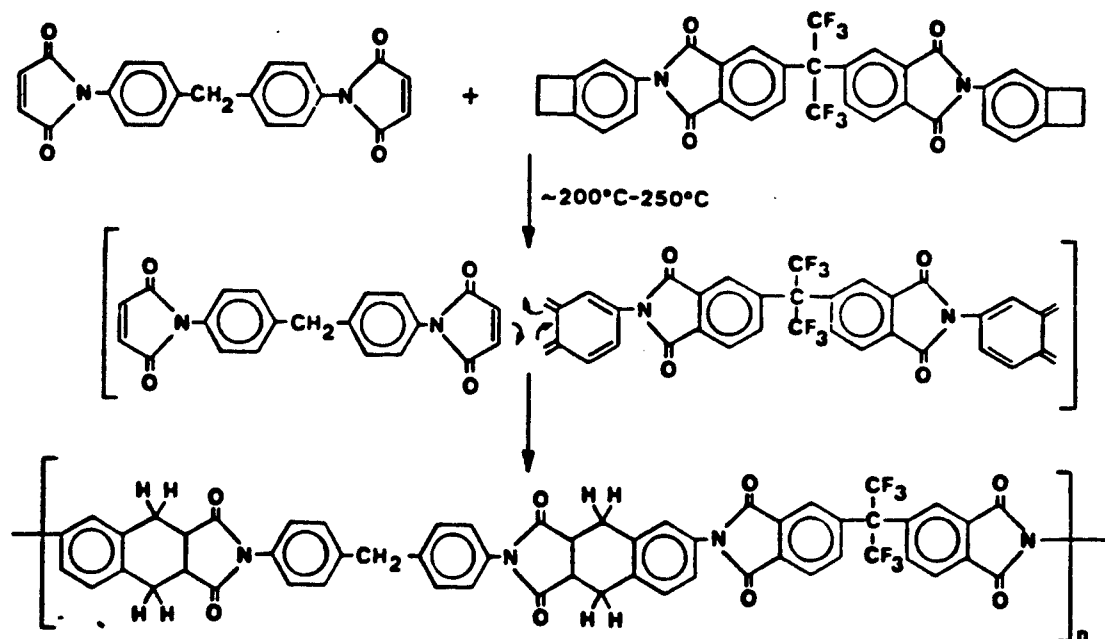


Figure 5. Idealized solid-state Diels-Alder polymerization of BCB and BMI via reactive o-xylylene intermediate.

THERMOXIDATIVE STABILITY ENHANCEMENT VIA AROMATIZATION

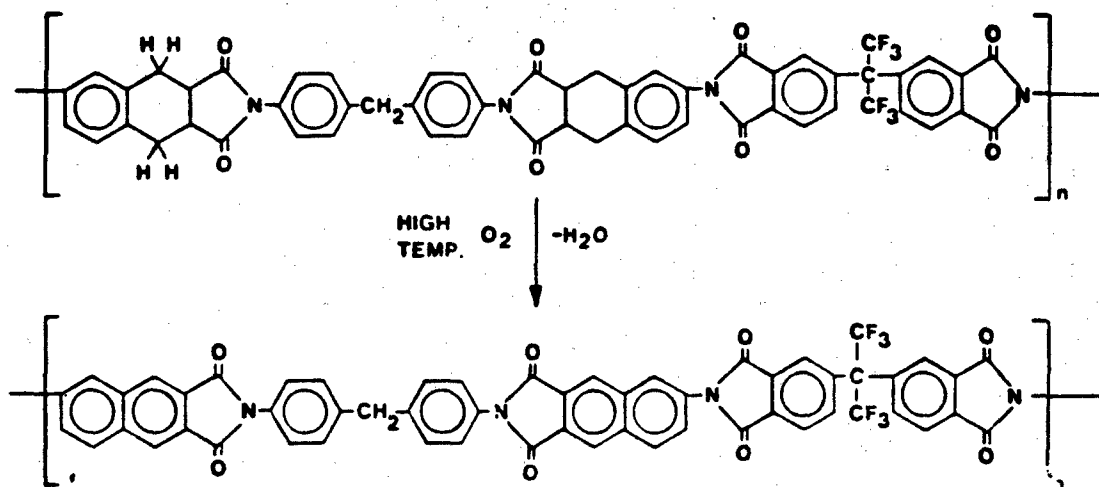


Figure 6. Idealized situation showing the thermo-oxidative stability enhancement of BCB/BMI thermosetting polymer via aromatization of the cure-site, i.e. 1,4-dihydro-2,3-naphthalimide structure.

THERMOXIDATIVE STABILITY ENHANCEMENT VIA BENZOQUINONE FORMATION

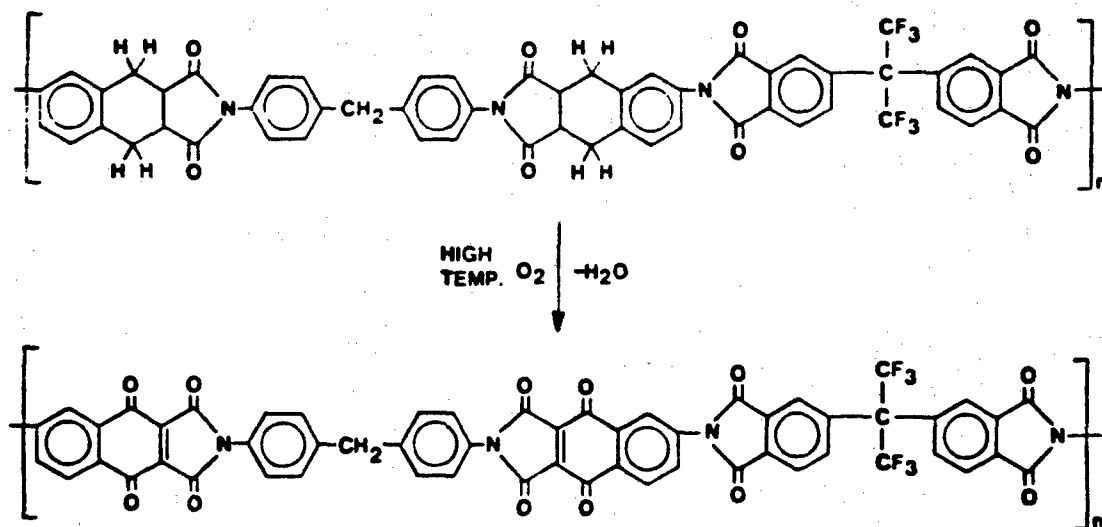


Figure 7. Idealized situation showing the thermo-oxidative stability enhancement of BCB/BMI thermosetting polymer via the formation of benzoquinone structure from that of 1,4-dihydro-2,3-naphthalimide at the cure-site.

SECTION III

EXPERIMENTAL

The preparation of 4-aminobenzocyclobutene was performed according to the procedure (with some modifications) described in the literature^{2,15-17}. 2,2-Bis(N-phthalic anhydrido)hexafluoropropane (6F-dianhydride) was purchased from American Hoechst Company and used without further treatment. Both N-phenylmaleimide¹⁸ and 1,1'-(methylene di-4,1-phenylene)bismaleimide (BMI) were obtained from Aldrich Chemical Company. The former was purified by vacuum-sublimation and the purification of the latter is provided below. Previous preparation of 2,2-bis[4-(N-4-benzocyclobutenyl phthalimido)]-hexafluoropropane (BCB) via thermal cyclo-dehydration of the corresponding amic acid in refluxing acetic acid resulted in ca. 59% yield^{8,19}. We have found that a better yield (89-90%) can be achieved if the synthesis were conducted in tow-step-one-pot-reaction fashion, using acetic anhydride/pyridine as the chemical dehydrating agent to convert the amic acid to the desired imide (*supra* *vida*).

Purification of BMI

1,1'-(Methylene di-e,1-phenylene)bismaleimide 5 (95% purity, 20.00 g) was dissolved in about 40 ml of methylene chloride. The resultant solution was then added to a chromatography column containing about 120 g of SiO₂. The column was eluted with CH₂Cl₂ and fractions were collected until the eluent became colorless. A dark band remained immobile at the top of the column. All fractions were combined and subjected to rotary evaporation. After all the solvent had been removed, pure BMI was obtained as a bright-yellow crystalline solid. Yield: 18.04 g (ca. 90% recovery). M.P. = 157-158°C. Anal. Calc. for C₂₁H₁₄N₂O₄: C, 70.38; H, 3.94; N, 7.82. Found: C, 69.95; H, 3.99; N, 7.65. DSC (10°/min, N₂) showed the following thermal transition: 162°C (T_m); 185°C (onset of polymerization exotherm); 239°C (maximum of exotherm, with tailing to ca. 420°C). Mass spectroscopy: M⁺ (358, 44.6%). Proton NMR (δ in ppm, CDCl₃): 4.06 (singlet, methylene protons, 2H); 6.85 (singlet, olefinic protons, 4H); 7.33 (singlet, aromatic protons, 8H). IR (KBr pellet): 1710 vs (maleimide group).

N-Benzocyclobutenyl Phthalimide

Phthalic anhydride (2.60 g, 17.6 mmol) was dissolved in about 50 ml of dry dimethyl acetamide. Freshly prepared 4-aminobenzocyclobutene (2.09 g, 17.6 mmol) was added subsequently and the resultant homogenous reaction mixture was stirred under nitrogen at room temperature for about 5 hours. Then, a mixture, which was composed of 3.59 g (35.2 mmol) of acetic anhydride and 2.79 g (35.3 mmol) of pyridine, was delivered to the reaction mixture. It was continuously stirred under nitrogen atmosphere at about 50°C for another 17 hours. Finally, the dark homogeneous reaction mixture was poured into a stirred 1N HCl solution (400 ml) in a 1-liter beaker. After about an hour of stirring at room temperature, the off-white mixture was filtered through a 600-ml medium-porosity fritted filter funnel. The collected crude product was washed with H₂O (4 X 400 ml) and air-dried (with suction) overnight. The crude product was extracted with about 150 ml of methylene chloride. The resultant CH₂Cl₂ solution was first dried over anhydrous MgSO₄, and then poured into a 150-ml coarse-porosity fritted filter funnel containing a bed of silica gel (chromatography grade), saturated with hexane. Two portions of 1:1 methylene chloride/hexane (50 ml) were used to wash the silica gel. The combined filtrate was subsequently subjected to rotary evaporation. The desired product was obtained as a light-tan solid. Yield: 3.95 g (90%). Anal. Calc. for C₁₆H₁₁NO₂: C, 77.09; H, 4.45; N, 5.62. Found: C, 76.97, H, 4.43; N, 5.68. Mass Spectroscopy: 249 (M⁺, 100%). Proton NMR (CDCl₃, δ in ppm): 3.25 (singlet, alicyclic protons, 4H); 7.10-7.28 (complex multiplet, benzocyclobutenyl aromatic protons, 3H); 7.71-8.14 (symmetrical octet, phthalic protons, 4H). IR (KBr pellet): 2985 vw, 2933 m (alicyclic C-H stretches); 1773 m, 1716 vs (symmetric and asymmetric stretches of the cyclic imide group) DSC (10°C/min; N₂) showed the following thermal transitions: 180.7° (T_m); 224.7°C (onset of exotherm); 266.5°C (maximum of exotherm; exotherm tailing to about 425°C). Rescanning of the sample, which had been heated to 450°C, showed a softening point (T_g (cure)) at 155.7°C. TGA (10°C/min; Air) showed three steps of weight loss, temperature (total weight loss in percent): 274.6°C (31.6%); 437.4°C (55.0%); 604.0°C (99.3%). Carbon-13 NMR (CDCl₃, δ in ppm. TMS internal standard): 29.33, 29.43 (alicyclic, sp³-carbons); 121.52, 123.40, 123.62, 125.96, 130.12, 131.80, 134.26, 146.08, 146.34 (aromatic, sp²-carbons); 167.54 (carbonyl, sp²-carbons).

Diels-Alder Adduct from the reaction of N-benzocyclobutenyl
phthalimide and N-phenylmaleimide

A mixture of N-benzocyclobutenyl phthalimide (0.262 g, 1.05 mmol) and N-phenylmaleimide (0.241 g, 1.39 mmol) was placed in a 25-ml 3 necked, round-bottomed flask, equipped with a reflux-condenser with a nitrogen adaptor attached, a thermometer/-adaptor and a glass stopper. The mixture was agitated with a spatula to ensure a thorough mix and then quickly heated under a stream of nitrogen on a heating mantle. At about 80°C, it melted into a yellow-green liquid and concomitantly some yellow sublimate started to appear on the top of the reaction flask. When the internal temperature reached ca. 150°C, the liquefied reaction mixture became dark amber and the amount of yellow sublimate also increased. As soon as the thermometer registered 200°C, heat source was turned off. The residual heat in the heating mantle caused the internal temperature to reach as high as 220°C. Then, the reaction mixture was allowed to cool to room temperature under nitrogen. The reaction mixture solidified. Hence, the yellow sublimate was carefully scraped from the top of the reaction vessel with a bent spatula. Subsequently, the reaction mixture was extracted with methylene chloride and the solution was carefully removed from the reaction flask with the help of a disposable pipet. The CH₂Cl₂ extract (ca. 20 ml) was filtered through a disposable pipet plugged with a piece of cotton. To the filtrate was added hexane to precipitate an off-white solid. The crude product was then collected, washed with hexane and dried. The yield of crude product was 0.37 g. It was redissolved in a minimal amount of methylene chloride in a 100-ml flask and hexane was carefully layered until cloudiness started to develop in the solution. The flask was then set aside. After a few days, a quantitative amount of a light-tan solid appeared in the flask. It was collected, washed with hexane and dried in vacuo at 70°C for 17 hours. Yield: 0.28 g (63%). Anal. Calc. for C₂₆H₁₈N₂O₄: C, 73.92; H, 4.29; N, 6.63. Found: C, 73.54; H, 4.36; N, 6.34. Mass Spectroscopy: 422 (M⁺, 42.8%). Proton NMR (CDCl₃, δ in ppm): 3.11-3.18, 3.40 (broad multiplet; alicyclic protons; 4H); 6.80-6.96, 7.16-7.47 (broad, complex multiplet; aromatic protons previously associated with benzocyclobutenyl group, 3H); 7.28 (singlet, phenyl protons previously associated with N-phenyl maleimide, 5H); 7.65-8.09 (symmetrical octet; phthalic protons). IR (KBr pellet, wavenumbers in cm⁻¹): 2850 vw, 2915 w, 2950 w (alicyclic C-H stretches); 1780 m, 1720 vs (symmetric and asymmetric stretches of the cyclic imide group). Carbon-13 NMR (δ in ppm, CDCl₃): 29.79, 30.17, 40.06, 40.21 (alicyclic sp³-carbons); 123.73

125.82, 126.19, 126.57, 128.66, 129.15, 130.83, 131.74, 134.42, 135.40, 136.17 (aromatic sp^2 -carbons); 167.20, 178.25 (carbonyl sp^2 -carbons).

2,2-Bis 4-(N-4-benzocyclobutenyl phthalimido) hexafluoropropane BCB

Freshly prepared 4-aminobenzocyclobutene (3.80 g, 31.9 mmol) was mixed with about 30 ml of dimethyl acetamide. To this solution was added 2,2-bis(4-phthalic anhydrido)hexafluoropropane (6.92 g, 15.6 mmol) in one portion, followed by addition of another 30 ml of dimethyl acetamide. The resultant reaction mixture, which was amber and homogeneous, was magnetically stirred at room temperature under nitrogen atmosphere for an hour and then at about 45°C for another 3 hours. A mixture of 6.51 g (63.8 mmol) of acetic anhydride and 5.05 g (63.8 mmol) of pyridine was added to the reaction mixture, which was stirred continuously at 45°C under nitrogen atmosphere for another 17 hours. After having been allowed to cool to room temperature, the dark, homogeneous reaction mixture was poured into a 2-liter beaker containing a stirred 1N HCl solution (ca. 1000 ml). The resulting off-white heterogeneous mixture was stirred at room temperature for about an hour and then filtered through a coarse-porosity 600-ml-capacity fritted filter funnel. The crude product was washed with copious amounts of H_2O and then with about 300 ml of hexane. The yield of the crude product, after having been air-dried overnight was about 9.40 g. The dry crude product was dissolved in about 100 ml of methylene chloride. A small amount of anhydrous magnesium sulfate was added to the CH_2Cl_2 solution, which was subsequently poured into a 150-ml coarse-porosity fritted filter funnel containing a bed of silica gel (chromatography grade), saturated with hexane. The fritted filter funnel was attached to a 500-ml filter flask, containing about 200 ml of hexane. Subsequently, the silica gel was washed with ethylene chloride (4 x 25 ml). The combined filtrate, which was homogeneous and yellow-green, was subjected to rotary evaporation. The desired product was obtained as a faint yellow-green microcrystalline solid. Yield: 8.95 g (88.9%). Needles were obtained from slow evaporation of 1:1 methylene chloride/hexane solution. M.P. = 219.4°C(DSC). Anal. Calc. for $C_{35}H_{20}F_6N_2O_4$: C, 65.02, H, 3.12; N, 4.33. Found: C, 65.02; H, 3.18; N, 4.34.. Mass spectroscopy: m/e 646 (M^+) 31.0 percent. Proton NMR ($CDCl_3$): 3.26 (singlet, alicyclic protons): 7.07-7.30, 7.85-8.81 (complex, aromatic protons). IR (KBr pellet): 2968 w, 2925 w (alicyclic C-H stretches); 1778 m 1717 vs (imide group stretches); 1243 s, 1188 s (asymmetric and symmetric stretches of $-C(CF_3)$ -group).

Preparation of Compatible BCB/BMI Mixtures

The following serves as the representative procedure for preparing the compatible mixtures of 2,2-bis[4-(N-4-benzocyclobutenyl phthalimide-4-oxy)phenyl]hexafluoropropane (BCB) and 1,1'-(methylene di-4,1-phenylene)bismaleimide (BMI): 0.1709 g (1.6669×10^{-4} mol) of BCB and 0.0523 g (1.675×10^{-4} mol) of BMI were dissolved completely in about 8 ml of CH_2Cl_2 . The resultant solution was slowly evaporated to dryness with the assistance of a heat-gun. Subsequently, the 1:1 molar BCB/BMI blend was then dried in an oven at 90°C in vacuo for 48 hours.

SECTION IV

CONCLUSION

Our studies demonstrate that with the right combination of bisdiene, in our case, an in situ-generated one and bis-dienophile, Diels-Alder polymerization can provide a viable curing pathway to attain high-temperature resistance thermosetting systems. Such remarkable thermo-oxidative stability may be explained by the molecular structure of the cure-site, which, for the BCB/BMI systems, is a six-membered ring fused to an aromatic ring on one side, and joined to an amide functional group on the other. The resultant structure has the capability of being transformed into a more thermodynamically stable aromatic structure. It is also reminiscent of that of ladder polymers, whose tolerance towards thermo-oxidative degradation is thought to be the direct consequence of their double-stranded backbone structure²⁰. The similarity of thermo-oxidative stability of the non-stoichiometric BCB/BMI (1:1.5) mixture to that of stoichiometric implies that BCB can help boost the thermo-oxidative stability of BMI (when utilized in a non-stoichiometric fashion), and also control its cross-linking density, since BMI itself forms highly cross-linked thermoset resins when thermally cured. The overall consequence is, that the BCB/BMI (especially 1:1 molar mixture) system will not only possess higher thermo-oxidative stability, but also have more toughness (due to the linear character of the Diels-Alder product), than BMI alone.

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