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### **Benzocyclobutenes: A New Class of High Performance Polymers**

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## **BENZOCYCLOBUTENES: A NEW CLASS OF HIGH PERFORMANCE POLYMERS**

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### **ABSTRACT**

Benzocyclobutenes are a family of thermally polymerizable monomers which can be classified into two groups: 1) monomers which contain only benzocyclobutene moieties and 2) monomers which contain sites of unsaturation in addition to benzocyclobutene moieties. The monomers can be partially polymerized (B-staged) by heating to form oligomers having processing advantages for various composite fabrication techniques. The polymerization proceeds through the thermally initiated cyclobutene ring opening to yield an *o*-quinodimethane intermediate (calculated to be a ground state singlet). Preliminary characterization of the network structures indicates that monomers which contained multiple benzocyclobutene moieties, optionally with sites of unsaturation, were transformed into multifunctional network junctions when the thermosets were fully cured. The 3-maleimidobenzocyclobutenes thermally polymerize to yield substantially linear, high glass transition temperature ( $T_g$ ) polymers. Thus benzocyclobutene polymers encompass materials which have properties ranging from high  $T_g$  thermosets to those of substantially linear thermoplastics. Some polymers exhibit an excellent retention of their room temperature mechanical properties to at least 200–250°C, making them useful as high performance polymers for applications in the aerospace

industry. Other polymers have outstanding electrical properties including very low dielectric constant and water pickup, making them useful in electronic applications.

## INTRODUCTION

The first documented synthesis of a benzocyclobutene (BCB) derivative was reported by Finkelstein in a 1909 paper dealing with the displacement reactions of aliphatic chlorides and bromides with iodide ion [1a]. During the course of this work, it was found that  $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene reacted with sodium iodide in ethanol to yield 1,2-dibromobenzocyclobutene. Following this initial report, there were apparently no further research efforts in benzocyclobutene chemistry until 1956 when Cava and coworkers repeated Finkelstein's work and prepared benzocyclobutene hydrocarbon for the first time [1b]. These workers also demonstrated that *o*-quinodimethanes were intermediates in the synthesis of benzocyclobutenes by Finkelstein's method. In 1959, Jensen and Coleman prepared 1,2-diphenylbenzocyclobutene and discovered that it readily reacted with maleic anhydride at room temperature to yield 1,4-diphenyl-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic acid anhydride [1c]. This product was proposed to arise from the thermal conversion of the benzocyclobutene to an *o*-quinodimethane which then entered into a Diels-Alder reaction with the maleic anhydride. As a result of these reports, other researchers entered the field and a steady growth in the understanding and applications of benzocyclobutene chemistry ensued. As these efforts progressed, many workers reported on the cycloaddition and dimerization reactions of benzocyclobutenes. These discoveries were often used in the synthesis of novel small molecules and diverse natural products.

In the late 1970s, Kirchoff at The Dow Chemical Company initiated a research program on the use of benzocyclobutenes in polymer synthesis and modification. These efforts culminated in 1985 with the issuance of the first patent describing the use of benzocyclobutenes in the synthesis of high molecular weight polymers [1d]. Similar work was reported separately and independently by Tan and Arnold working at the University of Dayton [2]. Since these initial discoveries, the field of benzocyclobutene polymers has rapidly expanded to currently include 44 patents and numerous papers. These numbers are expected to increase considerably since benzocyclobutenes constitute the basis of a new and versatile ap-

proach to the synthesis of high performance polymers for applications in the electronics and aerospace industries [1d-5].

The basic benzocyclobutene technology involves a family of thermally polymerizable monomers which contain one or more benzocyclobutene groups per molecule. Depending on the degree and type of additional functionality, these monomers can be polymerized to yield either thermosetting or thermoplastic polymers. The polymerization is believed to proceed through the thermally initiated ring opening of a benzocyclobutene to give an *o*-quinodimethane (*o*-xylylene) intermediate. The subsequent fate of this intermediate depends largely on the number and type of other functional groups present in the monomer molecule. For the class of monomers which contains only benzocyclobutene moieties as reactive groups (i.e., containing no reactive sites of unsaturation), the *o*-quinodimethane groups react rapidly with one another to give what are believed to be linear or cyclic polymeric structures which, for a bisbenzocyclobutene monomer, quickly lead to a highly crosslinked polymer.

Another class of benzocyclobutene monomers is the one which contains sites of unsaturation that are themselves capable of reacting with an *o*-quinodimethane to give cycloaddition products [6-10]. Typically, alkenes and alkynes have been used as the *o*-quinodimethane reactive moieties. In the particular case where the monomer molecule contains only one benzocyclobutene group and only one site of unsaturation, the cycloaddition polymerization goes on to produce what is essentially a linear thermoplastic polymer.

The benzocyclobutene monomers are typically solids at room temperature and appear to be indefinitely stable in air and to light at ambient temperatures. However, upon heating to above 170°C, the monomers rapidly and exothermically polymerize. The polymerization appears to be a strictly thermal process, and no catalysts are required to get it to proceed at a conveniently useful rate. Since the polymerization is fundamentally a ring-opening reaction which proceeds in the melt, there are no solvent molecules or gaseous by-products evolved which can potentially result in voids being present in the final polymerized part. This feature is in sharp contrast to the more typical situation with polyimides where both volatile solvents and condensation by-products are evolved during the polymerization process.

In the most useful examples, the benzocyclobutene monomers melt well below the temperature (170°C) where the polymerization rate starts to become rapid. Typically, the most preferred monomers melt at 150°C

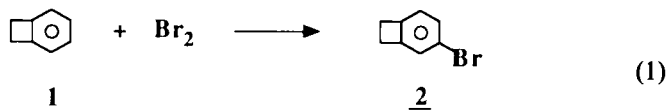
or below to give low viscosity liquids which are very suitable for a wide variety of coating and molding processes. The monomers can also be partially polymerized (B-staged) by heating them for various lengths of time at 160–180°C [11]. The oligomers resulting from this process typically have softening points below that of the pure monomers and, when molten, exhibit higher melt viscosities. These qualities offer certain processing advantages for various composite fabrication techniques.

As a family, the benzocyclobutene polymers encompass materials which have properties ranging all the way from those of high glass transition temperature ( $T_g$ ) thermosets to those of substantially linear thermoplastics and, in some instances, even elastomers. The type of polymer, thermoset or thermoplastic, depends strongly on the detailed structural features of precursor monomers. In general, low molecular weight monomers which contain two or more benzocyclobutene groups per molecule will, on polymerization, tend to give rise to highly crosslinked thermoset materials. In contrast, low molecular weight monomers which contain one benzocyclobutene group and one reactive site of unsaturation will yield substantially linear thermoplastic polymers upon polymerization. Monomers which have two or more benzocyclobutene groups per molecule and reactive sites of unsaturation almost always polymerize to yield highly crosslinked high  $T_g$  thermoset polymers. Superimposed upon these broad generalizations are the effects of the structural features of the functional groups which link the benzocyclobutene moieties with each other and/or with the reactive sites of unsaturation. The chemical make up of these linking groups can strongly influence many of the properties of the final polymer. To a certain and, in some instances, large extent, the properties of the final polymer will be a strong reflection of the intrinsic qualities of these linking groups. It is possible to prepare low ( $\sim 2.6$ ) dielectric constant hydrophobic benzocyclobutene polymers by starting with precursor monomers which contain hydrocarbon or siloxane groups interspersed between the reactive moieties of the monomer molecule. Overall, benzocyclobutenes provide a unique approach to the facile preparation of a wide variety of polymers. In particular, they have served as convenient vehicles for the preparation of high performance polymers for electronics and aerospace applications [12–18].

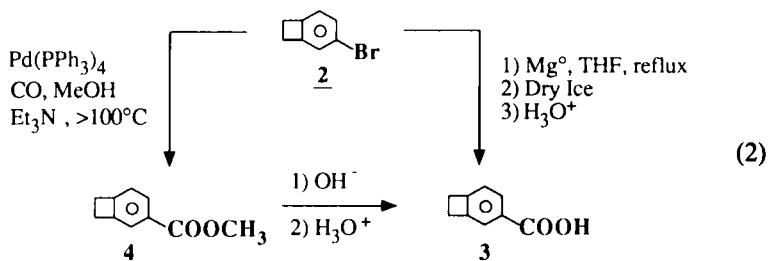
## MONOMER SYNTHESIS

Benzocyclobutene hydrocarbon [19a] **1** is the precursor to a wide variety of benzocyclobutene monomers. 3-Bromobenzocyclobutene **2** is

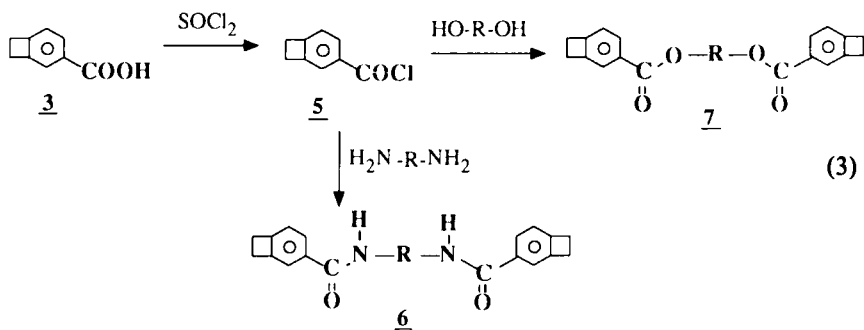
prepared from **1** in high yield by electrophilic aromatic bromination [19b, c] (Eq. 1).



Formation of the Grignard reagent ( $\text{Mg}^\circ/\text{THF}/\text{reflux}$ ) followed by addition of carbon dioxide (dry ice) affords the 3-benzocyclobutene carboxylic acid **3** in 60–70% yield [20]. Alternatively, acid **3** is available by hydrolysis of the ester **4** [21]. Ester **4** is prepared in one step from **2** through carboxymethylation by using a palladium zero catalyst in the presence of carbon monoxide and methanol [22, 23] (Eq. 2.).



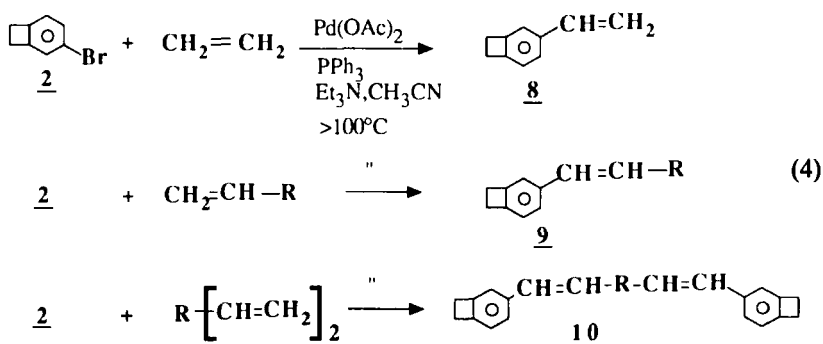
After acid **3** is converted to the acid chloride **5** via thionyl chloride, it can be reacted with either a diamine in the presence of a base to give a bisamide **6** or, with a diol under similar reaction conditions, to afford a bisester **7** [24–26] (Eq. 3).



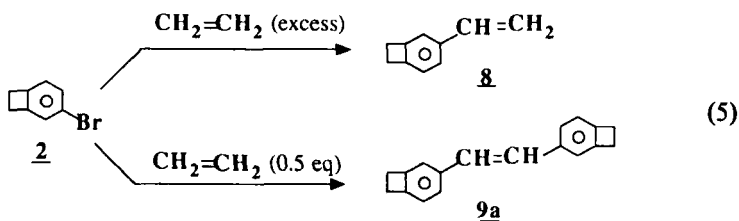
The R group between the bisamine or bisdiol functionality can be

widely varied to include straight chain and branched alkyl groups as well as additional functionality. Olefin and acetylene containing sections may also be present. R may also be an aromatic group which may or may not contain additional functionality. In general, all of the monomers of the general structure of **6** and **7** are crystalline solids and have melting points lower than the temperature required for the onset of efficient homopolymerization.

The bisamides and bisesters provide two different families of benzocyclobutene monomers and polymers derived from bromobenzocyclobutene **2**. Heck and coworkers demonstrated that aromatic bromides and iodides react with olefins in the presence of a palladium catalyst to afford the vinyl arylated product [23, 27, 28]. This technology has been used with **2** as the starting aromatic halide to prepare more highly functional bis- and monobenzocyclobutenes (Eqs. 4).

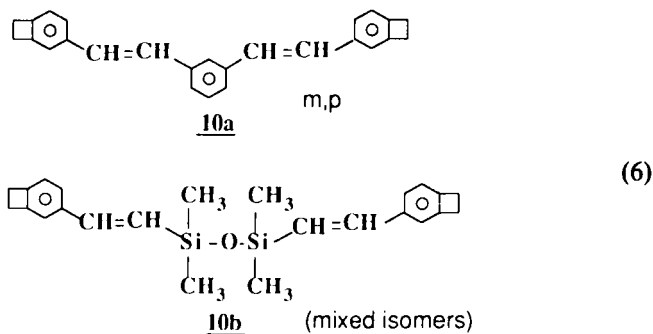


When the reaction is carried out with an olefin which is either a gas or a low boiling liquid, it must be run in a pressure vessel. Depending upon the product desired, the olefin is usually present in an excess concentration in order to insure formation of vinyl-substituted products (Eq. 5).



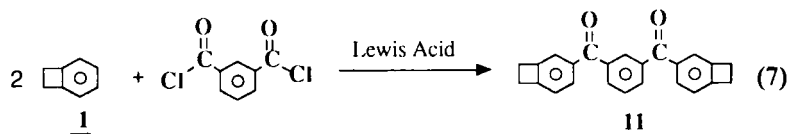
The reaction of **2** with terminal olefins such as styrenics and higher

alkyl substituted olefins is a general reaction which can lead to several different monomers which contain at least one benzocyclobutene. This same type of chemistry can be used to prepare bisbenzocyclobutenes if the starting olefin contains two olefins capable of undergoing the vinylic arylation reaction (Eq. 4, Reaction 3). Two important molecules prepared via this reaction are shown below:



Monomer **10a** is a crystalline solid which, when homopolymerized, affords a high  $T_g$  thermally stable polymer that has potential application in both the microelectronic and aerospace areas. Monomer **10b** (mixed isomers) is a liquid at room temperature and, when homopolymerized, also yields a high  $T_g$  thermally stable polymer that has a low moisture uptake and a low dielectric constant. This polymer has been targeted into the microelectronics area because of this interesting set of properties, combined with the prepolymer's unique ability to planarize over underlying topography.

The monomers described so far have all been prepared by starting with 3-bromobenzocyclobutene **2**. Another approach to the preparation of monomers begins with the parent hydrocarbon benzocyclobutene **1** by carrying out electrophilic aromatic substitution reactions [29]. Benzocyclobutene readily undergoes a Friedel-Crafts type of benzylation reaction (Eq. 7).

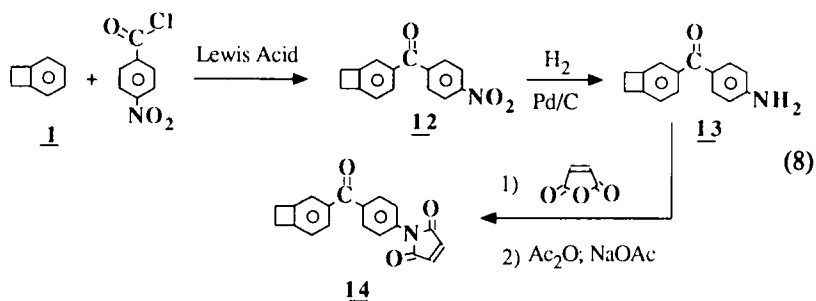


Many of the common Lewis acids which have been used for the Frie-



del-Crafts reaction, such as  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{SbCl}_5$ , and  $\text{FeCl}_3$ , also function effectively with benzocyclobutene **1**. In general, the catalyst must be present in greater than one equivalent for every equivalent of acid chloride functionality present. The reaction may be run with or without solvent and can be carried out at subambient to elevated temperatures depending upon the catalyst used. Some care must be exercised when running this type of reaction in order to minimize by-product formation. The principal by-product arises from the Lewis-acid-catalyzed reaction of  $\text{HCl}$  with the four-membered ring of benzocyclobutene. Monomer **11** ( $\text{mp} = 152^\circ\text{C}$ ) is being investigated as its homopolymer in high performance composite applications.

The use of the Friedel-Crafts type of technology can also be used for the preparation of monomers that contain one benzocyclobutene and a second functional group that will react with the benzocyclobutene. These types of molecules are commonly called AB monomers. An example of this class of monomer is shown in Eq. (8).



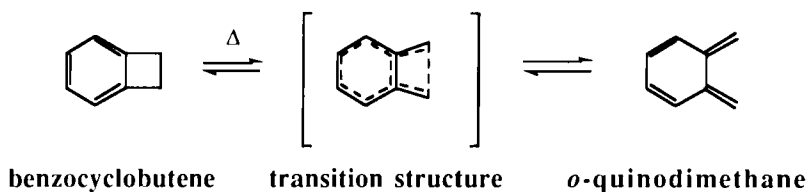
Reaction of 4-nitro-1-benzoyl chloride with benzocyclobutene **1** provides the benzoylated product **12** [29]. The nitro group of **12** can be hydrogenated in the presence of palladium on charcoal to afford the amine product **13** [30]. Reaction of the amine with maleic anhydride produces the amic acid which can be cyclodehydrated with acetic anhydride and sodium acetate at  $95^\circ\text{C}$  to afford the final maleimide product **14** [31–33].

## MECHANISM OF BENZOCYCLOBUTENE RING OPENING

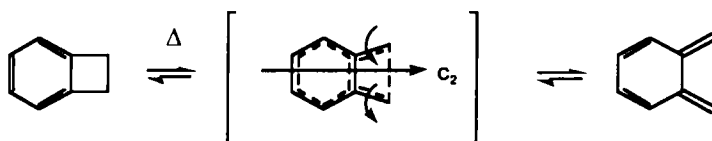
The first step in the reaction of a benzocyclobutene monomer is the thermal opening of the cyclobutene ring to yield an *o*-quinodimethane

derivative. A computational study of this benzocyclobutene  $\leftrightarrow$  *o*-quinodimethane interconversion has been carried out in order to determine the mechanism of the BCB ring opening as well as to characterize the transition state and/or intermediates that could exist and the ground state structure of *o*-quinodimethane. The studies were anticipated to yield an understanding of substituent and temperature effects as well as a description of the dimerization and polymerization processes.

The benzocyclobutene  $\leftrightarrow$  *o*-quinodimethane reaction pathway has been investigated by calculating the electronic structures of BCB, *o*-quinodimethane, and the transition structure for the ring-opening reaction. The transition structure is the energy maximum along the reaction path and cannot be isolated experimentally. The species that were computed are depicted in the reaction pathway shown below.

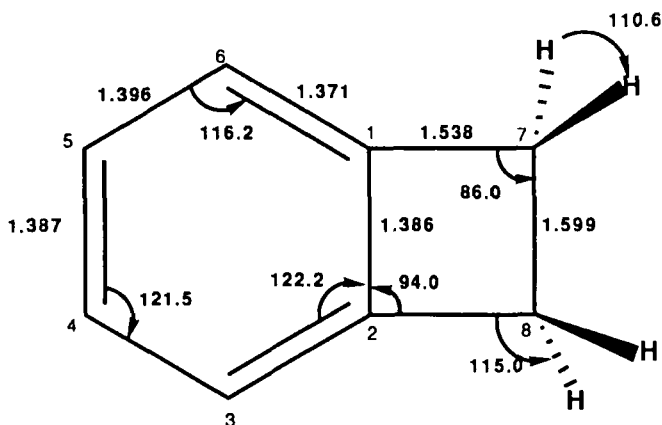


The structures of BCB, *o*-quinodimethane, and the transition structure were calculated using *ab initio* quantum mechanics and the 3-21G basis set [34]. This methodology is contained in the molecular orbital program package *Gaussian 86* [35]. Single-point calculations with second-order correlation energy corrections (MP2/3-21G//3-21G) were carried out on BCB, *o*-quinodimethane, and the transition structure [36]. In calculating the transition structure, a  $C_2$  symmetry constraint was imposed, consistent with the symmetry element in a conrotatory pathway (see below) [37]. The resulting energy maximum was proven to be a transition structure by calculating the vibrational frequencies using analytical second derivatives [35]. All the calculations were carried out on the VAX 8650 and IBM 3090-2VF computers.



## Benzocyclobutene

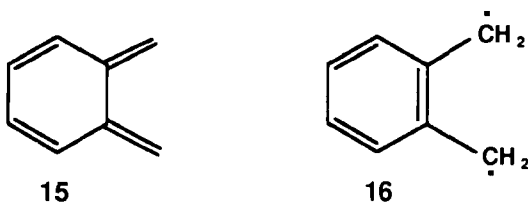
According to the 3-21G basis set, the ground state structure of benzocyclobutene has a  $C_{2v}$  symmetry. The bond lengths are in angstroms and the bond angles are in degrees.



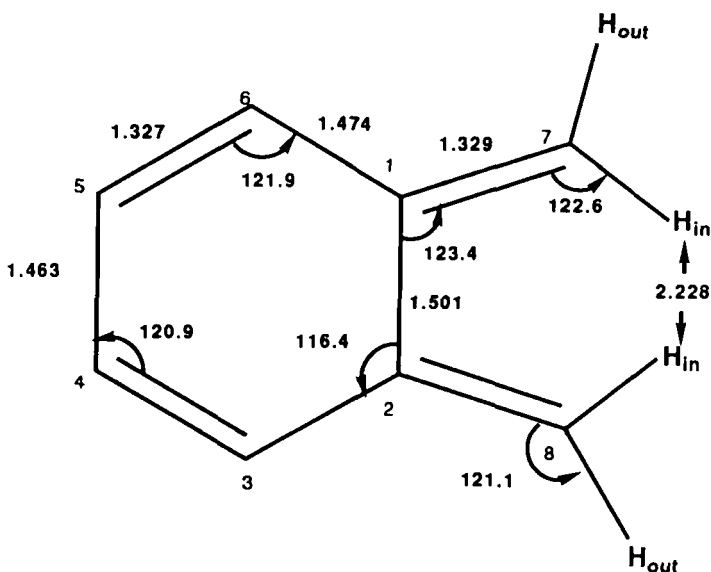
The aromatic character of the benzene moiety is maintained, as is evident from the small differences in the aromatic C=C bond lengths. The calculated Hartree-Fock energy is  $-305.84646$  atomic units (au). Upon inclusion of the correlation energy (MP2/3-21G//3-21G) correction, the total energy is lowered to  $-306.54086$  au. The zero-point vibrational energy is  $90.98$  kcal/mol and the computed entropy is  $74.3$  cal/mol·K.

## *o*-Quinodimethane

The electronic structure of *o*-quinodimethane has been extensively investigated both experimentally and theoretically. Interest in this particular species is attributed to the controversy regarding the ground state structure. Recent experimental and theoretical studies are consistent with the *o*-quinoid form **15** and not with the biradical structure **16** [38–40]. It was also concluded that the *o*-quinoid structure is planar and a ground state singlet.



The electronic structure of *o*-quinodimethane has now been computed, and it has been found that the ground state is indeed singlet and quinoid in structure. However, it was also found that *o*-quinodimethane is nonplanar and has a  $C_2$  symmetry, contrary to earlier contention by others [40]. The planar  $C_{2v}$  structure, which is also quinoid in form, is not an energy minimum because it has one imaginary frequency corresponding to the opposite twisting of the  $-\text{CH}_2$  groups. The nonplanar structure is an energy minimum not only because it is more stable than the planar structure by 0.14 kcal/mol, but most importantly, all vibrational frequencies are "real." *o*-Quinodimethane is quinoid in structure as evident from the C—C bond lengths. For example, the  $\text{C}_1\text{C}_7$  and  $\text{C}_5\text{C}_6$  bond lengths are 1.329 and 1.327 Å, respectively, typical of a double bond, while the  $\text{C}_1\text{C}_6$  and  $\text{C}_1\text{C}_2$  bond lengths are 1.474 and 1.501 Å, respectively. It is believed that if *o*-quinodimethane were a biradical, the electrons in the benzene moiety would be more delocalized so that all the CC bonds are aromatic and comparable in lengths.



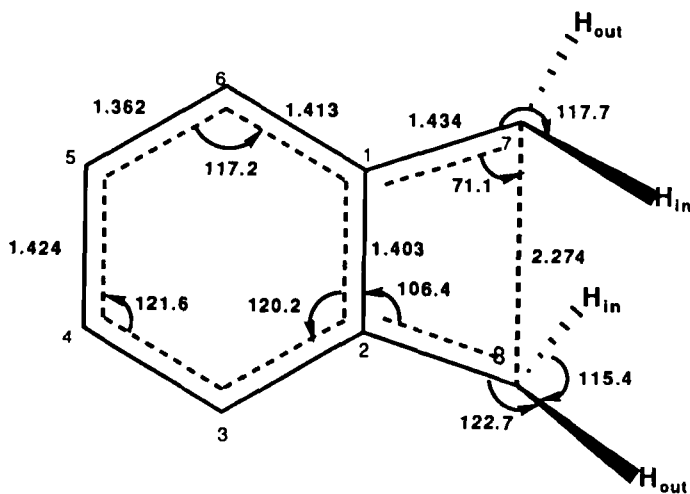
The dipole moment of the planar form is 0.0262 debye while that of the nonplanar is 0.0399 debye. The charge distribution between the two forms is comparable. The ionization potential of the nonplanar form is 7.38 electron volts (eV) while that of the planar form is 7.33 eV. The electron affinities are  $-1.99$  and  $-1.92$  eV for the nonplanar and planar

structures, respectively. From these results, we conclude that the experimental data for *o*-quinodimethane might also be explained by using the nonplanar structure.

The 3-21G total energy of nonplanar *o*-quinodimethane is  $-305.82335$  au. Inclusion of correlation energy correction lowers the energy to  $-306.51652$ . In contrast, the planar structure is less stable by  $0.14$  kcal/mol. The zero-point vibrational energy is  $89.76$  kcal/mol while the entropy is  $78.2$  cal/mol·K. For comparison, the zero-point vibrational energy of the planar form is  $89.73$  kcal/mol, comparable to that of the nonplanar, while the entropy is  $73.9$  cal/mol·K,  $4.3$  cal/mol·K lower than the nonplanar structure. Thus, entropy also favors the nonplanar form. According to these calculations, benzocyclobutene is more stable than *o*-quinodimethane by  $14.1$  kcal/mol. In other words, the interconversion from benzocyclobutene to *o*-xylylene is endothermic by  $14.1$  kcal/mol. This theoretical value is considerably larger than the experimental value reported by Roth [38] and Hehre [39]. However, the endothermic nature of the reaction is consistent in each of these studies.

### Transition Structure

The important geometrical parameters for the conrotatory transition structure of the benzocyclobutene  $\leftrightarrow$  *o*-quinodimethane interconversion are shown in the diagram below. The computed transition structure is nonplanar and has a  $C_2$  symmetry.



In the transition structure, the breaking  $C_7C_8$  bond length is  $2.274 \text{ \AA}$ ,

corresponding to reaction progress of 42%. The C<sub>1</sub>C<sub>7</sub> bond, which is a single bond in the reactant and becomes a double bond in the product, is 1.434 Å (60% reaction progress). The other CC bonds as well as bond angles show a smooth transition in going from the reactant to the product. That is, the double bonds in BCB that become single bonds in *o*-quinodimethane possess partial double bond character in the transition state. The 3-21G total energy of the BCB transition structure is -305.75932 au. Inclusion of the correlation energy correction (MP2/3-21G//3-21G) lowers the energy to -306.47444 au. The zero-point vibrational energy is 88.86 kcal/mol while the entropy is 74.2 cal/mol·K. The calculated 3-21G activation energy with zero-point energy corrections is 52.6 kcal/mol. Inclusion of correlation energy lowers the activation energy to 39.6 kcal/mol, in essentially perfect agreement with the experimental activation energy of 39.9 kcal/mol [38]. The small negative activation entropy (-0.1 cal/mol·K) is consistent with the experimental activation entropy of *cis*-diphenylbenzocyclobutene which is 0 cal/mol·K [41]. The computed activation energy for the reverse reaction, i.e., *o*-quinodimethane → BCB, is 25.5 kcal/mol. The 3-21G vibrational frequencies were calculated, and it was found that the computed transition structure is indeed authentic because it has an imaginary vibrational frequency. The imaginary vibrational frequency has a magnitude of 839 cm<sup>-1</sup>, corresponding to the stretching of the C<sub>7</sub>C<sub>8</sub> bond coupled with the conrotation of the two methylene groups.

The highest occupied molecular orbital (HOMO) of the transition structure is essentially the  $\sigma$ -orbital of the breaking C<sub>7</sub>C<sub>8</sub> bond, mixed in bonding fashion with one of the benzene  $\pi^*$ -orbitals ( $\sigma + \pi^*$ ). The lowest unoccupied molecular orbital (LUMO) is the C<sub>7</sub>C<sub>8</sub>  $\sigma^*$ -orbital mixed in antibonding fashion with one of the benzene  $\pi$ -orbitals ( $\sigma^* - \pi$ ). Stabilization of these orbitals increases if the orbital mixing increases. Stabilization of these orbitals would also lead to stabilization of the transition structure. That is, one of the possible consequences of orbital stabilization is the lowering of the activation energy of ring opening such that the transition structure will occur earlier. How then can the mixing of these orbitals be decreased? It is predicted that an electron-donating substituent at C<sub>7</sub> and/or C<sub>8</sub> will raise the energy of the  $\sigma$ -orbital such that it can mix more with the  $\pi^*$ . In other words, electron donors at the cyclobutene moiety (C<sub>7</sub> and/or C<sub>8</sub>) would ring open faster. Similarly, the stabilization of the transition structure can be increased if electron-withdrawing substituents are incorporated in the benzene moiety because in doing so the benzene  $\pi^*$  orbital energy is lowered so that it will have greater mixing with the C<sub>7</sub>C<sub>8</sub>  $\sigma$ -orbital. Thus, the best combination to

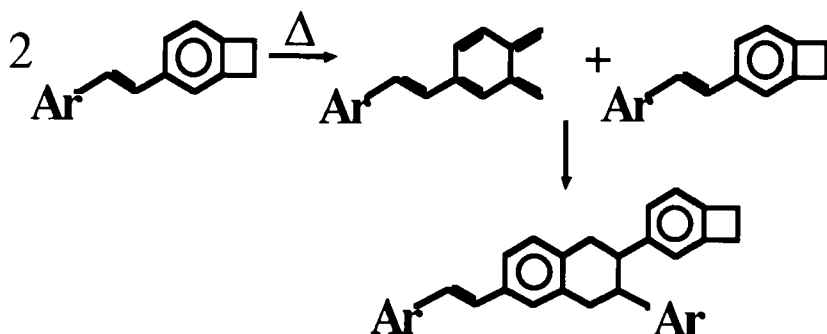


FIG. 1. Proposed reaction pathway for Diels-Alder type reactions.

lower the activation energy would be electron acceptors on the benzene ring and electron donors on the cyclobutene moiety.

### HOMOPOLYMERIZATION OF BCB MONOMERS

Benzocyclobutenes are a family of thermally polymerizable monomers which can be classified into two groups: 1) monomers which contain only benzocyclobutene moieties and 2) monomers which contain sites of unsaturation in addition to benzocyclobutene moieties. The *o*-quinodimethane structure described above is thought to be a key intermediate in each pathway. The reaction of a BCB group with an olefin, illustrated in Fig. 1, is referred to as the Diels-Alder pathway. The reaction between two BCB groups, illustrated in Fig. 2, is referred to as the BCB-BCB pathway.

#### Homopolymerization Kinetics

The reaction kinetics were investigated experimentally with differential scanning calorimetry (DSC). DSC is advantageous in that it allows the study of a thermoset throughout its polymerization and not just

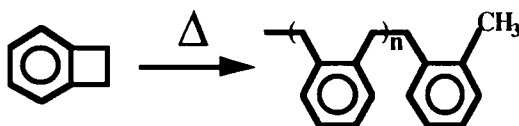


FIG. 2. Proposed reaction pathway for BCB-BCB type reactions.

prior to or after the gel point. Results for six BCB monomers are presented here. The reaction exotherm was analyzed by the method of Borchardt and Daniels [42] to obtain the reaction order  $n$ , the Arrhenius activation energy  $E_a$ , and preexponential factor  $\log Z$ . The highly exothermic reactions and volatile monomers required the use of small sample sizes, hermetically sealed sample containers, and vaporization corrections.

The structure, designation, and physical characteristics of the BCB monomers are shown in Table 1. The melting points reported in Table 1 were obtained from DSC measurements. All the DSC data were obtained with a Du Pont 1090 thermal analyzer. The heat evolved from each sample contained in hermetically sealed pans was measured relative to that of an empty pan. The BCB monomers were typically scanned from 60 to 400°C at 10°C/min. Each polymerization exotherm typically ranged between 500 and 1000 J/g, and had a single maximum near 258°C. Results were corrected for sample vaporization when the sample weight decreased during the DSC scan.

The measured enthalpies,  $\Delta H_{r \times n}$ , for all monomers in bulk are summarized in Table 2, assuming complete reaction. The reaction enthalpies can be combined with the reaction stoichiometry to ascertain the pathway favored by thermodynamics. Two moles of BCB moieties, that react according to the BCB-BCB type reaction, yield an average enthalpy of  $-53 \pm 3$  kcal. One mole of the BCB moieties, that react according to the Diels-Alder type reaction, yields an enthalpy of  $-44 \pm 3$  kcal. The BCB-BCB reaction is more exothermic by about 9 kcal and hence is favored thermodynamically. In contrast, homopolymerization products of monomers that could undergo both reaction pathways (e.g., **10b**) were dominated by the Diels-Alder type reaction [43]. This result would seem to indicate that the Diels-Alder pathway is kinetically preferred.

The kinetics results are summarized in Table 3. The reaction order is roughly unity for all the monomers studied except **18** [60].  $\log Z$  falls between 11 and 17  $\text{min}^{-1}$ , and  $E_a$  falls between 28 and 42 kcal/mol.  $E_a$  is determined with the best precision and characterizes the energy required to form the activated complex of the rate-limiting elementary step. This step is thought to be the ring-opening reaction of the BCB functionality for both reaction pathways (*vide supra*). Roth and coworkers [38] studied this ring opening in benzocyclobutene and found the reaction to be first order with an  $E_a$  of 39.9 kcal/mol. Both results are consistent with that observed for the homopolymerization of the BCB monomers and that theoretically calculated herein. Differences in the observed  $E_a$  rela-



TABLE 1. Physical Properties of Selected BCB Monomers

Monomer structure	Sample appearance at 25°C	Molecular weight, g/mol	Melting point, °C	$\Delta H_{\text{melt}}$ , kcal/mol
<p><b>10b</b> (mixed isomers)</p>	Clear/yellow liquid	390.7	Liquid	—
<p><b>17</b> m,p</p>	White crystalline solid	220.8	36–38	—
<p><b>18</b></p>	White crystalline solid	206.3	80–83	$5.28 \pm 0.05$
<p><b>19</b> (mixed isomers)</p>	Amber liquid	394.7	Liquid	—
<p><b>20</b></p>	White crystalline solid	234.3	82–86	$8.4 \pm 0.17$
<p><b>21</b> m,p</p>	Clear liquid	222.3	Liquid	—

TABLE 2. Reaction Enthalpies for Selected BCB Monomers

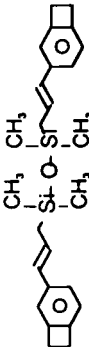

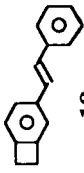
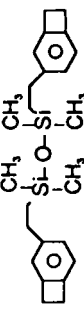
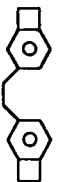

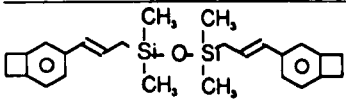
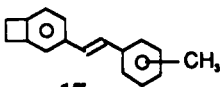
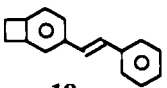
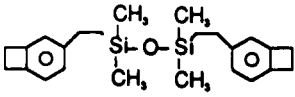
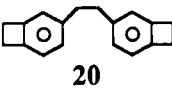
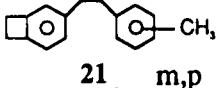
Monomer structure	Molecular weight, g/mol	Dominant reaction	$\Delta H_{\text{rxn}}$ , kcal/mol	$\Delta H_{\text{rxn}}$ , kcal/mol - BCB
	390.68	BCB + olefin	$-96.6 \pm 6.3$	$-48.3 \pm 3.2$
<b>10b</b> (mixed isomers)				
	220.81	BCB + olefin	$-43.1 \pm 2.6$	$-43.1 \bullet 2.6$
<b>17</b> m,p				
	206.29	BCB + olefin	$-42.2 \pm 1.0$	$-42.2 \pm 1.0$
<b>18</b>				
	394.71	BCB + BCB	$-49.1 \pm 2.7$	$-24.5 \pm 1.4$
<b>19</b> (mixed isomers)				
	234.34	BCB + BCB	$-53.2 \pm 2.0$	$-26.6 \pm 1.0$
<b>20</b>				
	222.33	BCB + BCB	$-28.9 \pm 3.0$	$-28.9 \bullet 3.0$
<b>21</b> m,p				

TABLE 3. Kinetic Parameters for Selected BCB Monomers

Monomer structure	Reaction order	$\log Z$ , $\text{min}^{-1}$	$E_a$ , kcal/mol
 <b>10b</b> (mixed isomers)	$1.03 \pm 0.01$	$15.7 \pm 0.1$	$38.5 \pm 0.2$
 <b>17</b> m,p	$0.86 \pm 0.13$	$14.6 \pm 1.0$	$35.8 \pm 2.4$
 <b>18</b>	$0.43 \pm 0.27$	$11.3 \pm 2.1$	$28.4 \pm 4.8$
 <b>19</b> (mixed isomers)	$1.24 \pm 0.3$	$17.0 \pm 1.2$	$41.8 \pm 3.1$
 <b>20</b>	$1.07 \pm 0.03$	$16.6 \pm 0.3$	$40.8 \pm 0.7$
 <b>21</b> m,p	$1.02 \pm 0.18$	$16.3 \pm 0.3$	$40.8 \pm 0.7$

tive to that of the ring-opening of BCB are presumed to be due to substituent effects. The  $E_a$  observed for **18** appears to be anomalously low, and the reason for this behavior is not yet understood [60].

The bulk thermally initiated homopolymerizations of the BCB monomers in Table 1 are assumed to share the same ring-opening, rate-limiting step exhibited by unsubstituted benzocyclobutene because: 1) all monomers belong to a set of BCB monomers that are substituted at the third carbon in the six-membered ring; 2) the thermal polymerizations are observed to be first order; 3) the  $E_a$ 's, with the exception of **18** (from 36–42 kcal/mol), fall within  $\pm 15\%$  of the  $E_a$  of benzocyclobutene (39.9 kcal/mol); and 4)  $E_a$  is independent of whether the reaction follows a

Diels–Alder or a BCB–BCB type reaction. The theoretical calculations also support this conclusion.

### Network Structures

Preliminary characterizations of the network structures formed by the thermal homopolymerization of BCB monomers have been undertaken. These studies involved measurement of the growth of the equilibrium shear modulus,  $G_e$ , during the bulk polymerization. The results have been compared to those predicted by a statistical model of the polymerization for interpretation of the network structure. The model was based on that of Flory [44] and Stockmayer [45] for the stepwise polymerization of nonlinear macromolecules from monomers with three or more reactive sites. The equivalent formalism of Miller and Macosko [46, 47] was used in developing models suitable for the thermal homopolymerization of BCB thermosets. This formalism was easier to apply to new types of monomers since average properties can be obtained without explicitly evaluating the distribution function.

The extent of reaction was measured with DSC. The structure, designation, and physical characteristics of the BCB monomers evaluated in this study are summarized in Table 1. The monomers were used as received.

The rheological data were measured with a Rheometrics RDSII dynamic mechanical spectrometer. All measurements of  $G_e$  were made using parallel-plate geometry. The thermosets were cured in bulk at 200°C. Stress relaxation and frequency sweep experiments were typically performed at 160°C. The growth of  $G_e$  at 200°C was sometimes approximated with the growth of the storage modulus,  $G'$ , measured at 0.1 rad/s. All measurement temperatures were chosen to exceed the glass transition temperature  $T_g$  of the thermoset. The growth of the  $T_g$  for each thermoset were measured with a Du Pont 942 thermal mechanical analyzer.

The results for a typical thermoset are illustrated in Fig. 3. At low extents of reaction,  $p < 0.33$ , the modulus of the **10b** thermoset was not observed and the network structure did not exist. Throughout this region, the average molecular weight of the macromolecules in the thermoset rose as  $p$  increased, and the macromolecules became more and more branched. At about  $p = 0.33$  the modulus was first observed and it rose steeply with increasing  $p$ . This point in the polymerization was identified as the gel point. It marked the onset of gelation and the first appearance of an infinite three-dimensional network.

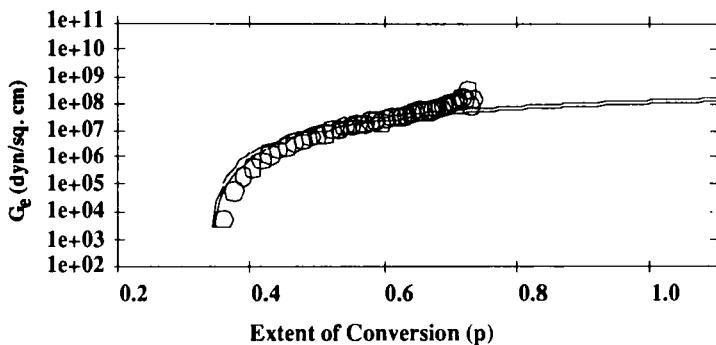


FIG. 3. Growth of the equilibrium shear modulus  $G_e$  for the homopolymerization of **10b** in bulk at 200°C. The data are well predicted by the statistical model for tetrafunctional monomers of the type  $A_2B_2$ .

The experimental data are well described by model predictions for a tetrafunctional monomer of type  $A_2B_2$  with a molecular weight corresponding to that of **10b**. The data observed near the gel point confirm that the highest functionality of each **10b** monomer never exceeds four. The set of all data confirms that each monomer is transformed into a tetrafunctional network junction when the thermoset is fully cured. The four reactive sites in **10b** are assumed to be the two internal olefinic groups as well as the two BCB groups. No evidence of BCB-BCB type reactions or of reactions solely involving the olefins were observed. Either reaction, if present, would change the observed functionality of the monomer. Using this information, along with the reaction kinetics data for this material discussed above, a picture of the network structure can be developed. For **10b**, a highly crosslinked network is formed via the Diels-Alder type reaction pathway, and each monomer is transformed into a tetrafunctional network junction in the fully cured thermoset.

The homopolymerization of **19** conformed to the predictions for tetrafunctional monomers of type  $A_4$  as expected for polymerizations via the BCB-BCB reaction pathway. Poly(*o*-xylene) was presumed to be the dominant reaction product since the postulated alternative products [dibenzocyclooctadiene or terminated poly(*o*-xylene)] would reduce the monomer functionality to three or less. The data were consistent with the expectation that each monomer was transformed into a tetrafunctional network junction in the fully cured thermoset. Similar  $G_e$  experiments have demonstrated that fully cured **20** thermosets are highly crosslinked and composed of a mixture of tri- and tetrafunctional network junctions.

Not all BCB monomers produce three-dimensional networks. In particular, **17**, **18**, and **21** never exhibited an equilibrium shear modulus. All three polymerized as bifunctional materials and formed thermoplastics. For **17** and **18**, which follow the Diels–Alder reaction pathway, the bifunctionality arose from the presence of only one BCB group and one olefinic group per monomer. No evidence for the BCB–BCB reaction pathway was observed for these monomers since this would have raised the monomer functionality to three or more, and produced a material with an equilibrium modulus. For **21**, each BCB group is presumed to act as two reactive sites as proposed in the BCB–BCB reaction pathway.

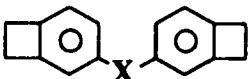
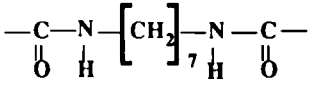
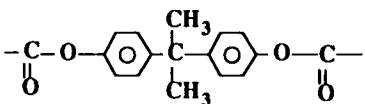
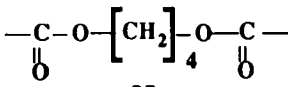
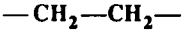
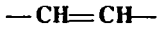

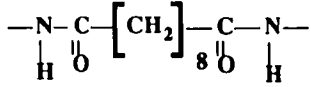
### POLYMER PROPERTIES

The synthesis of a wide variety of benzocyclobutene monomers, the theoretical basis for polymerization, and the thermal homopolymerization, including cyclobutene ring opening, polymerization kinetics, and network development, have been described. This section discusses the properties of the resultant homopolymers.

A general characteristic of the benzocyclobutene-derived polymers is that of high thermal stability [1–5, 48]. Thermal stability, for the purpose of this paper, is defined as the maximum temperature at which the polymer showed zero percent weight loss on a Du Pont 951 thermogravimetric analyzer (TGA) being ramped at a rate of 10°C/min under flowing nitrogen [5]. This experimental approach provides a measure of short-term thermal stability and is at best a first approximation as to what the long-term thermal stability of the polymer will be. In practice, this latter temperature will always be lower than the temperature observed by the procedure adopted herein. Table 4 shows the short-term zero percent weight loss temperatures for some representative bisbenzocyclobutene polymers. Of particular note is the good thermal stability of all of the polymers, including those such as the ester **25** which contain relatively large proportions of aliphatic linkages. The polymers derived from the all-hydrocarbon monomers **9a**, **10a**, **20**, **22**, **26**, and **28** are of particular note since they exhibit no appreciable weight loss up to 400–475°C (750–890°F).

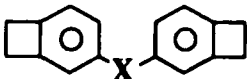
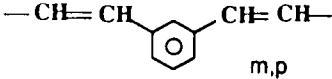

To a first approximation, the thermal stabilities of the polymers follow the conventional perception of functional group thermal stability. Entry **22**, with a direct bond between the aryl groups of the benzocyclobutene moieties, would be expected to give some indication of the ultimate thermal stability of a bisbenzocyclobutene polymer, since in this

TABLE 4. Thermal Stability of Polybisbenzocyclobutenes

Polymer from  X	Maximum temperature showing zero percent weight loss in N <sub>2</sub> by TGA: °C (°F)
None <b>22</b>	400 (752)
 <b>23</b>	385 (572)
 <b>24</b>	400 (752)
 <b>25</b>	370 (698)
 <b>20</b>	425 (797)
 <b>2a</b>	475 (887)
 <b>26</b>	410 (770)
 <b>27</b>	365 (689)

(continued)

TABLE 4 (continued)

Polymer from  X	Maximum temperature showing zero percent weight loss in N <sub>2</sub> by TGA: °C (°F)
 <u>10a</u>	425 (797)
 <u>28</u>	410 (770)

example there are no intervening functional groups. That is, the polymer from **22** should exhibit a thermal stability that is a strong reflection of the stability of the structures obtained by reacting two or more benzocyclobutenes via the proposed *o*-quinodimethane polymerization intermediates. That this assertion is not necessarily true is indicated by the data which show that the polymer from **22** is not, by this test, significantly more stable than a variety of other bisbenzocyclobutene polymers containing diverse aryl linking groups. Further, the data in Table 1 show that for some structures such as the ethane-, ethylene-, and ethynyl-linked bisbenzocyclobutenes **20**, **9a**, and **26**, the presence of nonaryl functional groups in fact enhances thermal stability. The data suggest that in these instances the linking groups are not in fact inert carriers of the benzocyclobutene moieties but rather take an active role in the polymerization process to modify the final polymer architecture. Independent evidence from rheological studies previously mentioned strongly supports the idea of the linking groups involvement in the polymerization process. Specifically, these studies (*vide supra*), along with others, suggest that the polymerization of monomer **9a** first involves almost exclusively the cycloaddition of a benzocyclobutene to the double bond followed by subsequent extensive crosslinking through the other benzocyclobutene groups at final higher functional group conversion. Such a highly crosslinked network would, on intuitive grounds at least, be ex-



pected to exhibit exceptional thermal stability. In fact, this notion is supported by the experimental facts in Table 4, using the TGA thermal stability method referenced above.

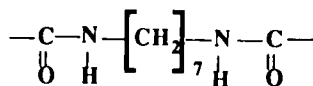
Thermal stability as measured by these ramped TGA experiments of the sort previously described are, of course, not the definitive test of a polymer's utility at elevated temperature. Rather, for a polymer to be useful at elevated temperatures, it must exhibit some significant retention of useful mechanical properties over a predetermined lifetime at the maximum temperature that will be encountered in its final end use application. In order to appropriately address this issue, several of the polymers which looked promising by the preliminary TGA screening were prepared in larger quantities and molded into test specimens for a mechanical properties evaluation protocol. Tables 5 and 6 show some of the preliminary mechanical data as well as some other physical properties of molded samples of polymers derived from amide monomer **23**, ester monomer **24**, diketone monomer **11**, and polysiloxane monomer **10b**. The use of the term polyamide, ester, etc. with these materials is not meant to imply that they are to be regarded as merely modified linear thermoplastics. Rather, these polymers are for the most part highly crosslinked thermosets.

As the data in Tables 5 and 6 indicate, these polymers exhibit an excellent retention of their room temperature mechanical properties to at least 200–250°C. Note in particular the very high  $T_g$  (> 350°C) of the tetramethyldivinylsiloxane bisbenzocyclobutene polymer made from monomer **10b**. Overall, the absolute values of some of these mechanical properties are quite comparable to those of other high temperature thermosets and suggest that the bisbenzocyclobutene polymers would be useful as matrix resins in this temperature range. Long-term thermal aging studies of polyester **24** and polydiketone **11** at 250°C suggest that this is the maximum continuous use temperature for these polymers.

Many of the bisbenzocyclobutene polymers are relatively unaffected by organic solvents and aqueous media. In Table 7 are shown some of the preliminary results obtained in a solvent pick-up study carried out on the bisbenzocyclobutene polyester **24** [5]. Of all of the solvents, only dimethylformamide, trichloroethylene, and methyl ethyl ketone were absorbed to any significant extent at 70°C over the 4-week course of the experiment. None of the polymer samples dissolved in the solvents tested, and only a slight swelling was observed with those liquids which were significantly absorbed. The small effect of aqueous sodium hydroxide on the bisbenzocyclobutene polyester is deserving of note since a

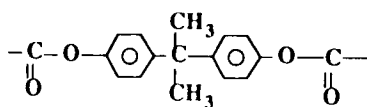
TABLE 5. Physical Properties of Polybisbenzocyclobutenes

Polymer properties from X =



23

"Amide"

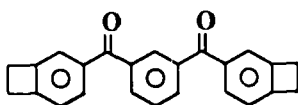


24

"Ester"

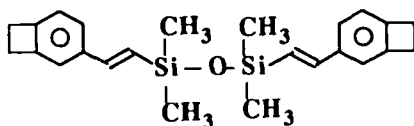
	Amide	Ester
Tensile modulus (psi):		
25°C	362,000	386,000
250°C	192,000	270,000
Shear modulus (psi):		
25°C	136,000	145,000
250°C	72,000	101,000
Tensile strength (psi):		
25°C	12,000	4,000
150°C	6,000	
Adhesion (tensile lab shear)	1,960 (25°C)	
psi, on steel	1,650 (200°C)	
Coefficient of thermal expansion		
(in./in./°C)		
25–250°C	$4.1 \times 10^{-5}$	$8 \times 10^{-5}$
250–325°C	$9.8 \times 10^{-5}$	
Water pick-up (% at 48 h, 100°C)	1.4	0.9
$T_g$	>270°C	>270°C
0% Weight loss temperature	385°C	400°C

TABLE 6. Properties of Poly:

**11**

$T_g$ (TMA)	310°C
Flexural strength	22 ksi
Flexural modulus	616 ksi (30°C)
DMA	426 ksi (300°C)
Coefficient thermal expansion:	
Below $T_g$	35 ppm/°C
Above $T_g$	150 ppm/°C
$G_{1c}$	80 J/m <sup>2</sup>
Elongation (at break)	4.1%
Thermal stability, 5% weight loss temperature (10°C/min)	445°C (N <sub>2</sub> )

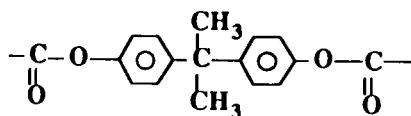
Properties of Poly:

**10b** (mixed isomers)

$T_g$ (TMA, DMA)	> 350°C
Flexural modulus (DMA, 25°C)	480 ksi
CTE, 25–300°C (TMA)	65–70 ppm/°C
Water absorption (24 h, 100°C)	0.25%
Weight loss at 350°C (N <sub>2</sub> ), 20 μm film on silicon 2 h	~ 2%
Dielectric constant:	
(1 MHz)	2.57
(10 GHz)	2.55
Dissipation factor:	
(1 MHz)	0.0008
(10 GHz)	< 0.002

TABLE 7. Solvent Resistance of a Polybisbenzocyclobutene

Polymer properties from X =

24

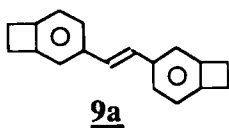
Solvent	Weight increase (%), 4 week exposure at 70°C
<i>N,N</i> -Dimethylformamide	17.0
Heptane	0.0
Isopropyl alcohol	0.6
Methyl ethyl ketone	18.0
Propylene glycol	0.0
5% Sodium hydroxide	0.3
Toluene	2.9
Trichloroethylene	47.0
Water	1.2

control sample of a commercial polyimide (Vespel) dissolved completely in 2 days under the conditions of this test.

Water absorption is a uniquely important property owing to water's ubiquitous nature and its ability to strongly influence a polymer's mechanical and electrical properties. In general, high water absorption is undesirable in a polymer, although in some cases, such as with the nylons and many biopolymers, absorbed water is critical to the proper functioning of the material. To a first approximation, water absorption of bisbenzocyclobutene polymers follows in an intuitive way the hydrophilic or hydrophobic character of the linking group  $x$  which connects the benzocyclobutene moieties in the parent monomer. It should be noted that all of the water absorption data shown in Tables 5, 6, 7, and 8 are rather small and for the most part consistent with what one would expect of a crosslinked polymer.

Bisbenzocyclobutene polymers have been used in a variety of electronic applications ranging from conductive metal-filled die-attach adhesives [57-59] to high  $T_g$  planarizing and insulating layers on silicon wa-

TABLE 8. Properties of Poly:



$T_g$ (TMA, DMA)	> 350°C
Flexural modulus (DMA, 25°C)	747 ksi
CTE, 25–300°C (TMA)	27 ppm/°C
Water absorption (24 h, 100°C)	0.87%
Weight loss at 350°C (N <sub>2</sub> ), 20 μm film on silicon 2 h	~0%
Dielectric constant (1 MHz)	2.7
Dissipation factor (MHz)	0.0004

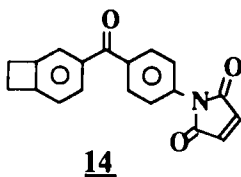
fers [12–18]. As with water absorption, the dielectric constant and dissipation factor of a bisbenzocyclobutene polymer depends strongly upon the group  $x$  which links the two benzocyclobutene moieties in the parent monomer. Highly polar linking functional groups tend to give polymers with relatively high (3.0–4.0) dielectric constants and larger dissipation factors. The more nonpolar linking groups such as siloxanes and hydrocarbons, on the other hand, yield polymers with dielectric constants less than 3.0. Tables 6 and 8 show some of the relevant properties of two bisbenzocyclobutene polymers that have been targeted for electronic applications. These particular polymers have, in addition to their good electrical properties, the advantage of having a very low water pickup. This means that the dielectric constant and dissipation factor of the polymers will be relatively insensitive to changes in environmental humidity. This is in sharp contrast to many polyimides which absorb relatively large amounts of water and whose electrical properties suffer accordingly.

A second major class of benzocyclobutene monomers is that family of materials which contains one benzocyclobutene group and one olefinic site of unsaturation per monomer molecule. Representative examples of these monomers are 3-vinylbenzocyclobutene [49, 50], 3-maleimidobenzocyclobutenes, and the family of 1-aryl-2-(3-benzocyclobutenyl) ethylenes [9, 10]. 3-Vinylbenzocyclobutene is a substituted styrene and readily enters into free radical, anionic, and Ziegler–Natta-type polymerizations [51–56].

The 3-maleimidobenzocyclobutenes undergo thermal homopolymer-

ization to yield high  $T_g$  polymers [33]. Table 9 shows some representative properties of the polymer derived from a maleimide-substituted benzocyclobutene. Note that the polymer has a relatively high  $T_g$  (310°C) and a very large fracture toughness as measured by the  $G_{1c}$  value of 610 J/m<sup>2</sup>. This contrasts sharply with the properties of the polymer derived from bisbenzocyclobutene diketone monomer **11** described in Table 6, which also has a  $T_g$  of 310°C but a fracture toughness of only 80 J/m<sup>2</sup>. This latter  $G_{1c}$  value of 80 J/m<sup>2</sup> is consistent with the expected properties of a highly crosslinked thermoset which is what the bisbenzocyclobutene polymers are believed to be. The much higher  $G_{1c}$  value of 610 J/m<sup>2</sup> for the polymaleimidobenzocyclobutene is reminiscent of a more linear and perhaps thermoplastic material. The polymerization mechanism proposed for the maleimidobenzocyclobutenes is a cycloaddition (Diels-Alder) polymerization in which the benzocyclobutene moiety first opens up to yield an *o*-quinodimethane which subsequently reacts with a maleimide double bond to yield a substituted tetralin. This tetralin would have a benzocyclobutene unit at one end of the molecule and a maleimide group at the other end and, as such, constitutes another larger maleimidobenzocyclobutene monomer which can go on to yield a linear polymer.

TABLE 9. Properties of Poly:



$T_g$	310°C
Flexural strength	29 ksi
Flexural modulus	515 ksi (30°C)
(DMA)	357 ksi (300°C)
CTE	
Below $T_g$	43 ppm/°C
Above $T_g$	193 ppm/°C
Elongation (at break)	6%
$G_{1c}$	610 J/m <sup>2</sup>
Thermal stability, TGA, 10°C/min,	
5% weight loss temperature	470°C (N <sub>2</sub> )

The limited data available thus far do in fact support the notion that maleimdobenzocyclobutenes such as **14** polymerize to yield substantially linear polymers.

## CONCLUSIONS

Benzocyclobutenes constitute the basis of a new and versatile approach to the synthesis of high performance polymers for applications in the electronics and aerospace industries. The basic technology involves a family of thermally polymerizable monomers which contain one or more benzocyclobutene groups per molecule. These monomers can be classified broadly into two groups: 1) monomers which contain only benzocyclobutene moieties and 2) monomers which contain sites of unsaturation in addition to benzocyclobutene moieties. The monomers can be partially polymerized (B-staged) by heating for various lengths of time at 160–180°C. The oligomers resulting from this process typically have softening points below those of the pure monomers and offer certain processing advantages for various composite fabrication techniques. Benzocyclobutene polymers encompass materials which have properties ranging all the way from those of high glass transition temperature ( $T_g$ ) thermosets to those of substantially linear thermoplastics and, in some instances, even elastomers.

The mechanism of thermal interconversion of benzocyclobutene to *o*-quinodimethane was examined theoretically. *o*-Quinodimethane was found to be a ground state singlet, *o*-quinoid structure, and not a biradical structure. This transformation is concerted and follows the Woodward–Hoffmann prediction of conrotatory motion. The reaction is endothermic and has a computed activation energy of 39.6 kcal/mol, in essentially perfect agreement with the experimental activation energy of 39.9 kcal/mol.

The reaction kinetics were investigated experimentally with differential scanning calorimetry. Monomers that contain only benzocyclobutene moieties yield an average enthalpy of  $-53 \pm 3$  kcal/mol, while monomers which contain sites of unsaturation in addition to benzocyclobutene moieties react by a Diels–Alder pathway and yield an enthalpy of  $-44 \pm 3$  kcal/mol. The benzocyclobutene only reaction is more exothermic by about 9 kcal and hence is favored thermodynamically. The Diels–Alder pathway is kinetically preferred.

Preliminary characterization of the network structures formed by the

thermal homopolymerization of BCB monomers was studied by the growth of the equilibrium shear modulus ( $G_e$ ) during the bulk polymerization. The results were compared to those predicted by a statistical model of the polymerization for interpretation of the network structure. Each monomer which contained either only multiple benzocyclobutene moieties or sites of unsaturation in addition to benzocyclobutene moieties was transformed into a tri- and/or tetrafunctional network junction when the thermoset was fully cured. Monomers which contain only one site of unsaturation and one benzocyclobutene moiety never exhibited an equilibrium shear modulus and polymerized to thermoplastics. The 3-maleimidobenzocyclobutenes thermally polymerize to yield substantially linear, high  $T_g$  polymers.

A general characteristic of the benzocyclobutene-derived polymers is that of high thermal stability. These polymers exhibit an excellent retention of their room temperature mechanical properties up to at least 200–250°C. The absolute values of some of these mechanical properties are quite comparable to those of other high temperature thermosets and suggests that the bisbenzocyclobutene polymers would be useful as matrix resins in this temperature range. The bisbenzocyclobutene polymers are relatively unaffected by organic solvents. The water absorption of bisbenzocyclobutene-derived polymers follows intuitively the hydrophilic or hydrophobic character of the linking group which connects the benzocyclobutene moieties in the parent monomer. All water absorption values are rather small and for the most part consistent with what one would expect of a crosslinked polymer.

Bisbenzocyclobutene polymers have been used in a variety of electronics applications ranging from conductive, metal-filled die-attach adhesives to high  $T_g$  planarizing and insulating layers on silicon wafers. Tetramethyldivinylsiloxane bisbenzocyclobutene has been targeted for electronics applications. The prepolymer has excellent planarization processability while the polymer has outstanding electrical properties and very low water pickup. This means that the dielectric constant and dissipation factor of the polymer will be relatively insensitive to changes in environmental humidity.

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