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Thermal Polymerization of Bis(benzocyclobutene) Monomers Containing α,β-Disubstituted Ethenes

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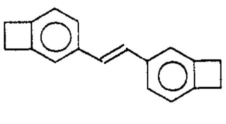
ABSTRACT: The thermally induced polymerization of monomers containing two benzocyclobutenes and one or two α,β-disubstituted alkenes has been studied. Polymers prepared from monomers of this type are highly cross-linked thermosets with high storage moduli. Spectroscopic analysis of partially polymerized monomers suggests that the dominant mode of polymerization is the Diels-Alder reaction of a reactive intermediate *o*-quinodimethane with α,β-disubstituted olefin. The rate of polymerization appears to be controlled by the first-order rearrangement of benzocyclobutene to *o*-quinodimethane. Rate constants for polymerization of two such monomers were calculated from residual monomer and FT-IR analyses. A relationship between molecular weight growth and functional group conversion based on the approach of Macosko and Miller[23] has been applied to the polymerization of monomers containing two benzocyclobutenes and one or two olefins. Molecular weight growth and gel point for a divinyltetramethyldisiloxane-linked bis(benzocyclobutene) was found to be well predicted by this model, and an energy of activation of 37 kcal/mol was calculated for the polymerization of this monomer. *trans*-1,2-Bis(3-benzocyclobutenyl)ethylene monomer was found to deviate substantially from the proposed mode of polymerization at functional group conversions approaching the gel condition. An earlier than predicted gel point and broadening of the molecular weight distribution during the polymerization of this monomer are thought to occur as a result of *o*-quinodimethane self-reaction as the olefin concentration decreases.

Introduction

The thermal polymerization of benzocyclobutene functional monomers has been used to provide an interesting array of polymers with diverse physical properties.[1-12] The use of the relatively nonpolar benzocyclobutene as a reactive end group allows for the preparation of hydrophobic materials with low dielectric constants (<2.7 at 1 MHz) which are particularly well suited for microelectronic applications. A previous study dealt[1] with the polymerization of a monomer which contained single benzocyclobutene and α,β-diarylethylene functionalities. This system was shown to polymerize exclusively by a Diels-Alder reaction to give a polytetrahydronaphthalene, up to ca. 65% conversion of the benzocyclobutene groups (Scheme I). The current work examines the thermal polymerization behavior of benzocyclobutene-alkene monomers which contain two benzocyclobutenes and at least one olefinic site per monomer molecule. Because the α,β-disubstituted alkenes are not reactive (except as dienophiles) during the polymerization, these systems present an opportunity to study the role of the benzocyclobutene reactive group during the polymerization reaction. The simplest example of this monomer type is the stilbene analog 1. Bis(vinylbenzocyclobutenes) with an equal number of benzocyclobutene and alkene functionalities have been prepared, including the tetramethyldisiloxane monomer 2 and *m*-phenylene monomer 3.[13] Experimentally, the thermolysis of all of these monomers has been found to lead to insoluble, highly cross-linked thermoset polymer systems.



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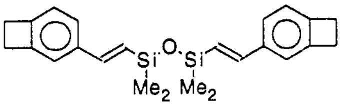

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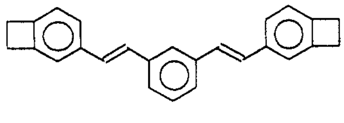

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Experimental Section

All of the arylbenzocyclobutene monomers were prepared using the Pd-catalyzed Heck vinylation reaction[14,15] (Scheme II). Monomer 1[16] (mp 130 °C) is prepared via the Pd-catalyzed reaction of 3-bromobenzocyclobutene with ethylene, followed by addition of a second mole of 3-bromobenzocyclobutene. Monomer 2 is prepared by Pd-catalyzed reaction of 3-bromobenzocyclobutene with 1,2-divinyl-1,1,2,2-tetramethyldisiloxane;[17] analysis of this monomer shows 97.9% purity, with some 1 present due to cleavage of the siloxane —Si—CH= bond during the reaction. Monomer 2 is an oil at room temperature and is found to contain a mixture of *cis*, *trans*, and *gem* alkene isomers. Because there are two alkenes per monomer molecule, there are a total of six configurational isomers with respect to the carbon-carbon double bonds: *trans-trans*, *trans-cis*, *cis-cis*, *gem-gem*, *trans-gem*, and *cis-gem*. Monomer 3 was prepared by Pd-catalyzed reaction of 3-bromobenzocyclobutene with divinylbenzene.[18] This monomer contains 90% *m*-phenylene linkages (mp 150 °C) and 10% *p*-phenylene linkages (mp 220 °C) as estimated from HPLC analysis.

Dynamic mechanical analysis was performed using a DuPont 983 dynamic mechanical analyzer at an oscillation frequency of 1 Hz and a peak-to-peak oscillation amplitude of 0.7 mm under a N_2 atmosphere. Due to the high moduli of these materials, a length correction factor for bending within the clamps was applied. Static flexural testing was performed using an Instron 1127 with a 50 000-lb load cell and a crosshead speed of 0.05 in./min. Thermomechanical analysis was performed using a DuPont 943 thermomechanical analyzer with a 1-g weight and a macroexpansion probe. All reported linear coefficient of thermal expansion values are averages of at least three measurements and were measured between 25 and 300 °C.

Size-exclusion chromatographic (SEC) determination of residual monomer in partially polymerized monomer 2 samples was performed using an HP 1090 liquid chromatograph, with a

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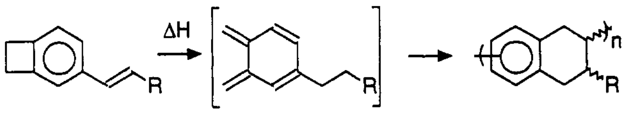
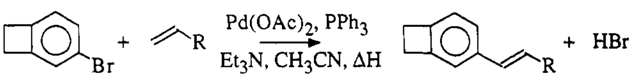
Scheme I



Scheme II



30 cm by 7.8 mm i.d. TSK-gel G2500 HXL column, a 1.0 mL/min tetrahydrofuran (THF) flow, and a differential refractive index detector. SEC determinations of residual monomer in partially polymerized monomer 1 were performed with a 30 cm by 7.8 mm i.d. TSK-gel G1000 HXL column and a UV detector at 210 nm. An external standard method was used in both systems in which monomer samples of known concentration were used to establish detector response. For the SEC quantitation of monomer 2, linearity was demonstrated over the sample concentration range analyzed, and a least-squares fit of the data gave a correlation coefficient (r^2) of 0.9994. The relative precision of the system was 0.4% on the basis of 5 replicate injections. SEC to determine the molecular weight distributions of partially polymerized monomer 1 samples was performed using THF eluent at 1 mL/min flow with a Waters Model 6000 pump through two 4000 HXL and one 2500 HXL columns. SEC to determine the molecular weight distributions of partially polymerized monomer 2 samples was performed using a Waters 510 pump and four Waters Ultrastyragel columns (500-, 103-, 104-, and 105-Å pore sizes) with THF as eluent flowing at 1.5 mL/min.

FT-IR spectra for monomer 2 and polymer prepared from it were obtained as thin films on KBr windows with a Nicolet 5PC FT-IR spectrophotometer.

Quantitative FT-IR spectra of monomer 1 and partially polymerized samples prepared from it were obtained as methylene chloride solutions using a Perkin-Elmer Model 1800 FT-IR. Measured absorbances in the quantitative FT-IR study were divided by the sample concentration to normalize these values.

Prepolymerization. Prepolymerization was performed in a 300-mL resin kettle which was equipped with an Ace Glass Trubore stirrer bearing, a glass stirring shaft with Teflon paddle, gas inlet adapter, and a stopper. To this vessel was added 15 g of monomer, and the vessel was assembled and sealed. The vessel was placed under vacuum for 5 min and refilled with dry nitrogen. The reactor was supplied with a positive pressure of dry nitrogen via mineral oil bubbler and was inserted into a silicone oil bath which was heated to temperature and stirred to maintain thermal uniformity. The temperature was measured throughout with an electronic thermometer which was traceable to the NIST standards. Samples were removed by pipet as required.

Thermal Polymerization. Polymerization was performed using a stainless steel plate mold which consisted of two 0.25-in. stainless steel plates with bolt holes drilled into the sides and bottom; the holes in one of the plates was threaded. The mold cavity was formed by assembling this apparatus with a 0.25-in.-thick Teflon shim around the outside edge. The plates were treated with a fluorocarbon mold release agent, and the mold was assembled. A prepolymer sample weighing 15 g was heated in a vacuum oven and when molten, was degassed by applying a vacuum for 30 min. The molten prepolymer was poured into the assembled mold, and the mold was placed in a nitrogen-purged oven. The sample was then heated to 180 °C for 1 h, 190 °C for 1 h, 200 °C for 1 h, 225 °C for 1 h, and 250 °C for 2 h.

Results and Discussion

Polymerization Chemistry. The monomers studied were polymerized thermally at 180 °C until conversion of the benzocyclobutene groups had occurred, and the polymerization was stopped prior to the gel point. Analysis of the prepolymers was undertaken to ascertain the products of the thermolytic reaction. Polymerization via Diels–Alder reaction should proceed to give *trans*-tetrahydronaphthalenic units (Scheme III) which can exist as four different regiochemical isomers.[1,19,20] ^{1}H and ^{13}C NMR spectra of a partially polymerized sample of the divinyldisiloxane monomer 2 show depletion of both benzocyclobutene methylene and olefinic methine moieties. ^{13}C attached proton[21] test spectrum (Figure 1) of this prepolymer shows new methylene signals at 39.3 ppm and two new methine (or methyl) signals, one at 42.7 ppm and another at 29.9 ppm. These resonances are consistent with a tetrahydronaphthalene ring system with a dimethylsiloxane and an aryl group on adjacent carbons of the saturated ring. Infrared spectroscopic analysis of monomer 2 and polymer prepared from it is given in Figure 2. Virtually complete elimination of resonances due to olefin (C–H out-of-plane mode, 988 cm^{-1}) and benzocyclobutene (aromatic in-plane ring mode, 1470 cm^{-1}) is again consistent with the proposed Diels–Alder mechanism.

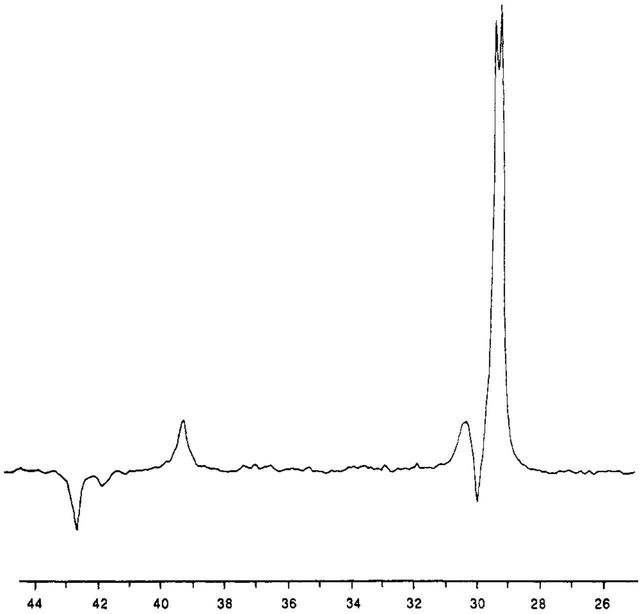
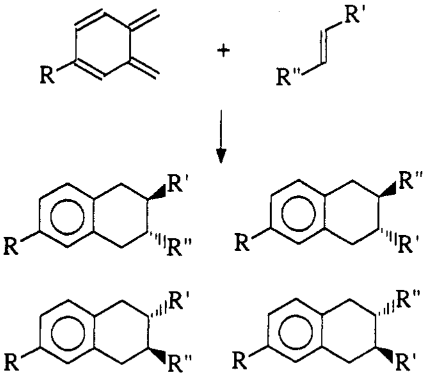


Figure 1. ^{13}C attached proton test spectrm of partially polymerized monomer 2 from 25 to 45 ppm.

Scheme III



Partial thermal polymerization of monomer 1 was performed to yield a soluble prepolymer. ^{13}C APT analysis of the high-field region of this material is shown in Figure 3; new methylene and methine resonances are observed, with chemical shifts similar to those previously reported for thermally prepared poly[3-(4-methylstyryl)benzocyclobutene].[1] In addition, the strong *trans* C–H out-of-plane infrared absorption at 965 cm^{-1} decreases dramatically during the thermolysis. These spectral data are consistent with the depletion of both benzocyclobutenyl and ethenyl functionality during polymerization. Thermal treatment of monomer 3 proceeds in a similar fashion: new methine resonances at 45.5–47 ppm and new meth-

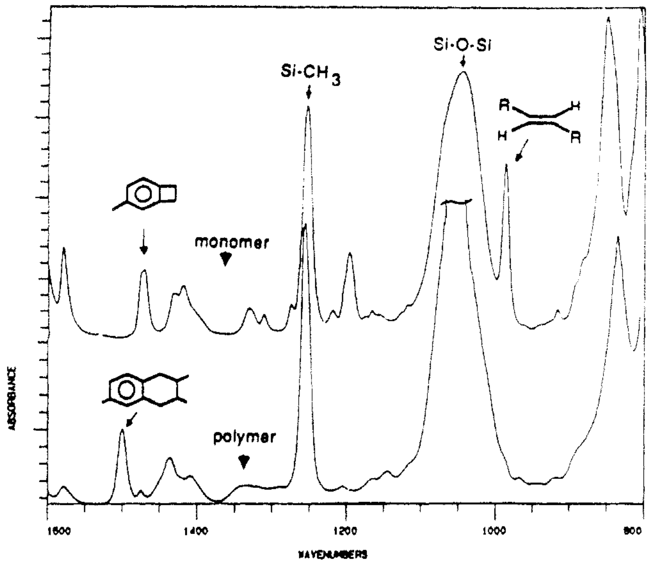


Figure 2. Infrared spectra of monomer 2 and polymer prepared by thermolysis of monomer 2.

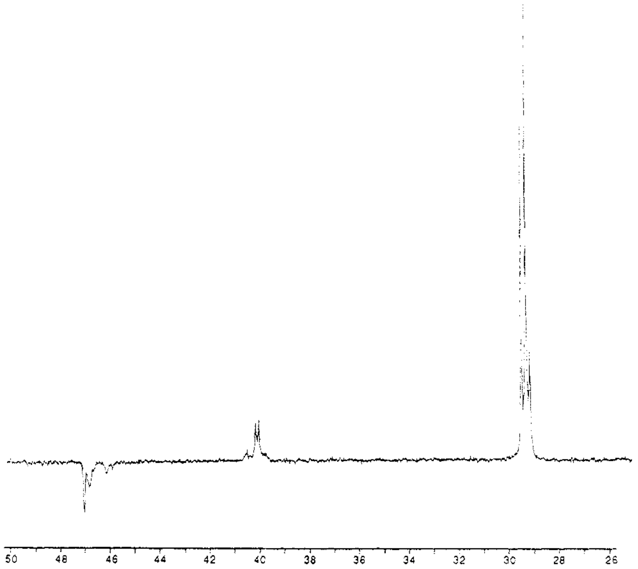


Figure 3. ^{13}C attached proton test spectrum of partially polymerized monomer 1, 25–50 ppm.

Table I. Physical Properties, Ethenyl Bis(benzocyclobutene) Polymers

α, μm/m °C[a]	refractive index	E′, 25 °C, kpsi	flexural strength, kpsi	critical surface energy, dyn/cm
1) 28		750	6.25	26.4
2) 64	1.55	480	10.30	23.3
3) 29	1.65	725		

[a] Linear coefficient of thermal expansion, measured between 25 and 300 °C.

ylene resonances at 39 ppm, with diminution of the *trans* olefinic IR band at 965 cm^{-1}.

Polymer Properties. Fully cured polymer samples were prepared by heating samples of prepolymer slowly to a final cure temperature of 250 °C, to ensure complete conversion of the benzocyclobutene groups. Some physical properties for these polymers are given in Table I. Dynamic mechanical analysis (Figure 4) shows these polymers to be high modulus materials, with no major thermal transitions between room temperature and 400 °C. Polymer prepared from the divinyldisiloxane monomer 2 has a lower storage modulus than that prepared from the two hydrocarbon monomers and undergoes a proportionately larger modulus decrease at temperatures approaching 400 °C; this difference is presumably due to the flexible siloxane linkage. All three polymers show only broad, weak loss modulus peaks over the temperature range studied (Figure 5). Above 350 °C, all of the polymers begin to undergo some weight loss, which may account for decreases in the storage modulus (especially in polymer from monomer 2) at higher temperatures.[2-4]

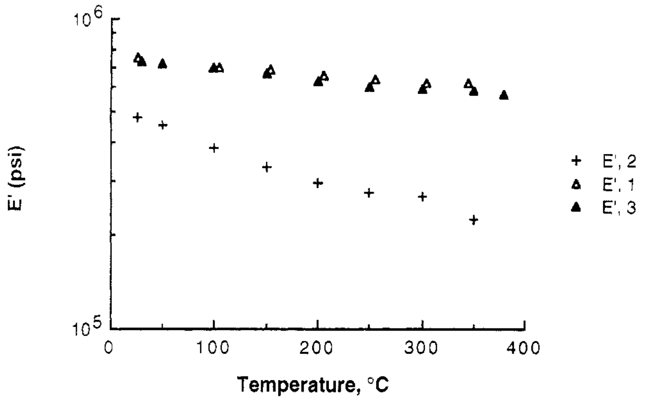


Figure 4. Flexural storage modulus with respect to temperature for polymers prepared thermally from monomers 1–3.

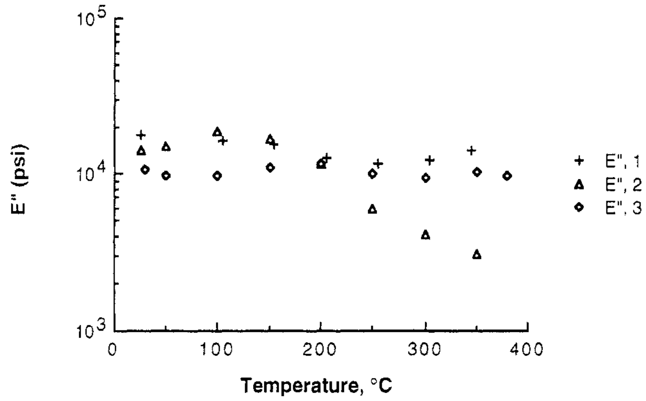


Figure 5. Flexural loss modulus with respect to temperature for polymers prepared thermally from monomers 1–3.

Polymer Formation. Previous work has shown that, at temperatures below 200 °C, polymerization of a monomer containing both benzocyclobutene and stilbene functionality proceeds via a mechanism which consumes both benzocyclobutene and olefinic sites at identical rates; kinetic and molecular weight growth data, along with spectroscopic evidence, suggest strongly that this mechanism is the Diels–Alder reaction.[1] Monomer 1 differs from the system previously studied in that the ratio of benzocyclobutene to stilbene units is no longer stoichiometric, possessing an excess of benzocyclobutene functionality. If only the Diels–Alder mechanism operates, thermolysis of this monomer would give a branched poly(tetrahydronaphthalene) with pendant benzocyclobutene groups (Figure 6). Network formation for this system requires benzocyclobutene–benzocyclobutene interactions.[1,8,9,11] Monomers 2 and 3, which contain two benzocyclobutenes and two olefinic sites, should achieve a cross-linked network early in the polymerization process. An idealized segment of polymer prepared from monomer 2, in which only Diels–Alder polymerization has occurred, is present in Figure 7. If fully polymerized, these monomers would be expected to give highly cross-linked polymeric materials.

Kinetics of Polymerization. A kinetic model has been proposed for Diels–Alder polymerization of vinyl benzocyclobutenes[1] in which the rate-controlling step involves

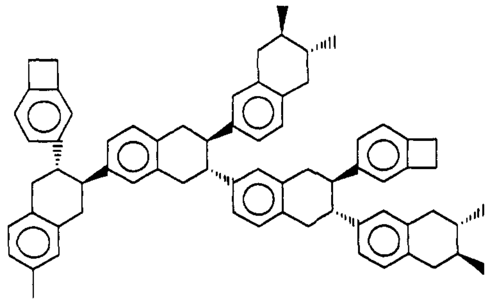


Figure 6. Idealized polymer structure of monomer 1, in which only benzocyclobutene–alkene Diels–Alder reactions have occurred.

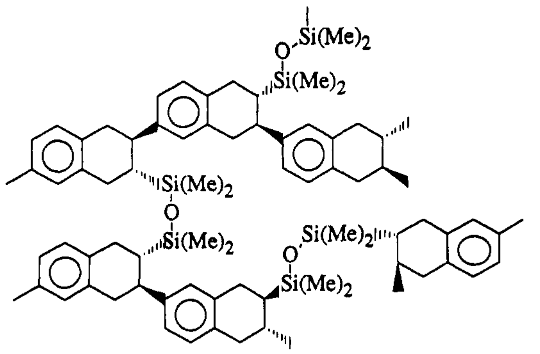
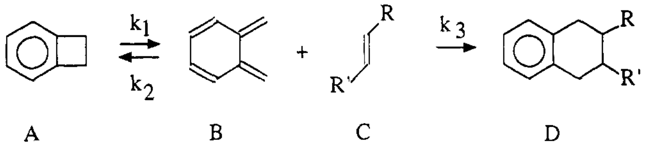


Figure 7. Idealized polymer structure of monomer 2, in which only benzocyclobutene–alkene Diels–Alder reactions have occurred.

Scheme IV



the opening of the benzocyclobutene ring A, followed by a rapid Diels–Alder reaction between the reactive *o*-quinodimethane B and *trans* olefin C (Scheme IV). The decay of benzocyclobutene can be expressed by the rate of ring opening and ring reclosure:

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_1[\mathrm{A}] - k_2[\mathrm{B}] \qquad (1)$$

The rate of ring closure of *o*-quinodimethane B to benzocyclobutene A is several orders of magnitude slower than the ring opening.[22] The rate of the Diels–Alder reaction is thought to be much faster than the ring opening reaction, such that the concentration of the *o*-quinodimethane is assumed to be at steady state (d[B]/dt = 0), and the rates of olefin depletion and tetrahydronaphthalene formation are limited by the rate of initial ring opening:

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = \mathrm{d}[\mathrm{D}]/\mathrm{d}t = -\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_1[\mathrm{A}] \qquad (2)$$

The rate of benzocyclobutene reaction can be obtained from the rate of change of monomer concentration in the thermal polymerization with respect to time via the integrated form of eq 1 (ignoring the slow ring closure step):

$$\ln(A_t/A_0) = -k_1 t \qquad (3)$$

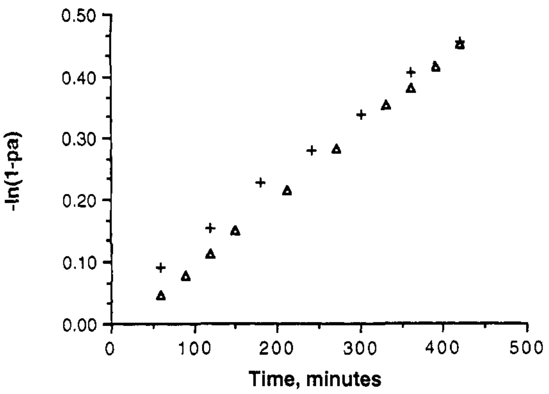


Figure 8. Plot of $-\ln(1 - p_a)$ with respect to time at 180 °C for monomer 1 (+) and monomer 2 (Δ).

where A_0 is the initial number of moles of functional group and A_t is the functional group quantity at time t. The fraction of functional groups reacted is denoted p_a. The fraction of benzocyclobutene functional groups remaining, $1 - p_a$, equals the ratio of reacted functional groups to initial functional groups, such that changes in functional group with respect to time can be given as

$$\ln(1 - p_a) = -k_1 t \qquad (4)$$

or

$$p_a = 1 - \exp(-k_1 t) \qquad (5)$$

Several simplifying assumptions are required in order to relate functional group conversion to changes in the system molecular weight. The mode of polymerization is assumed to be only the Diels–Alder reaction, such that no benzocyclobutene–benzocyclobutene or alkene–alkene reactions occur. It is also assumed that no intramolecular reactions take place, and all functional groups are equally reactive, regardless of whether or not other functional groups on the same molecule have reacted. The extent of functional group conversion can then be directly related to the weight of residual monomer remaining in the system. For tetrafunctional monomers **2** and **3**, with equivalent numbers of A and B functional groups, if functional groups are depleted only by A–B reactions, the fraction of B functional groups reacted, p_b, will equal the fraction of A functional groups reacted, p_a. The weight fraction monomer W_{4t} for these systems is related to the probability that any functional group remains unreacted:

$$W_{4t} = (1 - p_a)^2(1 - p_b)^2 = (1 - p)^4 \qquad (6)$$

For monomer **1**, which has two A-type and one B-type functional group ($p_b = 2p_a$), assuming only A–B reactions, the weight fraction monomer W_{3t} can be given as

$$W_{3t} = (1 - p_a)^2(1 - p_b) = (1 - p_a)^2(1 - 2p_a) \qquad (7)$$

Monomers **1** and **2** were thermally polymerized at 180 °C, the polymerization was sampled at regular intervals, and the quantity of residual monomer was determined by SEC. Fractional benzocyclobutene conversion was calculated from the weight fraction monomer using eqs 6 and 7. A plot of $-\ln(1 - p_a)$ with respect to time (Figure 8) was linear, with a slope equal to the rate constant k_1. The rate of reaction of benzocyclobutene (k_1) was determined from these data as 1.0×10^3 min^{-1} for monomer **1** and 1.1×10^3 min^{-1} for monomer **2**. These values are in excellent agreement with the rate constant of 1.1×10^3 min^{-1} measured previously for the thermal polymerization of 3-(4-methylstyryl)benzocyclobutene[1] at 180 °C. Functional group conversion data obtained by residual monomer quantitation for the thermal polymerization of monomer **2** at 171, 180, and 191 °C are shown in Figure 9. The linearity of these plots is consistent with the suggested first-order ring opening reaction which is thought to initiate the polymerization sequence. Application of the Arrhenius equation to the rate data thus obtained

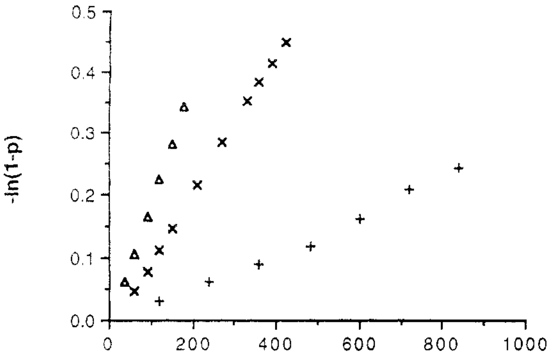


Figure 9. Plot of $-\ln(1 - p_a)$ with respect to time for monomer 2 at 171 °C (△), 180 °C (×), and 191 °C (+).

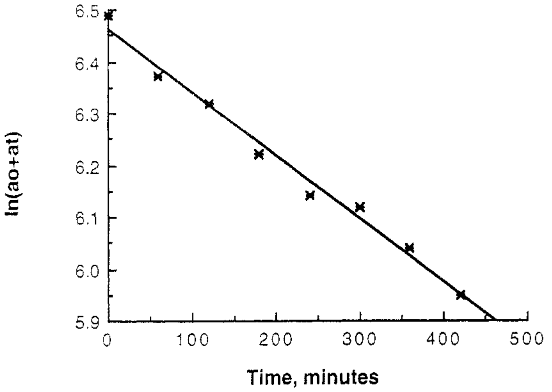


Figure 10. Plot of $\ln(a_0 + a_t)$ with respect to time for monomer 1 polymerized at 180 °C.

provides an activation energy of 37 kcal/mol, compared to the activation energy of 35.4 kcal/mol measured for the 3-(4-methylstyryl)benzocyclobutene polymerization[1] and 39.9 kcal/mol measured for the reaction of the parent hydrocarbon benzocyclobutene with maleic anhydride.[22]

Samples of partially polymerized monomer 1 were analyzed by infrared analysis to quantify changes in the olefin concentration. The strong resonance at 966 cm^{-1} (olefinic C–H out-of-plane deformation) was monitored with respect to time at 180 °C. Equation 4 can be rewritten to reflect the relationship between spectrophotometric absorption measurements of the olefinic absorption and time. Because the initial concentration of A is twice that of B ($A_0 = 2B_0$), it can be shown that the concentration of A at any time during the polymerization (A_t) is equal to $B_0 + B_t$. Substituting into eq 4 gives the relationship between reaction time and the concentration of the olefin, B:

$$\ln[(B_0 + B_t)/2B_0] = -k_1 t \qquad (8)$$

If the concentration of B during the reaction obeys Beer's law ($a_0 = B_0\epsilon b$ and $a_t = B_t\epsilon b$, where ϵ is the molar absorptivity and b is the path length), eq 8 can be rewritten in terms of absorption:

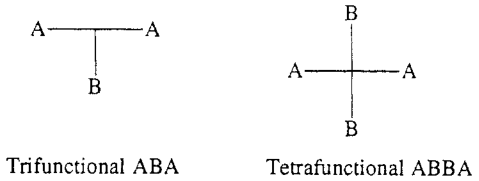
$$\ln[(B_0 + B_t)\epsilon b/2B_0\epsilon b] = \ln[(a_0 + a_t)/2a_0] = -k_1 t \qquad (9)$$

which can be expressed as

$$\ln(a_0 + a_t) = \ln a_0 + \ln 2 - k_1 t \qquad (10)$$

Assuming that the molar absorptivity is the same for monomeric and polymeric alkenes, a plot of $\ln(a_0 + a_t)$ with respect to time should provide a linear plot with a slope equal to the rate constant and an intercept equal to ($\ln a_0 + \ln 2$), as shown in Figure 10. The rate constant k_1 at 180 °C was calculated as 1.2×10^3 min^{-1}, which agrees well with the k_1 calculated from residual monomer data and further reinforces the proposed role of the *trans*-α,β-disubstituted olefin in this type of polymerization reaction. It is important to note that all of the rate measurements based on residual monomer and IR data were obtained on soluble materials. Because these monomers form thermoset networks, only prepolymer samples of low functional group conversions were studied. Polymerization kinetics beyond the gel point for monomer 2 have been reported by Stokich as measured by FT-IR.[5]

Chart I



Molecular Weight Growth and Network Formation. Analyses which focus on changes in the concentration of functional groups allow for the definition of the kinetics of the polymerization reaction. It is of fundamental importance to understand how changes in functional group conversion are translated into molecular weight growth. The molecular weight averages of samples which polymerize via coupling of reactive site A specifically with reactive site B can be predicted from functional group conversion data using the recursive method of Miller and Macosko.[23] The monomers studied in this work take the form of trifunctional ABA and tetrafunctional ABBA shown in Chart I. The simplifying assumptions used to relate residual monomer concentration to the extent of reaction (only intermolecular, A to B reactions occur) are required for this model.

During the polymerization of a trifunctional monomer such as 1, a fraction of benzocyclobutene A type groups (p_a) and a fraction of alkenyl B type groups (p_b) will have reacted. The expected weight on any A-type group which has reacted looking out from the parent monomer to which it is attached, $E(W_A^{\text{out}})$, is given by

$$E(W_A^{\text{out}}) = p_a E(W_B^{\text{in}}) + 0(1 - p_a) = p_a E(W_B^{\text{in}}) \qquad (11)$$

where $E(W_B^{\text{in}})$ is the molecular weight on any B unit looking into its parent monomer. The expected weight on any B looking into its parent monomer is given by the molecular weight of the trifunctional monomer (m_3) plus the sum of the expected weight on each of the remaining arms:

$$E(W_B^{\text{in}}) = m_3 + 2E(W_A^{\text{out}}) \qquad (12)$$

The expected weight on any B functional group looking out of its parent monomer is given by

$$E(W_B^{\text{out}}) = p_b E(W_A^{\text{in}}) = 2p_a E(W_A^{\text{in}}) \qquad (13)$$

where $E(W_A^{\text{in}})$ is the expected weight on any A unit looking into its parent monomer. The expected weight on any A-type reactive group looking into its parent monomer is given by the molecular weight of the monomer plus the sum of the expected weights on each of the remaining arms:

$$E(W_A^{\text{in}}) = m_3 + E(W_A^{\text{out}}) + E(W_B^{\text{out}}) \qquad (14)$$

For the trifunctional monomer 1 it follows that

$$E(W_A^{\text{out}}) = p_a m_3/(1 - 2p_a) \qquad (15)$$

$$E(W_B^{out}) = 2m_3p_a(1-p_a)/(1-2p_a)^2 \qquad (16)$$

The weight-average molecular weight of the system is calculated by selecting a unit of mass (i.e., a repeating unit) at random and summing the repeating unit mass and the total expected weight looking out from all of the reactive groups:

$$M_W = m_3 + 2E(W_A^{out}) + E(W_B^{out}) = m_3(1-2p_a^2)/(1-2p_a)^2 \qquad (17)$$

The number-average molecular weight is given by the total mass of the system, m_t, divided by the number of moles in the system. If no intramolecular reactions occur, the number of moles is given by the initial number of moles, N_0, minus the number of new bonds formed, N_b, as every Diels–Alder reaction diminishes the number of moles by 1. The following equivalencies exist:

$$m_t = m_3A_0/2 \qquad (18)$$

$$N_0 = A_0/2 \qquad (19)$$

$$N_b = p_aA_0 \qquad (20)$$

The number-average molecular weight can thus be expressed:

$$M_n = m_t/(N_0 - N_b) = m_3/(1-2p_a) \qquad (21)$$

For tetrafunctional monomers 2 and 3, the number of A and B groups in the system are identical, such that $p_a = p_b$. The expected weight on any A-type reactive group looking out of its parent molecule is

$$E(W_A^{out}) = pE(W_B^{in}) + 0(1-p) = pE(W_B^{in}) \qquad (22)$$

The expected weight no any B functional group looking into its parent molecule is the molecular weight of tetrafunctional monomer, m_4, plus the sum of the expected weights on each of the remaining arms:

$$E(W_B^{in}) = m_4 + 2E(W_A^{out}) + E(W_B^{out}) \qquad (23)$$

The expected weight on any B functional group looking out of its parent molecule is

$$E(W_B^{out}) = pE(W_A^{in}) + (1-p)0 = pE(W_A^{in}) \qquad (24)$$

The expected weight on any A functional group looking into its parent molecule is given by the molecular weight of the monomer plus the sum of the expected weights on each remaining arm:

$$E(W_A^{in}) = m_4 + 2E(W_B^{out}) + E(W_A^{out}) \qquad (25)$$

Simultaneous solution of eqs 20–23 yields

$$E(W_B^{out}) = E(W_A^{out}) = pm_4/(1-3p) \qquad (26)$$

The weight-average molecular weight is calculated by selecting a unit of mass (i.e., a repeat unit) at random and summing the repeat unit mass and the total expected weight looking out from all its reactive groups:

$$M_w = m_4 + 2E(W_A^{out}) + 2E(W_B^{out}) = m_4(1+p)/(1-3p) \qquad (27)$$

The number-average molecular weight is again given by the total mass of the system divided by the number of moles in the system. The initial number of moles N_0 is equivalent to $A_0/2$, total mass is $m_4A_0/2$, and the number of bonds formed N_b is equivalent to pA_0, such that M_n for the tetrafunctional monomers is

$$M_n = m_4/(N_0 - N_b) = m_4/(1-2p) \qquad (28)$$

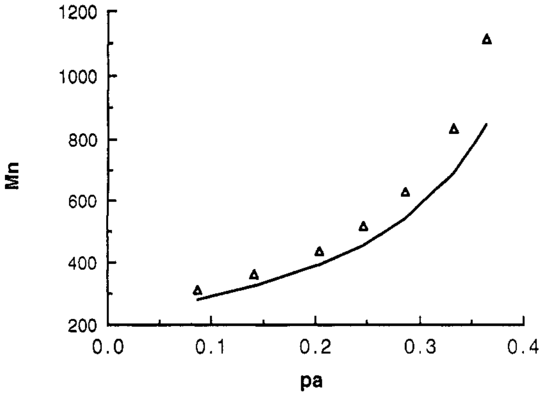


Figure 11. M_n with respect to benzocyclobutene conversion p_a for monomer 1 polymerized at 180 °C, estimated (–) and measured (Δ) with respect to SEC calibration using oligomer molecular weight SEC.

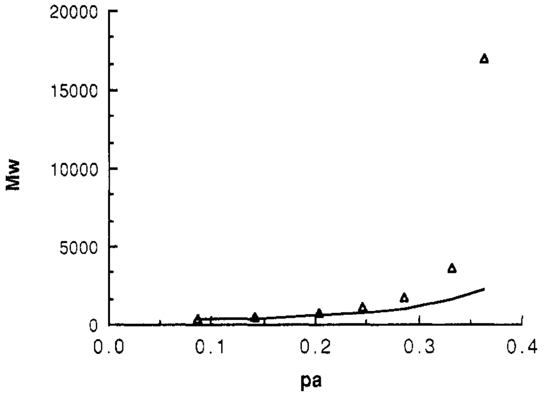


Figure 12. M_w with respect to benzocyclobutene conversion p_a for monomer 1 polymerized at 180 °C, estimated (–) and measured (Δ) with respect to SEC calibration using oligomer molecular weights.

Molecular weight averages of partially thermally polymerized samples of monomer 1 were determined by obtaining SEC chromatograms and extrapolating the oligomer molecular weights to provide a molecular weight calibration. These measured values were compared to molecular weight averages predicted using values for functional group conversion obtained from residual monomer quantitation. Figure 11 shows the measured and predicted M_n values, and Figure 12 shows the predicted and measured M_w values with respect to benzocyclobutene functional group conversion for monomer 1 at 180 °C. The measured M_n values agree well with calculated M_n values, while M_w values increase much more rapidly than is predicted from functional group conversion data. The increase in M_w leads to an overall broadening of the molecular weight distribution (Figure 13) with increasing functional group conversion.

The gel point is that point in the polymerization at which M_w becomes infinite. For monomer 1, if only the Diels–Alder mechanism of polymerization were to operate (e.g., non benzocyclobutene–benzocyclobutene reactions occur), this condition would occur only at complete conversion ($p_a = 0.5$, $p_b = 1$). Experimentally, the system gels at when $p_a = 0.37$–0.39 and $p_b = 0.72$–0.78, as determined from residual monomer quantitation. It is clear from these data and from the molecular weight analysis that, although the rate of benzocyclobutene ring opening occurs as predicted at 180 °C, benzocyclobutene–benzocyclobutene

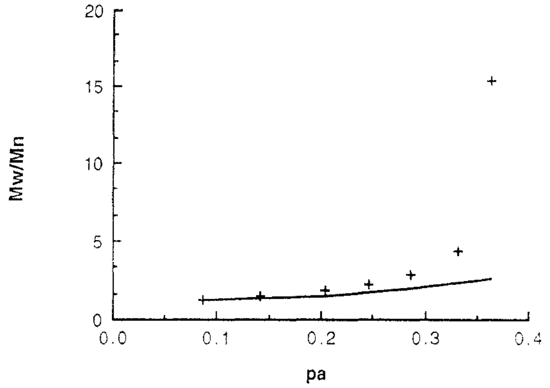


Figure 13. M_w/M_n with respect to benzocyclobutene conversion p_a for monomer 1 polymerized at 180 °C, estimated (–) and measured (+) with respect to SEC calibration using oligomer molecular weights.

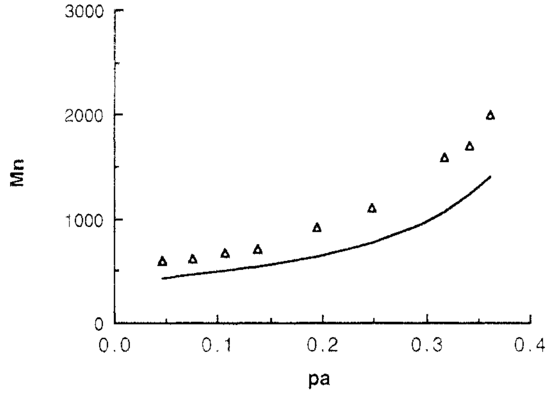


Figure 14. Apparent M_n with respect to benzocyclobutene conversion p_a for monomer 2 polymerized at 180 °C, estimated (–) and measured (△) with respect to polystyrene standards.

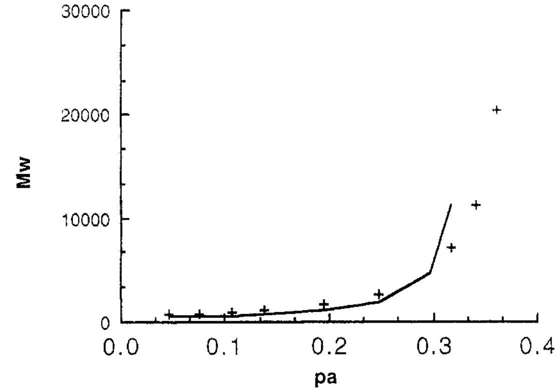


Figure 15. Apparent M_w with respect to benzocyclobutene conversion p_a of monomer 2 polymerized at 180 °C, estimated (–) and measured (+) with respect to polystyrene standards.

reactions begin to compete with the Diels–Alder reaction significantly prior to exhaustion of the olefinic sites. Benzocyclobutene homopolymerization is thought to proceed to give poly-*o*-xylylene chains of short duration termination by proton abstraction.[1,8,9,11,24] The increased operation of this mode of polymerization just prior to the gel point is consistent with the divergence of the molecular weight distribution from predicted values.

Apparent molecular weight averages for partially polymerized samples of monomer 2 were obtained as compared to narrow molecular weight polystyrene standards (Figures 14 and 15). Although differences between polystyrene and polymer prepared from monomer 2 make a detailed analysis problematic, low-angle light scattering on one sample polymerized for 270 min (p_a = 0.25) had an M_w of 1900, in excellent agreement with the value of 1880 predicted from functional group conversion. For monomer 2, the trend in the predicted M_n with increasing conversion agrees well with changes in the apparent M_n values obtained from SEC. The apparent M_w values agree well with those predicted on the basis of functional group conversion until the reaction approaches the gel point. Figure 16 shows the changes in apparent polydispersity with respect to p_a for monomer 2 polymerized at 180 °C and the values calculated using the model. These data also suggest that M_w/M_n increases less rapidly than expected near the gel point. For monomer 2, the gel condition is predicted to occur when $p = 0.33$ (from eq 24). Experimentally, this system was observed to gel at ca. $p = 0.36$, as determined from residual monomer concentration. The small difference between predicted and observed gel points may be due to the small amount of monomer 1 which is known to be present in samples of monomer 2, although prediction of the molecular weights of mixtures of ABA and ABBA monomer systems containing 1% of the ABA[25] monomer are only slightly different than those for the tetrafunctional monomer alone. The observation that measured gel points occur at higher functional group conversions than predicted in the polymerization of multifunctional polymers has been made for a number of systems.[26–29] This has been attributed to the presence of some cyclization (intramolecular) reactions, which lead to depletion of functional groups but do not give rise to an increase in the molecular weight. In addition, it is difficult experimentally to determine exactly when the gel condition has been reached; visual indicators including dramatic viscosity changes are probably observed after the true gel point has been achieved. The polymerization of monomer 2 proceeds to give good qualitative agreement between predicted and measured molecular weights, and between predicted and observed gel points. The high concentration of olefins in the system at conversions below the gel point allows this polymerization to proceed in a manner more consistent with the proposed mechanism than monomer 1.

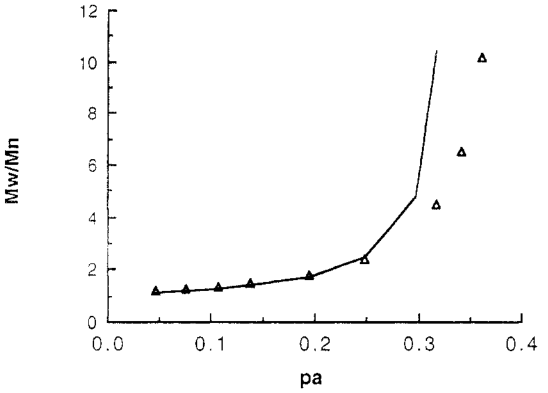


Figure 16. Apparent M_w/M_n with respect to benzocyclobutene conversion p_a for monomer 2 polymerized at 180 °C, estimated (–) and measured (△) with respect to polystyrene standards.

Figure 17 shows the viscosity of monomer 3 with respect to time at 200 °C. At 200 °C, the kinetics of the ring opening reaction predict that the gel condition, identical with that expected for monomer 2 ($p = 1/3$), should occur at 63 min; the measured gel point occurs at ca. 66 min.

Conclusions

The thermal polymerization of bis(benzocyclobutenes) with α,β-disubstituted alkenes proceeds to give high modulus thermoset materials. For all of these systems, the polymerization rate is controlled by the first-order ring opening reaction of benzocyclobutene to the reactive

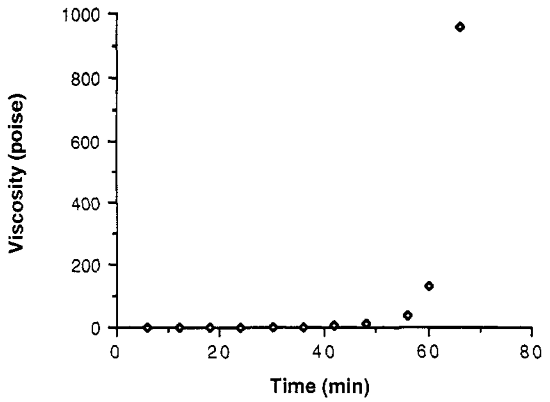


Figure 17. Viscosity in poise with respect to time for monomer 3 polymerized at 200 °C.

o-quinodimethane intermediate. Analysis suggests that the polymerization proceeds largely by Diels–Alder reaction of the o-quinodimethane with α,β-disubstituted alkenyl sites. Tetrafunctional monomers containing 2 benzocyclobutenes and 2 alkenes polymerize to gel when about 1/3 of the functional groups have reacted. A trifunctional monomer containing 2 benzocyclobutenes and a single olefin gels at lower extents of conversion than predicted by the model put forth for benzocyclobutene–alkene reactions; it is suspected that the o-quinodimethane intermediates react with themselves as the alkene concentration is depleted. In both of these systems, the polymerization reaction was studied at relatively low temperatures, where the instantaneous concentration of the reactive o-quinodimethane intermediate is expected to be low compared to that of the alkene. For monomer 1, the alkene concentration decreases quickly with the onset of benzocyclobutene thermolysis, such that the concentration of alkenes becomes similar to the concentration of the reactive o-quinodimethane species at p_a values approaching 0.5. For this reason, it seems likely that the gel point phenomena and the physical properties of polymer prepared from monomer 1 may be affected by the thermal treatment afforded it, because the concentration of o-quinodimethanes will differ greatly with polymerization temperature. Conversely, monomers such as 2 and 3, where even at the gel point the olefin concentration is higher than that of the reactive o-quinodimethane, would not be expected to be as strongly influenced by the temperature used for thermal polymerization. This postulate is consistent with the work of Stokich,[5] who found that the FT-IR spectrum of polymer prepared from monomer 2, when monitored *in situ*, was the same whether the monomer was polymerized at 150 or 300 °C.

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