Macromolecules **1992,** *25,* 1539–1545

Thermally Induced Polymerization of an Arylvinylbenzocyclobutene Monomer

Stephen F. Hahn,* Steven J. Martin, and Marianne L. McKelvy

Central Research and Analytical Sciences Laboratories, The Dow Chemical Company, Midland, Michigan 48674

Received September 11, 1991; Revised Manuscript Received November 8, 1991

ABSTRACT: The thermal polymerization of *trans-p*-(vinyltolyl)benzocyclobutene provides a soluble polymer of modest molecular weight. Spectroscopic analysis of this polymer suggests that the dominant mode of polymerization is the Diels–Alder reaction of the *trans*-α,β-disubstituted olefin with an intermediate *o*-quinodimethane which arises from the thermally induced rearrangement of the benzocyclobutene functionality. The kinetics of this polymerization were studied by sampling an active polymerization and analyzing the reaction mixture via spectroscopic and chromatographic methods. A kinetic model for this polymerization is proposed in which the rate-limiting step is the first-order ring-opening rearrangement of the benzocyclobutene four-membered ring, followed by a relatively rapid Diels–Alder reaction. Observed rate constants calculated from the residual monomer content, alkene concentration, concentration of tetrahydronaphthalene repeat units, and oligomer molecular weights were in good agreement with the proposed polymerization mechanism and kinetics. The activation energy for the rate-limiting ring-opening rearrangement was calculated to be 35.4 kcal/mol.

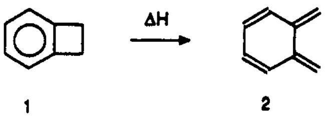
Introduction

Polymeric materials prepared by thermally initiated polymerization of monomers based on benzocyclobutene (1) have attracted interest due to the unusual physical property profiles available from these materials.[1-5] The polymerization of benzocyclobutene monomers is thought to proceed as a result of the thermal rearrangement of benzocyclobutene to the reactive intermediate *o*-quinodimethane or *o*-xylylene (2; Scheme I). Polymers prepared from some multifunctional benzocyclobutene monomers exhibit a combination of low dielectric constant and dissipation factor, little moisture sensitivity, and good thermal stability, leading to the use of these materials in microelectronic applications.[6,7]

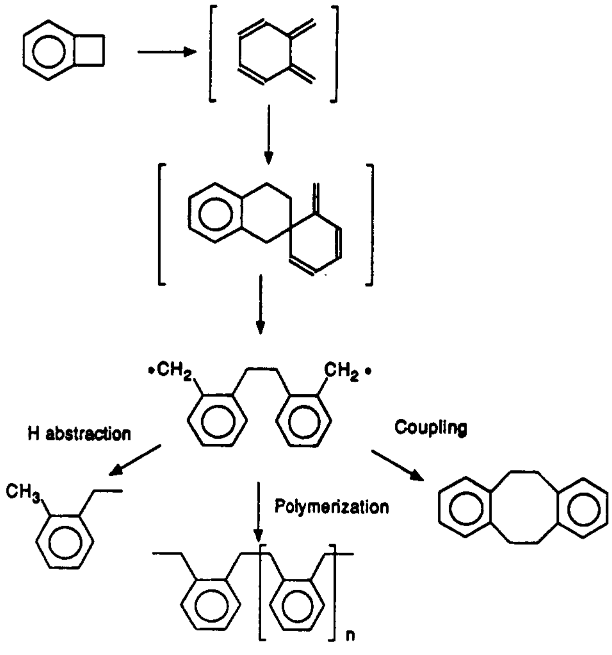
Benzocyclobutene monomers can be separated into two distinct categories. The first type includes molecules which contain a benzocyclobutene functionality as the only reactive species: polymers of this type would polymerize solely through interactions of thermally activated benzocyclobutenes.[1,2] The thermally activated polymerization of bisbenzocyclobutenes has been proposed[1,2] to proceed via an initial Diels–Alder reaction of two *o*-quinodimethanes, one a diene and one a dienophile, to yield an intermediate spirodimer (Scheme II). This spirodimer has been at prepared subambient temperatures[8-10] but has not been directly identified as an intermediate in the thermal polymerization. The dimer then fragments to give a benzylic diradical species. This diradical may undergo intramolecular coupling to give dibenzocycloocta-1,5-diene or oligomerize to provide poly(*o*-xylene). The formation of poly(*o*-xylene) is terminated by proton abstraction.

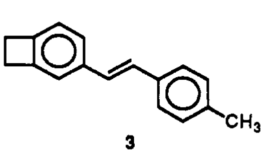
The propensity for the *o*-quinodimethane to function as a diene in the Diels–Alder reaction has been well documented.[11-14] This facility has led to the second benzocyclobutene monomer type, which contains both a benzocyclobutene functionality and a Diels–Alder dienophile.[3,4] Several monomers have been prepared in which α,β-disubstituted alkenes (such as maleimides) provide dienophilic sites. While maleimides are known to thermally homopolymerize, α,β-diarylethylenes (stilbenes) are resistant to homopolymerization at elevated temperatures.[15] Diels–Alder polymerization of an α,β-diarylethylene monomer in which one of the rings is benzocyclobutene would give rise to a linear poly(tetrahydronaphthalene) (Scheme III). It was our aim to study the polymerization chemistry of a stilbene-containing benzocyclobutene monomer; this paper describes an investigation into the thermal polymerization of *p*-(vinyltolyl)benzocyclobutene monomer (3).

Scheme I



Scheme II

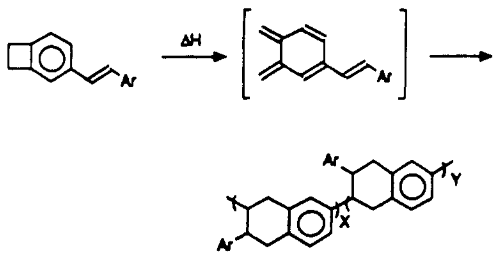




3

0024-9297/92/2225-1539$03.00/0

Scheme III



Experimental Section

p-(Vinyltolyl)benzocyclobutene (**3**) was prepared via the Pd-catalyzed coupling of 3-bromobenzocyclobutene[16,17] with *p*-vinyltoluene (Aldrich Chemical Co.) in acetonitrile according to the procedure of Heck.[18,19] The recovered yield was 80%, and the monomer was recrystallized from ethanol and dried in vacuo at 30 °C: mp 90–92 °C, melt endotherm 93 J/g; IR (KBr) 3025, 2920, 1513, 1473, 965, 820 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.4–6.9 (m, 9 H), 3.1 (s, 4 H), 2.3 (s, 3 H); ^{13}C NMR (CDCl$_3$) δ 21.1, 29.2, 29.4, 119.8, 122.6, 125.9, 126.2, 127.2, 128.8, 129.3, 134.8, 136.4, 137.0, 145.3, 146.0. This monomer is 99.5% pure by GC analysis. The only other component is isomeric with the monomer: it is likely that the impurity is a benzocyclobutene ring isomer which arises from the presence of a small amount of 2-bromobenzocyclobutene in the starting material.

Partial Polymerization Procedure. The prepolymerization was performed in a 300-mL resin kettle with a positive pressure of dry nitrogen supplied via a mineral oil bubbler. A glass stirring shaft and Teflon paddle were used to stir the reaction mixture thoroughly during polymerization. Heat was supplied with a silicone oil bath. The bath was stirred to maintain a uniform temperature, and the bath temperature was measured directly adjacent to the resin kettle with a thermometer which was calibrated using a mercury immersion thermometer which was traceable to the National Bureau of Standards. A total of 6 g of monomer **3** was entered into the vessel, and the vessel was immersed into the oil bath. The reaction mixture was sampled by removing small aliquots from the vessel.

Polymer and Oligomer Characterization. The residual monomer was quantitated using a Hewlett-Packard 5880A gas chromatograph equipped with a 25-m column (0.2 mm i.d.) with an SE-564 stationary phase. An area ratio/weight ratio calibration curve was measured for monomer **3** with benzonitrile (Aldrich Chemical Co.) as the internal standard. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet 5PC FT-IR (KBr samples) and a Perkin-Elmer 1800 FT-IR (dichloromethane solutions). UV spectra were obtained using tetrahydrofuran solutions on a Perkin-Elmer Lambda 3 UV/visible spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Associates Gemini 300 nuclear magnetic resonance spectrometer (NMR). All spectra were obtained from deuteriochloroform solutions with tetramethylsilane as the internal standard. Size-exclusion chromatography was performed in tetrahydrofuran at a 1 mL/min eluent flow through a single 2500 HXL column, and the output was detected with a differential refractometer. Molecular weights of partially polymerized samples of monomer **3** were determined by correlation of the retention volumes of oligomers with their molecular weight and extrapolation to include higher molecular weight species.

Results and Discussion

Analysis of the Polymerization Product of Monomer 3. A sample of monomer **3** was thermally polymerized by heating a sample of the monomer at 180 °C for 1 h, 190 °C for 1 h, 200 °C for 1 h, and finally at 250 °C for 1 h. The clear, light brown polymer was soluble in THF and chloroform; no remaining benzocyclobutene functionality was observed by IR or ^{13}C NMR analyses. This polymer had an intrinsic viscosity of 0.25 dL/g, and GPC analysis (Figure 1) indicates a low molecular weight polymer (Table I) with a broad distribution. DSC analysis of this polymer shows a glass transition temperature at 240 °C (Figure 2). By comparison, thermolysis of the phenyl ester of benzocyclobutenyl-3-carboxylic acid (which contains no good Diels–Alder dienophile) gives an oligomeric mixture with a much lower molecular weight and a glass transition of 79 °C.

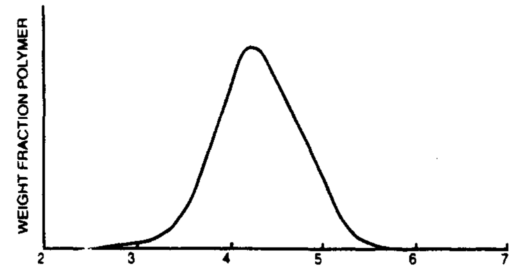


Figure 1. GPC chromatogram of thermally polymerized *p*-(vinyltolyl)benzocyclobutene.

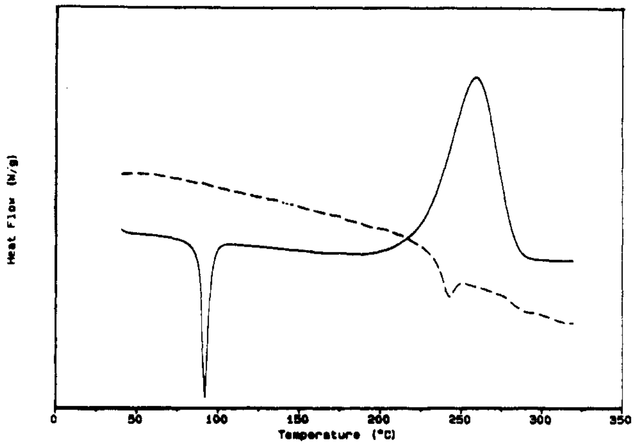
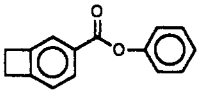
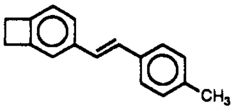
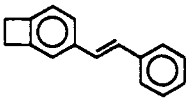


Figure 2. Differential scanning calorimetry of monomer **3** (solid line) and fully polymerized monomer **3** (dashed line).

Table I
Apparent Molecular Weights of Thermally Polymerized Monobenzocyclobutenes

	T_g, °C	M_n	M_w	M_w/M_n
	79	1230	4570	3.7
	240	9810	43580	4.4
	235	9640	34540	3.6

Infrared spectra of monomer **3** and partially thermally polymerized monomer (ca. 60% conversion of benzocyclobutenes by NMR) are shown in Figure 3. Several absorptions which are due to benzocyclobutene shift during polymerization: these include methylene stretches at 2920 and 2825 cm^{-1}, an in-plane aromatic ring stretch at 1473 cm^{-1}, and a methylene hydrogen deformation at 1204 cm^{-1}.[20] The trans olefin gives a strong C–H out-of-plane deformation (wag) at 965 cm^{-1}. This characteristic band decreases dramatically upon polymerization but is not completely exhausted in samples in which the benzocyclobutene functionality is no longer detectable by IR or ^{13}C NMR.

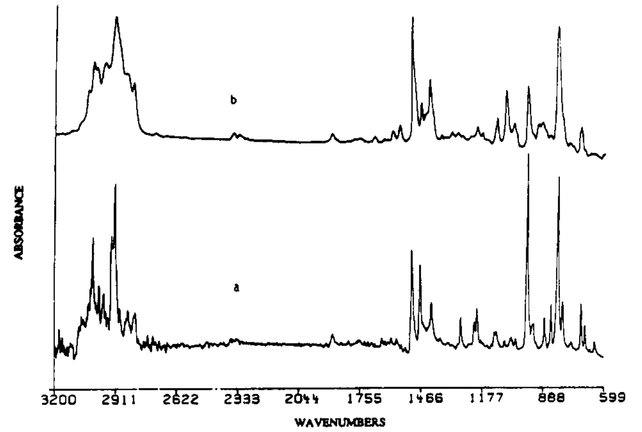


Figure 3. Infrared spectra of monomer 3 (a) and monomer 3 thermally polymerized to 60% benzocyclobutene conversion (b).

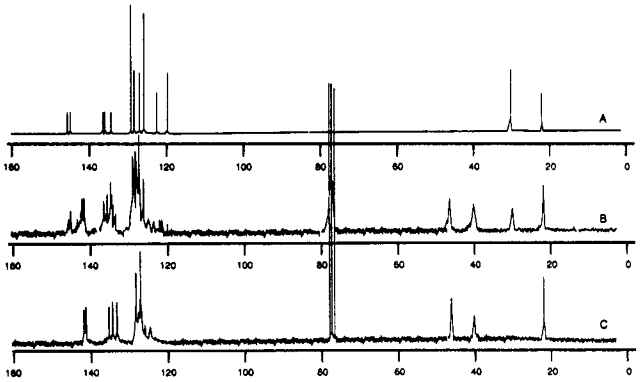


Figure 4. ^{13}C NMR spectra of monomer 3 (A), partially polymerized monomer 3 (B), and fully polymerized monomer 3 (C).

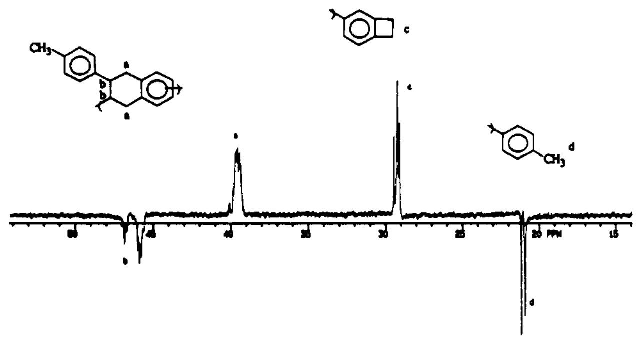


Figure 5. ^{13}C NMR attached proton test spectrum, in the 15–55 ppm region, of partially polymerized monomer 3 (CH_3, CH up; CH_2, quaternary carbons down).

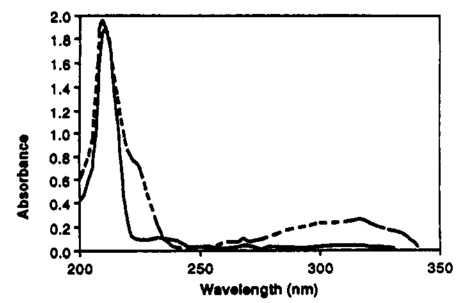
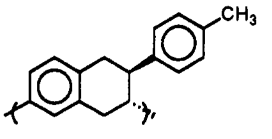
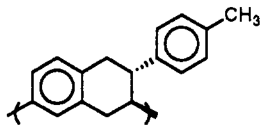


Figure 6. UV spectra of monomer 3 (dashed line) and thermally polymerized monomer 3 (solid line).

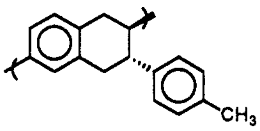
^{13}C NMR spectra of monomer 3, partially polymerized monomer 3, and polymer 3 are shown in Figure 4. A decrease in the resonance due to the methylene carbons from the benzocyclobutene four-membered ring is accompanied by the formation of two new carbon signals near 39 and 46 ppm, which are of equal peak area (as determined by quantitative ^{13}C NMR). Figure 5 shows the analysis of the high-field region of the ^{13}C NMR attached proton test (APT) spectrum of partially polymerized monomer 3 in which ca. 60% of the benzocyclobutene functionality has been reacted; this analysis suggests that these resonances are due to new methylene and methine moieties, respectively. This is consistent with the formation of a tetrahydronaphthalene repeat unit formed by the Diels–Alder reaction detailed in Scheme III. The multiplicity of resonances in the ^{13}C NMR spectrum would necessarily arise from the regiochemically isomeric units which can arise from the Diels–Alder reaction. The Diels–Alder reaction proceeds such that the *p*-methylphenyl ring and the continuing polymer chain must exist in a trans configuration on the saturated tetrahydronaphthalene ring. In addition, the dienophilic alkene can enter into the Diels–Alder reaction such that the polymer chain continues either through the 2 and 6 carbons or the 2 and 7 carbons of the tetrahydronaphthalene. As a result, four different tetrahydronaphthalene repeat units (4–7) can exist. Assignment of chemical shifts for individual regioisomers and their possible linear combinations (e.g., diads, triads) which can occur has not been pursued.



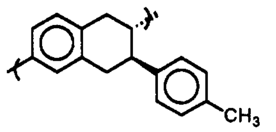
4



5



6

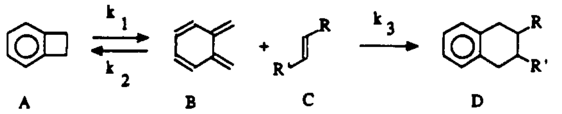


7

The chemistry of aromatic rings with fused cycloalkanes has been studied extensively due to an unusual rehybridization of the aromatic ring carbon skeleton imposed by the strained ring (the Mills–Nixon effect).[21-24] The ring strain imposed by the fused four-membered ring makes the ring junction carbons in benzocyclobutene more electropositive than those in an unstrained ring, such that the chemical shifts of these carbons in 3, 145 and 146 ppm, are considerably further downfield than the ring junction carbons of indane (143.3 ppm) or tetrahydronaphthalene (136.4 ppm).[25] Upon polymerization by ring opening, this strain is released, and the ring junction carbons shift upfield to 142 and 142.5 ppm. The rehybridization of the benzocyclobutene carbon skeleton due to the constraints of the four-membered ring also causes an upfield shift of the benzocyclobutene ring carbons ortho to the ring junction carbons in 3 (120 and 122 ppm) as compared to unstrained systems; these resonances shift downfield during the polymerization, consistent with the relief of ring strain due to rearrangement of the benzocyclobutene functionality. The olefinic carbons (127 and 129 ppm) decrease in intensity but are still discernible in the fully cured (i.e., no residual benzocyclobutene) polymer. The carbons in the *p*-methylphenyl ring are essentially identical in monomer and polymer; the methyl resonance shifts upfield by about 0.2 ppm upon reaction of the alkene.

Figure 6 shows the UV spectra of the monomer and polymer of 3. Monomer absorbances at 230 and 320 nm are absent or greatly diminished in the polymer sample. This is consistent with eradication of the majority of alkenyl sites.

Scheme IV



The spectral data are consistent with the proposed Diels–Alder mechanism in which the α,β-diaryl olefinic site acts as a dienophile for a majority of the *o*-quinodimethane units which are thermally generated. The limited molecular weight growth and broad molecular weight distribution of the polymer prepared from monomer **3** suggest that this is not the sole product of thermolysis. Reaction of an *o*-quinodimethane with a second *o*-quinodimethane would have the effect of coupling two growing polymer chains through the benzocyclobutenes alone, interrupting the stoichiometry of the polymerization and leaving some olefinic sites unreacted.

The rate of ring opening of the hydrocarbon benzocyclobutene at elevated temperatures followed by Diels–Alder trapping with maleic anhydride has been examined.[26] The following reaction sequence (Scheme IV) was proposed based on this study: benzocyclobutene A rearranges reversibly to *o*-quinodimethane B, followed by reaction with a dienophile C to provide the tetrahydronaphthalenic product D. The rate of depletion of the benzocyclobutene functionality, A, can be given by eq 1 and the

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

concentration of the intermediate *o*-quinodimethane B is given by eq 2. Measurements by Roth have shown that

$$\mathrm{d}[\mathrm{B}]/\mathrm{d}t = k_1[\mathrm{A}] - k_2[\mathrm{B}] - k_3[\mathrm{C}][\mathrm{B}] \qquad (2)$$

the rate of reversion of B to A is about 5 orders of magnitude slower than the rate of ring opening. If the rate of the Diels–Alder reaction is fast compared to the ring-opening rearrangement, the *o*-quinodimethane is assumed to be at steady state ($\mathrm{d}[\mathrm{B}]/\mathrm{d}t = 0$). The rate of change of the dienophile concentration can then be expressed by eq 3. If ring closure of *o*-quinodimethane back to benzocyclobutene is slow with respect to the Diels–Alder reaction ($k_3[\mathrm{C}] \gg k_2$), the rate of change of the concentration of alkene C will be directly related to the rate of benzocyclobutene rearrangement:

$$-\mathrm{d}[\mathrm{C}]/\mathrm{d}t = (k_1k_3[\mathrm{A}][\mathrm{C}])/(k_2 + k_3[\mathrm{C}]) \qquad (3)$$

$$-\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_1[\mathrm{A}] \qquad (4)$$

Similarly, the rate of formation of tetrahydronaphthalene product D can be determined from the rates of reaction of A and C:

$$\mathrm{d}[\mathrm{D}]/\mathrm{d}t = (k_1k_3[\mathrm{A}][\mathrm{C}])/(k_2 + k_3[\mathrm{C}]) \qquad (5)$$

As with the rate of reaction of the dienophile, if the rate of formation of the product is much greater than that of cycloreversion to benzocyclobutene, the concentration of D will be controlled by the rate of *o*-quinodimethane formation:

$$\mathrm{d}[\mathrm{D}]/\mathrm{d}t = k_1[\mathrm{A}] \qquad (6)$$

A series of polymerizations of monomer **3** were carried out in an apparatus which allowed the reaction mixture to be sampled during the course of the reaction. Dependences of the monomer quantity and the concentrations of benzocyclobutene, olefin, and product species on time were thus determined, and these data were analyzed to determine the validity of the proposed polymerization mechanism and kinetic scheme.

Table II
Weight Fraction of Monomer and Fraction Functional Group Conversions for the Polymerization of Monomer 3 at 180 °C

	GC		NMR		GPC:
time, min	W_{2t}	p_a	p_a	p_d	p_a
120	0.79	0.11	0.09	0.13	0.18
240	0.57	0.24	0.24	0.26	0.31
360	0.35	0.41			0.37
480	0.27	0.48	0.46	0.44	0.45
600	0.25	0.50	0.52	0.51	0.52
720	0.19	0.56	0.59	0.59	0.58
840	0.14	0.63	0.65	0.65	0.64
960	0.11	0.66	0.67	0.69	0.68

Quantitation of Residual Monomer by Gas Chromatography. The amount of residual monomer in partially polymerized samples of monomer **3** treated at 180 °C was determined via gas chromatography with an internal standard present. The weight fraction of residual monomer for a difunctional monomer, W_{2t}, can be calculated from the probability that neither of the functional groups (in this case benzocyclobutene or olefin) on a given monomer molecule has reacted. The fraction of functional groups reacted is designated p, the fraction of benzocyclobutenes reacted p_a, and the fraction of olefins reacted p_c. Polymerization solely via a Diels–Alder mechanism requires that $p_a = p_c$, so that the fraction of unreacted functional groups is given by $1 - p_a$ for benzocyclobutene or $1 - p_c$ for olefin. The weight fraction of monomer can be related to the fraction of functional groups which have reacted:

$$W_{2t} = (1 - p)^2 \qquad (7)$$

In order to determine the rate of benzocyclobutene depletion (assuming that ring closure does not compete effectively with Diels–Alder reaction), the integrand of eq 1 is given as eq 8 where A is the quantity of benzocyclobutene present initially and A_0 represents the quantity at time t. Because $A/A_0 = (1 - p_a)$, the rate constant for the reaction of A can then be determined with respect to p_a:

$$\ln (A/A_0) = -k_1t \qquad (8)$$

$$\ln (1 - p_a) = -k_1t \qquad (9)$$

It is also possible to express the rate constant in terms of the weight fraction of monomer:

$$\ln W_{2t} = -2k_1t \qquad (10)$$

The weight fraction of monomer and p_a values for a sample of **3** treated at 180 °C were determined and are given in Table II. Figure 7 shows a plot of $-\ln (1 - p_a)$ with respect to time; the slope of this plot represents the observed rate constant for the ring-opening reaction and, by the kinetic model invoked, the Diels–Alder reaction of olefin. A k_1 value of 1.1×10^{-3} min^{-1} was obtained from these data. The linearity of these data is consistent with the first-order kinetics predicted for this reaction, although the reaction was only carried to 66% conversion of the functional groups.

Olefin Quantitation by Infrared Spectrophotometry. The kinetic model proposed for the thermal polymerization of monomer **3** requires that the Diels–Alder reaction take place quickly with respect to reversion of

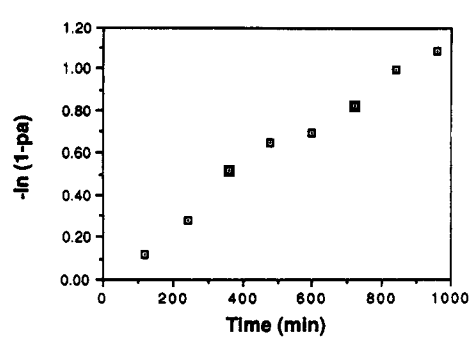


Figure 7. $-\ln(1 - p_a)$ with respect to reaction time during the polymerization of monomer 3 from residual monomer quantitation by gas chromatography.

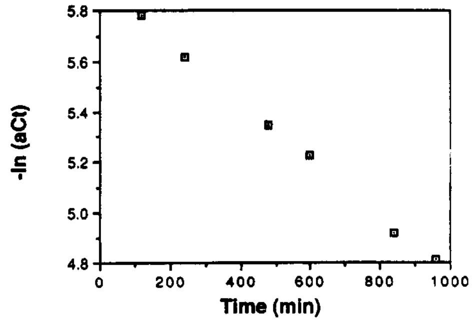


Figure 8. $-\ln a_{C_t}$ with respect to reaction time during the polymerization of monomer 3 at 180 °C as measured by infrared spectrophotometric analysis of the alkenyl C–H peak at 965 cm^{-1}.

o-quinodimethane to benzocyclobutene. Infrared spectrophotometry was used to determine changes in the amount of olefin over the course of the reaction. The 965-cm^{-1} band which arises from the C–H out-of-plane deformation of the trans-alkenyl protons was monitored with respect to time at a polymerization temperature of 180 °C. The structure of monomer 3 requires that the quantity of benzocyclobutene, A_0, and the initial quantity of olefinic species, C_0, be equal. The reaction model proposes that, at any time t, the concentration A_t remains equal to the concentration C_t. The change in the concentration C with time can then be expressed by modifying eq 8:

$$\ln(C_t/C_0) = -k_1 t \tag{11}$$

Equation 11 can be rewritten as

$$\ln C_t = \ln C_0 - k_1 t \tag{12}$$

If the concentration C is directly proportional to the magnitude of the absorbance, a, at 965 cm^{-1} (from Beer's law, $a_{C_0} = C_0 \epsilon b$ and $a_{C_t} = C_t \epsilon b$, where ϵ is the molar absorptivity and b is the path length), eq 12 can be rewritten to express the relationship of the rate constant k_1 to changes in absorbance of the olefinic species:

$$\ln a_{C_t} = \ln a_{C_0} - k_1 t \tag{13}$$

Figure 8 shows a plot of $-\ln a_{C_t}$ with respect to time for samples polymerized at 180 °C. The plot is linear, with a value k_1 of -1.1×10^{-3} min^{-1} given by the slope of the best fit line through the data. The agreement between k_1 from IR data, which depends upon the olefin concentration alone, and the k_1 obtained from residual monomer data, which relies on the reaction of both functional groups, reinforces the supposition that the ring opening of benzocyclobutene is accompanied by reaction of the olefin; the Diels–Alder reaction is one mechanism which is consistent with this observation.

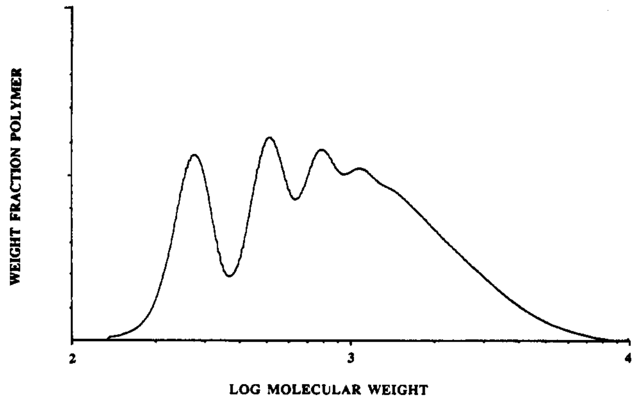


Figure 9. GPC trace of partially thermally polymerized monomer 3.

Quantitation of Benzocyclobutene Decay and Product Formation by ^{13}C NMR Analysis. ^{13}C NMR analysis can be used to monitor the decay of resonances due to the benzocyclobutene functionality and the increase in resonances due to the tetrahydronaphthalene product as the reaction proceeds. ^{13}C NMR spectra were obtained such that proton decoupling was complete, but the NOE signal enhancement was suppressed. In addition, t_1 values for the resonances used to monitor the reaction were measured, and spectra were obtained with a pulse delay equal to 10 times the longest t_1. Values for the fraction of the benzocyclobutene group reacted, p_a, and fractional increases in the product resonances, designated p_d, are given in Table II. The p_d values shown were calculated from the methine carbons: the integral values for the methine and methylene carbons due to the tetrahydronaphthalene product were virtually identical. Using eq 9, a k_1 value of 1.2×10^{-3} min^{-1} was calculated for both benzocyclobutene decay and tetrahydronaphthalene formation. These data suggest that the rates of change of benzocyclobutene decay, olefin decay, and tetrahydronaphthalene formation are essentially identical (within the limits of the measurements) at 180 °C.

Functional Group Quantitation via Size-Exclusion Chromatography. The molecular weight growth of a difunctional monomer can be monitored to determine the extent of reaction of the two functional groups. The molecular weights of partially polymerized samples of monomer 3 were analyzed by size-exclusion chromatography to determine the extent of reaction. A calibration curve was constructed by correlating the retention times of oligomers $n = 2$ through $n = 6$ and extrapolating this relationship to include higher molecular weight species (Figure 9 shows an SEC trace of prepolymer of monomer 3). M_n and M_w values were measured for the 180 °C polymerization series. The extent of reaction for these samples can be calculated using the approach put forth by Macosko and Miller.[27] To make use of this model, several simplifying assumptions must be made. These assumptions are that the only mechanism of polymerization is the Diels–Alder reaction and that benzocyclobutene/benzocyclobutene and olefin/olefin interactions do not occur. It is also assumed that no intramolecular reactions (cyclizations) occur, that all functional groups are equally reactive (without regard to the size of the molecule to which they are attached), and that these groups react independently of one another. It is further assumed that the fate of one functional group on a given monomer molecule does not influence the reactivity of the other; for instance, the reactivities of a benzocyclobutene on a monomer molecule and a benzocyclobutene on a monomer whose olefinic site has been removed via Diels–Alder

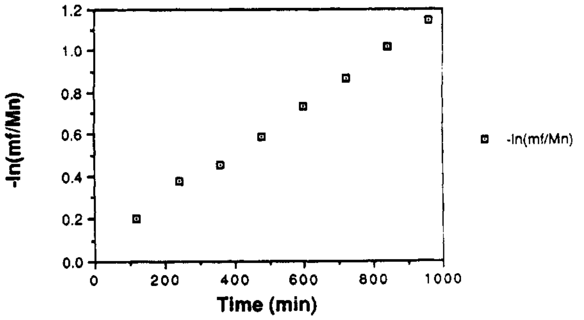


Figure 10. $-\ln (m_f/M_n)$ with respect to reaction time for the polymerization of monomer 3 at 180 °C, as measured by GPC analysis.

reaction are assumed to be identical. The fraction of functional groups reacted, p, can be related to the number-average molecular weight. 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. Every reaction thus reduces the number of moles by 1, while the mass remains constant. The number-average molecular weight can then be expressed as

$$M_n = m_t/(N_0 - N_b) \qquad (14)$$

where N_0 is the initial number of moles in the system and N_b is the number of new tetrahydronaphthalene groups formed. The total mass of the system is given by the initial concentration of functional groups A (or C) multiplied by the molecular weight of the monomer, m_f:

$$m_t = m_f A_0 \qquad (15)$$

The number of new tetrahydronaphthalene groups formed, N_b, is determined from the probability that a functional group has reacted and the initial concentration of that functional group:

$$N_b = p_a A_0 \qquad (16)$$

Because the number of moles of monomer 3 is equivalent to the number of A or C functional groups, it is possible to rewrite eq 14 to give the relationship between M_n and the fraction of functional group conversion:

$$M_n = m_f/(1 - p_a) \qquad (17)$$

The rate constant can then be calculated from the number-average molecular weight:

$$\ln [m_f/M_n] = -k_1 t \qquad (18)$$

Figure 10 shows a plot of $-\ln [m_f/M_n]$ with respect to time for partially polymerized samples of monomer 3 treated at 180 °C. The k_1 value obtained via this treatment was 1.1×10^{-3} min^{-1}. These data are consistent with those obtained by spectroscopic methods and show little deviation from the expected molecular weight values for the predicted polymerization mode, although the polymerization was not followed above ca. 66% conversion of functional groups. Calculated fractional functional group conversions obtained from molecular weight measurements are given in Table II. The degree of functional group conversion can also be related to the weight-average molecular weight distribution:

$$M_w = m_f[(1 + p_a)/(1 - p_a)] \qquad (19)$$

The polydispersity index of the monomer is 1; as the polymerization proceeds, the polydispersity index should approach a maximum value of 2 (the theoretical molecular weight distribution for any condensation polymerization). Figure 11 shows polydispersity indices with respect to fractional functional group conversion as measured for the 170 °C polymerization samples (using p_a values from GPC data) and calculated from p_a via eqs 17 and 19. The measured and theoretical data are in reasonable agreement for the range of functional group conversions examined here. The fact that the polydispersity index exceeds the expected value of 2 as p_a approaches complete reaction suggests that the Diels–Alder mechanism gives way to another polymerization mechanism at high functional group conversion.

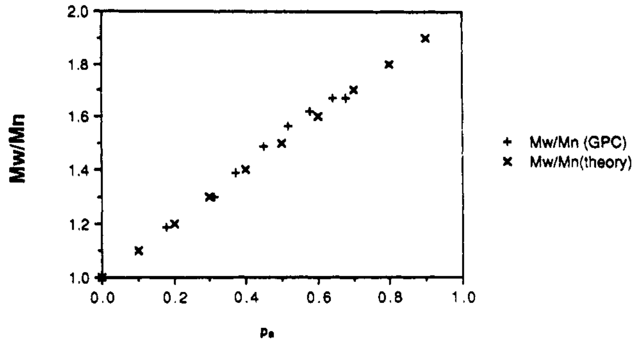


Figure 11. M_w/M_n with respect to fractional benzocyclobutene conversion of theoretical (×) and GPC-generated (+) data.

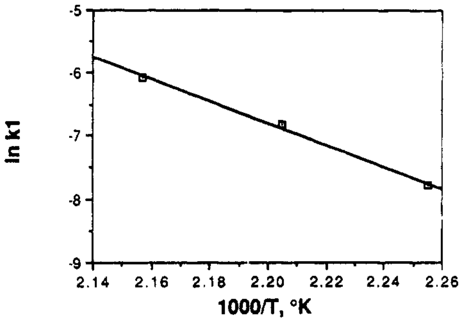


Figure 12. Arrhenius plot of ln k_1 versus reciprocal temperature for the polymerization of monomer 3.

Temperature Dependence of the Polymerization Rate of Monomer 3. Measurement of the rate constant for the loss of benzocyclobutene in the thermal polymerization of monomer 3 was studied at two other temperatures to determine the dependence of reaction rate on temperature. Two further polymerizations were performed, at 190.2 and 170.6 °C, and the extent of polymerization was monitored by residual monomer analysis using the gas chromatographic method previously discussed. Reaction rates were calculated from these data: at 170.6 °C, $k_1 = 4.2 \times 10^{-4}$, and at 190.2 °C, $k_1 = 2.3 \times 10^{-3}$. If the ring-opening reaction is an activated process, the activation energy E_a for this process can be evaluated from the rate data at different temperatures via the Arrhenius equation (eq 20), where R is the ideal gas constant

$$\ln k_1 = -[E_a/RT] + Z \qquad (20)$$

and Z is a constant. Figure 12 shows an Arrhenius plot of ln k_1 versus the reciprocal temperature. From this analysis, an activation energy of 35.4 kcal/mol was calculated for the polymerization of 3 (E_a for the thermally activated Diels–Alder reaction of the hydrocarbon benzocyclobutene with maleic anhydride has been reported as 39.9 kcal/mol[26,28-30]). This energy of activation allows for estimation of the rate of reaction of 3 at temperatures outside of the range reported herein, assuming that the same reaction processes are occurring (eq 21). The temperature dependence of the half-life of the benzocy-

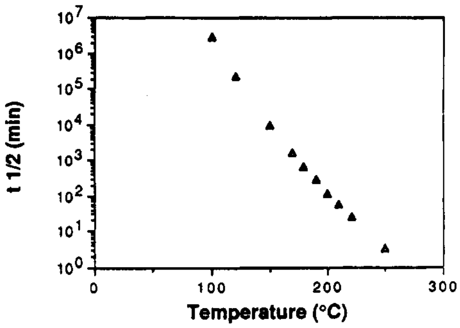


Figure 13. Estimated half-life of the benzocyclobutene moiety in monomer 3 with respect to temperature, based on an energy of activation of 35.4 kcal/mol.

clobutene functional group (the time required to obtain a system where $p_a = 0.5$) for the thermal polymerization

$$\ln (k_2/k_1) = (E_a/R) ([1/T_1] - [1/T_2]) \qquad (21)$$

of monomer 3 can thus be estimated from the calculated E_a for the ring-opening rearrangement (Figure 13). This estimation of the benzocyclobutene lifetime assumes that the reaction proceeds through the same first-order rearrangement reaction mechanism at temperatures outside of the range included in this study.

Conclusions

The thermal polymerization of a molecule containing both benzocyclobutene and stilbene (α,β-diarylethylene) functionalities appears to proceed solely (within the limits of analysis) by the Diels–Alder reaction of the highly reactive *o*-quinodimethane intermediate. The reaction kinetics for this polymerization have been measured from time rate of change data obtained via residual monomer quantitation, molecular weight growth, and spectral analysis of benzocyclobutene, olefin, and tetrahydronaphthalene species for monomer 3 treated at 180 °C. These data are consistent with a model for the polymerization reaction in which the rate of molecular weight growth is limited by the first-order rearrangement of a benzocyclobutene moiety to an *o*-quinodimethane, followed by the relatively fast Diels–Alder reaction of this reactive species with an alkenyl site. The fact that this monomer does not polymerize to provide a high molecular weight polymer and a high polydispersity index at high functional group conversion suggests that some process not detected by this study is also operating. It is possible that at high degrees of functional group conversion, low concentrations of both alkene and *o*-quinodimethane allow for the formation of other chemical species (possibly via proton abstraction or *o*-quinodimethane/*o*-quinodimethane interactions) which do not contribute to continued molecular weight growth.

Acknowledgment. Molecular weight analyses were performed by George Murphy and Deidre Strand. Ms. Lori Hugo performed the GC monomer quantitation experiments. Dr. Alan K. Schrock first prepared and polymerized the monomers described in this study and has offered much helpful advice and many excellent suggestions.

References and Notes

(1) Iwatsuki, S. *Advances in Polymer Science*; Springer-Verlag: Berlin, Heidelberg, 1984.
(2) Tan, T. S.; Arnold, F. E. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1819.
(3) Tan, L. S.; Arnold, F. E. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 3159.
(4) Tan, L. S.; Arnold, F. E. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 3103.
(5) Hahn, S. F.; Townsend, P. H.; Burdeaux, D. C.; Gilpin, J. A. *Polymeric Materials for Electronics and Interconnection*; Lupinski, J. H., Moore, R. S., Eds.; ACS Symposium Series 407; American Chemical Society: Washington, DC, 1989.
(6) Johnson, R. W.; Phillips, T. L.; Jaeger, R. C.; Hahn, S. F.; Burdeaux, D. C. *IEEE Trans. Compon., Hybrids, Manuf. Technol.* **1989**, *12*, 185.
(7) Johnson, R. W.; Phillips, T. L.; Weidner, W. K.; Hahn, S. F.; Burdeaux, D. C.; Townsend, P. H. *IEEE Trans. Compon., Hybrids Manuf. Technol.* **1990**, *13*, 347.
(8) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949.
(9) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1973**, *95*, 5802.
(10) Trahanovsky, W. S.; Macias, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 6820.
(11) Klundt, I. L. *Chem. Rev.* **1970**, *70*, 471.
(12) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873.
(13) Oppolzer, W. *Synthesis* **1978**, 793.
(14) Kametani, T.; Honda, T.; Ebisawa, Y.; Ichikawa, H. *Tetrahedron* **1985**, *41*, 3643.
(15) Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*; Wiley-Interscience: New York, 1967; p 331.
(16) IUPAC nomenclature gives the name bicyclo[4.2.0]octa-(1,3,5)-triene for the C_8H_8 hydrocarbon commonly known as benzocyclobutene. In this paper, the common name will be used, with carbon 1 assigned to the ring junction carbon.
(17) Lloyd, J. B. F.; Ongley, P. A. *Tetrahedron* **1965**, *21*, 245.
(18) Heck, R. F.; Nolley, J. P. *J. Org. Chem.* **1972**, *37*, 2320.
(19) Plevyak, J. F.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2454.
(20) These assignments are based on simulation of IR spectra using ab initio calculations performed by Dr. Nelson G. Rondan.
(21) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510.
(22) Finnegan, R. A. *J. Org. Chem.* **1965**, *30*, 1330.
(23) Streitweiser, A.; Ziegler, G. R.; Mowery, P. C.; Lewis, A.; Lawter, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 1357.
(24) Thummel, R. P. *Acc. Chem. Res.* **1980**, *13*, 70.
(25) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; VCH Publishers: New York, 1987; pp 264 and 265.
(26) Roth, W. R.; Beirmann, M.; Dekker, H.; Jochems, R.; Mosselman, C.; Hermann, H. *Chem. Ber.* **1978**, *111*, 3892.
(27) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.
(28) Stokich, T. M., Jr.; Lee, W. M.; Peters, R. A. Proceedings of the Materials Research Society, April 1991, Anaheim, CA.
(29) Heistand, R. H.; DeVellis, R.; Manial, T. A.; Kennedy, A. P.; Garrou, P. E.; Stokich, T. M.; Townsend, P. H.; Adema, G. M.; Berry, M. J.; Turlik, I. Proceedings of the International Society of Hybrid Microelectronics, Orlando, FL, 1991.
(30) Bruza, K. J.; Carriere, C. J.; Kirchhoff, R. A.; Rondan, N. G.; Sammler, R. L. *J. Macromol. Sci.*, in press.