Synthesis and Thermal Properties of Thermosetting Bis-benzocyclobutene–terminated Arylene Ether Monomers

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ABSTRACT: A series of new bis-benzocyclobutene-encapped arylene ether monomers was prepared and characterized. Whereas 2,6-bis(4-benzocyclobutenyloxy)benzonitrile (BCB-EBN) could be prepared in good yield using the standard procedure (K2CO3/NMP/toluene/Dean–Stark trap/120°C), other bis(benzocyclobutene) (BCB)-terminated monomers containing ether-benzophenone (BCB-EK), ether-phenylsulfone (BCB-ES), and ether-6F-benzoxazole (BCB-EBO) moieties were invariably contaminated by monencapped products under similar reaction conditions. This can be attributed to a much greater activating effect of the nitrile group on the ortho-fluorides in the aromatic nucleophilic displacement reaction than the carbonyl, sulfonyl, and benzoxazolyl groups. However, the latter monomers could be synthesized (70–80%) from 4-trimethylsiloxynitrobenzocyclobutene and respective aromatic fluorides in the presence of CsF at 140°C. Similar curing behaviors under N2 (DSC: extrapolated onset and peak temperatures at 227–230°C and 260–262°C, respectively) characterized all four monomers. BCB-EK, BCB-ES, and BCB-EBN showed melting transitions at 108, 119, and 146°C, in that order. As BCB-EBO contained more rigid benzoxazole segments, it only exhibited a glass transition (Tg) at 85°C prior to curing exotherm, after it had been previously heated to 125°C. The following Tg,s were observed for the cured materials: BCB-EK (201°C), BCB-EBN (224°C), BCB-ES (264°C), and BCB-EBO (282°C). The relative thermal stability according to TGA (He) results is: BCB-ES < BCB-EBN < BCB-EK < BCB-EBO. Finally, the results from thermal analysis, infrared spectroscopic, and variable temperature microscopic studies indicated that the nitrile group plays an important role in the cure chemistry, thermal, and microstructural properties of BCB-EBN. © 1998 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 36: 2637–2651, 1998

Keywords: benzocyclobutene; cesium fluoride; 4-hydroxybenzocyclobutene; 4-trimethylsiloxybenzocyclobutene; thermosets; arylene ether monomers

INTRODUCTION

Motivated by the versatile reaction chemistry of benzocyclobutene (BCB) as well as the combined advantages of processability and material properties, BCB-based polymers have emerged as a new generation of high-performance materials for a spectrum of structural and electronic applications.1-4 The cure chemistry of benzocyclobutene is based upon the propensity of the four-membered ring to undergo electrocyclic ring opening at elevated temperatures to provide reactive o-quinodimethane that will undergo dimerization and polymerization, or react with an attendant dieno-
Previously, we reported the preparation of a bis(benzocyclobutene)-terminated monomer derived from 4-HOBCB as a matrix material for a rigid-rod polyimide-based, thermoset molecular composite.\textsuperscript{10} We also briefly described the synthesis of 2,6-bis(4-benzocyclobutenyloxy)benzonitrile (BCB-EBN), which was an intermediate for the amine-bearing thermoset matrix resin utilized to demonstrate the concept of in situ molecular composites based on the rigid-rod polyimide derived from pyromellitic dianhydride and tetra-methylbenzidine. In an effort to develop a more complete picture of the effect of the linking groups on the thermal properties of the BCB-terminated arylene-ether monomers and their cured products, we proceeded to prepare three new monomers to complement BCB-EBN.

In this article we provide the details for the synthesis and thermal characterization of BCB-EBN and three other BCB-terminated arylene ether monomers based on 4-HOBCB.

RESULTS AND DISCUSSION

Synthesis of 4-Hydroxybenzocyclobutene and 4-Trimethylsiloxybenzocyclobutene

4-HOBCB was first prepared from bis(4-aminobenzocyclobutene) sulfate under diazotization condition (H\textsubscript{3}PO\textsubscript{4}/NaNO\textsubscript{2}).\textsuperscript{11,12} It can also be synthesized from benzocyclobutene-4-carboxaldehyde via a modified Baeyer–Villiger reaction using permoposphoric acid prepared from 70% H\textsubscript{2}O\textsubscript{2} solution and P\textsubscript{2}O\textsubscript{5}.\textsuperscript{13} In addition, it has been demonstrated that benzocyclobutene could be enzymatically dioxygenated to an intermediate diol that underwent facile dehydration to form 4-HOBCB.\textsuperscript{3,9} We reported\textsuperscript{14} that 4-HOBCB can also be easily prepared from the demethylation of 4-methoxybenzocyclobutene by AII.\textsuperscript{15} 4-Methoxybenzocyclobutene was prepared via the flash vacuum pyrolysis of 6-methoxy-3-isochromane using a similar procedure reported in the literature.\textsuperscript{16} 4-Trimethylsiloxybenzocyclobutene (4-TMSO-BCB) was prepared from 4-HOBCB and chlorotrimethylsilane in the presence of triethylamine.

Bis(benzocyclobutene)-terminated Aryl Ether Monomers

As mentioned briefly in our previous work,\textsuperscript{10,17} the synthesis of 2,6-bis(4-benzocyclobutenyloxy)benzonitrile (BCB-EBN) from 4-HOBCB...
and 2,6-difluorobenzonitrile was carried out in the presence of excess anhydrous potassium carbonate in N-methylpyrrolidinone and toluene, which was to remove azeotropically the water of reaction. However, the reaction temperature was kept at 120–130°C so as to avoid the premature ring opening of the benzocyclobutene groups. To drive the reaction to completion, excess 4-HOBCB and a longer reaction time were used. Good yield of the desired BCB-EBN was obtained (see Scheme III).

The syntheses of the other new monomers are summarized in Scheme IV. 4,4'-difluorobenzophenone and 4,4'-difluorodiphenylsulfone were commercially available compounds. Although 2,2-bis[2-(4-fluorophenyl)benzoxazol-6-yl]hexafluoropropane had been prepared from the condensation reaction of 2,2-bis(3- amino-4-hydroxyphenyl)-hexafluoropropane and 4-fluorobenzoic acid, we found that shorter reaction time (12 h vs. 2–4 days) and lower cyclodehydration temperature (180°C vs. 260°C) were needed in the presence of trimethylsilyl polyphosphate. As benzocyclobutene would undergo ring opening in solution at the temperature at which the syntheses of polyetherketones and polyethersulfones were typically conducted, our initial attempts in preparing

**Scheme 3.** Synthesis of 2,6-bis(4-benzocyclobutenyloxy)benzonitrile.

The benzophenone and diphenylsulfone monomers using potassium carbonate as the base was conducted at temperature no higher than 140°C.

At these temperatures, we found that in both cases, a mixture of mono-encapped and bi-encapped monomers was obtained as evidenced by liquid chromatographical (see Fig. 1) and mass spectral results. Prolonged heating and using more than 10 mol % excess of 4-HOBCB were futile. This is in contrast to the synthesis of 2,6-bis(4-benzocyclobutenyloxy)benzonitrile, as described in the foregoing paragraph. Both the mass spectral and high-performance liquid chromatographic data did not show the presence of mono-encapped product. Ostensibly, this is because the nitrile is a stronger activating group than the keto, sulfonyl, or benzoxazole group, and of the fact that both fluorides are situated at the positions ortho to the nitrile, whose activating effect can be exerted without attenuation, as in the case of para-positions. Similar observations on the reactivity of 2,6-difluorobenzonitrile have also been reported by other researchers. As a consequence, we turned to the more reactive combination of 4-TMSO-BCB and CsF. The use of CsF or KF to induce greater nucleophilicity of phenols, O-trimethylsilylated phenols, and N-trimethylsilylated amines is well documented. Indeed, the aromatic nucleophilic substitution reactions between 4-TMSO-BCB, and the respective aromatic difluorides in the presence CsF went to completion when the keto, sulfonyl, and benzoxazole functions were used as the activating groups.

These monomers were all characterized by elemental analysis, FTIR, nuclear magnetic resonance, and mass spectroscopic methods. The results of characterization are presented in the
Thermal Properties

All four monomers were subjected to differential scanning calorimetry (DSC, N₂, 10°C/min.) and thermogravimetry analysis (TGA, helium or air; 10°C/min.). Whereas BCB-EBN is a yellow microcrystalline compound, the other arylene ether monomers are all white, microcrystalline solids. No glass transition (T_g) was observed for BCB-EK when its DSC scan and rescan were run from room temperature to 130°C. BCB-ES exhibited a glass transition (T_g) temperature of 27°C during similar scan and rescan. Although the initial DSC runs of two BCB-EBO samples showed relatively sharp endotherms at 88 and 93°C, the rescans of both samples after heating to 125°C and cooling to 25°C unraveled the T_g at 85°C as an inflexion in the baseline. The virtual melt endotherm may be attributed to the thermally induced molecular relaxation of BCB-EBO molecules in solid state. Similarly, BCB-EBN showed a set of two closely coupled, endotherms at 140°C (larger endotherm) and 146°C (smaller endotherm) on initial scan to 160°C (see Fig. 4). Upon rescan, a small, slightly broad endotherm appeared around 70°C, and a sharp endotherm at 146°C. We assigned the latter transition as the melting transition for BCB-EBN. The smaller endotherm appeared to be more first order than second order, and we are not sure of its origin without a separate, detailed morphological study. In any event, the DSC results hinted that some interesting, thermally induced changes in crystal morphology may be taking place in BCB-EBN, and we proceeded to conduct a variable-temperature microscopic study (vide infra).

The exotherms ascribable to the ring opening of BCB group and the subsequent network-forming reactions all started at 227–230°C (extrapolated onset temperature), and reached the peak temperature at 260–262°C. Upon rescan of the samples to 325–400°C after previously heating to 325–400°C and cooling to 25°C, the cured materials derived from these monomers revealed their T_g's from 201 to 282°C. All in all, the DSC results indicated that these materials other than BCB-EBO have excellent processing windows (T_{onset} – T_m) of 83–122°C.

Thermogravimetric analysis of the BCB-terminated monomers showed that they were thermally (helium environment) and thermo-oxidatively (air environment) stable. It is noteworthy that except for BCB-EBN, the other three monomers displayed a small weight gain (~ 1%) in air...
atmosphere between the onset of BCB reaction exotherm and catastrophic degradation. Apparently, the curing mechanisms for BCB-EK, BCB-ES, and BCB-EBO differ in inert and air atmospheres. We have made similar observations in our previous work when an aromatic polyamide with a keto-benzocyclobutene pendant was heated under air and inert atmospheres under DSC and TGA conditions. In the case of BCB-EBN, weight losses of 2.99% (221°C, in air) and 4.06% (229°C, in helium) were observed. Because BCB-EBN is the only monomer that contains a dienophile (nitrile) in its molecular structure, we suspected that the Diels–Alder reaction between the nitrile function and α-quinodimethane generated from benzocyclobutenyl group may be rather significant (see Scheme V). Although nitrile function is a moderate dienophile, under suitable conditions, the Diels–Alder reaction between a nitrile group and α-quinodimethane is reported to be quite facile. Indeed, after a sample of BCB-EBN (13.3 mg) was heated to 300°C at 10°C/min under nitrogen atmosphere in a DSC cell and kept at 300°C for 5 min before cooling down to room temperature, the resultant amber disk was subjected to infrared spectral analysis, which indicated that the characteristic stretching band due to the nitrile group at 2229 cm⁻¹ had almost completely disappeared (see Fig. 5). This is in contrast to the reported inertness of the nitrile pendants of the thermoplastic counterparts, poly(arylene ether nitrile). For example, the poly(arylene ether nitrile) derived from resorcinol and 2,6-difluorobenzenitrile showed that its nitrile group remained intact after being heated at 230°C for 5 h in air. Also, we noticed that the TGA sample of BCB-EBN, after it had been heated to 900°C under helium, consolidated into a relatively tough char with the circular shape of the sample pan, whereas the other cured monomers only gave black, brittle powders. This is also reflected in a higher char yield (51.4%) for BCB-EBN than the other monomers (40.0–47.2%). Finally, with respect to the onset temperature of catastrophic degradation, TGA results in all cases seem to suggest slightly higher stability in air than in helium.
As we are intrigued by the reports\textsuperscript{23,24c} that polyethers derived from 2,6-dihalobenzonitrile and 1,3-dihydroxybenzene (resorcinol) or dihydroquinone are crystalline, insoluble in common organic solvents, and possess high melting temperatures (312–386°C), we wondered about the role that the benzonitrile-2,6-diyi moiety might play in the crystalline properties of these polymers, which is quite in contrast to conventional thinking that meta catenation usually leads to amorphous character in thermoplastic polymers with relatively low melting temperatures. Because the DSC results indicated that only BCB-EBN showed a crystallization exotherm upon cooling from 160°C, we conducted a hot-stage photomicroscopic study to examine its birefringent crystalline morphologies as the functions of both temperature and temperature history.

Thus, a thin film of BCB-EBN was prepared by preheating two microscope coverglass slides to \( T = 160°C \) on one of the temperature-controlled surfaces of a custom heating stage.\textsuperscript{31} A single powder particle was placed on one cover slip and quickly melted to a clear liquid drop. Subsequent placement of the second coverslip spread the drop to a thin film with a thickness of approximately 5 \( \mu \)m. The glass–monomer–glass stack was then quickly quenched to 50°C on another temperature-controlled, cooler surface of the heating stage, at which point spherulites were observed to grow to the point of impingement over a period of five minutes.

The crystalline (impinged spherulite) material was observed using polarizing optical microscopy (POM) during a heating scan from 25°C through melting, using a heating rate of 10°C/min. Figure 7 shows photomicrographs for this heating run, where the temperatures shown are (a) 25, (b) 100, (c) 120, (d) 140, (e) 144, and (f) 145°C. For \( T = 145°C \), the polarizers were slightly uncrossed to provide an acceptably low photographic exposure time. Several features are evident from the photomicroscopy sequence shown in Figure 7. First, relatively large spherulites were present for all of the temperatures observed below the sample melting temperature, indicating a somewhat low number density as well spatial homogeneity of the crystal nuclei. Little change in sample morphology was observed for temperatures below \( T = 120°C \), at which temperature the color was dramatically shifted from pink-red to green, indicating a lowering of the crystalline birefringence occurring between 110°C (not shown) and 120°C. Further heating led to significant disorder of the spherulites [Fig. 7(e)] and complete melting at 145°C.

On slow cooling from 145°C at 10°C/min, which was slower than the quenching thermal history for Figure 7, a dramatically different morphology

![Figure 4. Composite DSC scans of BCB-EBN in nitrogen atmosphere (scanning rates at 10°C/min).](image-url)
Table I. DSC Data for Bis-benzocyclobutene–Terminated Arylene Ether Monomers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$T_g$ (ini) ($^\circ$C)</th>
<th>$T_g$ (Cure) ($^\circ$C)</th>
<th>Onset (°C)</th>
<th>Max. (°C)</th>
<th>Polym Enthalpy (kcal/mol)</th>
<th>$T_g$ (Cure) ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCB–EBN</td>
<td>—</td>
<td>146</td>
<td>229</td>
<td>261</td>
<td>−45.4</td>
<td>224$^f$</td>
</tr>
<tr>
<td>BCB–EK</td>
<td>—$^c$</td>
<td>108</td>
<td>230</td>
<td>262</td>
<td>−53.7</td>
<td>201$^g$</td>
</tr>
<tr>
<td>BCB–ES</td>
<td>27$^d$</td>
<td>119</td>
<td>230</td>
<td>262</td>
<td>−54.4</td>
<td>264$^g$</td>
</tr>
<tr>
<td>BCB–EBO</td>
<td>85$^e$</td>
<td>—</td>
<td>230</td>
<td>262</td>
<td>−51.2</td>
<td>282$^h$</td>
</tr>
</tbody>
</table>

$^a$ Conducted under N$_2$ at 10°C/min. All $T_g$ values are inflection points.
$^b$ Sample re-scanned after previously heated to 160°C. Initial scan showed two endotherms at 140°C (13.90 cal/g) and 146°C (5.07 cal/g).
$^c$ Not detected; sample re-scanned after previously heated to 120°C.
$^d$ Sample re-scanned after previously heated to 130°C.
$^e$ Sample re-scanned after previously heated to 125°C.
$^f$ Sample re-scanned after previously heated to 400°C.
$^g$ Sample re-scanned after previously heated to 325°C.
$^h$ Sample re-scanned after previously heated to 325°C and then 360°C.

was formed during rapid crystallization at $T = 113^\circ$C, shown in Figure 8(a), in the form of a striated, angular, and coarse microstructure. Continued cooling to 40°C [Fig. 8(b)] led to only small changes in the sample birefringence. Figure 8(c)–(e) shows the POM micrographs for (c) 80°C, (d) 120°C, and (e) 140°C, with complete melting occurring at $T = 145^\circ$C. Clearly, different thermal histories would lead to a dramatically different crystalline morphology in this monomeric material, as seen, for example, by comparing Figure 7(d) and Figure 8(e) for $T = 140^\circ$C.

Given the morphological similarity shown in Figure 8(e) with a nematic mesophase, the presence of fluidity was tested by shearing the glass–monomer–glass stack with tweezers at $T = 140^\circ$C. Such a shearing force was unable to easily displace the glass coverslips relative to one another. This indicated that the monomer film was a solid, and therefore, ruled out the possibility of liquid crystallinity. The absence of a nematic mesophase is not surprising, given the nonlinear conformation of the BCB–EBN molecule, as shown in Figure 3.

The influence of crosslinking on crystallization was investigated by thermally annealing a fresh thin film of BCB material in a similar glass–monomer–glass stack at $T = 225^\circ$C for 60 min and subsequently cooling at a rate of 10°C/min to room temperature. Following the specified thermal history in using POM showed that no crystallization during cooling had occurred, indicating that thermal crosslinking had led indeed to the formation of an amorphous solid.

**CONCLUSION**

As an extension of our effort in developing new thermosetting resins for various space and aerospace applications, we have successfully synthesized a new class of bis(benzocyclobutene)(BCB)-terminated monomers containing ether-benzonitrile (BCB–EBN), ether-benzophenone (BCB–EK), ether-phenylsulfone (BCB–ES), and ether-6F-benzoxazole (BCB–EBO) bridging groups. These monomers could be synthesized in good yields (70–80%) from 4-trimethylsiloxybenzocyclobutene and respective aromatic difluorides in the presence of CsF. However, only BCB–EBN could be prepared from 4-hydroxybenzocyclobutene and 2,6-difluorobenzonitrile via the standard procedure without the contamination of mono-end-capped product. The BCB arylene ether monomers exhibited practically similar curing behaviors under N$_2$ (DSC: extrapolated onset and peak temperatures at 227–230°C and 260–262°C, respectively). BCB–EK, BCB–ES, and BCB–EBN showed only melting transitions at 108, 119, and 146°C, in that order, and BCB–EBO exhibited only a glass transition ($T_g$) at 85°C and cured without melting. The cured materials of these monomers showed the following $T_g$ values: BCB–EK (201°C), BCB–EBN (224°C), BCB–ES (264°C), and BCB–EBO (282°C). Also, the results from thermal analysis, infrared spectroscopic and variable temperature microscopic studies indicated that the nitrile group played an important role in the cure chemistry, thermal, and crystalline properties of BCB–EBN. Finally, the relative
The thermal stability according to TGA (He) results is: BCB-ES < BCB-EBN < BCB-EK < BCB-EBO. Thus, thermal analyses of these thermosetting systems suggested that they are potentially high-temperature matrix materials with excellent melt processing windows.

**EXPERIMENTAL**

Both 4-Methoxybenzocyclobutene and 6-methoxy-3-isochromanone were custom synthesized following literature procedures with slight modification. 4-Methoxybenzocyclobutene was obtained in

<table>
<thead>
<tr>
<th>Monomer</th>
<th>TGA in Helium$^a$</th>
<th>TGA in Air$^a$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$T^b$ (onset)</td>
<td>$T_{5%}$</td>
</tr>
<tr>
<td>BCB-EBN</td>
<td>443$^c$</td>
<td>417</td>
</tr>
<tr>
<td>BCB-ES</td>
<td>430</td>
<td>415</td>
</tr>
<tr>
<td>BCB-EK</td>
<td>456</td>
<td>430</td>
</tr>
<tr>
<td>BCB-EBO</td>
<td>473</td>
<td>463</td>
</tr>
</tbody>
</table>

$^a$ Scan rate: 10°C/min; $^c$ extrapolated values; $^d$ A weight loss of ~ 4% was detected around 229°C.  
$^e$ A weight loss of ~ 3% was observed around 221°C.  
$^f$ A small weight gain (− 1%) was observed between the onset temperature of curing (200–230°C) to the onset of degradation.
60–70% yield via the flash vacuum pyrolysis of 6-methoxy-3-isochromanone, which was prepared in 30% yield from the reaction of 3-methoxyphenylacetic acid (Aldrich) with 37% formalin (Aldrich) in a mixture of acetic acid and concentrated hydrochloric acid at room temperature for 135 h. 4-Hydroxybenzocyclobutene was prepared from All3-mediated demethylation of 4-methoxybenzocyclobutene as previously described.14 2,2-[(Bis-(3-amino-4-hydroxyphenyl)hexafluoropropene was obtained from DayChem under a custom synthesis contract and used without further purification. Trimethylsilyl polyphosphate (PPSE) was purchased from Fluka and used as received.

Hot-stage photomicroscopy experiments were performed to examine birefringent crystalline morphologies as functions of both temperature and temperature history. For this purpose, a custom conductive heating stage91 was employed, featuring a nitrogen purge and temperature control better than ±1.0°C. The heating stage was mounted on an aus Jena Jenalumar polarizing optical microscope, which was used with the polarizer and analyzer crossed, a Tungsten lamp light source, and a 25× long working distance objective lens. The total magnification to printed film was 250×.

4-Trimethylsiloxybenzocyclobutene

To 3.14 g (0.026 mol) of 4-hydroxybenzocyclobutene taken up in 10 mL anhydrous benzene was added 2.64 g of triethylamine in a nitrogen-swept three-necked flask. Chlorotrimethylsilane (4.16 g, 0.038 mol) in 5 mL benzene was added at 15°C over a period of 15 min. The mixture was kept at 20°C overnight and was refluxed for about 2 h to complete the reaction. The precipitated triethylamine hydrochloride was filtered off under a nitrogen blanket and more benzene (25 mL) was filtered through the solid to extract all the product. A pale yellow oil was obtained after removing the solvents by distillation under nitrogen pressure. The residual volatiles were removed, and the crude product was vacuum distilled (65–67°C, 0.5 mm Hg) to collect a colorless oil (1.2 g, 24% yield).

ANAL. Calc. for C11H15OSi: C, 68.69%; H, 8.38%. Found: C, 69.94%; H, 8.33%

A larger batch of 4-trimethylsiloxybenzocyclobutene was synthesized from 6.56 g of 4-hydroxybenzocyclobutene and 5.54 g of triethylamine, taken up in 15 mL anhydrous benzene followed by the addition of a nearly three molar excess of chlorotrimethylsilane (20 mL in 15 mL dry benzene) to the reaction mixture maintained at 5°C. An instant white precipitation of triethylamine hydrochloride was observed. The solution was allowed to warm up on its own to 15°C in about 5 h, and the reaction mixture was kept stirred overnight. It was warmed to 40°C and maintained for about 3 h. The reaction mixture was cooled and the isolation of the product was done exactly as described before. The weight of the light yellow oil (crude) was 7.93 g, 76% yield. Total amount of the colorless oil obtained from vacuum distillation was 7.07 g.

ANAL. Calc. for C11H15OSi: C, 68.69%; H, 8.38%. Found: C, 69.15%; H, 8.44%

Mass spectrum: (M⁺, m/z 192, relative abundance 100%). Infrared spectrum: (neat, cm⁻¹): 3080 (aromatic CH), 2967 (CH₃ stretch), 2931 (benzocyclobutenyl CH₂ stretch), 1594 (aromatic C=C), 1471 (CH₂ deformation), 1270 (benzocyclobutenyl CH₂ stretch) and 951 (Ar—OSiMe₃).¹H-NMR (CDCl₃, no TMS, ppm): 0.28 (s, 9H, —OSiMe₃), 3.12 (s, 4 H, benzocyclobutenyl CH₃), 6.61, 6.62 (d, 1 H, aromatic proton ortho to both OSiMe₃ and alicyclic group), 6.69–6.72 (dd, 1 H, aromatic proton gauche to Osime₃ and protons of the alicyclic group).
Figure 7. Photomicrographs of BCB-EBN taken at (a) 25°C; (b) 100°C; (c) 120°C; (d) 140°C; (e) 144°C, and (f) 145°C.

aromatic proton ortho to alicyclic group and meta to OSiMe₃ and 6.91, 6.94 (d, 1 H, aromatic proton ortho to OSiMe₃ group and meta to alicyclic group). ¹³C-NMR (CDCl₃, no TMS, 77 ppm for CDCl₃ as reference): 0.18–0.64 (OSiMe₃ carbons), 28.68, 28.92 (benzocyclobutanyl CH₂), 114.95 (sp²C meta to C—OSiMe₃ and ortho to alicyclic), 119.84 ((sp²C ortho to C—OSiMe₃ and ortho to alicyclic), 123.42 (sp²C ortho to C—OSiMe₃ and meta to alicyclic), 138.16 (sp²C cyclobutene para to C—OSiMe₃), 146.34 (sp²C cyclobutene meta to C—OSiMe₃), and 154.40 (sp²C-OSiMe₃).

2,6-di-(4-Benzocyclobutenyloxy)benzonitrile (BCB-EBN)

In a 250 mL, three-necked round-bottomed flask equipped with a Dean–Stark trap/reflux condenser/nitrogen adaptor, an overhead mechanical stirrer and a thermometer/adaptor were placed 2,6-difluorobenzonitrile (3.85 g, 27.68 mmol.), anhydrous potassium carbonate (8.00 g, 57.88 mmol.), and 4-hydroxybenzocyclobutene (7.50 g, 62.42 mmol). N-methylpyrrolidinone (NMP) (120 mL) and 80 mL of dry toluene were added to the mixture. The resultant reaction mixture was vigorously stirred and heated rapidly in an oil bath under a nitrogen blanket. The internal temperature of the reaction mixture was maintained at about 120–130°C for 48 h. The final reaction mixture was dark, with the precipitated solid forming a ring on the walls just above the surface of the solution. After the reaction mixture had cooled down to room temperature, it was filtered and the reaction vessel was rinsed with methylene chloride. The combined filtrate was transferred to a 500-mL round-bottomed flask and subjected to rotary evaporation to remove methylene chloride and toluene at 90°C. The remaining dark liquid was then poured into a stirred, cold aqueous HCl
solution (100 mL of concentrated HCl + 1400 mL of distilled water). The brown precipitate formed was allowed to stand at room temperature for several hours and then collected by suction filtration, washed with copious amount of water until the filtrate was neutral to a litmus paper. After the crude product had been air dried (with suction) overnight, it was redissolved in ca. 200 mL of methylene chloride. The resulting solution was dried over anhydrous MgSO₄ and filtered. The filtrate was subjected to rotary evaporation. After the volume of the filtrate had been reduced to about 50 mL, 100 mL of hexane was added. Rotary evaporation was resumed to remove completely the solvents. About 9.15 g of crude product was obtained. The crude product was dissolved in ca. 100 mL of ethyl acetate, and the resulting solution was added to a small quartz column containing ca 100 g of silica gel saturated with hexane. The column was then eluted with 1:4 ethyl acetate/hexane. The first fraction was collected, and complete removal of the solvent via rotary evaporation led to the isolation of the desired product. The crude yield was 8.70 g (93%). Recrystallization of a small sample (0.76 g) of the crude product from hot i-PrOH/EtOH (denatured ethanol from Aldrich) resulted in 0.56 g (74%) recovery of BCB-EBN as a yellow, microcrystalline solid.

**ANAL. Calc. for C₂₃H₁₇NO₂:** C, 81.39%; H, 5.05%; N, 4.14%. Found: C, 81.08%; H, 4.99%; N, 3.92%. Mass spectrum: M⁺, m/z 339, relative abundance 19.25%. Infrared spectrum: (KBr, cm⁻¹): 3080 (aromatic CH), 2969, 2930 (benzocyclobutenyl CH₂ stretch), 2229 (CN stretch), 1596 (aromatic C=O), 1577, 1456 (CH₂ deformation), 1245 (benzocyclobutenyloxy stretch), 1215, 1115, 1080, 1017, 876, 827, 778, 726, 557.
**1H-NMR (CDCl₃, TMS, δ in ppm):** 3.15 (s, 8 H, benzocyclobuteny 1 CH₂), 6.36, 6.39 (d, 2 H, aromatic protons meta to O— and ortho to cyclobutenyl ring), 6.82, 6.83 (d, 2 H, aromatic protons ortho to O— and ortho to cyclobutenyl ring), 6.91, 6.92, 6.94, 6.95 (dd, 2H, aromatic protons ortho to O— and meta to cyclobutenyl ring), 7.04, 7.07 (d, 2H, protons meta to CN), 7.17, 7.20, 7.23 (t, 1 H, proton para to CN). **13C-NMR (CDCl₃, ppm):** 28.91, 28.97 (benzocyclobutenyl CH₂), 108.82, 115.50, 119.52, 124.03, 133.93 (protonated aromatic carbons), 94.08 (nonprotonated aromatic carbon attached to CN), 142.37, 146.92 (nonprotonated aromatic carbons, cyclobutenyl), 153.77, 161.95 (nonprotonated aromatic carbons forming ether linkage) and 113.31 (CN-carbon resonance).

**4,4′-bis(4-Oxybenzocyclobuteny)benzophenone (BCB-EK)**

4-Trimethylsiloxybenzocyclobutene (0.9695 g, 0.0050 mol) was heated with p,p′-difluorobenzophenone (0.5216 g, 0.0024 mol) in the presence of 0.923 g (0.006 mol) of CsF and 10 mL anhydrous DMAC in the temperature range 125–130°C for 24 h under nitrogen. The cooled mixture was poured into 250-mL ice-cold water; the precipitated gummy, yellow solid was extracted into 300 mL CH₂Cl₂, the organic extract washed with 10% NaOH to remove excess 4-hydroxybenzocyclobutene, and then with water. The organic layer was dried over anhydrous MgSO₄, and the product after solvent evaporation solidified on standing (0.8 g, yield 80%). This was recrystallized from hot ethanol to an off-white crystalline solid and dried in vacuum overnight at acetone reflux (0.5 g, m.p., 102–103°C, DSC endotherm at 106°C).

Mass spectrum: (M⁺, m/z 418, 100% relative abundance). IR spectrum (cm⁻¹, KBr disc): 3065 (aromatic CH), 2957, 2926 (CH₃, 1651 (keto carbonyl), 1594 (aromatic C=C) and 1240 (arlyoxy stretch). **1H-NMR (CDCl₃, TMS, ppm):** 3.16 (s, 8 H, benzocyclobutenyl CH₂), 6.81–7.06 (m, 10 H, aromatic) and 7.74–7.78 (d, 4 H, aromatic). **13C-NMR (CDCl₃, ppm):** 29.11 (benzocyclobutenyl CH₂), 115.50, 116.60, 119.52, 124.12, 132.17 (protonated aromatic carbons), 131.90 (nonprotonated aromatic carbon attached to carbonyl), 141.83, 147.09 (nonprotonated aromatic carbons, cyclobutenyl), 154.67, 162.19 (nonprotonated aromatic carbons forming ether linkage), and 194.23 (carbonyl carbon resonance).

The DSC of the bis-BCB-terminated monomer showed a melting endotherm at 106°C and a homopolymerization exotherm at a maximum of 262°C. The Tg of the homopolymerized material, on DSC scan, was 201°C.

A second crop of glistening white crystals (0.10 g) was obtained from the ethanol filtrate. This was filtered and dried in vacuum overnight at 65°C, m.p. 107–108°C.

**ANAL. Calc. for C₂₅H₂₂O₃:** C, 83.23%; H, 5.29%.

**Found:** C, 83.42%; H, 5.03%.

**Mixture of 4-Oxybenzocyclobuteny-4'-fluoro-benzophenone and 4,4'-bis(4-Oxybenzocyclobuteny)benzophenone**

4,4′-Difluorobenzophenone (3.66 g, 16.77 mmol), 4-hydroxybenzocyclobutene (4.38 g, 36.46 mmol), anhydrous potassium carbonate (8.00 g, 57.88 mmol) and 50 mL of dry N-methylpyrrolidinone were placed in a 250-mL three-necked, round-bottomed flask, which was equipped with a reflux condenser with a nitrogen adaptor, a thermometer/adaptor, and a glass stopper. The initial heterogeneous mixture was heated slowly to 120°C under nitrogen and maintained at 120–125°C for 17 h. The resultant dark, heterogeneous reaction mixture was allowed to cool to room temperature and poured into a 1-liter beaker containing 30 mL of 12 N HCl and about 600 mL of ice water. White precipitates appeared initially, but upon standing at room temperature for about an hour, the precipitates became brown and gummy. The product was separated by careful filtration. The filtrate was colorless and had the characteristic smell of 4-hydroxybenzocyclobutene. The gummy residue was washed with water until the pH of the washing was neutral. It was then extracted with diethyl ether. About 150 mL of the diethyl ether extract was poured into a 500-mL separatory funnel and washed with aq NaOH (10 g in 200 mL of water) and then with water (2 × 200 mL). The ether phase was then dried over anhydrous magnesium sulfate, filtered directly into a 500-mL round-bottomed flask, and rotavapped, initially at room temperature and then at 70°C after all solvent had been removed. An amber oil was obtained and dried under vacuum overnight (yield: 5.58 g). Mass spectrum and liquid chromatographic results of the amber oil indicated the presence of mono- (M⁺, 318), and bi-end capped (M⁺, 418) products. Similar results were obtained when the reaction temperature was raised to
140°C and >10% excess of 4-hydroxybenzocyclobutene was used.

Mixture of 4-Oxybenzocyclobutanyl-4'-fluoro-diphenylsulfone and 4,4'-bis-(4-Oxybenzocyclobutanyl)diphenylsulfone

4,4'-Difluorodiphenylsulfone (3.15 g, 12.39 mmol), 4-hydroxybenzocyclobutene (3.00 g, 24.97 mmol), anhydrous potassium carbonate (6.90 g, 49.94 mmol) and 60 mL of dry N-methylpyrrolidone were placed in a 250-mL three-necked, round-bottomed flask, which was equipped with a reflux condenser with a nitrogen adaptor, a thermometer/adaptor, and a glass stopper. The initial heterogeneous mixture was heated slowly to 125°C under nitrogen and maintained at 125–130°C for 17 h. The resultant dark, heterogeneous reaction mixture was allowed to cool to room temperature and poured into a 1-liter beaker containing 50 mL of 12 N HCl and about 700 mL of ice water. White fluffy precipitates formed, but upon standing at room temperature for about 6 h, the precipitates densified into a light brown, gummy solid. The product was separated by careful filtration. The gummy residue was washed with aq. NaOH (5 g in 600 mL of water) and then with water until the pH of the washing was neutral. After drying overnight, the crude product was extracted with methylene chloride. About 200 mL of the methylene chloride was dried over anhydrous magnesium sulfate, filtered directly into a 500-mL round-bottomed flask, and rotavapped, initially at room temperature and then at 70°C after all solvent had been removed. An amber oil was obtained and dried under vacuum overnight (yield: 5.60 g). Mass spectrum and liquid chromatographic results of the amber oil indicated the presence of mono- (M+, 354), and bi-endcapped (M+, 454) products. Similar results were obtained when the reaction temperature was raised to 140°C and >10% excess of 4-hydroxybenzocyclobutene was used.

2,2-Bis[2-(4-fluorophenyl)benzoxazol-6-yl]hexafluoropropene

4-Fluorobenzoic acid (2.12 g, 15.13 mmol) and 2,2-bis-(3-amino-4-hydroxyphenyl)hexafluoropropene (2.55 g, 6.96 mmol) were placed via a ground-joint glass funnel in a 100-mL round-bottomed flask together with a stir-bar, followed by the addition of 15 mL of 1,2-dichlorobenzene. Trimethylsilyl polyphosphate (also known as polyphosphoric acid trimethylsilyl ester or PPSE, 17.21 g) was added subsequently, followed by rinsing with 15 mL of 1,2-dichlorobenzene. The
resultant light yellow, heterogeneous reaction mixture was heated to gentle reflux (~ 180°C) under nitrogen in an oil bath. The reaction mixture became completely homogeneous about 100°C, and was kept at reflux for about 12 h. The reaction mixture was allowed to cool to room temperature. The resultant clear, amber solution was then poured into a 1-liter beaker containing about 300 mL of methanol. Initially, only a clear, yellow solution resulted. Then, upon scratching the walls of the beaker, white microcrystalline solid began to form. The mixture was covered and allowed to stand at room temperature for about 4 h. Finally, the product was collected on a fritted filter funnel, washed with methanol, and air dried overnight. TLC of the crude product showed only one spot (eluted with 2:1 v/v CH₃Cl₂/hexane) (yield: 3.05 g). It was used in the subsequent preparation without further purification.

m.p. 185.6–187.5°C, 184.2°C (DSC), (lit. m.p. 195–197°C). Mass spectrum: M⁺, 574, 100% relative abundance. ¹H-NMR (CDCl₃, TMS, δ in ppm): 7.17, 7.18, 7.21, 7.24 (4H; proton ortho to fluorine); 7.37, 7.40 (2H; proton ortho to oxygen); 7.52, 7.55 (2H; proton para to nitrogen); 7.93 (2H; proton ortho to nitrogen); 8.21, 8.23, 8.23, 8.24, 8.25, 8.26 (4H; proton meta to fluorine).

2,2-Bis[2-(4-benzoclobutenyloxy-4-phenyl)benzoxazol-6-yl]hexafluoropropane (BCB-EBO)

2,2-Bis[2-(4-fluorophenyl)benzoxazol-6-yl]hexafluoropropane (1.50 g, 0.0026 moles) and 4-trimethylsiloxybenzoclobutene (1.22 g, 0.0063 mol, 2.4 mol relative to the benzoxazole) were heated to 140°C in presence of 1.22 g CsF (0.0080 mol, 3 mol relative to the benzoxazole) and 18 mL DMAc under a dry nitrogen atmosphere for 24 h. The solution obtained was deep brown in color. The solution was cooled and poured into 1 liter of ice water with stirring and an instant off-white precipitate was formed. The precipitate was filtered off using a house vacuum and washed several times with water. When still partially dry, the solid was dissolved in methylene chloride. The pale yellow solution was stirred two times with 10% NaOH solution and shaken thoroughly in a separatory funnel. Because of the emulsion formation, more solvent was added and the layers gradually separated. The organic layer (500 mL volume) was washed with water and dried over MgSO₄. Solvent removal in a rotary evaporator resulted in a viscous liquid that solidified to a glistening, foamy, off-white solid after vacuum was applied. Yield of the crude compound = 1.53 g (yield 75%). Mass spectrum showed a single component and confirmed the presence of the expected product (M⁺ 774, base peak). IR spectrum (KBr, cm⁻¹): 2977, 2938 (benzoclobutenyl CH₂ stretch), 1605 (mixed vibration, C=N and aromatic C=C), 1495 (aromatic ring), 1466 (benzoclobutenyl CH₂ deformation) and 1245 (aryloxy).

The crude solid in CH₂Cl₂ was passed through silica gel in a filter funnel, but the appearance of the recovered solid was still foamy. Attempted recrystallization from MeOH resulted in the formation of a hard light yellow solid that was dried in vacuum at 100°C overnight (1.1 g). HPLC using CH₂Cl₂ as the eluent showed a single component that eluted later than the starting benzoxazole compound.

ANAL. Calc. for C₄₄H₃₈F₆N₂O₄: C, 69.77%; H, 3.64%; N, 3.62%. Found: C, 69.58%; H, 3.53%; N, 3.49%.

IR spectrum (KBr, cm⁻¹): 3076 (aromatic CH), 2969, 2935 (benzoclobutenyl CH₂ stretch), 1604 (aromatic C=C and C=N), 1467(CH₂ deformation), and 1263 (aryloxy stretch). ¹H-NMR (CDCl₃, TMS, δ in ppm): 3.17 (8H, s, benzoclobutenyl CH₂); 6.84 (2H; aromatic H ortho to both the ether and cyclobutenyl ring); 6.92, 6.95 (2H; aromatic protons ortho to ether and meta to the cyclobutenyl ring); 7.04, 7.06 (4H; aromatic protons ortho to ether and meta to the oxazolyl ring); 7.07, 7.09 (2H; aromatic protons ortho to oxazolyl oxygen and meta to C(CF₃)₂); 7.34, 7.37 (2H; aromatic protons meta to ether and ortho to the cyclobutenyl ring); 7.51, 7.55 (2H; aromatic protons para to oxazolyl nitrogen and ortho to C(CF₃)₂); 7.90 (2H); aromatic protons ortho to both the oxazolyl ring and C(CF₃)₂); 8.18, 8.15 (4H; aromatic protons ortho to the oxazolyl ring and meta to ether). ¹C-NMR (CDCl₃, TMS): 29.09, 110.05, 115.53, 117.48, 119.50, 120.48, 122.15, 124.11, 126.93, 129.52, 130.15, 141.90, 142.19, 147.08, 150.60, 154.57, 161.94, 164.07 (for tentative assignment of the peaks, see Fig. 2). DSC analysis did not show any Tm, but a Tg (when rescanned after first heating to 125°C) was detected at 85°C and a BCB homopolymerization exotherm with the onset at 230°C and a maximum at 262°C.

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REFERENCES AND NOTES


