Polymer Bulletin 33, 385–388 (1994)

**Polymer Bulletin**

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# Benzocyclobutenes as crosslinking agents in synthetic polyolefins

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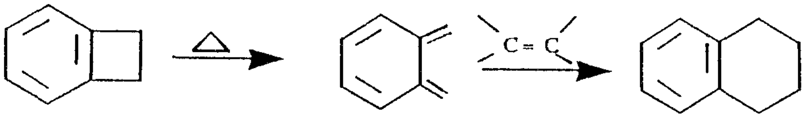
## Summary

4-Allylbenzocyclobutene was synthesized and copolymerized with 1-hexene and a non-conjugated diene, and the resulting terpolymer was cured thermally, under pressure, in the presence of carbon black. Mechanical properties of the crosslinked polymer containing allylbenzocyclobutene with two different dienes (5-methyl-1,4-hexadiene and 7-methyl-1,6-octadiene) were studied and are presented. Similar properties of a standard sulfur-cured polymer composed of 1-hexene and the two dienes were measured for comparison.

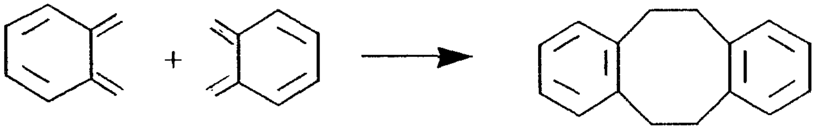
## Introduction

We have reported that benzocyclobutene (BCB) derivatives, incorporated in various molecules, oligomers, or polymers, can be used as crosslinking agents (2,3,4,5,6). In addition, BCB end-capped polystyrene was synthesized and thermally induced to form a graft copolymer with a polyolefin containing some pendant double bonds (7).

The four-membered strained ring on BCB opens thermally, around 200 °C, to give o-xylylene, which undergoes Diels-Alder reactions with suitable dienophiles:



In the absence of a dienophile, the o-xylylene group reacts with itself, to give:



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Crosslinking reactions occur thermally in polymers containing the BCB functionality according to the above methods.

## Experimental

Physical Methods. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian VXR 300 MHz spectrometer using $CDCl_3$ as the solvent; the residual proton signal at 7.24 ppm was used as the calibration reference for proton spectra, whereas the solvent triplet served as the calibration for the carbon spectra.

Gel permeation chromatography was carried out on a Waters Associates Model 150 C GPC instrument using THF as the solvent. A standard microgel column was used, and the polymer concentration was 2.5 mg/ml (0.25%).

Materials. Niobium pentachloride (Aldrich, 99.9%), titanium trichloride (Stauffer) and triethylaluminum (Aldrich, 1.0 M in hexanes) were used as received. 1,5-Hexadiyne (Wiley) and 5-chloro-1-pentyne (Aldrich) were distilled under reduced pressure and passed through a column of neutral alumina. 1-Hexene (Aldrich), 5-methyl-1,4-hexadiene (Wiley), and 7-methyl-1,6-octadiene (Biddle Sawyer) were distilled; the middle cuts were taken and passed through neutral alumina.

4-(3-Iodopropyl)benzocyclobutene was prepared by the cross trimerization reaction of 5-chloro-1-pentyne with 1,5-hexadiyne, followed by an iodine for chlorine exchange, according to literature methods (4,7,8). Allyl-BCB was synthesized by dehydroiodination of 4-(3-iodopropyl)BCB by treatment with potassium t-butoxide (4).

Terpolymers containing the desired ratios of 1-hexene, 5-methyl-1,4-hexadiene (MHD) or 7-methyl-1,6-octadiene (MOD) and allyl-BCB were prepared using $TiCl_3/AlEt_3$ as the catalyst in heptane solvent, under argon, according to literature methods (4,7).

Physical Testing Methods. Polymer samples that were to contain additives such as carbon black, sulfur, or accelerators were mixed an a Brabender Internal Mixer, and end-rolled 10 times on a two-roll rubber mill.

Polymers were cured in a heated hydraulic press at 670 psi. The optimum temperature and time for sulfur cures were determined on a Monsanto rheometer. Cure conditions for the BCB-containing polymers varied.

Tensile tests were carried out on an Instron Tensile Tester, according to ASTM guidelines for rubber, at room temperature, in air. Grip separation speed was 50 cm/min.

## Results and Discussion.

The terpolymers containing 2 and 3% allyl-BCB, 3% MHD or MOD, and 94 or 95% 1-hexene were characterized by $^1H$ and $^{13}C$ NMR spectroscopy. The proton spectra clearly exhibit the salient signals of the BCB group and the pendant diene. The aromatic ring of the BCB resonate between 6.5-7.0 ppm, and the strained four-membered ring protons show a sharp singlet at 3.1 ppm, which is characteristic for the BCB ring. The pendant double bond proton resonates at 5.2 ppm. The upfield hydrocarbon pattern is typical for a saturated carbon chain. The $^{13}$C NMR spectra show no multiplets, indicating a stereoregular structure for the polymer. This type of polymer has been shown to be stereoregular (head to tail) in other work (9).

GPC measurements showed that the molecular weight distributions are heavily skewed toward the high molecular weight chains. The weight-average MW's of the terpolymers are in the 970-990 x 10$^3$ range.

A control experiment was carried out on a copolymer composed of 1-hexene (99%) and 1% allyl-BCB (no diene), to determine if crosslinking could occur from BCB-BCB interactions in a carbon black-filled polymer. Crosslinking actually occurred to a measurable extent, showing that both Diels-Alder and BCB-BCB reactions can occur (see Table 1, sample D). Table 1 shows the results of the tests of the mechanical properties.

Table 1. Terpolymer Mechanical Properties

| Sample | Cure Time (min) | Ultimate Elongation (%) | Tensile Strength (psi) | Stress at 100% Strain (psi) | Stress 300% (psi) |
|---|---|---|---|---|---|
| A | 10 | 895 | 681 | 128 | 331 |
| A | 20 | 463 | 968 | 190 | 664 |
| A | 30 | 285 | 1318 | 392 | -- |
| B | 10 | 403 | 1154 | 186 | -- |
| B | 20 | 363 | 1315 | 230 | 1012 |
| B | 30 | 273 | 1354 | 364 | -- |
| C | 10 | 1600 | 212 | 111 | 151 |
| C | 20 | 1380 | 294 | 78 | 168 |
| C | 30 | 910 | 681 | 135 | 317 |
| C | 40 | 650 | 1031 | 154 | 443 |
| C | 60 | 551 | 1192 | 176 | 587 |
| D | 10 | >1800 | 204 | 84 | 130 |
| D | 20 | >1800 | 317 | 88 | 150 |
| D | 30 | 1355 | 532 | 98 | 227 |
| E | 45 | 400 | 1531 | 309 | 1141 |
| F | 45 | 308 | 1262 | 344 | -- |

All polymers cured at 210$^0$C at 670 psi pressure. A = 1-hexene/3% allyl-BCB/3% MOD; B = 1-hexene/3% allyl-BCB/3% MHD; C = 1-hexene/2% allyl-BCB/2% MHD; D = 1-hexene/1% allyl-BCB; E = 1-hexene/3% MHD/sulfur cured; F = 1-hexene/3% MOD/sulfur cured. All samples were loaded with 50 phr carbon black (Columbia Carbon, Raven 600).

The samples were loaded with carbon black to determine whether crosslinking would occur in that medium. In previous studies using 1,2-bis(benzocyclobutenyl)ethane in crosslinking reactions with SBR, it was found that crosslinking occurred readily for the pure gum, but was inhibited significantly in the carbon-black filled samples (3). This study shows that crosslinking occurs readily in the presence of carbon black.

Samples A and B (Table) consist of 3% BCB and 94% 1-hexene, differing only in the nature of the diene: sample A contains 3% MOD while B has 3% MHD. The MHD samples clearly show superior tensile strength, as do the corresponding sulfur-cured polymers (E and F). As the time of curing increases, ultimate elongation decreases because of greater crosslinking, and tensile strength and moduli increase. The mechanical properties of the 1-hexene/3% allyl-BCB/3% MHD terpolymer, cured through thermally induced Diels-Alder and BCB-BCB reactions to form new carbon-carbon bonds, are somewhat comparable to those of the sulfur-cured system. Whereas the terpolymers containing 2% allyl-BCB and 2% MHD show lower tensile strength and moduli than the corresponding 3% samples, at a 60 minute cure time, the mechanical properties become somewhat comparable. This indicates that longer cure times result in a greater number of crosslinks.

Swell test confirm this contention. The 3% allyl-BCB/3% MHD sample showed a 180 weight percent increase (toluene uptake) for the 30 minute cure, but a 339% weight increase for the 10 minute cure. In the 2% samples, the 10-minute cure resulted in a 436% weight increase, but the 60 minute cure gave a 221% weight increase, again, somewhat comparable to the 3% samples at 30 minute cure time. The weight percent increases of the samples varied inversely almost linearly with cure time.

Acknowledgement. The Ohio Department of Development, Thomas Edison Seed Grant, and AcroMed Corp. are gratefully acknowledged for support of this work.

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Received: 30 June 1994/Accepted: 10 July 1994