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Crosslinking of styrene-butadiene rubber with polyurethanes bicapped with benzyocyclobutene*

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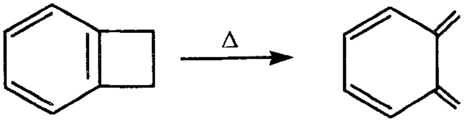
Summary

A polyurethane prepared from 1,9-nonanediol and toluene-2,4-diisocyanate with M_n=11,840, was capped on both ends in a reaction with 4-(benzocyclobutenyl)methanol. The polyurethane was used to crosslink styrene-butadiene rubber through Diels-Alder reactions on the benzocyclobutene functionality. The synthesis and characterization of 4-(benzocyclobutenyl)methanol, a molecule not reported previously, is presented. The crosslinking reaction was carried out on intimate mixtures of the telechelic polyurethane and SBR at elevated temperature and pressure. Various physical properties of the crosslinked material were studied.

Introduction

Benzocyclobutene (BCB) reacts thermally to open the strained 4-membered ring to o-xylylene, which readily undergoes Diels-Alder reactions to form new carbon-carbon bonds.



Many examples of monomers bicapped with benzocyclobutenes have been reported to undergo $4\pi + 2\pi$ reactions to give polymers. For example, various high polymers were prepared from bis(benzocyclobutene) monomers and oligomers and bis(maleimides)[1,2] Kirchhoff prepared oligomers containing both BCB and a dienophile, which reacted to form high molecular weight polymers.[3]

There are at least two methods of using benzocyclobutenes for crosslinking purposes: preparation of a copolymer containing a BCB monomer, and the use of a bifunctional BCB monomer or macromonomer with a polymer

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containing double bonds. In the former example, Bower and Farona used several ethynylbenzocyclobutenes as comonomers in polymers with various alkynes, and then subjected the polymers to crosslinking conditions.[4] Copolymers of vinylbenzocyclobutene and appropriate monomers were prepared and similarly crosslinked.[5] An example of the latter type utilized bis(benzocyclobutene) derivatives to crosslink EPDM's or copolymers based on 1,3-dienes.[6]

Recently, Wong synthesized block copolymers containing BCB, which reacted with maleic anhydride, modifying the pendant BCB molecules. The resulting polymer could then be crosslinked with primary diamines, or the anhydride could be hydrolyzed and the polymer crosslinked with a polyvalent metal ion.[7]

Grafting with polymers endcapped with BCB groups has only recently been reported. An aromatic polyester endcapped with a BCB group was grafted to a polyacrylate elastomer containing some carbon-carbon double bonds.[8]

Experimental

Materials and Solvents. N-butyllithium (Aldrich, 1 M in hexanes), chlorotrimethylsilane (Aldrich, 98%), pyridinium-p-toluenesulfonate (Aldrich, 98%), and cyclopentadienylcobalt dicarbonyl (Strem 95%) were used as received. Propargyl alcohol (Farchan, 97%) was distilled and stored over molecular sieves. Styrene-butadiene copolymer (Harwick, institute grade SBR-1502, $M_n=1x10^6$) was used as received. Toluene-2,4-diisocyanate (Eastman Kodak, reagent grade) was distilled under nitrogen and stored over molecular sieves, as was 1,9-nonanediol. Solvents were purified by standard methods.

Physical Methods. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Spectrograde $CDCl_3$, DMSO-d_6 and acetone-d_6 were used as solvents and also internal references.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on a DuPont 9900 Thermal Analyzer. All of the profiles were recorded under a nitrogen atmosphere.

Molecular weights were obtained by gel permeation chromatography using THF as the solvent.

Cure profiles were obtained from a Monsanto R-100 oscillating disk rheometer. A constant 3° arc was utilized for all the samples. Polymers were compression molded on a Dake Hydraulic Press at a pressure of 637 psi and at temperatures ranging from 160° to 200°C.

The stress-strain behavior of the polymer specimens was studied on an Instron tensile tester utilizing a crosshead speed of 5 cm/min.

Scanning electron microscopy was performed on an Ektascope 1. Elemental analyses were determined by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y.

Preparation and Characterization of Polyurethanes.

Several diols were used in the preparation of various polyurethanes (PU), to test their miscibilities with SBR 1502. Because of the great difference in the viscosities of the two component polymers, mechanical methods of blending failed to give an adequate level of dispersion, and precipitation from THF, a common solvent for both species, was employed. The blends were then stained by placing them over a 4% aqueous solution of OsO_4 for 20 minutes, causing the double bonds in the SBR to be stained blue. These samples were then visually inspected for gross phase separation at a magnification of 400x. It was concluded that the PU prepared from 1,9-nonanediol and toluene-2,4-diisocyanate was miscible over a sufficient range of compositions to be utilized in the crosslinking studies.

A dry, round bottom flask was charged with the desired amounts of THF, 1,9-nonanediol, and 4-(benzocyclobutenyl)methanol, and purged with dry nitrogen for 60 minutes. Toluene-2,4-diisocyanate was added and the reaction mixture brought to reflux. A catalytic amount of triethylamine was added and the mixture was refluxed for 12 h. The polymer was precipitated from a 1:1 mixture of methanol and water, and dried in a vacuum oven for 24 h at 65°C. The resulting material was crushed into a fine powder and continuously extracted in a Soxhlet apparatus with chloroform for 24 h. After extraction, the PU was dried in a vacuum oven for 24 h at 100°C.

Two samples were prepared such that in one case, the stoichiometric imbalance was 0.94 and in another, 0.80. Both polymers were obtained in final yields of 85-90%. Molecular weight determinations were carried out by gel permeation chromatography. Approximately 2.5 mg/ml polymer solutions were analyzed at a flow rate of 1 ml/min using UV and RI detectors. Elution counts were calibrated with polystyrene and polyisobutylene standards. In the case where the stoichiometric imbalance was 0.94, M_n of the PU was 11,840; where the stoichiometric imbalance was 0.80, M_n of the PU was 3,650.

Preparation of 4-(5-trimethylsilylbenzocyclobutenyl)methanol. Propargyl alcohol was converted to tetrahydro-2-(2-propynyloxy)-2H-pyran by reaction with 3,4-dihydro-2H-pyran in the presence of pyridinium-p-toluenesulfonate, according to literature methods.[9]. This product was converted to tetrahydro-2-(3-trimethylsilyl-2-propynyloxy)-2H-pyran in a reaction with n-butyllithium and chlorotrimethylsilane.[10] The resulting product was cyclotrimerized with 1,5-hexadiyne in the presence of $CpCo(CO)_2$ in a procedure outlined by Vollhardt.[11] A dry, round bottom flask was charged with 500 ml of n-octane and 14.2 g (50 mmol) of tetrahydro-2-(3-trimethylsilyl-2-propynyloxy)-2H-pyran and purged with dry nitrogen for 60 min. The contents of the flask were heated to 125°C and 0.2 ml of $CpCo(CO)_2$ was added. Then 3.49 g (2.75 ml, 25 mmol) of 1,5-hexadiyne diluted to 50 ml with n-octane was added via a syringe pump at 0.075 ml/min. After the addition was complete, the reaction mixture was refluxed for 24 h. Celite was added, the mixture was filtered, and the crude product was concentrated on a rotary evaporator. The pyran group was removed by diluting the crude product with a solution of glacial acetic acid, THF, and water (3:1:1, v/v). The reaction mixture was stirred for 12 h at 50°C, extracted with water and methylene chloride, and the organic extracts were collected. The combined methylene chloride extracts were washed with 10% NaOH, 10% $NaHCO_3$ and saturated NaCl solution, dried over $MgSO_4$, and concentrated on a rotary evaporator. The pure product was obtained as a yellow oil by distillation under reduced pressure (142°C, 0.1 mm). The yield was 6.43 g, or 71%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 9H, $Si(CH_3)_3$); 2.97 (s, 4H, strained ring on BCB); 3.43 (s, 1H, -OH); 4.54 (s, 2H, $-CH_2-OH$); 6.89 (s, 1H, aromatic) 7.17 (s, 1H, aromatic). The singlet at 3.43 ppm was identified as the hydroxyl proton by deuterium exchange. ^{13}C NMR (300 MHz, $CDCl_3$: ppm, 0.1, 28.9, 64.4, 122.0, 128.1, 136.0, 144.2, 145.3, 147.6. Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.8; H, 8.8; O, 7.8; Si, 13.6%. Found: C, 69.5; H, 8.9; O, 7.9; Si, 14.1%.

Preparation of 4-(benzocyclobutenyl)methanol. A round bottom flask was charged with 25 ml of a 10% aqueous solution of HF and 4.2 g (15 mmol) of 4-(5-trimethylsilylbenzocyclobutenyl)methanol and the reaction mixture heated to 80°C. The reaction was followed by thin layer chromatography. When the presence of the starting material could no longer be detected (~6 h) the reaction mixture was extracted with methylene chloride and the organic extracts collected. The combined organic extracts were washed with 10% $NaHCO_3$ and saturated NaCl solution, dried over $MgSO_4$, and concentrated on a rotary evaporator. The final product was obtained as a white solid (m.p.=45°C) by sublimation (126°C, 0.1 mm). The yield was 0.836 g, or 54%. ^1H NMR (300 MHz, $CDCl_3$): δ 315 (s, 4H, strained ring on BCB); 4.62 (s, 2H, $-CH_2-OH$); 7.02 (d, J=8.1 Hz, 2H, aromatic); 7.07 (s, 1H, aromatic); 7.17 (d, J=7.9 Hz 1H, aromatic). ^{13}C NMR (300 MHz, $CDCl_3$): 29.5, 66.2, 122.0, 122.8, 126.3, 139.8, 145.9, 146.5. Anal. Calcd for $C_9H_{10}O$: C, 80.6; H, 7.4; O, 11.9%. Found: C, 80.1; H, 7.5; O, 12.4%

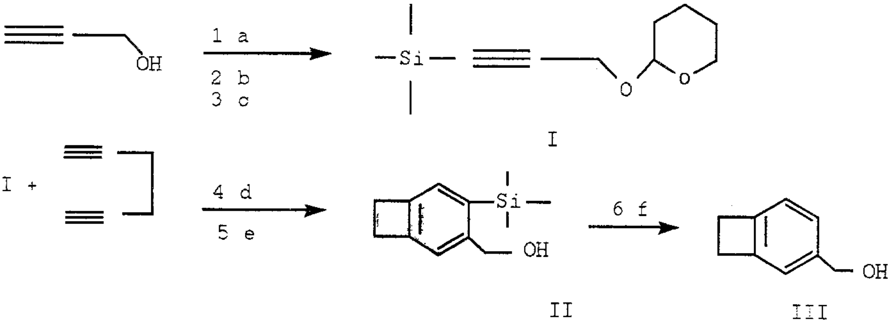
Results and Discussion

The key molecule in the preparation of the crosslinking polyurethanes is 4-BCB-methanol, which is herein reported for the first time. Although the catalyst niobium(V) chloride gives superior yields of cross-trimerized products of 1,5-hexadieyne with acetylenes to give benzocyclobutenes than $CpCo(CO)_2$,[12] the Nb catalyst is not active in the presence of heteroatoms. Therefore, the cobalt catalyst, whose versatility in organic synthesis was shown by Vollhardt,[13] was used.

Initial attempts to cross-trimerize 1,5-hexadiyne with propargyl alcohol or methylpropiolate led only to very poor yields of the desired product, because the monoalkynes readily cyclotrimerize with themselves. Therefore a bulky protecting group, 3,4-dihydro-2H-pyran, was used on the alcoholic group, and a trimethylsilyl group was substituted on the acetylenic end.

This product, with sterically hindering groups on both sides of the triple bond, did not undergo homocyclotrimerization reactions in the presence of $CpCo(CO)_2$. The bulky ether, however, cross-trimerized with 1,5-hexadiyne to give the benzocyclobutene derivative, which after removal of the pyran group, gave 4-(5-trimethylsilylbenzocyclobutenyl)methanol. Figure 1 shows the salient synthetic steps. The trimethylsilyl group can be removed with a 10% solution of HF; the product was obtained in 54% yield. The compounds II and III were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

The polyurethane of M_n 11,840 was bicapped with BCB-methanol, but spectroscopic evidence for the BCB groups was inconclusive, due to the relatively high molecular weight of the polymer. Similarly, when the PU was bicapped with BCB-methanol containing the trimethylsilyl group (compound II), spectroscopic evidence for the presence of the BCB group was indistinct, although analysis showed the presence of Si. Therefore, an oligomer of the polyurethane of M_n=3650 was prepared and bicapped



a. Methylene chloride, PPTS, dihydropyran
b. n-BuLi, THF, -78°C
c. Trimethylchlorosilane
d. $CpCo(CO)_2$, n-octane, 129°C
e. H_2O, THF, acetic acid
f. 10% HF

Figure 1. Synthesis of 4-(benzocyclobutenyl)methanol

with compound II. The NMR spectrum of this material clearly showed the methyl signals of the trimethylsilyl groups in proper integration with respect to the nonane methylenes of the oligomer. Since the procedure for bicapping was the same for both polyurethanes, it was assumed that the polymer of M_n=11,840 was also bicapped.

Before any crosslinking studies were carried out, it was necessary to investigate whether SBR 1502 and the polyurethane would be thermally stable in the temperature range needed to effect ring opening.

TGA studies were carried out on the polymers separately, utilizing both scanning and isothermal methods. The polyurethane exhibited significant weight loss beginning at 275°C. At a constant temperature of 200°C, the polyurethane showed a 6% weight loss after 60 minutes. The SBR 1502 showed a 2% weight loss at 200°C, but was then stable up to 375°C, after which degradation occurred. At a constant temperature of 200°C the SBR 1502 exhibited a 4.5% weight loss after 60 minutes. From these data, it was determined that both polymers were sufficiently thermally stable to be processed.

Samples of mixtures of SBR 1502 and PU (M_n=11,840) were prepared at PU loadings of 5, 10, and 20%, and subjected to crosslinking conditions. Nitrogen analysis was performed to determine the level of PU incorporation in the final material. The results are presented in Table 1.

Table 1. Nitrogen Analysis of SBR 1502 Crosslinked with Polyurethane

Loading, %	% N (calcd)	% N (found)	% PU
0	0	0	0
5	0.42	0.47	5.0
10	0.84	0.86	10.0
20	1.68	1.44	17.1
100	8.4	8.5	-

The analytical data indicate that loadings of PU up to 10% are fully incorporated into SBR 1502, while the 20% loading is approaching the upper limit of miscibility. The loss may be caused by PU macrophase separation, thus preventing the BCB from reacting with the double bonds of SBR 1502 by occlusion of the chain ends in the macrophase.

Stress/strain studies and percent volume swell were performed on the samples. The data are presented in Table 2. Shown for comparison is sulfur-cured SBR 1502, which was vulcanized as follows: 100 parts SBR 1502, 1.5 sulfur (RM-104), 0.75 tetramethylthiuram disulfide accelerator, 2.0 stearic acid and 5.0 zinc oxide; 22 minute cure time, 160°C.

Table 2. Physical test results of Crosslinked Material

Loading of PU, %	Tensile, psi	M @ 300%, psi	Elongation	% Volume Swell %
5	234	131	534	794
10	236	144	564	711
20	153	147	353	660
S-Cured SBR	405	212	317	440

No conclusions can be drawn from the limited data in Table 2. However, comparing the S-cured SBR with the 20% PU material (actually 17% according to N analysis), the S-cured material contains 50% more crosslinks (swell data), and shows a modulus 44% greater. It is clear that BCB-capped PU can crosslink SBR. Further studies on the extent of crosslinking with the bicapped polymers are required.

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