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Copolymers of substituted acetylenes and ethynylbenzocyclobutenes

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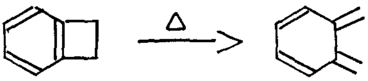
Summary

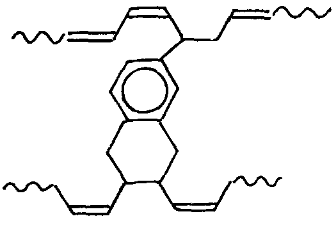
Random coploymers of substituted acetylenes with various amounts of similarly substituted ethynylbenzocyclobutenes were synthesized: phenylacetylene/ethynylbenzocyclobutene; 1-phenylpropyne/1-(4-benzocyclobutenyl)-1-propyne; and 1-chloro-2-phenylacetylene/1-chloro-2-benzocyclobutenylacetylene. Successful cures were obtained only for the chloro-substituted alkynes; the other two coploymers partly degraded under the elevated temperatures and pressures of the curing conditions.

Introduction

Benzocyclobutene (BCB) has been well represented in the chemical literature because of theoretical interest in the effect of the strained ring on the aromaticity of the benzene ring [1], the challenge of efficient synthesis of BCB and its derivatives [2], and in particular, the thermal reactivity and chemistry of the strained ring [3], which is known to open thermally to o-xylylene and participate in reactions (e.g., Diels-Alder) to form new carbon-carbon bonds.



Diels-Alder reactions are of particular interest in promoting cures of polyalkynes with BCB derivatives. Two methods are possible: reaction of a homopolyalkyne with a bifunctional BCB molecule (e.g., 1,2-bis(benzocyclobutenyl)ethane and synthesis of copolymers consisting of an alkyne monomer and an ethynyl-BCB molecule of similar structure to that of the alkyne monomer. In this work, several copolymers of alkyne and ethynyl-BCB monomers were synthesized, characterized, and subjected to thermal crosslinking reactions. To the best of our knowledge, there have not been any reports of attempted BCB cures with polyconjugated backbones. A section of a polyconjugated polymer with a Diels-Alder crosslink is shown below.



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Experimental

Starting materials and solvents. Cuprous iodide and triphenylphosphine were purchased from Fisher and used as received. Toluene (Fisher) was refluxed over calcium hydride and distilled under nitrogen. Triethylamine (Fisher) was distilled from phenylisocyanate before used. Lithium amide, niobium pentachloride, tungsten hexachloride, potassium carbonate and tetraphenyltin were obtained from Aldrich and used as received. Phenylacetylene (Aldrich) was vacuum distilled from calcium hydride and p-toluenesulfonyl chloride was recrystallized from pentane before used. Dichlorobis(triphenylphosphine)palladium(II) was purchased from Strem and used as received. 1-Phenyl-1-propyne was purchased from Farchan and vacuum distilled from calcium hydride, and trimethylsilylacetylene (Farchan) was used as received. 4-Bromobenzocyclobutene was a gift from Dow Chemical Company and used as received.

Physical methods. Infrared spectra were recorded on a a BioRad FTS-7 spectrophotometer; liquid and resinous samples were recorded neat between NaCl plates, and solids were sampled as either KBr pellets or neat-cast films. Nuclear magnetic resonance (^{1}H and ^{13}C) spectra were recorded on a Varian Gemini 300 MHz spectrometer, using $CDCl_3$ as the solvent. For proton spectra, the residual proton signal at 7.24 ppm was used to calibrate the spectra, and the solvent carbon triplet was the reference for ^{13}C spectra. ^{13}C NMR spectra of solid samples were taken on a Chemagnetic 200 MHz spectrophotometer. Gel permeation chromatographic analyses were performed on a Water Associates Model 150C GPC using THF as the solvent. A standard column of microstyryl gel was used. Six column sets of pore size 10^6, 10^5, 10^4, 10^3, 500 and 100 Å were used to determine the molecular weights of the polymers. Approximately 0.25% polymer solutions in THF were used at a flow rate of 1 ml/ min at 30°C. Elution counts were calibrated by polystyrene standards. Mass spectra were recorded on a VG Auto Spec tandem mass spectrometer. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were conducted on a DuPont 9900 instrument.

General experimental conditions. The glassware used for reactions was washed in Alconox wash water, rinsed with hot water and acetone, and dried in an oven. Magnetic stirring was employed in all reactions except those involving lithium amide, where a stir rod driven by a motor was used. All reactions were carried out under an atmosphere of dry nitrogen. Cure studies were performed on a Rake Heat Press with a 5 inch diameter ram, at 1,025 psi and 190°C for 10 minutes. Samples were then tested for solubility in toluene and carbon tetrachloride after cure. Swell tests were done in toluene.

Synthesis of monomers and polymers

4-Ethynylbenzocyclobutene. The method of Kirchhoff, et al., [4] was used to prepare 1-trimethylsilyl-2-(4-benzocyclobutenyl)acetylene. It was desilylated by treatment with a saturated solution of K_2CO_3 in methanol, and after the methanol was removed, an aqueous solution of K_2CO_3 was added. The organic compound was extracted with methylene chloride, dried over magnesium sulfate, and the solvent was removed by rotary evaporation. Distillation gave 6.5 g (93% yield) of pure product, as determined by the absence of trimethylsilyl signals in the ^{1}H NMR spectum. ^{1}H NMR: δ, ppm. 3.1 (s, 1H, acetylenic); 3.2 (m, 4H, methylenes of strained ring); 7.2 (s, 1H, aryl C-3); 7.0 and 7.4 (m, 2H, aryl C-5 and C-6).

1-Chloro-2-phenylacetylene. The monomer was prepared according to the method of Brandsma [5] except that p-toluenesulfonyl chloride was used as the chlorinating agent. The NMR spectrum of the product showed only the presence of aryl protons. MS; 126, 138, m/e.

1-Chloro-2-(4-benzocyclobutenyl)acetylene. This was synthesized in a manner similar to that of 1-chloro-2-phenylacetylene, and the product was obtained in 30% yield. ^{1}H NMR: δ, ppm: 3.2 (m, 4H, CH_2); 6.9-7.4 (m, 3H, aryl). MS: 182, m/e.

1-(4-Benzocyclobutenyl)-1-propyne. To a three necked, 500 ml, round bottom flask equipped with a dry ice/acetone condenser, gas adapter, stir bar and septum was added 35 ml of triethylamine, 0.012 g (0.017 mmol) of dichlorobis(triphenylphosphine)palladium(II), 0.067 g (0.255 mmol) of triphenylphosphine, 0.014 g (0.074 mmol) of cuprous iodide, and 5.0 g (27 mmol) of 4-bromobenzocyclobutene. Propyne was bubbled into the mixture through a needle while the temperature was raised to 75°C using an oil bath. Propyne was added periodically over a 12 h period. The system was allowed to cool to room temperature and the white precipitate was removed by suction filtration. The solvent was removed by rotary evaporation, and the resulting oil was washed with 10% HCl solution and extracted with methylene chloride. The solution was dried over magnesium sulfate, the liquid was decanted, and the solvent removed on a rotary evaporator. Vacuum distillation yielded 4 ml of crude product, 20% of which was shown by ^{1}H NMR to be the desired product, and the remainder was 4-bromobenzocyclobutene. This mixture was used without further purification; 4-bromobenzocyclobutene was assumed to be inert to polymerization conditions.

Homopolymerization of phenylacetylene and copolymerization of phenylacetylene and 4-ethynylbenzocyclobutene. These reactions were carried out according to the method of Masuda, et al., [6] using WCl_6 and $Sn(C_6H_5)_4$ as the catalyst. The reactions were carried out for 24 h at room temperature. For the copolymerization reactions, volume loadings of 2, 4, 6 and 8% ethynyl-benzocyclobutene were run side by side. The polymers were precipitated in methanol, filtered, dried, and purified by chromatography on an alumina column with CCl_4. A quantitative yield of polymer was obtained in all cases.

Homopolymerization of 1-chloro-2-phenylacetylene and copolymerization of 1-chloro-2-phenylacetylene and 1-chloro-2-benzocyclobutenylacetylene. These polymerizations were carried out in the manner described by Masuda, et al., [7] using $Mo(CO)_6/CCl_4$ under 335 nm irradiation. The reaction mixture after irradiation of the catalyst, was stirred for 24 h, followed by precipitation of the polymer in excess methanol. Copolymers were synthesized with 6, 10, and 25% loadings of 1-chloro-2-benzocyclobutenylacetylene. The yield of the homopolymer was 70% and those for the 6, 10 and 25% loadings were 65, 60, and 50%, respectively.

Homopolymerization of 1-phenylpropyne and copolymerization of 1-phenylpropyne and 1-(4-benzocyclobutenyl)-1-propyne. These reactions were carried out according to the method reported by Masuda, et al., [8] using $NbCl_5/Sn(C_6H_5)_4$ as the catalyst. The reactions were carried out at 80°C for 24 h. The copolymer was made from 94% 1-phenylpropyne and 9% benzocyclobutenylpropyne. The yield of homopolymer was 80% while that of the copolymer was 65%.

Results and Discussion

The homopolymers were synthesized in order to compare various properties with those of the copolymers containing a benzocyclobutene group. The ^{1}H NMR spectra are sensitive indicators to determine whether copolymerization was achieved or not. The methylene groups of the strained 4-member ring resonate at about 3.2 ppm, which is a unique signal for the polymers investigated. In the ^{1}H NMR spectra of all copolymers prepared, the signal at 3.2 ppm is obvious, showing clearly the incorporation of the benzocyclobutenyl monomers. Infrared data also show the presence of the methylene groups; medium intensity absorbances around 2900 cm^{-1} show the presence of the cyclobutenyl group in the copolymers.

Table 1 shows molecular weight data of the polymers and copolymers prepared in this work.

Table 1. Homopolymer and Copolymer Molecular Weights

Sample	Physical Form	$M_w x10^3$	Mw/Mn
PPA	orange powder	11.7	1.99
PPA/EBCB (2%)	orange powder	12.7	2.02
PPA/EBCB (4%)	orange powder	14.1	2.16
PPA/EBCB (8%)	orange powder	23.6	1.84
PCPA	yellow film	110.6	2.20
PCPA/CBCBA (6%)	yellow film	261.8	5.49
PCPA/CBCBA (10%)	yellow film	137.2	6.32
PCPA/CBCBA (25%)	yellow film	64.6	22.7
PPP	white powder	55.8	1.91
PPP/BCBP	white powder	89.7	2.10

Abbreviations: PPA = polyphenylacetylene; EBCB = ethynylbenzocyclobutene; PCPA = poly(chlorophenylacetylene); CBCBA = chlorobenzocyclobutenylacetylene; PPP = poly(phenylpropyne); BCBP = benzocyclobutenylpropyne.

Polyphenylacetylene/ethynylbenzocyclobutene. The thermal stability of polyphenylacetylene is poor. Whereas the DSC trace shows no apparent melting point below 230°C, the TGA curve shows a 17% weight loss below 230°C. An attempted cure of the 2% copolymer resulted in a soluble, copper-brown material which showed a molecule weight of 6,000, about half of that of the original molecular weight. Percec has demonstrated that chain scission reactions occur above 130°C in cis-polyphenylacetylene. [9] It is reasonable to suppose that a similar phenomenon occurs here around 200°C. Polymer degradation was also noted in the attempted crosslinking of the 8% copolymer.

Polyphenylpropyne/benzocyclobutenylpropyne. The pressure-thermal cure of this copolymer gave a white, elastic material that did not hold its shape in hot toluene. While some crosslinking had occurred, a true cure was not achieved.

Poly(1-chloro-2-phenylacetylene)/1-chloro-2-benzocyclobutenylacetylene. The NMR spectrum of the copolymer containing 10% benzocyclobutene monomer showed an aryl:BCB strained ring proton ratio of 15.5, somewhat higher than 12, which is the ratio expected for 10% incorporation of BCB monomer. This indicated that only 7.8% of 1-chloro-2-benzocyclobutene is actually incorporated in the polymer.

This copolymer was successfully cured, becoming insoluble but brittle, and incurring a color change from yellow to deep red. Whereas the DSC plot of the copolymer showed an exotherm starting at 221°C with a maximum at 266°C, representing the crosslinking reaction, that of the post-cure copolymer showed only a sharp exotherm at 325°C and the TGA showed no weight loss below 230°C and only about 8% weight loss at 325°C. This represents good thermal stability for a polyconjugated polymer, in contrast to polyphenylacetylene or polyphenylpropyne. Swell tests of the cured copolymers showed less than 50% solvent uptake, indicating a high crosslinking density.

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