Polymer Bulletin 40, 9–13 (1998)

Polymer Bulletin

Photolytic generation of an *o*-quinodimethane derivative and its reactions with unsaturated polymers

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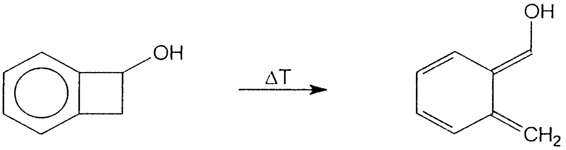
Received: 19 September 1997/Accepted: 24 November 1997

Summary

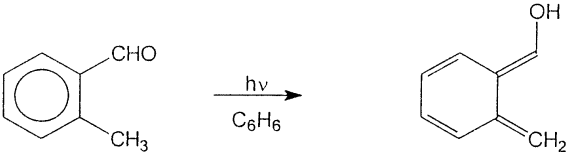
Polybutadiene was treated with o-tolualdehyde under UV irradiation to produce random copolymers through Diels-Alder reactions on the backbone double bonds. The physical properties of the polymer products change as more of the aldehyde attaches to it. The copolymers were characterized by NMR spectroscopy. A bifunctional o-tolualdehyde was synthesized and used as a crosslinking agent.

Introduction

In contrast to benzocyclobutene (BCB) which opens thermally to o-quinodimethane (QDM) above 200°C, 1-hydroxybenzocyclobutene opens to 1-hydroxy-o-quinodimethane under much lower temperatures.



It was found that the QDM generated from 1-hydroxybenzocyclobutene added to multiple bonds, including those containing heteroatoms (1,2). Griesbeck and Stadtmuller reported that o-tolualdehyde, under the influence of UV light, was converted to 1-hydroxy-o-quinodimethane, exactly the same species as that obtained from the thermal opening of 1-hydroxybenzocyclobutene (3).



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Since 1-hydroxy-QDM added readily to double bonds, and since o-tolualdehyde gives 1-hydroxy-QDM upon irradiation, it seemed plausible that similar reactions to the former would occur with the latter system. The results of the reaction of o-tolualdehyde with polybutadiene under the influence of UV light is the subject of this research report.

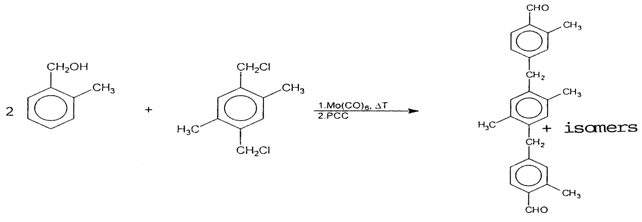
Experimental

Materials and Solvents. Polybutadiene (phenyl terminated, Mn = 1800, 45% 1,2, 10% trans-1,4, 5% cis-1,4), o-tolualdehyde, 2-methylbenzyl alcohol, and 2-pentene were purchased from Aldrich and used as received. Molybdenum hexacarbonyl (Strem), and 2,5-bis(chloromethyl)-p-xylene (Lancaster) were used without further purification. Solvents were purified by standard methods.

Physical Methods. ^{1}H NMR spectra were recorded on a Bruker DRX nuclear magnetic spectrometer, using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. Gas chromatography-mass spectrometry (GC-MS) data were gathered on a Hewlett-Packard 5890 Series II and HP 5971 Series mass selective detector. Benzene was used as the solvent. Infrared spectra were taken on a MIDAC M series FTIR spectrophotometer or a MIDAC Prospect FTIR spectrophotometer. The samples were held either between NaCl plates or as KBr pellets. The irradiation experiments were carried out in a Rayonet Photochemical Reactor using RPR 3000 Å lamps.

Irradiation Method. All irradiation experiments were carried out by the following general procedure. The substrates to be irradiated were dissolved in benzene and placed in a 20 x 150 mm Pyrex test tube containing a magnetic stirrer. Nitrogen gas was bubbled through the solution for 20 min to purge the system of oxygen. A cold finger was placed in the test tube and sealed with parafilm. Water was run through the cold finger, after passing it through an ice-water bath, so that the reaction mixture could be maintained at 10-15°C throughout the experiment. The reaction solution was irradiated for about 24 hr, the solvent removed by rotary evaporation, and the product obtained was examined and characterized by various physical methods.

Preparation of a Bis-o-tolualdehyde. To a three-necked, 100 mL flask was added 2.5 g (20 mmol) of 2-methylbenzyl alcohol, and 1.5 g (7 mmol) of 2,5-bis(chloromethyl)-p-xylene. The system was purged of oxygen by bubbling nitrogen through it for 20 min, and $Mo(CO)_6$ (0.010 g, 0.027 mmol) was added as the Friedel-Crafts catalyst (4). The reaction mixture was heated to 110°C with magnetic stirring until the evolution of HCl ceased (about 8 hr). The crude product was dissolved in a minimum amount of methylene chloride, and added all at once to 20 mL of a methylene chloride solution containing 2.5 g of pyridinium chlorochromate. The oxidation reaction was allowed to continue for 2 hr, and then stopped by the addition of 50 mL of anhydrous ether. The volume of the ether solvent was reduced under rotary evaporation, and the product was purified by passing it through a Florisil column. The product was characterized by NMR and IR spectroscopy. The reactions to prepare the bis-o-tolualdehyde are shown below.



Irradiation of o-Tolualdehyde and Polybutadiene. Polybutadiene (1 g, 0.2 mmol) was dissolved in 20 mL of benzene. Several experiments were carried out using varying amounts of o-tolualdehyde: 1,2,3, and 5 mL (8.2, 16, 25 and 41 mmol, respectively). The reaction solutions were irradiated for 24 hr, and methanol was added to the solution until a precipitate formed. The supernatant liquid was decanted, and the product was redissolved in benzene and precipitated with methanol. This process was repeated three times, and the product was dried by rotary evaporation. The products from these reactions were elastomeric solids of varying melting points, depending on the amount of o-tolualdehyde used. The polymers were characterized by NMR and IR spectroscopy.

Crosslinking of Polybutadiene with the Bis-o-tolualdehyde. The his-o-tolualdehyde obtained from the Friedel-Crafts reaction was dissolved in the minimum amount of benzene and added to a solution of 1 g of polybutadiene dissolved in 10 mL of benzene. The solution was irradiated as described above, and a small amount of material precipitated from solution. The precipitate was isolated by filtration, and 0.01 g was recovered. The material, which was not soluble in common organic solvents, was characterized by IR spectroscopy.

Results and Discussion

Several control reactions were carried out to determine whether the changes in polybutadiene were the result of a Diels-Alder reaction with o-tolualdehyde, or arose from other reactions. In one reaction, o-tolualdehyde was irradiated with itself. The resulting product was a viscous liquid, which, by gas chromatographic measurements, contained at least 10 products. This viscous liquid was present in all reactions where o-tolualdehyde was used as a reactant. In order to show that a Diels-Alder reaction was feasible with polybutadiene, o-tolualdehyde was irradiated in the presence ofa mixture of cis and trans 2-pentene. The resulting viscous liquid product was subjected to GC-MS, and, besides the products arising from the reaction of o-tolualdehyde with itself, two products separated by GC showed a m/e ratio of 190 in the mass spectrum. These products of molecular weight 190 are the expected isomers of a Diels-Alder reaction of o-tolualdehyde with 2-pentene. We also irradiated 2-pentene with itself, and polybutadiene with itself (no other reactant). In both cases, the starting material was isolated unchanged, as shown by NMR spectroscopy. Therefore, all photolytic reactions of polybutadiene with o-tolualdehyde proceed with an attack of the aldehyde on the polymer.

Photolytic reactions of 1,2,3, and 5 ml of o-tolualdehyde, each with 1 g of polybutadiene resulted in a change in physical properties of the polymer. Whereas polybutadiene used in this work is a viscous liquid, the products, after reaction with o-tolualdehyde ranged from a tacky, elastomeric solid to a soft elastomeric solid, depending on the amount of the aldehyde used. Furthermore, the melting points of the polymers increased with increasing amounts of the aldehyde used in the reaction. Table 1 shows these changes in physical properties.

Table 1. **Changes in the Physical Properties of Polybutadiene**

o-Tolualdehyde (mL)	Physical Appearance	MP,°C
0	viscous liquid	---
1	tacky elastomeric solid	30-40
2	tacky elastomeric solid	43-60
3	soft elastomeric solid	52-70
5	soft elastomeric solid	65-78

All reactions were carried out using 1 g of polybutadiene_

Proton NMR spectra of the products show changes in the aliphatic:olefinic hydrogen integrated intensities. Clearly, the aliphatic:olefinic proton ratio increase with increasing amounts of o-tolualdehyde used in the reaction. Since each addition of the aldehyde to a double bond of the polymer results in the gain of 5 aliphatic protons and the loss of 2 olefinic protons, simple calculations allow us to estimate the number of reactions that occur per backbone of the polymer. Whereas polybutadiene shows an aliphatic:olefinic hydrogen ratio of 2: 1, the same ratio after reaction with 1.0 mL of the aldehyde was 2.49:1. This amounts to an average of 3.2 attachments per polymer chain. Therefore, 1.78 mmol of o-tolualdehyde reacted with the polymer, or 20% of the initial amount used. Table 2 shows the aliphatic:olefinic hydrogen ratios for the reactions.

Table 2. **Aliphatic:Olefinic Hydrogen Ratios**

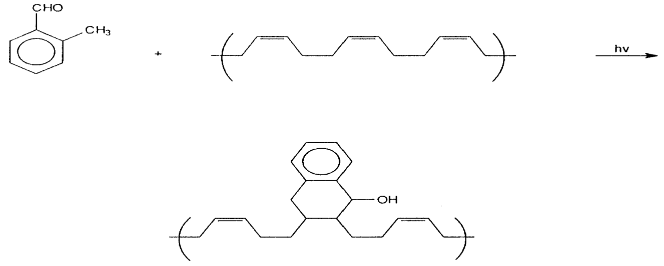
o-Tolualdehyde (mL)	Aliphatic:Olefinic Hydrogen Ratio	# Molecules Attached	% Reacted
0.0	2.07:1	0	--
1.0	2.49:1	3.2	20.0
3.0	2.84:1	5.2	11.6
5.0	2.88:1	5.4	7.3

All reactions were carried out using 1 g ofpolybutadiene.

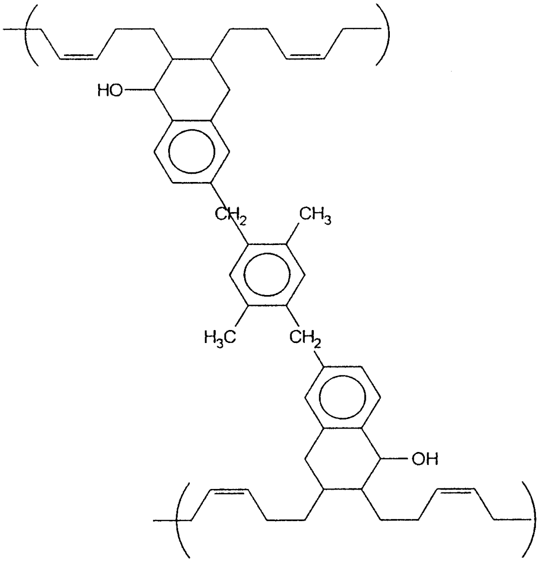
As can be seen in Table 2, it is evident that as more o-tolualdehyde is added as a reactant, more of it attaches to polybutadiene, but the efficiency of the reaction falls off considerably, dropping from 20% for 1 mL to 7.3% for 5 mL of o-tolualdehyde. Apparently, there is a limited amount of the aldehyde which can attach to the polymer.

It should also be mentioned that the hydroxide group on the six-membered ring of the product, which was not detected in the NMR spectrum of the polymers, is clearly observed at 3385 cm^{-1} in the infrared spectra of all the product polymers.

It is clear that o-tolualdehyde reacts with the double bonds of polybutadiene under photolytic conditions, as evidenced by the change in physical properties and the aliphatic:olefinic hydrogen ratios. Since the substrate polymer contains 45% vinyl (from 1,2 polymerization), 10% trans, and 5% cis double bonds, the question arises as to which is the preferred reaction site. This can be determined by comparing the ratios of the three different kinds of olefinic hydrogens. Whereas the total olefinic hydrogen integrated intensities decrease with respect to the aliphatic intensities, those of the cis and trans double bonds decrease with respect to the vinyl protons. This indicates that the reaction preferentially occurs on the backbone double bonds, even thought they are in the minority. The reaction amounts to changing a homopolymer into a random copolymer as shown below.



Finally, we synthesized a molecule containing two o-tolualdehyde functionalities to test this species as a crosslinking agent. The result of the photolytic reaction of the bifunctional molecule with polybutadiene was a precipitate which was insoluble in all common organic solvents. The infrared spectrum of this material is similar to those of the random copolymers produced above, and it also exhibited the O-H stretching band at 3385 cm^{-1}. The crosslinked product is shown below.



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