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Ring-opening polymerization of spirobislactones in a solid acrylic matrix

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Summary

Acrylic resins have been made with pendant spirobislactone functional groups. These resins form films at room temperature. When heated at 120 °C for 24 h, the films are crosslinked by the reaction of spirobislactone, hydroxyl, and glycidyl groups in the polymer, and an insoluble film is produced.

Introduction

Conventional addition polymerization proceeds with shrinkage, for atoms in van der Waals contact as monomers fuse to form a covalent bond in the polymer. Shrinkage can form voids, cracks, and other defects which shorten the life of the matrix. One strategy to avoid shrinkage is to use a proportion of bicyclic monomers in the reaction mixture. Suitable "expanding monomers" contain two or more rings joined at a common carbon atom, and contain functional groups so situated that attack initiates multiple bond breaking; atoms pairs moving apart in a number which exceeds atoms pairs moving together should produce expansion. Polymerizations in which two or more bonds are broken for each new bond formed are being evaluated in epoxy coatings (1), carbon fiber composites (2), and adhesives (3).

Nearly one hundred "expanding monomers" of this type have been prepared and polymerized (4). Not all polymerization reactions are straightforward, however, and two major complications have been documented. First, multiple ring opening is not the preferred pathway for all polymerizations. Examples are reported in which monomers react by opening of only one ring (5), by addition polymerization through vinyl groups (6), by elimination reactions (7), and by combinations of these pathways (8). The volume of the reactants does not increase when any of these pathways dominate.

A second complication arises because ring-opening reactions of polycyclic monomers are appreciably faster than addition

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polymerization of conventional epoxy or urethane resins (9). Thus all of the increase in volume is wasted because it occurs when the resin mass is liquid, and the resin subsequently cures with its characteristic shrinkage.

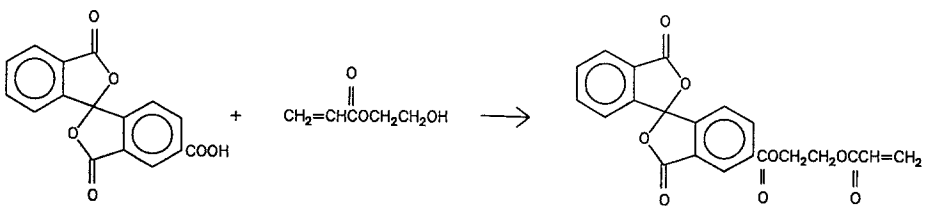
In order for double ring-opening reactions to achieve their potential in controlling volume change during polymerizations, it is necessary to use a monomer which reacts exclusively by a double ring-opening pathway. It is also essential to ensure that the monomer reacts after the polymer matrix has solidified, so that volume changes take place in a solid phase.

We report here a new and novel method of conducting a double ring-opening polymerization within a solid polymer matrix. In earlier work on the copolymerization of spirobislactones and epoxy resins (10), it was shown that both rings in the spirobislactones open unambiguously by reaction with hydroxyl and glycidyl groups in the epoxy resin. Here the same chemistry is exploited within a preformed solid acrylic matrix.

Experimental

Materials. Glycidyl acrylate, 2-hydroxyethyl acrylate, 4-hydroxybutyl acrylate, 4-dimethylaminopyridine (all from Aldrich), and azobis(isobutyronitrile) (K & K Laboratories) were used as received. 4-Carboxy-7,7'dioxo-2,2'spirobi-(benzo[*c*]tetrahydrofuran) (**1**) was prepared as described previously (10). Glassware was oven-dried and solvents were dried over 4 Å molecular sieves before use.

Characterization. Fourier transform infrared (FTIR) spectra were measured on a Perkin-Elmer Model 1800 spectrophotometer operating in the double-beam mode at a resolution of 2 cm^{-1}. Spectra were obtained for films cast from acetone or methylene chloride on KBr flats and dried at 120 °C. Peak intensities are given as strong (s), medium (m), and weak (w). ^{1}H and ^{13}C NMR spectra in deuterated benzene were recorded at room temperature on a Bruker 300 MHz MSL-FT-NMR spectrometer.

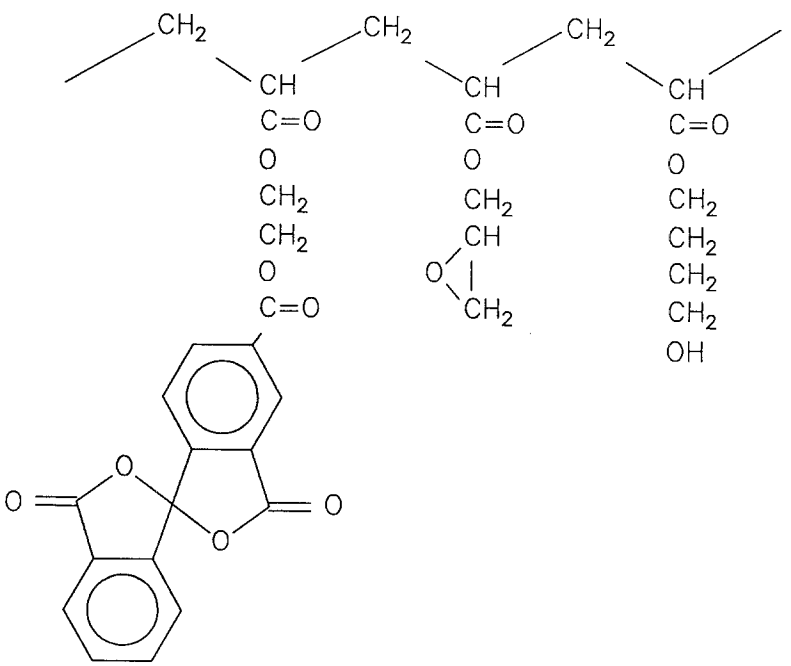


1 **2** **3**

4-(Acryloxyethyleneoxycarbonyl)-7,7'dioxo-2,2'spirobi(benzo-[c]tetrahydrofuran) (**3**). Acid **1** (9.17 g, 31.0 mmol) and 2-hydroxyethyl acrylate (**2**) (3.57 g, 30.8 mmol) were dissolved in

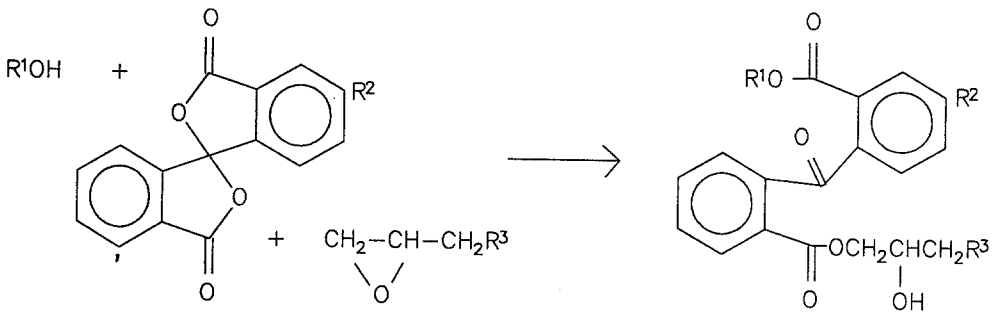
200 mL of tetrahydrofuran (THF). Powdered 4-dimethylaminopyridine (3.89 g, 31.9 mmol) was added to the solution, followed by a solution of dicyclohexyl carbodiimide (7.50 g, 36.4 mmol) in 50 mL THF. The reaction was very exothermic, and a precipitate formed within 2 min. After 16 h the precipitate was filtered and THF was removed on a flash evaporator. The residue was taken up in methylene chloride and washed with 200-mL portions of water (three times), 10% hydrochloric acid (twice), 2.5% sodium bicarbonate (twice), and water (three times). The organic layer was dried over anhydrous magnesium sulfate and stored at -20 °C for 24 hours, which caused dicyclohexyl urea to precipitate. The liquid was then filtered and evaporated to dryness, yielding 6.61 g (16.8 mmol, 55%) of a white chalky solid: mp 243-245 °C; IR 3075 (w), 2930 (w), 2845 (w), 1795 (s), 1740 (s), 1625 (vw), 1607 (vw), 1464 (m), 1343 (m), 1307 (m), 1276 (m), 1252 (w), 1210 (m), 1185 (m), 1155 (m), 1125 (w), 1088 (m), 1028 (m), 1009 (m), 961 (m), 913 (m), 876 (m), 864 (m), 785 (m), 767 (w), 743 (w), 713 (w), 695 (m), and 670 (w) cm^{-1}; ^1H NMR (C_6D_6, 22 °C) δ 3.97 (4 H, m, $-OCH_2CH_2O-$), 6.34 (1 H, q, $-CH=$), 6.85 (2 H, m, ϕH), 6.88 (2 H, m, $=CH_2$), 7.29, (2 H, o, ϕH), 7.40 (1 H, d, ϕH), 7.48 (1 H, q, ϕH), and 7.80 (1 H, q, ϕH); ^{13}C NMR (C_6D_6, 22 °C) δ 61.56, 63.59, 77.40, 122.63, 123.81, 124.85, 126.04, 126.33, 131.71, 133.81, 134.44 and 135.09.

Acrylic terpolymer **4**. A slurry of **3** (299 mg, 0.76 mmol), glycidyl acrylate (2.58 g, 20 mmol), and 4-hydroxybutyl acrylate (27 mg, 0.19 mmol) in 7 mL tetrahydrofuran was stirred at 70 °C



under nitrogen. Azobis(isobutyronitrile) (4 mg) was added and a solution was formed within 5 min; a precipitate began to form within 10 min. After 4 h, an infrared spectrum of the liquid from the reaction mixture showed only trace absorption at 1635 cm^{-1}. The reaction mixture was filtered; the precipitate was washed with hexane and dried to yield 3.5 g (97%) of an off-white solid polymer **4**: IR 3052 (w), 2969 (m), 2863 (m), 1797 (m), 1738 (s), 1635 (vw), 1483 (m), 1449 (m), 1344 (w), 1257 (s), 1176 (s), 1081 (s), 986 (m), 910 (s), 857 (m), 824 (w), 813 (m), and 698 (w) cm^{-1}. The polymer did not melt below 350 °C, but sintered and became discolored above 280 °C, probably as a result of crosslinking reactions.

Crosslinking. Polymer **4** was dissolved in methyl ethyl ketone or methylene chloride and cast as a film on 76- by 152-mm steel panels. The film could easily be removed by rubbing with a cotton ball soaked in methyl ethyl ketone. The steel panel was placed in an oven at 120 °C for 24 h, after which the coating could not be removed by vigorous rubbing with solvent. An FTIR spectrum of the starting film showed the spirobislactone carbonyl band at 1792 cm^{-1}; this band was absent in the FTIR spectrum of the heat-treated film, but new bands at 1729 (ester) and 1675 cm^{-1} (diphenyl ketone) were present (10).



Results and Discussion

An acrylic ester containing the spirobislactone functional group (**3**) was prepared by condensing hydroxyethyl acrylate with acid **1**. Ester **3** was copolymerized with 4-hydroxybutyl acrylate and glycidyl acrylate to produce terpolymer **4**.

Terpolymer **4** has the same mixture of functional groups as an epoxy-spirobislactone reaction mixture reported earlier (10), but has the advantage of being a solid rather than a syrup at room temperature. Thus **4** can be used as a conventional solution acrylic resin; a solution of **4** can be applied to various surfaces and evaporated to form a dry film of acrylic polymer. This film has potential practical uses, but in this state it can be redissolved by the same solvents used to form it.

Films of acrylic polymer **4** are crosslinked by heat. Treatment at 120 °C for 24 h leads to crosslinked films which lack the carbonyl absorption bands of the spirobislactone functional group. The polymerization has been shown to proceed in two steps (10). Reaction of a hydroxyl group with a spirobislacone carbonyl carbon forms an ester and opens both lactone rings, producing a benzophenone carbonyl group and a carboxylic acid. In the second step, the acid reacts with an oxirane ring to form an ester and a hydroxyl group. In this crosslinked condition the film cannot be redissolved in the solvent used to deposit it.

It is possible to adjust the rate and extent of the crosslinking reaction by controlling the proportion of spirobislactone, hydroxyl, and glycidyl groups in the polymer.

The reaction of spirobislactone, glycidyl, and hydroxyl groups proceeds smoothly in the solid phase at elevated temperature, and effectively forms crosslinks. The expansion in volume during this reaction may diminish the formation of voids and other defects in the resin, and may promote bonding between the resin and fibers, fillers, or the substrate.

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