

Unsaturated Polyester Containing Myrcene–Maleic Anhydride Diels–Alder Adduct

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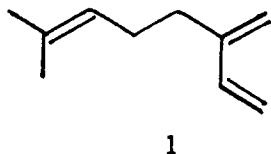
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SYNOPSIS

Myrcene–maleic anhydride Diels–Alder adduct and the corresponding diacid were used as monomers for unsaturated polyesters. The polyesters exhibited air-drying properties on cross-linking with styrene.

INTRODUCTION

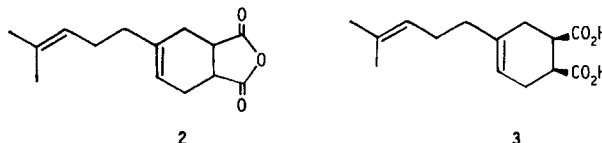
Uncertainties in the long-term availability of petrochemical feedstocks for the polymer industry have sparked considerable interest in polymers derived from renewable resources.^{1–3} The monoterpene myrcene (**1**), which occurs naturally in such plants as bay, verbena, and hops, is of particular interest because it is available in substantial quantities by the vapor-phase thermal isomerization of β -pinene,⁴ a major constituent of turpentine. Furthermore, myrcene possesses a 2-substituted 1,3-butadiene structure:



hence, it is capable of undergoing polymerization analogous to that of isoprene to yield elastomeric polydienes. Indeed, several papers have been published^{5–12} describing free-radical, cationic, anionic, and Ziegler–Natta polymerizations or copolymerizations of myrcene. More recently, hydroxy-terminated polymyrcenes have been incorporated into polyurethane formulations.^{13–15}

The purpose of this study was to determine the feasibility of using 4-(4-methyl-3-pentenyl)-4-cyclohexene-1,2-dicarboxylic anhydride (**2**) (the

readily available⁴ Diels–Alder adduct of myrcene and maleic anhydride) or the corresponding diacid (**3**) as an ingredient for unsaturated polyesters. It was anticipated that the resultant polyester resins might exhibit air-drying characteristics on curing by virtue of the two isolated double bonds in the myrcene-derived moiety:



EXPERIMENTAL

Monomers

Freshly distilled myrcene (Aldrich technical grade) was converted to its Diels–Alder adduct with maleic anhydride by the procedure of Goldblatt and Palkin.⁴ Phthalic anhydride, maleic anhydride, and diethylene glycol were obtained from commercial sources and used without further purification. Styrene was distilled prior to use.

Synthesis of Diacid (3)

Myrcene–maleic anhydride Diels–Alder adduct (**1**) was added slowly with stirring to excess ice-cooled 6*M* sodium hydroxide solution. The resultant solution was extracted twice with methylene chloride and acidified with 3*M* sulfuric acid. The precipitated product was isolated in quantitative yield by vacuum

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filtration, mp 117–119°C (literature value⁴ 122.5–123.5°C).

Polyester Synthesis

Polyester from Diacid 3

Diacid **3** (28.0 g, 0.111 mol), maleic anhydride (14.7 g, 0.150 mol), and diethylene glycol (29.5 g, 0.274 mol) were charged to a 100 mL three-neck flask equipped with mechanical stirrer, thermometer, inert gas delivery tube extending below the liquid surface, and distilling adapter with condenser for collecting water of esterification. The mixture was heated rapidly to 200°C with stirring while purging with nitrogen or argon and maintained at that temperature for 3.25 h. The polyester was poured from the flask while hot.

Polyester from Phthalic Anhydride

The same procedure was followed using 22.2 g (0.150 mol) of phthalic anhydride, 14.7 g (0.150 mol) of maleic anhydride, and 33.4 g (0.315 mol) of diethylene glycol.

Polyester from Anhydride 2

Diels–Alder adduct **2** was prepared in the reaction flask by mixing myrcene (15.1 g, 0.111 mol) and maleic anhydride (10.9 g, 0.111 mol) with external cooling to control the very vigorous reaction. When the reaction had subsided, maleic anhydride (14.7 g, 0.150 mol) and diethylene glycol (29.5 g, 0.274 mol) were added, and the polyester was processed as above.

Curing

Solutions containing 70 parts polyester and 30 parts styrene by weight were prepared with warming. Benzoyl peroxide (1% by weight) as a paste in tricresyl phosphate (Luperco ATC) was dissolved in the solution, followed by *N,N*-dimethylaniline (0.5% by weight). In some experiments, pure benzoyl peroxide was dissolved in the styrene prior to dissolving polyesters. Cobalt (0.05% by weight) as cobalt(II) acetylacetonate was added to some samples. The solutions were poured into aluminum dishes prior to gelation. Cross-linking was highly exothermic.

RESULTS AND DISCUSSION

Styrene-compatible unsaturated polyesters were prepared without difficulty from myrcene–maleic

anhydride Diels–Alder adduct (**2**) or the corresponding diacid (**3**), maleic anhydride, and a 5 mol % excess of diethylene glycol. The polyesters were compared with a similarly formulated polyester containing phthalic anhydride. Each polymer contained the same level of maleic unsaturation (2.3 mmol/g of polymer) corresponding to that of a conventional phthalic anhydride/maleic anhydride/diethylene glycol polyester having a 1 : 1 : 2 mol ratio. In the case of the myrcene-derived polyesters, careful attention had to be paid to processing time at 200°C to avoid premature gelation. In the small-scale formulations tested, viscosity increased very rapidly to the gel point after about 3.5 h; therefore, 3.25 h was chosen as the optimum processing time. The acid number after 3.25 h was approximately 32. The polyesters formed clear solutions with styrene and were cured with benzoyl peroxide and *N,N*-dimethylaniline to clear, light brown, rigid disks in aluminum dish molds.

The tendency toward gelation is probably a result of polymerization (bodying) involving the ring or side-chain unsaturation, as evidenced by a marked decrease in the infrared absorption at 810 cm⁻¹ arising from C—H out-of-plane bending at the trisubstituted double bond.¹⁶ Apart from peak broadening, no other significant changes occur in the infrared spectrum during processing; hence, reorganization of the carbon framework characteristic of many terpenes¹⁷ apparently does not occur under the polyesterification conditions.

A major problem with conventional unsaturated polyesters is inhibition by atmospheric oxygen of the free radical-promoted copolymerization with styrene, particularly in thin-film applications where the cross-linking exotherm is readily dissipated. To circumvent this problem, manufacturers apply a variety of strategies such as adding wax that rises to the surface, modifying the polymers with drying oils or allyl ethers, or using monomers that contain isolated double bonds such as tetrahydrophthalic anhydride or 2-dodecenylsuccinic anhydride that air-dry in the same manner as drying oils.¹⁸

Monomers **2** and **3** each contain two isolated double bonds; hence, they were expected to have the additional advantage of imparting air-drying properties to polyester resins. The highly viscous polyesters prepared from **2** and **3**, prior to solution in styrene, did, in fact, develop a surface skin on standing at room temperature. The cured disks exhibited moderate air-drying characteristics. Samples that were processed almost to the point of gelation formed tack-free surfaces within 72 h. Polyesters processed for 3.25 h were almost tack-free after 2

weeks if cobalt(II) acetylacetonate was added, but in the absence of cobalt, they retained a slight tackiness after several weeks. Phthalic anhydride polyesters remained very tacky in the same time period.

Because terpenes are often susceptible to skeletal rearrangement under acidic conditions, it was considered possible that **2** or **3** might rearrange under processing conditions.

CONCLUSIONS

Unsaturated polyesters compatible with styrene may be synthesized without difficulty from the Diels–Alder adduct of maleic anhydride and myrcene, one of the most readily accessible of the conjugated monoterpenes. Upon cross-linking with styrene, the polyesters exhibit moderate air-drying properties. These results suggest that more extensive testing of the adduct in a variety of polyester formulations is warranted.

Diels–Alder adducts of maleic anhydride and “terpene hydrocarbons” (the composition of which was not specified) have been investigated as cross-linking agents for epoxy polymers¹⁹; hence, anhydride **2** might also prove useful in that regard.

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