

Unsaturated Polyesters. II. Structure and Properties of Polyester Resins Based on Cinnamylsuccinic Acid

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Synopsis

Unsaturated polyester resins were prepared by the reaction of cinnamylsuccinic acid with saturated diols, namely, ethylene, diethylene, propylene, dipropylene, tetramethylene, and hexamethylene glycols, and the unsaturated diols, namely, 1,4-butene- and 1,4-butyndiols. All the polyester resins obtained have been characterized and were found to cure with styrene, with relatively low conversions. The properties of the cured polyesters in the form of films were determined. IR and $^1\text{H-NMR}$ spectroscopy were used for both qualitative and quantitative analyses of the polyesters and their hydrolyzate products, after curing with styrene.

INTRODUCTION

Unsaturated polyesters^{1,2} are conveniently prepared by melt copolyesterification of the saturated and unsaturated dicarboxylic acids with a glycol at elevated temperatures above the melting points of the resulting polyesters. Curing of the unsaturated polyesters with styrene to form solid thermoset materials may have markedly improved properties.^{1,3} In our previous work,⁴ the kinetics of polyesterification of cinnamylsuccinic anhydride with ethylene glycol were studied. The work is now extended to find the optimal general conditions for the preparation of a number of unsaturated polyesters based on the condensation of cinnamylsuccinic acid with some glycols. Further, the reactions between these unsaturated polyesters and styrene have been also studied.

EXPERIMENTAL

Cinnamylsuccinic acid (mp 144°C) was prepared by the reaction of allylbenzene and maleic anhydride according to the method of Christian and Randestvedt.⁵ All chemicals and solvents used were of AR or equivalent grade.

Polyesterification Reactions. The polyesterification reactions were carried out by heating equimolar amounts of the acid and glycol in presence of oxygen-free nitrogen. The time-temperature program for each polyester is illustrated in Table I. The polyesters were purified twice by dissolving in chloroform and precipitating with light petroleum, and then were dried under reduced pressure.

TABLE I
Variation of Degree of Oxidation of Gamma-irradiated PVC with Temperature

| Temp (°C) | Dose Mrad | 10 Mrad | | 15 Mrad | |
|--------------|--------------|--|-------------------|--|-------------------|
| | | Absorbances of the C=O band at 1720 cm ⁻¹ | Carbonyl index | Absorbances of the C=O band at 1720 cm ⁻¹ | Carbonyl index |
| 25 | | 0.385 | 0.26 | 0.245 | 0.38 |
| 44 | | 0.122 | 0.94 | 0.081 | 0.84 |
| 60 | | 0.117 | 1.19 | 0.117 | 0.76 |
| 80 | | 0.140 | 0.48 | 0.053 | 0.73 |
| 100 | | 0.146 | 0.86 | 0.102 | 0.91 |
| 120 | | 0.066 | 0.91 | 0.094 | 0.49 |
| 140 | | 0.119 | 0.87 | 0.081 | 0.84 |
| 160 | | 0.087 | 0.91 | 0.089 | 0.94 |
| 170 | | 0.102 | 1.08 | 0.071 | 1.31 |

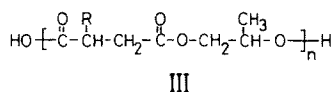
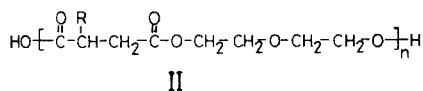
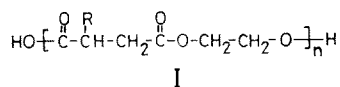
Curing of the Polyester Resins with Styrene. Each of the prepared unsaturated polyesters was copolymerized⁶ with styrene, in the molar ratio of 70:30, using benzoyl peroxide as initiator (1%) and dioxane as solvent. The cured polyesters were casted as films on glass and tin plates. The films were tested for resistance to hot and cold water⁷ and to acids and alkalis.⁸

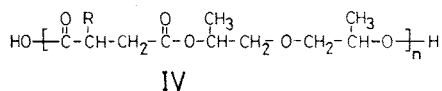
Degradation of the Cured Polyesters. The cured polyesters were subjected to alkaline hydrolysis,⁶ and the soluble product in each case was purified and characterized by studying its infrared and ¹H-NMR spectra.

Viscosity measurements were carried out by an Ostwald Viscometer using a 1% solution in dioxane at 30°C. The molecular weight of the prepared polyesters were determined by the end group analysis for —COOH using KOH.⁹ The infrared spectra were recorded by a Beckman 4220 Infrared Spectrophotometer in the range 4000–600 cm⁻¹. The ¹H-NMR spectra (in CDCl₃ as a solvent and using TMS as a zero reference) were measured with a Varian EM-390 Spectrometer operating at 90 MHz.

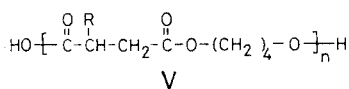
RESULTS AND DISCUSSION

In the present study, unsaturated polyester resins (I–VIII) were prepared by the reaction of cinnamylsuccinic acid with the saturated diols namely, ethylene, diethylene, propylene, dipropylene, tetramethylene and hexamethylene glycols; and the unsaturated diols namely, 1,4-butene- and 1,4-butyne-diols.

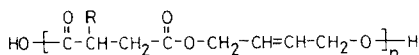




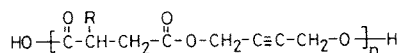
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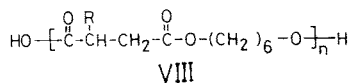
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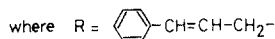
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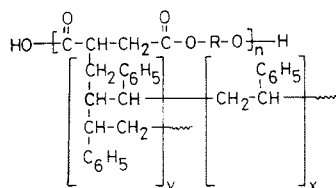
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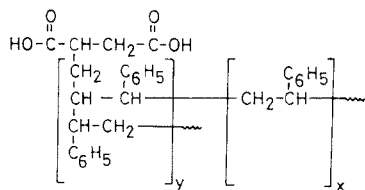
VIII



The prepared polyesters (I-VIII) were yellow, viscous materials, soluble in most organic solvents except alcohol, *n*-hexane, and light petroleum. These unsaturated polyesters showed greater resistance to homopolymerization and remained soluble after long storage periods. Some of the physical properties of these polyesters are presented in Table II. Trials to prepare polyesters with higher molecular weights by increasing the reaction temperature or the condensation time failed because of the formation of an insoluble gel during the synthesis due to the cinnamyl double bonds. This behavior was clear in case of polyesters VI and VII, which contain the cinnamyl double bonds as well as the unsaturated glycol residues.



IX



Segment B

Segment A

X

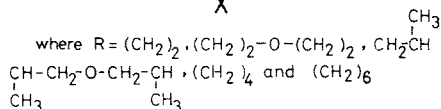


TABLE II
Physical Characteristics of the Polyester Resins

| Polyester | Nature of polyester | Acid value | Mol. wt. | n | $[\eta]_{inh.}$ |
|-----------|---------------------|------------|----------|------|-----------------|
| I | Low melting solid | 29.28 | 4145 | 15.9 | 0.043 |
| II | Syrupy mass | 33.04 | 3428 | 11.3 | 0.058 |
| III | Low melting solid | 54.55 | 2057 | 7.5 | 0.062 |
| IV | Low melting solid | 30.32 | 3700 | 11.1 | 0.046 |
| V | Syrupy mass | 37.14 | 3022 | 11.5 | 0.060 |
| VI | Syrupy mass | 42.79 | 2628 | 9.2 | 0.050 |
| VII | Low melting solid | 69.31 | 1619 | 5.7 | 0.041 |
| VIII | Syrupy mass | 15.03 | 7516 | 23.8 | 0.057 |

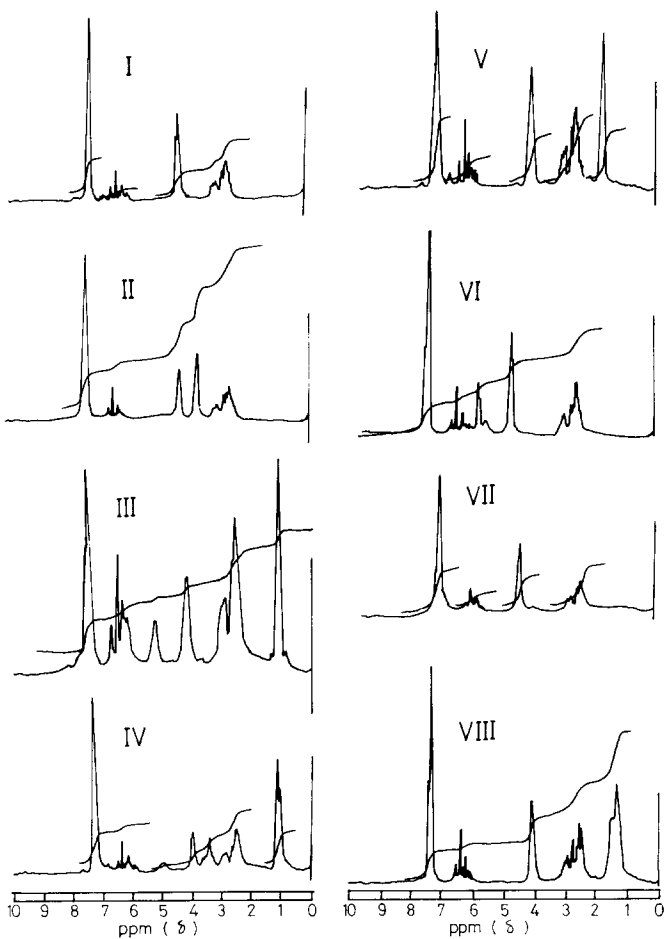


Fig. 1. ^1H -NMR spectra of polyesters (I-VIII).

TABLE III
¹H-NMR Spectral Data of Polyesters (I-VIII)

| Polyester | Component | Chemical shift (ppm) | Assignment | Peak area integration | Relative mol amount | Mol % |
|-----------|-----------|-----------------------|---|-----------------------|---------------------|-------|
| I | Glycol | 4.35 | $-\text{O}-\overset{ }{\text{CH}_2}-\overset{ }{\text{CH}_2}-\text{O}-$ | 24.00 | 6.00 | 50.00 |
| | Acid | 2.35-3.30 & 5.90-7.60 | $-\overset{ }{\text{CH}_2}-\overset{ }{\text{CH}}-\overset{ }{\text{CH}_2}-$ and $5\text{Ar}+$ and $-\text{CH}=\text{CH}-$ | 72.00 | 6.00 | 50.00 |
| II | Glycol | 3.59 & 4.20 | $-\text{CH}_2-\text{O}-\overset{ }{\text{CH}_2}-$ and $2(-\overset{ }{\text{CH}_2}-\text{O}-)$ | 60.00 | 7.50 | 51.23 |
| | Acid | 2.30-3.20 & 5.87-7.50 | $-\overset{ }{\text{CH}_2}-\overset{ }{\text{CH}}-\overset{ }{\text{CH}_2}-\overset{ }{\text{CH}_2}-$ and $5\text{Ar}+$ and $-\text{CH}=\text{CH}-$ | 85.68 | 7.14 | 48.77 |
| III | Glycol | 1.18, 4.11, & 5.16 | $\overset{ }{\text{CH}_3}-\overset{ }{\text{C}}-, -\text{O}-\overset{ }{\text{CH}_2}-, \text{and } -\text{CH}-\text{O}-$ | 37.50 | 6.25 | 49.33 |
| | Acid | 2.30-3.20 & 5.87-7.60 | $-\overset{ }{\text{CH}_2}-\overset{ }{\text{CH}}-\overset{ }{\text{CH}_2}-$ and $5\text{Ar}+$ and $-\text{CH}=\text{CH}-$ | 77.00 | 6.42 | 50.67 |
| IV | Glycol | 1.15 & 3.30-5.20 | $2(\overset{ }{\text{CH}_3}-\overset{ }{\text{C}}-)$ and $2(-\overset{ }{\text{CH}_2}\text{O}-)$ + $2(-\text{CH}-\text{O}-)$ | 60.00 | 5.00 | 50.00 |
| | Acid | 2.30-3.10 & 5.90-7.45 | $-\overset{ }{\text{CH}_2}-\overset{ }{\text{CH}}-\overset{ }{\text{CH}_2}-$ and $5\text{Ar}+$ and $-\text{CH}=\text{CH}-$ | 60.00 | 5.00 | 50.00 |
| V | Glycol | 1.70 & 4.20 | $-\overset{ }{\text{CH}_2}-\overset{ }{\text{CH}_2}-$ and $2(-\overset{ }{\text{CH}_2}-\text{O}-)$ | 96.00 | 12.00 | 50.00 |
| | Acid | 2.35-3.30 & 5.95-7.55 | $-\overset{ }{\text{CH}_2}-\overset{ }{\text{CH}}-\overset{ }{\text{CH}_2}-$ and $5\text{Ar}+$ and $-\text{CH}=\text{CH}-$ | 144.00 | 12.00 | 50.00 |
| VI | Glycol | 4.78 & 5.82 | $2(-\overset{ }{\text{CH}_2}-\text{O}-)$ and $-\text{CH}=\text{CH}-$ | 33.00 | 5.50 | 49.64 |
| | Acid | 2.30-3.25 & 6.00-7.51 | $-\overset{ }{\text{CH}_2}-\overset{ }{\text{CH}}-\overset{ }{\text{CH}_2}-$ and $5\text{Ar}+$ and $-\text{CH}=\text{CH}-$ | 67.00 | 5.58 | 50.36 |

TABLE III. (Continued from the previous page.)

| Polyester | Component | Chemical shift (ppm) | Assignment | Peak area integration | Relative mol amount | Mol % |
|-----------|-----------|-----------------------|---|-----------------------|---------------------|-------|
| VII | Glycol | 4.60 | $-\text{O}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-\text{O}-$ | 32.00 | 8.00 | 50.00 |
| | Acid | 2.20-3.10 & 5.70-7.35 | $-\text{CH}_2-\text{CH}-\text{CH}_2-$ and 5Ar + $-\text{CH}=\text{CH}-$ | 96.00 | 8.00 | 50.00 |
| VIII | Glycol | 1.10-1.79 & 4.15 | $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ and 2($-\text{CH}_2-\text{O}-$) | 70.00 | 5.83 | 50.35 |
| | Acid | 2.35-3.20 & 5.89-7.63 | $-\text{CH}_2-\text{CH}-\text{CH}_2-$ and 5Ar + $-\text{CH}=\text{CH}-$ | 69.00 | 5.75 | 49.65 |

The structure of cinnamylsuccinic acid as well as the prepared polyester resins (I–VIII) were established by studying their IR and $^1\text{H-NMR}$ spectra. The infrared spectra of the eight prepared polyesters show bands at 3450–3480, 3020–3060, 2850–2970, 1730–1740, and 700, 750 cm^{-1} characteristic for ν_{OH} , ν_{CH} (aromatic and olefinic), ν_{CH_2} , $\nu_{\text{C=O}}$, and γ_{CH} of aromatic (five adjacent), respectively. The $^1\text{H-NMR}$ spectra (Fig.1) of the prepared polyester resins (I–VIII) are studied, and the method of Baddar et al.¹⁰ was used in our present work for the quantitative analysis of these polyesters by $^1\text{H-NMR}$ spectroscopy. The results of both qualitative and quantitative analyses of the polyester resins are shown in Table III. From Table III, it is clear that the mol % ratio of the glycol to the acid, calculated for polyesters (I–VIII) are 50:50.

The prepared polyesters (I–VIII) were found to cure with styrene to form insoluble crosslinked polymers (IX), with variable levels of conversions: 48.41%, 35.17%, 5.21%, 9.39%, 27.87%, 45.18%, 53.96%, and 35.23%, respectively. The properties of these cured polyesters in the form of films (Table IV) show that they have a considerable film properties on glass and metal plates. Curing of polyesters VI and VII with styrene gave a very hard cured products with good film properties (Table IV) which could not be hydrolyzed. The cured polyester (IX) were subjected to hydrolysis, and the hydrolyzate products (X) were characterized by IR and $^1\text{H-NMR}$ spectra: Thus, their infrared spectra exhibit bands at 1710 ($\nu_{\text{C=O}}$), 3440 (ν_{OH}), 3025 ($\nu_{\text{C-H}}$ of aromatic), 2840 ($\nu_{\text{sC-H}}$ of CH_2), and 2920 cm^{-1} ($\nu_{\text{asC-H}}$ of CH_2). Also the aromatic C—H bending (five adjacent) appears at 700 and 750 cm^{-1} . Also, their $^1\text{H-NMR}$ spectra show two signals at $\delta 6.65$ and 7.15 ppm, indicating the presence of phenyl groups in two rather different chemical environments. Beside that, their $^1\text{H-NMR}$ spectra show two broad bands centered at $\delta 1.3$ and 1.8 ppm, corresponding to the aliphatic protons (CH—CH_1). From the integrated areas and from the position of signals, it was concluded that the copolymer (X) contains phenyl groups in two different environments, i.e., the hydrolyzate molecule is built up of two segments, segment A ($\delta 7.15$) composed of styrene molecules and segment B ($\delta 6.65$) composed of styrene with cinnamylsuccinic acid. The average molar ratios of styrene and cinnamylsuccinic acid residue in the hydrolyzate products (X) (Table V) were deduced from the oxygen content as well as the $^1\text{H-NMR}$ spectral data.

TABLE V
Molar Ratio of Styrene to Cinnamylsuccinic Acid Residue in Hydrolyzate Products Calculated from Oxygen Content and from $^1\text{H-NMR}$ Spectral Data

| Hydrolyzate products of polyesters | Calculated from oxygen content | Calculated from $^1\text{H-NMR}$ |
|------------------------------------|--------------------------------|----------------------------------|
| I | 8.64 | 8.89 |
| II | 7.21 | 7.00 |
| III | 4.64 | 4.33 |
| IV | 7.43 | 7.20 |
| V | 4.93 | 5.19 |
| VIII | 6.78 | 6.51 |

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Received April 10, 1984

Accepted May 7, 1984

Corrected proofs received February 21, 1985