

Unsaturated Polyesters: Part I—Kinetics of Polyesterification of Cinnamylsuccinic Anhydride with Ethylene Glycol

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The polyesterification of cinnamylsuccinic anhydride with ethylene glycol, in the presence or absence of *p*-toluenesulphonic acid as a catalyst, follows a second order rate equation. Curing of the prepared polyester with styrene was studied. IR and PMR spectroscopy have been used for both qualitative and quantitative analyses of the polyester resin and its hydrolyzate product after curing with styrene.

Kinetics of polyesterification of dibasic acids with glycols have been reported by various authors. Flory^{1,2} concluded that in the case of aliphatic diacids and glycols, the initial reaction was third order and second order in the absence and presence of catalyst, respectively. Baddar *et al.*³ studied the polycondensation reactions of γ -arylitaconic anhydrides with ethylene glycol and reported that both the catalyzed and self-catalyzed reactions followed a second order rate equation. These conflicting results prompted us to undertake the title investigation. Further, the reaction between the product poly-(ethylene glycol cinnamylsuccinate) with styrene has also been studied.

Materials and Methods

Cinnamylsuccinic anhydride (m.p. 104°) was prepared by the reaction of allylbenzene and maleic anhydride according to the method of Christian and Rondestvedt⁴. Ethylene glycol was fractionally distilled and the fraction, b.p. 197° was collected. Styrene (E. Merck) was freed from inhibitor by distillation under reduced pressure and the centre cut was retained for use. All solvents used were of reagent grade and purified by distillation before use.

Bulk polyesterification reaction of cinnamylsuccinic anhydride (1 mol) with ethylene glycol (1 mol) was carried out under a stream of dry carbon dioxide gas. Kinetic runs were made at 130°, 150°, and 170°C using a thermostatically controlled oil-bath. The reaction was followed by titration of the total free carboxyl in samples (≈ 0.2 g) removed from the reaction mixture at suitable time intervals, against alcoholic KOH, using phenolphthalein as indicator. Reactions catalyzed by *p*-toluenesulphonic acid were carried out similarly except that the calculated amount of the catalyst (0.004 mol per mol of glycol) needed for the three runs was

dissolved in the glycol in order to keep the catalyst concentration constant, and then the calculated amount of the glycol for each experiment was taken from this mixture. The extent of the reaction (*P*) or the fraction of the functional groups that reacted at time *t*, was calculated from the equation:

$$P = \frac{C'_0 - C'}{C'_0} \quad \dots (1)$$

where *C'*₀ and *C'* are the acid values before the reaction and after time *t* respectively.

Curing of the polyester resin with styrene was carried out by dissolving a mixture of polyester and styrene (in the ratio of 7:3 by weight) in dioxane using benzoyl peroxide (1%) as initiator. The reaction mixture was successively heated for 24 hr at 80°, for 24 hr at 100° and then for 6 hr at 130°C.

Results and Discussion

The esterification of cinnamylsuccinic anhydride (I) with ethylene glycol (II) occurs by a mechanism shown in Scheme 1 (steps 2-4).

The proton catalyzing the reaction (3) comes from *p*-toluenesulphonic acid in the case of catalyzed polyesterification. That the formation of half-ester (step 2) is a rapid process is supported by the rapid drop in the acid value to nearly half in the first 30 min. The polycondensation occurs by a repetition of step (4).

For the self-catalyzed reactions at 130°, 150°, and 170°C the reactions between $1/1-P$, $1/(1-P)^{3/2}$ and $1/(1-P)^2$ have been plotted graphically against time using the least squares method. The best linear plots were obtained by plotting $1/1-P$ versus time (Fig. 1), indicating that the reaction satisfies the second order rate equation (Eq. 5).

$$C_0 k_2 t = (1/1-P) - 1 \quad \dots (5)$$

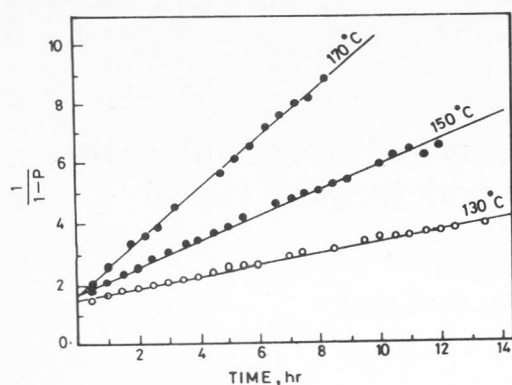


Fig. 1—Plots of $1/1-P$ versus time for the self-catalysed polyesterification of cinnamylsuccinic anhydride (1 mol) with ethylene glycol (1 mol) at different temperatures

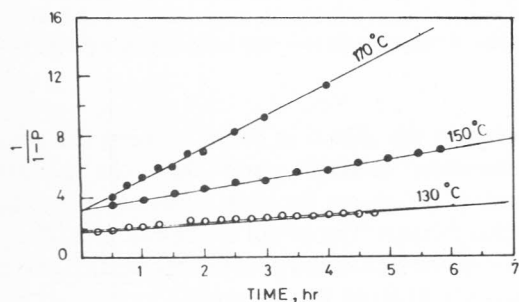


Fig. 2—Plots of $1/1-P$ versus time for the catalysed polyesterification of cinnamylsuccinic anhydride (1 mol) with ethylene glycol (1 mol) at different temperatures

where C_0 is the initial concentration, k_2 is the second order rate constant and t is the time.

The catalysed polyesterification is also found to satisfy second order kinetics (Fig. 2). The rate constants for both the uncatalyzed and catalyzed polyesterification reactions have been calculated and these values are presented in Table 1.

The energies of activation (ΔE_a) of the uncatalyzed and catalyzed reactions are found to be 57.20 ± 2.30 kJ mol⁻¹ and 79.79 ± 2.43 kJ mol⁻¹ respectively. It appears that the uncatalyzed polyesterification is slower than the catalyzed one, in spite of the fact that the activation energy is less in former case. Similar results were obtained by Baddar *et al.*³ in the reactions of γ -arylitacnic anhydrides with ethylene glycol. This indicates that the frequency factor in Arrhenius equation is much greater for the reaction involving a charged catalyst as indicated by the increase in the entropy of activation (ΔS^\ddagger) by about 64 JK⁻¹mol⁻¹ in the catalyzed reaction (the entropies of activation for both the uncatalyzed and catalyzed reactions were calculated at 130°C and were found to be -206.15 ± 8.28 and -142.43 ± 4.35 JK⁻¹mol⁻¹ respectively). The low negative values of ΔS^\ddagger may be due to the high viscosity of the reaction medium and the restricted freedom of the transition state in the reaction.

Table 1—Rate Constants for Uncatalyzed and Catalyzed Polyesterification of Cinnamylsuccinic Anhydride by Ethylene Glycol

Temp. (°C)	$k_2 \times 10^5$ (mol ⁻¹ dm ³ s ⁻¹)	
	Uncatalyzed	Catalyzed
130	1.23 ± 0.02	1.60 ± 0.12
150	2.74 ± 0.05	4.47 ± 0.12
170	5.75 ± 0.11	13.74 ± 0.43

Table 2—Molecular Weights of Polyester Resins Obtained in Catalyzed and Uncatalyzed Reactions

Temp. (°C)	Without catalyst			With catalyst		
	Time (min)	Mol. wt	n	Time (min)	Mol. wt	n
130	810	1060.64	4.08	540	1215.55	4.68
150	720	1801.02	6.93	420	2238.13	8.61
170	495	2445.00	9.40	240	3133.76	12.05

Polyester resins produced from either uncatalyzed or catalyzed reactions at 130°C, 150°C, and 170°C, are yellowish transparent solids soluble in most organic solvents except *n*-hexane and light petroleum. Average molecular weights for these polyester resins obtained at advanced stages of polyesterification reactions, were calculated by the end group analysis for $-\text{COOH}$ using KOH⁵ (Table 2). It is clear from the data in Table 2 that polyester resins contain 4-12 repeating units (n) per molecule and that resins with high molecular weights are obtained during catalyzed reactions.

The infrared spectrum of the polyester resin, as thin film exhibits a strong band at 1735 cm⁻¹ ($\nu\text{C}=\text{O}$) and a broad band at 3500 cm⁻¹ (νOH). The two bands at 2970 and 3040 cm⁻¹ are due to the $\nu\text{C}-\text{H}$ of the CH_2 and $\text{CH}=\text{CH}-$ groups respectively. The presence of mono-substituted benzene ring is confirmed by the appearance of two bands at 700 and 750 cm⁻¹. The PMR spectra of both cinnamylsuccinic anhydride and its polyester resin with ethylene glycol were recorded on a Varian EM 360L instrument in CDCl_3 (chemical shifts in δ -scale down field zero TMS internal reference). The spectrum of the acid anhydride displays signals at $\delta 2.4-3.35$ ($\text{CH}_2-\text{CH}-\text{CH}_2$), $5.8-6.5$ ($\text{CH}=\text{CH}$) and $6.5-7.5$ (five aromatic protons). The PMR spectrum of the poly(ethylene glycol-cinnamylsuccinate) also exhibits these signals, in addition to a peak centered at $\delta 4.25$ due to $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$. The method of Badder *et al.*⁶ was used for the quantitative analysis of this polyester by PMR spectroscopy. It was found that the polyester resin contained ethylene glycol-cinnamylsuccinic anhydride in the ratio of 50:50.

The unsaturated polyester was ester-cured with styrene in dioxane as a solvent and benzoyl peroxide as

initiator, to give solid insoluble cross-linked product (VI) in 85% yield. The cured product was subjected to alkaline hydrolysis⁷ to reduce the complex polymer to a simple structure (VII) more amenable to analysis.

The average molar ratio (X) of styrene (St) and cinnamylsuccinic acid residue in the hydrolyzate was deduced from the oxygen content and was found to be 7.67 when calculated according to Eq. (6).

$$\% \text{ of oxygen} = \frac{64 \times 100}{x(104 + 234)} \dots (6)$$

The infrared spectrum of the hydrolyzate product (VII) exhibits bands at 1710 ($\nu_{\text{C=O}}$), 3440 (broad, ν_{OH}), 3025 (aromatic C-H), 2850 ($\nu_{\text{S C-H}}$ of CH_2)

and 2930 cm^{-1} ($\nu_{\text{as C-H}}$ of CH_2). Also, the aromatic CH bending (five adjacent) appears at 700 and 750 cm^{-1} .

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