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Copolymerization of Vinyl Cinnamate with Vinyl Acetate: Infrared Spectral Studies

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ABSTRACT

Vinyl cinnamate (C) was synthesized and copolymerized with vinyl acetate (A) in benzene at 60° using benzoyl peroxide as initiator. Monomer distributions in the resulting copolymers were determined by the infrared spectral technique. A calibration curve was obtained for this purpose. Reactivity ratios as calculated by Kelen and Tüdös method were found to be $r_C = 1.401 \pm 0.210$, $r_A = 0.043 \pm 0.006$.

INTRODUCTION

The cyclopolymerization of vinyl cinnamate (C) has been reported [1] as has the copolymerization of C and vinyl acetate (A) in benzene at 70°C using AIBN as initiator [2]. It was considered of interest to study these polymers from the point of view of their possible application as photoresists. C would contribute pendant cinnamoyl groups which can undergo photodimerization in the solid state to yield cross-

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linked, insoluble products whereas A is expected to improve film-forming properties. Determination of copolymer composition is therefore critical. Infrared spectral techniques have been widely used in the analysis of polymers [3]. In the present investigation an infrared spectral technique was used to determine the composition of copolymer and the reactivity ratios of the monomer.

EXPERIMENTAL

Materials

Vinyl acetate was purified by washing with 10% sodium hydroxide to remove stabilizer, followed by repeated washings with water until the aqueous washings were neutral. It was then dried over anhydrous sodium sulfate and distilled (bp 72-73°C) over 4Å molecular sieves.

Cinnamic acid (mp 132-134°C) was recrystallized from hot water.

Mercuric acetate (chemically pure grade) was used without further purification.

Benzoyl peroxide (Bz_2O_2) was purified by dissolving it in chloroform at room temperature, then adding excess methyl alcohol and crystallizing at 10°C in a refrigerator. Crystals of the initiator were then dried in a vacuum dessicator.

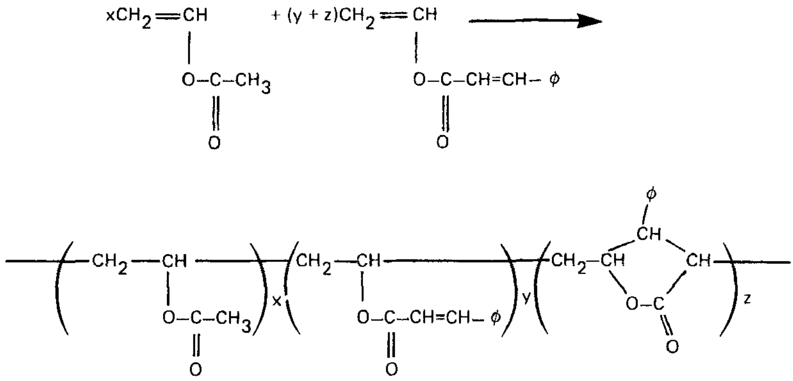
Preparation of Vinyl Cinnamate

Vinyl cinnamate was prepared according to the method described by Swern and Jordan [4].

To 206.4 g (2.4 mol) of vinyl acetate and 59.2 g (0.4 mol) cinnamic acid was added 1.6 g of mercuric acetate. The flask was shaken vigorously for 30 min, the mixture was refluxed for 6 h, after which sodium bicarbonate was added to neutralize excess acid. The reaction mixture was distilled at standard pressure up to 125°C. The ester was then obtained by distillation under reduced pressure (130°C/8 mm). The structure was confirmed by mass and infrared spectroscopic techniques. The mass spectrum of the substance was obtained on a Hitachi mass spectrometer and the infrared spectrum was run on liquid film using a Perkin-Elmer spectrophotometer. The mass spectrum showed major peaks at m/e 174 (parent peak), 131 (C_6H_5–CH=CH–C=O$^+$), 103 (C_6H_5–CH=CH$^+$), 77 ($C_6H_5^+$), and 43 (CH_2=CH–O$^+$). The infrared spectrum showed a combination of peaks at 1725, 1630, 1150, and 980 cm^{-1} characteristic of the –CH=CH–COO grouping and at 1449, 1310, and 950 cm^{-1} due to –CH=CH_2.

Copolymerization of Vinyl Cinnamate with Vinyl Acetate

Required amounts of C, A, Bz_2O_2, and benzene were charged in glass test tubes and sealed after flushing with nitrogen. The tubes were placed in a thermostatically controlled bath maintained at 60 ± 5°C for 15 h. The tubes were then broken and the contents poured into a large amount of n-hexane. The polymer, obtained as a white powder, was filtered and washed several times with n-hexane. The purified polymer was dried to constant weight. The reaction scheme is



Characterization of Copolymers

Viscosity measurements were done in benzene at 30°C using a KPG Ubbelohde suspended level viscometer with a Schott-Gerade automatic measuring unit. The spectra of the copolymers were run in KBr using a Perkin-Elmer spectrophotometer.

Infrared Spectral Analysis

A calibration curve was plotted according to the method used by various authors [5-7]. Homopolymers of C and A were dissolved in varying molar proportions to give solutions of constant concentration in chloroform. The infrared spectra of the solutions were run between 1600 and 1800 cm^{-1}. Similarly, solution of the copolymers of the same concentrations as above were prepared in chloroform and their spectra were recorded in the same range.

The peak at 1770 cm^{-1} associated with the C=O of γ-lactone and that at 1730 cm^{-1} due to the C=O of saturated and unsaturated ester groups were chosen for quantitative analysis. These bands were found to be optimum for the present investigation. Quantitative analysis was done using the band ratio technique. Baselines were drawn connecting minima on either side of the analytical peaks. Absorbances were measured from the baseline to maxima. All bands were below an intensity of 0.9A, thus ensuring optimization of analytical accuracy.

RESULTS AND DISCUSSION

Homopolymers of C and A as well as their copolymers were prepared under identical conditions. The results are summarized in Table 1. Intrinsic viscosities of the copolymers are also given in Table 1. Bulk polymerization of C in the presence of free radical initiators yields insoluble polymers. However, polymers prepared as dilute solutions were found to be soluble in common organic solvents. The greater proximity of growing chains in the former case allows the formation of interchain cross-links, giving rise to an insoluble polymer. In the latter case a largely linear structure results due to the absence of cross-linking.

The infrared spectra of the copolymers recorded in KBr show peaks at 1630 (C=C), 1235 (C–O), 1020 (CH=CH), 1770 (C=O of γ-lactone), and 1160 cm^{-1} (C–O of lactone) due to C and 2925 (CH_3), 1370 (CH_3), and 950 cm^{-1} (C–CH_3) associated with A. Figure 1 shows a typical spectrum.

TABLE 1. Preparation of Homopolymers and Copolymers of C and A[a]

Sample code	Vinyl cinnamate added (mL)	Vinyl acetate added (mL)	Intrinsic viscosity,[b] $[\eta]$ (dL/g)
C	2.5	0	.31
C_4A_1	2.0	0.5	.31
C_3A_2	1.5	1.0	.35
C_2A_3	1.0	1.5	.38
C_1A_4	0.5	2.0	.44
A	0	2.5	.54

[a] Polymerization conditions: benzoyl peroxide (0.05 g) and benzene (7.5 mL) were added, 60 ± 5°C.

[b] Intrinsic viscosity determined in benzene at 30 ± 0.1°C.

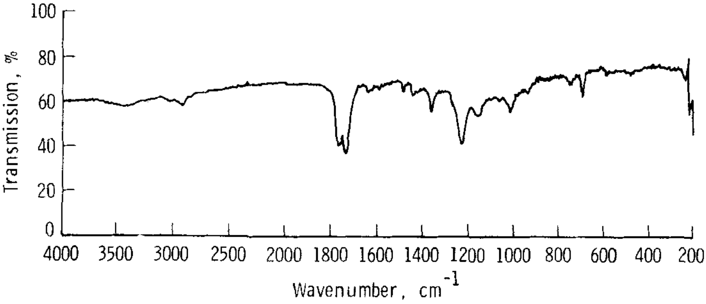


FIG. 1. Infrared spectrum of copolymer A_4C_1.

Infrared Spectral Analysis

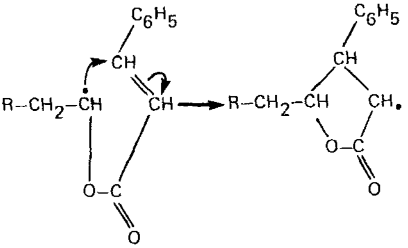
Compositions of solutions of C and A homopolymers (Table 2) were used for preparing calibration curves. Figure 2 shows the spectra obtained. The resulting ratios of absorbances at 1770 cm^{-1} to those at 1730 cm^{-1} (A_{1770}/A_{1730}) are also given in Table 2, and Fig. 3 shows the calibration curve obtained from the results. Figure 4 gives the spectra obtained for the various copolymers of C and A. Table 3 summarizes the data obtained.

Reactivity ratios were calculated by the method described by Kelen and Tüdős [8]. This is a linear graphic method which improves on and eliminates the disadvantages of the Fineman-Ross method [9].

The reactivity ratios for this system were found to be $r_C = 1.401 \pm 0.21$ and $r_A = 0.043 \pm 0.006$.

These values agree with those obtained by Roovers and Smelt ($r_C = 1.2$, $r_A = 0.04$) within the limits of experimental error.

The results reflect the high reactivity of C in comparison to A. This agrees with the suggestion made by the above authors on the formation of a pseudo-cyclic benzyl stabilized radical on addition of the vinyl double bond.



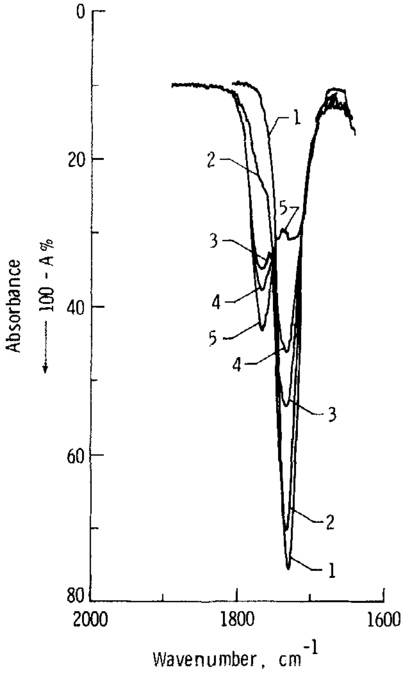


FIG. 2. Infrared curves of C and A homopolymer solutions: (1) 0, (2) 20, (3) 50, (4) 67, and (5) 100 mol% C.

TABLE 2. Composition of C and A Homopolymer Solutions for Infrared Spectral Analysis[a]

Weight of homopolymer (g)			
C	A	Mole fraction C	A_{1170}/A_{1730}
2.3760	0	1.00	1.625
1.9052	0.4708	0.67	0.855
1.5901	0.7859	0.50	0.571
0.7981	1.5779	0.20	0.216
0	2.3760	0	0.031

[a] Solutions were prepared in 100 mL of chloroform.

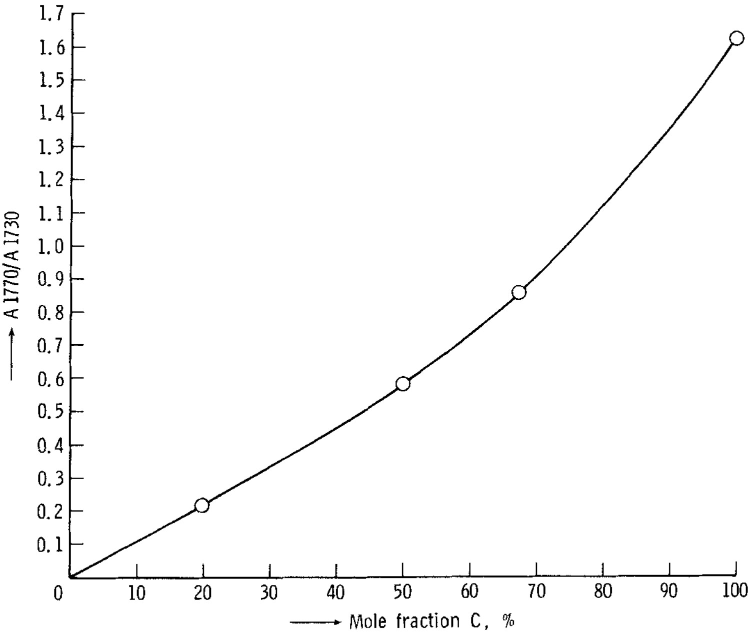


FIG. 3. Calibration curve of A_{1770}/A_{1730} vs mole fraction.

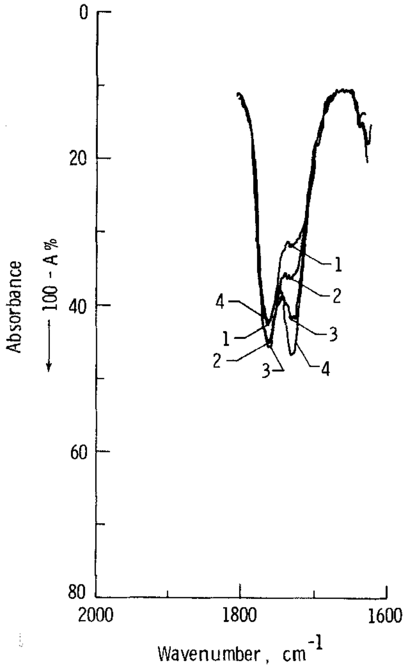


FIG. 4. Infrared curves of copolymers of C and A: (1) C_4A_1, (2) C_3A_2, (3) C_2A_3, and (4) C_1A_4.

TABLE 3. Monomer Distribution from IR Data for Various Copolymers of C and A

Copolymer code	A_{1770}/A_{1730}	Mole fraction C in Monomer feed	Mole fraction C in Copolymer[a]
C_4A_1	1.561	0.692	0.94
C_3A_2	1.373	0.467	0.875
C_2A_3	1.145	0.273	0.775
C_1A_4	0.877	0.135	0.680

[a] As derived from calibration curve.

Thus, copolymers of C and A were analyzed quantitatively using infrared spectral technique to determine monomer distribution. The method was found to afford a fast and simple means of copolymer analysis.

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