

Cyclopolymerization

III. Kinetics of Polymerization and Copolymerization of Vinyl-*trans*-Cinnamate*

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Dedicated to G. NATTA on the occasion of his 60th birthday

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SUMMARY:

The kinetics of cyclopolymerization and cyclo-copolymerization of vinyl cinnamate have been studied. The mechanism of chain propagation during the cyclopolymerization of vinyl cinnamate has first been considered. By determination of the residual unsaturation of the polymer (I.R. and U.V. spectrometry and bromometry) at different monomer concentrations, it was possible to evaluate the ratio of the cyclization rate constant to the vinyl propagation rate constant; it is equal to 13.

In the range of low monomer concentrations the polymerization of vinyl cinnamate is of first order with respect to monomer concentration, and of one half order with respect to initiator concentration. At monomer concentration higher than three mole·l.⁻¹ the reaction becomes independent of monomer concentration, and first order with respect to the initiator.

Modified copolymer composition equations have been derived taking due account of the different reactivity of the monomer radical before and after cyclization; consequently three reactivity ratios r_1 , r_2 , and r_3 have been defined, and the experimental methods for their evaluation determined.

On the basis of these equations the following reactivity ratios have been evaluated: vinyl cinnamate(M_1)-vinyl acetate $r_3 = 1.2 \pm 0.1$ and $r_2 = 0.04$; M_1 -vinyl pyrrolidone $r_3 = 1.15-1.30$ and $r_1 = 0.01$; M_1 -methacrylonitrile $r_3 = 0.15$ and $r_2 = 4$; M_1 -styrene $r_1 = 0.25 \pm 0.1$ and $r_2 = 1.25 \pm 0.1$. The interpretation of these data suggests formation of a pseudo-cyclic benzyl radical stabilized by resonance before addition of the second vinyl monomer.

ZUSAMMENFASSUNG:

Die Kinetik der Cyclopolymerisation und Cyclo-Copolymerisation von Zimtsäurevinylester wurde studiert. Zuerst wurde der Mechanismus des Kettenwachstums während der Cyclopolymerisation von Zimtsäurevinylester betrachtet. Die Bestimmung der restlichen Doppelbindungen im Polymeren (durch IR- und UV-Spektroskopie und Bromometrie) erlaubte die Bestimmung des Verhältnisses von Cyclisierungs- zu Vinylwachstums-Geschwindigkeitskonstanten; es ergibt sich zu 13.

*) Preceding paper: J. MERCIER and G. SMETS, J. Polymer Sci. **57** (1962) 763.

Im Bereich kleiner Monomerkonzentrationen ist die Polymerisation von Zimtsäurevinylester eine Reaktion 1. Ordnung bezüglich Monomerkonzentration und 0,5. Ordnung bezüglich Initiatorkonzentration; sind die Monomerkonzentrationen größer als $3 \text{ Mole} \cdot \text{l}^{-1}$, wird die Reaktion von der Monomerkonzentration unabhängig und 1. Ordnung bezüglich des Initiators.

Unter entsprechender Berücksichtigung der unterschiedlichen Reaktivität des Monomer-radikals vor und nach der Zyklisierung wurden modifizierte Copolymerisationsgleichungen aufgestellt; 3 Copolymerisationsparameter r_1 , r_2 und r_3 wurden definiert, und die experimentellen Methoden zu ihrer Bestimmung wurden angegeben.

Auf Grund dieser Gleichungen wurden als Wert der Copolymerisationsparameter bestimmt: Zimtsäurevinylester (M_1)-Vinylacetat $r_3 = 1,2 \pm 0,1$ und $r_2 = 0,04$; M_1 -Methacrylnitril $r_3 = 0,15$ und $r_2 = 4$; M_1 -Styrol $r_1 = 0,25 \pm 0,1$ und $r_2 = 1,25 \pm 0,1$. Eine Diskussion dieser Werte legt die Bildung eines pseudo-cyclischen Benzylradikals nahe, das durch Resonanz stabilisiert ist, bevor das 2. Vinylmonomere addiert wird.

I. Introduction

It has been shown recently by VAN PAESSCHEN, JANSSEN and HART¹⁾ that the polymerization of vinyl-*trans*-cinnamate proceeds through alternate propagation and cyclization steps, according to a cyclopolymerization mechanism²⁻⁴⁾. Indeed, by comparison of the infrared spectra of polyvinyl cinnamate synthesized by polymerization of the monomer with that of polyvinyl cinnamate prepared by esterification of polyvinyl alcohol with cinnamoyl chloride, they have demonstrated that the polymerization of vinyl cinnamate proceeds mainly by cyclopolymerization with formation of a γ -lactone ring; some residual unsaturated ester groups are nevertheless present.

The results that we have obtained with infrared spectrometry are in complete agreement with their conclusions and need not be repeated; it may be worthwhile to mention that a weak shoulder band at 950 cm^{-1} may be indicative of a small amount of free vinyl ester group in the polymer.

In fact, the study of the copolymerization of vinyl cinnamate is especially attractive because it concerns two double bonds of very different chemical nature, which are known to copolymerize very difficultly. From this point of view, the problem is much more complicated than that of acrylic anhydride, which contains two identical double bonds, and whose kinetics of polymerization was described recently by one of us⁵⁾.

In the present paper we will consider first the structure of polyvinyl cinnamate in relation with the kinetics of chain propagation; thereafter the overall kinetics of free radical polymerization and copolymerization will be considered.

II. Experimental

Vinyl cinnamate was prepared by transvinylation of cinnamic acid (1 mole) with vinyl acetate (10 moles) in the presence of mercury acetate and boron fluoride as catalysts⁶. The yield was 70–80%. It was purified by three fractional distillations *in vacuo*. Refractive index: $n_D^{25} = 1.5844$; b.p.: 92°C./1 mm. Hg; specific volume V_{sp} at 70°C.: 0.9744.

Polymers of vinyl cinnamate were isolated by pouring their chloroform solutions in four times its volume in diethylether; this procedure was repeated twice. The polymers were dried *in vacuo* at 40°C. during 48 hrs.

Polyvinyl cinnamate-S was obtained by treating polyvinyl alcohol in pyridine solution with cinnamoyl chloride⁷).

Ethyl cinnamate and *ethyl- β -phenyl propionate* were prepared by direct esterification with an excess of ethyl alcohol in the presence of sulfuric acid as catalyst.

Ethyl cinnamate b.p.: 137°C./13 mm. Hg, 111°C./3 mm. Hg

Ethyl- β -phenyl propionate b.p.: 127°C./15 mm. Hg.

Ethyl cinnamate has been copolymerized at 75°C. with styrene in benzene solution in order to evaluate the reactivity of its double bond. The composition of the copolymers were determined by infrared analysis, using the C=O double bond as analytical band (1729 cm^{-1}); ethyl- β -phenyl propionate was used as substance of reference.

Table 1. Copolymerization of Styrene and ethyl cinnamate

Styrene mole $\cdot \text{l}^{-1}$	Molar fraction styrene in monomer	Time min.	Degree of conversion	Molar fraction styrene in copolymer
1.862	0.848	135	9.4	0.898
1.49	0.691	135	6.3	0.821
1.117	0.528	135	3.8	0.75
0.740	0.358	195	2.15	0.707
0.372	0.183	2 days	4.8	0.61

From these results the copolymerization reactivity ratios have been calculated: $r_{St} = 2.7 \pm 0.3$; $r_{EtCinn} = 0.05$. These values are consistent with those for the systems butadiene/methyl-chloro cinnamate⁸) and styrene/methyl cinnamate⁹); they confirm the low reactivity of the cinnamic double bond with respect to the polymerization¹⁰). The copolymerization of ethyl cinnamate with methyl methacrylate failed, only polymethyl methacrylate was obtained. With vinyl acetate practically no polymerization occurred at all.

Rate measurements were carried out by the dilatometric method; the high vacuum technique as described by MATHESON and coworkers¹¹) has been followed. The decrease of specific volume, due to a one percent conversion, is 0.00208 and 0.00231 at 60.25 and 69.95°C. respectively.

Table 2 gives a typical series of measurements.

Osmotic molecular weights were determined in a FUOSS-MEAD osmometer in chloroform solution at 25°C. Intrinsic viscosities were also determined in chloroform solution at 25°C.

Table 2. Rate of polymerization of vinyl cinnamate at 69.95°C.
 $[M] = 3.85 \text{ mole} \cdot \text{l}^{-1}$, $[AIBN] = 1.88 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$, solvent: benzene

Time in sec.	$-\Delta[M]$	Time in sec.	$-\Delta[M]$
540	0.0072	4.500	0.0882
960	0.0144	4.860	0.0983
1.320	0.0219	5.220	0.1040
1.800	0.0323	5.700	0.1133
2.160	0.0414	7.200	0.1415
2.520	0.0476	7.800	0.1547
2.880	0.0552	8.400	0.1666
3.300	0.0648	9.000	0.1772
3.900	0.0760		

The *unsaturation* of the polymers has been determined:

- by infrared spectrometry (PERKIN-ELMER Model 112 C double beam spectrometer) in 5% chloroform solution using the carbon-carbon double bond (1635 cm^{-1}) as analytical band, with polyvinyl cinnamate-S and ethyl cinnamate as reference substances;
- by ultraviolet spectrometry (UNICAM U.V. spectrometer) in ethanol solution at 274 m μ in dioxane solution.
- bromometry using the method described by BUCKWALTER and WAGNER¹²). The polymer was hydrolyzed in alkaline medium; after hydrolysis, the solution was neutralized and freeze-dried. Free cinnamic acid was extracted with carbon tetrachloride and titrated bromometrically¹¹).

Copolymerizations were carried out in sealed glass tubes under nitrogen atmosphere at 70°C. Before use, the monomers and solvents were distilled twice in an inert atmosphere. The copolymers were isolated and purified by dissolving and precipitating twice. The solvent/precipitant systems were for:

- Vinyl cinnamate-vinyl pyrrolidone copolymers: acetone/diethyl ether
- Vinyl cinnamate-vinyl acetate copolymers: toluene/heptane
- Vinyl cinnamate-methacrylonitrile copolymers: acetone/heptane
- Vinyl cinnamate-styrene copolymers: butanone/methanol.

Analyses of the copolymers

Carbon and hydrogen contents were determined microanalytically (Dr. A. BERNHARDT, Mülheim, W. Germany); these data were used for the determination of the vinyl acetate or styrene content of corresponding copolymers.

Nitrogen percent was determined by the KJELDAHL method (vinyl pyrrolidone and methacrylonitrile).

The unsaturation of the copolymers of vinyl cinnamate with vinyl acetate and vinyl pyrrolidone was determined by ultraviolet spectrometry in dioxane solution (analytical band λ_{mx} : 274 m μ); for the copolymers with methacrylonitrile the determination was carried out by infrared spectrometry on the basis of the carbon-carbon double bond absorption (1635 cm^{-1}) using *sym.* tetrachloroethane as solvent. By infrared analysis it was

Kinetics of Cyclopolymerization

shown that for these three systems δ -lactone groups and vinyl ester side groups are absent. Consequently the content of cyclized units (γ -lactone groups) was calculated by difference. In case of styrene copolymers, the unsaturation due to cinnamic double bonds was also determined by ultraviolet and infrared spectrometry. However, the infrared spectra show appreciable amounts of vinyl side groups, which result from the direct copolymerization of styrene with the cinnamyl double bond (instead of the vinyl double bond).

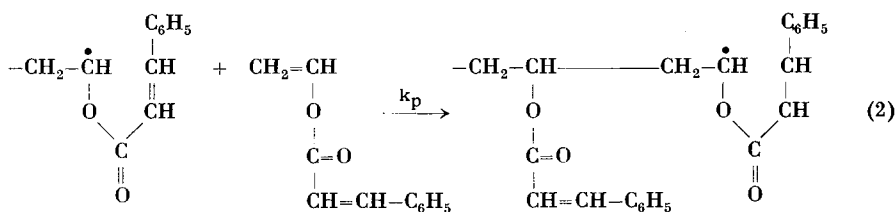
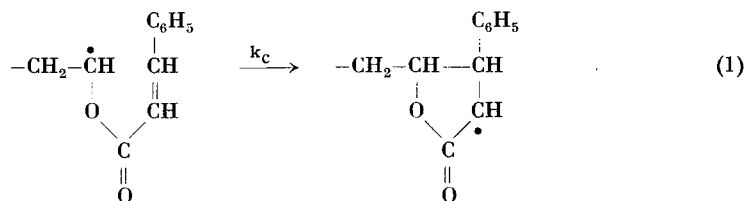
The graphical evaluation of the r_2 and r_3 parameters was based on the case of Eqs. 10 and 11 (*v.i.*). In Table 3 the corresponding values, calculated from the experimental data, are summarized.

Table 3. Determination of r_2 and r_3 copolymerization parameters

Comonomer	R	$\rho \cdot$	$\frac{I}{R} \left\{ \frac{\rho}{1 + \frac{[M_1]}{K_c}} - 1 \right\}$	$\frac{\rho}{R^2 \left[1 + \frac{[M_1]}{K_c} \right]}$	σ	$\frac{\sigma-1}{R}$	$\frac{\sigma}{R^2}$
Vinyl acetate	1.00	2.59	1.25	2.28	2.10	1.09	2.10
	0.67	1.95	1.07	3.82	1.59	0.88	3.54
	0.35	1.55	0.97	11.2	1.27	0.77	10.50
	0.23	1.26	0.48	21.0	1.05	0.22	19.9
Vinyl pyrrolidone	4.07	5.13	(0.78)	(0.25)	4.34	(0.83)	(0.27)
	1.00	2.34	1.05	2.05	2.07	1.07	2.07
	0.67	2.05	1.13	4.00	1.86	1.30	4.30
	0.25	1.32	0.96	20.0	1.26	1.08	20.5
	0.11	1.06	0.26	103	1.04	0.36	104.0

III. Kinetics of Chain Propagation

The internal structure of polyvinyl cinnamate is determined by the relative importance of the cyclization reaction(1) with respect to the vinyl propagation reaction (2). Indeed, it is the competition between both reactions which is responsible for the unsaturation of the polymer.



If R_v and R_c indicate the rates of vinyl propagation and cyclization respectively, their ratio is equal to

$$\frac{R_v}{R_c} = \frac{k_p[M\bullet][M]}{k_c[M\bullet]} = \frac{k_p}{k_c} [M] = K[M] \quad (3)$$

The fraction of cyclized units f_c is equal to $\frac{R_c}{R_c + R_v}$; consequently

$$1/f_c = 1 + K[M] \quad (4)$$

Eq. 4 permits a graphical evaluation of the ratio k_c/k_p from a plot of the reciprocal of the percent of cyclized units *vs.* monomer concentration. It is, however, only valid for polymers obtained at low degree of conversion, where the monomer concentration can be considered as constant and chain branching remains negligible.

The experimental results are summarized in Table 4.

Table 4. Unsaturation of polyvinyl cinnamate — Influence of the monomer concentration
 $t = 70^\circ\text{C.}$, $[\text{AIBN}] = 1.88 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$, solvent: benzene

[M] mole·l ⁻¹	% Unsaturation			1/ f_c
	I.R.	Bromometry	U.V.	
0.26	9.6	—	—	1.11
0.50	10.8	—	—	1.12
0.66	11.2	—	—	1.13
0.97	13.1	—	12.0	1.15
1.63	18.1	—	—	1.22
2.25	20.5	—	20	1.26
2.94	21.2	22.5	—	1.275
3.06	22.8	—	—	1.29
4.50	—	—	21.8	—
5.87	25.9	28.7	23.0	1.35

From these data k_p/k_c was evaluated to $0.075 \text{ mole}^{-1} \cdot \text{l}$.

Table 5. Unsaturation of polyvinyl cinnamate — Influence of temperature
 $[\text{AIBN}] = 1.88 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$, solvent: benzene

t (°C.)	% Unsaturation	
	[M] = 1.63 mole·l ⁻¹	[M] = 4.00 mole·l ⁻¹
45	16.5	—
60	18	19.3
70	18.1	—
80	17	21.6
87	17.7	—
97	19.3	20.5

The degree of cyclization of polyvinyl cinnamate is thus higher than that of polyacrylyl anhydride at equal monomer concentration⁵⁾. It is, however, practically independent of the temperature of polymerization, as can be seen from Table 5.

IV. Overall Kinetics of Polymerization

a) Influence of the monomer concentration

The rate of polymerization of vinyl cinnamate has been determined in benzene and dioxane solutions at 69.95°C., in the presence of azo-bis-isobutyronitrile (AIBN) as initiator. The data are summarized in Table 6.

As can be seen from Fig. 1, the polymerization of vinyl cinnamate is a first order reaction with respect to the monomer concentration in the range of 0 to 3 mole·l⁻¹; above this upper concentration, the rate increases only slightly and becomes independent of the monomer concentration.

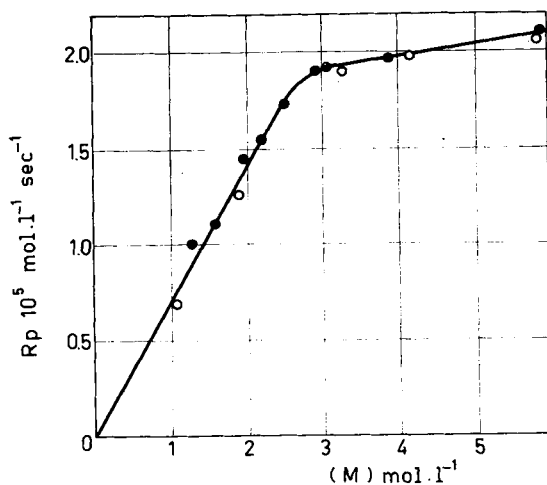


Fig. 1. Polymerization of vinyl cinnamate
Influence of the monomer concentration
[AIBN] = $1.88 \cdot 10^{-2}$ mole·l⁻¹ $t = 69.95^\circ\text{C}$.
● benzene ○ dioxane

b) Influence of the concentration of initiator

Three series of experiments were carried out at constant monomer concentration, one in bulk, the others in benzene solution. The data are given in Table 7.

Table 6. Polymerization of vinyl cinnamate — Influence of monomer concentration
 $t = 69.95^{\circ}\text{C.}$, $[\text{AIBN}] = 1.88 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$

Solvent	[M] mole \cdot l $^{-1}$	Solvent mole \cdot l $^{-1}$	$R_p \cdot 10^5$ mole \cdot l $^{-1} \cdot$ sec $^{-1}$	Degree of conversion	Mol.wt. $\cdot 10^{-3}$ osmot.	$[\eta]$
Benzene	1.31	8.20	1.025	—	—	—
	1.63	7.36	1.11	—	—	—
	1.97	7.10	1.42	5.5	22.8	0.20
	2.25	6.36	1.53	—	—	—
	2.56	5.93	1.73	—	—	—
	2.94	5.28	1.91	8.8	44.1	0.33
	3.06	5.03	1.93	—	—	—
	3.85	3.65	2.00	7.1	53.3	0.37
	5.87	—	2.10	4.7	58.4	0.44
	4.50	—	—	6.1	53.7	0.40
Dioxane	1.10	9.00	0.70			
	1.91	7.48	1.26			
	3.20	5.30	1.93			
	4.22	3.13	1.97			
	5.87	—	2.10			

Table 7. Polymerization of vinyl cinnamate — Influence of concentration of initiator

t ($^{\circ}\text{C.}$)	[M] mole \cdot l $^{-1}$	$[\text{AIBN}] \cdot 10^2$ mole \cdot l $^{-1}$	$R_p \cdot 10^5$ mole \cdot l $^{-1} \cdot$ sec $^{-1}$
60.25	(bulk)	10.57	3.22
		7.78	2.55
		5.75	1.93
		4.42	1.62
		3.77	1.49
69.95	1.72	6.95	2.75
		5.70	2.40
		4.33	2.00
		2.99	1.50
		1.88	1.22
69.95	3.85	5.75	4.97
		3.93	3.50
		2.85	2.71
		1.89	2.00

From a logarithmic diagram of the rate of polymerization *vs.* the concentration of initiator it was found that in dilute monomer solution (1.72 mole \cdot l $^{-1}$) the order of reaction with respect to the initiator is 0.58, while

in more concentrated medium and in bulk (3.85 and 5.95 mole \cdot l $^{-1}$ respectively) this order is practically equal to one (0.93). In the range of low monomer concentration the polymerization of vinyl cinnamate follows practically a normal course, *i.e.* a first order with respect to the monomer, and a square root relationship for the initiator concentration; contrarily, at high monomer concentration, the reaction becomes independent of the monomer concentration and first order with respect to the initiator. In this last region the molecular weights of the polymer vary only very little.

It is also noteworthy to remark that the kinetic significance of the molecular weights is much more complicated than in the case of usual vinyl polymerization. Indeed, as can be seen from Table 8 the molecular weight increases very strongly with increasing degree of conversion, and this strong increase must be related to the residual side double bonds and consequently to chain branching.

Table 8. Molecular weight of polyvinyl cinnamate and degree of conversion
 $t = 70^{\circ}\text{C.}$, $[\text{M}] = 1.97 \text{ mole} \cdot \text{l}^{-1}$, $[\text{AIBN}] = 1.88 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$, solvent: benzene

Time of polymerization, hrs.	Degree of conversion	Mol. wt. osmot.	D. P.	$[\eta]$
1.45	5.5	22.800	131	0.20
3.30	10.1	55.000	316	
6	17.2	106.000	609	
7.30	22.0	342.00	1,965	0.46
8		gel		

It is admitted that the abnormal kinetic behavior of this polymerization at high monomer concentration must be attributed to a progressive gelation and precipitation of polymer particles. The increasing heterogeneity of the medium not only affects the values of the different rate constants, but also causes trapping of radicals and consequently a higher order for the initiator concentration. The presence of trapped radicals was demonstrated previously in the case of polyacrylic anhydride, prepared by cyclopolymerization of acrylic anhydride⁵).

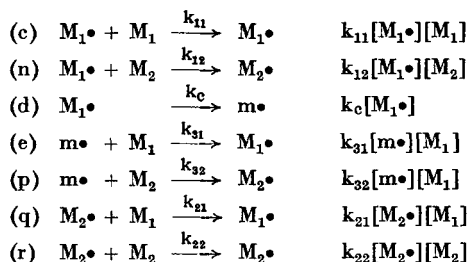
V. Kinetics of Cyclo-copolymerization

It was demonstrated in the previous section that the degree of cyclization of polyvinyl cinnamate depends on the monomer concentration. It is therefore evident that the polymerization of vinyl cinnamate (M_1) in

the presence of a comonomer (M_2) will be also concentration dependent; moreover, it must be expected that the amount of cyclization will be influenced by the nature of the comonomer, its reactivity and its polarity.

1. Copolymer composition equations

When a diene monomer (M_1) participating in copolymerization undergoes cyclization, the number of propagation reactions increases, on account of the different reactivity of this monomer radical before (M_1^\bullet) and after cyclization (m^\bullet). From this point of view, at least, six bimolecular propagation steps and one monomolecular cyclization reaction (d) must be considered.



If the kinetic chain lengths are sufficiently large and if we assume a stationary state for the different types of radicals, the concentration of the cyclized radical $[m^\bullet]$ and of the comonomer $[M_2^\bullet]$ can be expressed as a function of the stationary concentration of the open diene unit radical $[M_1^\bullet]$

$$[m^\bullet] = \frac{k_c[M_1^\bullet]}{k_{31}[M_1] + k_{32}[M_2]} \quad \text{and} \quad [M_2^\bullet] = \frac{[M_1^\bullet][M_2]}{k_{21}[M_1]} \left\{ k_{12} + \frac{k_{32}k_c}{k_{31}[M_1] + k_{32}[M_2]} \right\} \quad (5)$$

By introducing these values in the rate expression of consumption of monomers (M_1 und M_2), and by putting $r_1 = k_{11}/k_{12}$; $r_2 = k_{22}/k_{21}$; $r_3 = k_{31}/k_{32}$; $K_c = k_c/k_{11}$ $K'_c = k_c/k_{12}$, one obtains

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2] + K'_c}{\left\{ r_2[M_2] + [M_1] + K'_c \left[\frac{r_2[M_2] + [M_1]}{r_3[M_1] + [M_2]} \right] \right\}} \quad (7)$$

Eq. 7 relates the copolymer composition to the absolute monomer concentration; it becomes identical with a usual ALFREY-PRICE equation when K'_c is very high, i.e. when the tendency to cyclization is strongly pronounced.

Similar equations relating the total amount of diene monomer (M_1) or comonomer (M_2) to the amount of cyclized units in the copolymer (m) can also be derived

$$\frac{d[M_1]}{d[m]} = 1 + \frac{[M_1]}{K_c} + \frac{[M_2]}{K'_c} \quad (8)$$

$$\frac{d[M_2]}{d[m]} = [M_2] \left\{ 1 + r_2 \frac{[M_2]}{[M_1]} \right\} \left[\frac{1}{K'_c} + \frac{1}{r_3[M_1] + [M_2]} \right] \quad (9)$$

Eqs. 7, 8, and 9 give the composition of the copolymers as a function of the initial monomer concentration, and make it possible to evaluate K'_c , r_1 , r_2 , and r_3 .

If the degree of cyclization of the diene is independent of the presence of a second monomer ($k_{12} \rightarrow 0$), these three equations can be simplified to the following equations:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left[\frac{r_3[M_1] + [M_2]}{r_2[M_2] + [M_1]} \right] \left\{ 1 + \frac{[M_1]}{K_c} \right\} \quad (7a)$$

$$\frac{d[M_1]}{d[m]} = 1 + \frac{[M_1]}{K_c} \quad (8a)$$

$$\frac{d[M_2]}{d[m]} = \frac{[M_2]}{[M_1]} \left[\frac{r_2[M_2] + [M_1]}{r_3[M_1] + [M_2]} \right] \quad (9a)$$

Eqs. 7a and 8a are independent of each other; indeed Eq. 7a contains only the initial monomer concentrations and the copolymer composition, while Eq. 8a necessitates the determination of unsaturation of the polymer.

By putting

$$\frac{d[M_1]}{d[M_2]} = \rho, \quad \frac{[M_1]}{[M_2]} = R \quad \text{and} \quad \frac{d[m]}{d[M_2]} = \sigma$$

both equations can be rewritten in a more adequate form, and permit a graphic evaluation of the r_2 and r_3 parameters:

$$1/R \left\{ \frac{\rho}{1 + [M_1]/K_c} - 1 \right\} = r_3 - r_2 \cdot \left\{ \frac{\rho}{R^2 (1 + [M_1]/K_c)} \right\} \quad (10)$$

$$\text{and} \quad \frac{\sigma - 1}{R} = r_3 - r_2 \left(\frac{\sigma}{R^2} \right) \quad (11)$$

2. Experimental results and discussion

a) Copolymerization with vinyl acetate

Two series of experiments were carried out, one at constant $[M_1]/[M_2]$ ratio, but increasing total monomer concentration, the other at constant vinyl cinnamate concentration ($[M_1] = 1.49 \text{ mole} \cdot \text{l}^{-1}$) but increasing vinyl acetate concentration. On infrared analysis it was shown that δ -lactone and vinyl ester groups are absent in these copolymers.

The results are given in Table 9.

Table 9. Copolymerization of vinyl cinnamate (M_1) and vinyl acetate (M_2)
 $t = 70^\circ\text{C}$., $[\text{AIBN}] = 1.83 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$, solvent: benzene

$[M_1]/[M_2]$	$[M_1] + [M_2]$ $\text{mole} \cdot \text{l}^{-1}$	$[m_2]$ mole %	$[m_1]$ mole %		% Unsaturation of m_1
			Cinnamic units	γ -Lactone	
1	1.365	29.2	8.8	62.0	12.4
	2.685	28.0	12.9	59.1	17.7
	3.325	27.6	14.0	58.4	19.3
	5.067	24.1	15.1	60.7	19.9
$[M_1]$	$[M_1]/[M_1] + [M_2]$				
1.49	0.500	27.8	13.5	58.7	18.6
	0.402	33.9	12.2	54.0	18.4
	0.260	39.2	10.8	50.0	17.7
	0.188	44.1	9.5	46.4	17.0

These data show that the percent of open cinnamic ester structure varies very slightly in the presence of variable amounts of vinyl acetate (last column, second series). By plotting $d[M_1]/d[m]$ as function of the concentration of vinyl acetate $[M_2]$ following Eq. 8, the slope $1/K'_c$ is practically zero, i.e. k_{12} is very small and practically negligible. Consequently the addition of vinyl acetate proceeds practically only on cyclized vinyl cinnamate units. In order to determine the copolymerization parameters r_2 and r_3 , as defined in the preceding paragraph, Eqs. 10 and 11 have been used separately. The values calculated are given in the experimental part; the agreement between these two methods was fairly good (Fig. 2) $r_2 = 0.04$, $r_3 = 1.20 \pm 0.10$.

b) Copolymerization with vinyl pyrrolidone

Two series of experiments were also carried out with vinyl pyrrolidone; one at constant $[M_1]/[M_2]$ ratio and increasing total monomer concen-

tration, the other at constant overall monomer concentration but in different proportions. The results are summarized in Table 10.

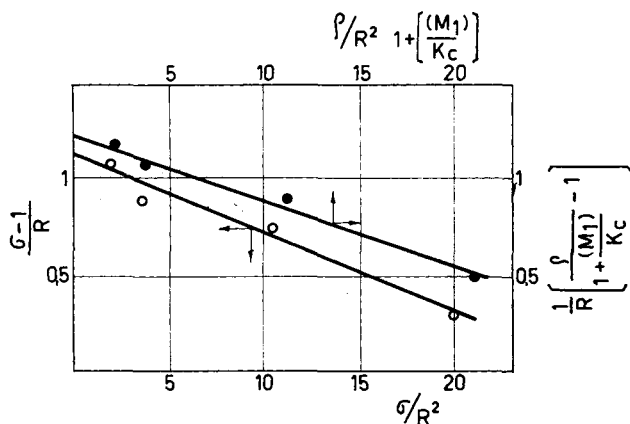


Fig. 2. Copolymerization of vinyl cinnamate and vinyl acetate
Evaluation of r_2 and r_3 copolymerization parameters following
● Eq. 10 ○ Eq. 11

Table 10. Copolymerization of vinyl cinnamate (M_1) and vinyl pyrrolidone (M_2)
 $t = 70^\circ\text{C.}$, $[\text{AIBN}] = 0.61 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$, solvent: benzene

$[M_1]/[M_2]$	$[M_1] + [M_2]$ $\text{mole} \cdot \text{l}^{-1}$	$[m_2]$ $\text{mole} \%$	$[m_1]$ mole %		% Unsaturation of m_1
			Cinnamic units	γ -Lactone	
1	1.426	26.0	7.4	66.6	10.0
	2.900	29.9	8.3	61.8	11.8
	4.826	32.1	9.1	58.8	13.5
$[M_1] + [M_2]$ $\text{mole} \cdot \text{l}^{-1}$	$[M_1]/[M_1] + [M_2]$				
2.90	0.950	6.4			
	0.904	10.5			
	0.803	16.3	12.9	70.8	18.2
	0.602	22.9			
	0.500	29.9	8.3	61.8	11.8
	0.403	32.9	5.8	61.3	9.4
	0.201	43.2	2.0	54.8	3.8
	0.105	48.5	1.0	50.5	2.0

For this system, too, K'_c was found to be very high so that k_{12} tends again towards zero. The parameters r_2 and r_3 were evaluated graphically on the basis of Eq. 10:

$$r_2 = 0.01 \quad r_3 = 1.15 \pm 0.1$$

and of Eq. 11 (see experimental part)

$$r_2 = 0.01 \quad r_3 = 1.30 \pm 0.1$$

It may be worthwhile to mention that the calculation of r_2 and r_1 parameters based on the usual ALFREY-PRICE equation without taking into account the cyclopolymerization of vinyl cinnamate, gives $r_2 = 0.01$ and $r_1 = 1.20$.

c) Copolymerization with methacrylonitrile

In order to compare the behaviour of a monomer of different polarity and reactivity, copolymerization experiments with methacrylonitrile have been carried out. The results are given in Table 11.

Table 11. Copolymerization of vinyl cinnamate (M_1) and methacrylonitrile (M_2)
 $t = 70^\circ\text{C}$., $[\text{AIBN}] = 0.61 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$, solvent: cyclohexanone

$[\text{M}_1] + [\text{M}_2]$ $\text{mole} \cdot \text{l}^{-1}$	$[\text{M}_2]$	$[\text{m}_2]$ $\text{mole} \%$	$[\text{m}_1]$ mole %		% Unsaturation of m_1
			Cinnamic units	γ -Lactone	
2.375	1.917	95.5	3.7	0.8	82
	1.585	90.6	6.3	3.1	67
	1.180	82.2	9.1	8.6	53
	0.925	77.0	12.3	10.6	52
	0.829	70.9	13.9	15.1	47
	0.480	54.0	18.7	27.3	40
$[\text{M}_1]$ $\text{mole} \cdot \text{l}^{-1}$					
1.436	0.925	77.0	12.3	10.6	53
	1.876	84.8	10.0	5.2	65
	3.822	89.2	5.6	5.1	52
	7.694	95.4	3.3	1.3	71
1.676	0.504	61.2	17.7	21.0	45
	0.963	77.8	13.1	9.4	60
	1.420	80.8	11.7	7.4	61
	1.846	83.7	9.6	6.6	59

In the first series of experiments the overall concentration of the two monomers was kept constant and equal to $2.375 \text{ mole} \cdot \text{l}^{-1}$. As can be seen in Table 11, the percent of vinyl cinnamate units incorporated as open ester units is much higher than in the homopolymerization and in the two previous copolymerizations; indeed, with vinyl acetate and vinyl pyrrolidone, this content never exceeded 20%. By application of Eq. 8 K'_c could be evaluated; a more accurate determination was possible by

means of experiments with constant vinyl cinnamate and increasing methacrylonitrile concentration. Fig. 3 shows the plot of

$$\frac{d[M_1]}{d[m]} - \frac{[M_1]}{K_c} \text{ vs. } [M_2];$$

K'_c was found equal to 1

$$K'_c/K_c = k_{11}/k_{12} = 0.10 \pm 0.01$$

Substituting these values in Eqs. 7 and 9 the copolymerization parameters r_2 and r_3 were calculated:

$$r_2 = 4 \quad r_3 = 0.15$$

In first approximation it can be admitted that $r_1 = r_3$; indeed, using the ALFREY-PRICE equation, r_2 and r_1 were found equal to 4.6 ± 0.4 and 0.15 ± 0.06 respectively, values which agree fairly well with $r_2 = 4$ and $r_3 = 0.15$.

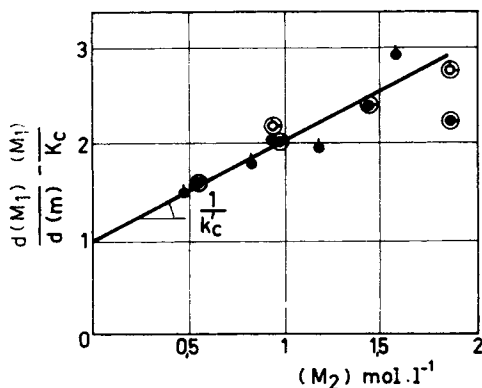


Fig. 3. Copolymerization of vinyl cinnamate (M_1) and methacrylonitrile (M_2) following Eq. 8

$$\frac{d[M_1]}{d[m]} - \frac{[M_1]}{K_c} = 1 + \frac{[M_2]}{K'_c}$$

d) Copolymerization with styrene

It is well known that in copolymerizations of styrene with vinyl acetate, vinyl benzoate or vinyl chloride, only very small amounts of these monomers are incorporated in the polymer. It is assumed that this effect is due to the low reactivity of these monomers toward the stabilized styryl radical.

From this point of view the copolymerization of vinyl cinnamate with styrene is especially interesting, and some experiments are reported in Table 12. Column 4 of this table indicates the molar percent of vinyl cinnamate units built into the copolymer either as γ -lactone or as unsaturated vinyl side groups. Indeed, in this case the vinyl absorption band in the infrared is very appreciable.

Table 12. Copolymerization of vinyl cinnamate (M_1) and styrene (M_2)
 $t = 70^\circ\text{C.}$, $[\text{AIBN}] = 0.61 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$, solvent: benzene
 $[\text{M}_1] + [\text{M}_2] = 2.89 \text{ mole} \cdot \text{l}^{-1}$

$[\text{M}_2]$	$[\text{m}_2]$ mole-%	Cinnamic units mole-%	Δ
2.332	84.7	1.2	14.1
1.891	72.6	2.4	24.8
1.457	63.3	3.2	33.4
1.020	54.8	6.1	39.0
0.583	34.2	7.4	58.4

Therefore, only apparent copolymerization parameters r'_1 and r'_2 were determined on the basis of the ALFREY-PRICE equations; they are equal to

$$r'_1 = 0.25 \pm 0.1 \quad r'_2 = 1.25 \pm 0.1$$

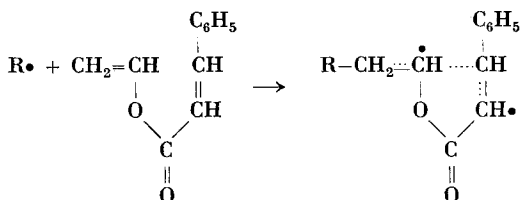
3. Conclusions

The results of these four copolymerization systems can be summarized best in a survey of the rate constant ratios which have been determined experimentally.

System	$K_c = k_c/k_{11}$	$K'_c = k_c/k_{12}$	$r_1 = k_{11}/k_{12}$	$r_2 = k_{22}/k_{21}$	$r_3 = k_{31}/k_{32}$
Vinyl cinnamate (M_1) .	11				
(M_1) + vinyl acetate . . .		high		0.04	1.20
(M_1) + vinyl pyrrolidone		high		0.01	1.15
(M_1) + methacrylonitrile		1	0.10	4	0.15
(M_1) + styrene			(0.25)	(1.25)	

From this table it is evident that the reactivity of vinyl cinnamate is intermediary between that of usual vinyl esters and that of (meth)acrylic monomers. The high K'_c values obtained in the presence of vinyl acetate

and vinyl pyrrolidone suggest a pseudo-cyclic benzyl stabilized radical as soon as the vinyl double bond has been added.



A similar suggestion was already put forward by MARVEL in the case of the cyclopolymerization of 1,5-hexadiene¹⁴.

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