

Experimental Study of Copolymerization. III. Copolymerization Behavior of Polychloroethylenes

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INTRODUCTION*

SEVERAL investigators¹⁻⁴ have observed that 1,2 disubstituted ethylenes exhibit copolymerization behaviors quite different from those of vinyl and vinylidene monomers. It is common for such 1,2 disubstituted monomers to copolymerize more or less readily with vinyl compounds, although they do not polymerize (or polymerize only with great difficulty) by themselves. This fact has been interpreted as an indication that the specific rate constant for the self-propagation step is unusually low, rather than as evidence for a low rate of chain initiation, or for an unusually high rate of chain termination. This assumption is substantiated by the fact that in such copolymerization studies, when the monomer M_2 is a 1,2 disubstituted ethylene, the reactivity ratio r_2 has been found to equal zero within experimental error. This means that the rate constant for self-propagation of such monomers is vanishingly small.

The structural origin of this effect, however, is somewhat in doubt. Most of the 1,2 disubstituted monomers which have been studied have been symmetrically substituted, *e.g.*, maleic anhydride and maleic esters. The peculiar reluctance to self-propagation could therefore be attributed to the balanced electrical charge distribution in the double bond. On the other hand, it is possible that this is a steric effect, and that a 1,2 disubstituted alkyl free radical has difficulty in approaching a 1,2 disubstituted ethylene.

We have therefore studied the copolymerization behavior of a number of 1,2 disubstituted ethylenes of both the symmetrical and unsymmetrical type. The present paper presents experimental results on the copolymerization of *cis*-dichloroethylene, *trans*-dichloroethylene, and trichloroethylene, with vinyl acetate and styrene. The unsymmetrical compound—trichloroethylene—exhibited the same reluctance to add to itself in the growing chain as did the two dichloroethylenes. This result (as well as similar results with other unsymmetrical 1,2 polysubstituted ethylenes recently obtained in this laboratory) would seem to indicate that the effect in question has its origin in steric interference rather than in a balanced electrical character of the double bond.

* *Note added in proof:* A very similar study of the copolymerization properties of the chloroethylenes has been reported by K. W. Doak, in a paper presented at the 112th Meeting of the American Chemical Society, September 1947 (*J. Am. Chem. Soc.*, *in press*).

¹ T. Alfrey, Jr., E. Merz, and H. Mark, *J. Polymer Research*, **1**, 37-43 (1946).

² P. Agron, T. Alfrey, Jr., J. Bohrer, H. Haas, and H. Wechsler, *J. Polymer Sci.*, **3**, 157-166 (1948).

³ T. Alfrey, Jr., and E. Lavin, *J. Am. Chem. Soc.*, **67**, 2044 (1945).

⁴ T. Wagner-Jauregg, *Ber.*, **63**, 3213 (1930).

EXPERIMENTAL

Vinyl acetate (Niacet) was purified by vacuum distillation. *Cis*- and *trans*-dichloroethylenes (Dow) were used as received. Styrene monomer was washed several times with dilute caustic solution to remove inhibitor, and was then washed several times with distilled water, dried over calcium chloride, and distilled under vacuum. Trichloroethylene was purified by vacuum distillation.

The monomers were mixed in the proportions described in the tables. All mixtures contained 0.1% by weight of benzoyl peroxide. Immediately before sealing, carbon dioxide was passed through the solutions. The tubes were then sealed and placed in a 68°C. constant temperature bath. The copolymers containing vinyl acetate were purified by precipitating in hexane and redissolving in benzene. This was done at least three times to separate all the monomer from the copolymer. The copolymers containing styrene were dissolved in methyl ethyl ketone and precipitated with methanol. The copolymers were then dried in a vacuum oven at 50°. Chlorine analyses were carried out by Raymond J. Bunker.

The following tables, Systems I through V, indicate the composition of the initial monomer mixture, the time allowed for conversion, the per cent yield of polymer, the chlorine analysis, and the molar composition of the copolymer.

SYSTEM I. VINYL ACETATE (M_1)-*trans*-DICHLOROETHYLENE (M_2)

Tube No.	Time, hours	M_2^*	Per cent chlorine in polymer	m_2^{**}	Conversion, %
1-1	11	0.223	15.13	0.192	0.98
1-2	15	0.462	26.55	0.339	11.9
1-3	46	0.722	36.2	0.466	11.9
1-4	46	0.607	32.9	0.424	3.5
1-5	19	0.309	19.75	0.252	4.35
1-6	4	0.084	6.90	0.088	7.3

* Mole fraction of vinyl chloride in monomer mixture.

** Mole fraction of vinyl chloride in copolymer.

SYSTEM II. VINYL ACETATE (M_1)-*cis*-DICHLOROETHYLENE (M_2)

Tube No.	Time, hours	M_2	Per cent chlorine in polymer	m_2	Conversion, %
2-1	83	0.777	31.1	0.387	0.28
2-2	10.5	0.565	17.2	0.216	6.7
2-3	7.5	0.472	14.06	0.175	11.1
2-4	7.5	0.087	3.26	0.039	15.7

SYSTEM III. STYRENE (M_1)-*trans*-DICHLOROETHYLENE (M_2)

Tube No.	Time	M_2	Per cent chlorine in polymer	m_2	Conversion, %
3-1	11 days	0.895	24.1	0.327	1.47
3-2	4 "	0.815	7.6	0.108	9.1
3-3	2 "	0.645	5.5	0.081	15.2
3-4	29 hrs.	0.506	3.2	0.047	13.5
3-5	8 "	0.298	0.05	0.005	7.4
3-6	1.5 "	0.109	0.05	0.005	1.43

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SYSTEM IV. STYRENE (M_1)-*cis*-DICHLOROETHYLENE (M_2)

Tube No.	Time	M_2	Per cent chlorine in polymer	m_2	Conversion, %
4-1	12 days	0.907	4.5	0.071	3.8
4-2	27 hr.	0.813	1.96	0.029	6.7
4-3	27 "	0.665	0.84	0.012	12.9
4-4	10 "	0.490	0.05	0.0007	5.8
4-5	3 "	0.254	0.05	0.0007	5.6
4-6	3 "	0.099	0.05	0.0007	3.5

SYSTEM V. VINYL ACETATE (M_1)-TRICHLOROETHYLENE (M_2)

Tube No.	Time	M_2	Per cent chlorine in polymer	m_2	Conversion, %
5-1	5 hrs.	0.110	16.5	0.142	15.5
5-2	5 "	0.175	23.2	0.205	7.2
5-3	10 "	0.282	29.8	0.270	25.6
5-4	24 "	0.495	38.8	0.372	25.6
5-5	3 days	0.590	41.35	0.405	22.7
5-6	3 "	0.815	46.45	0.465	3.97

DISCUSSION OF RESULTS

The experimental results for System II and System V are shown in Figures 1 and 2, respectively. In both these cases, the reactivity ratio r_2 is equal to zero,

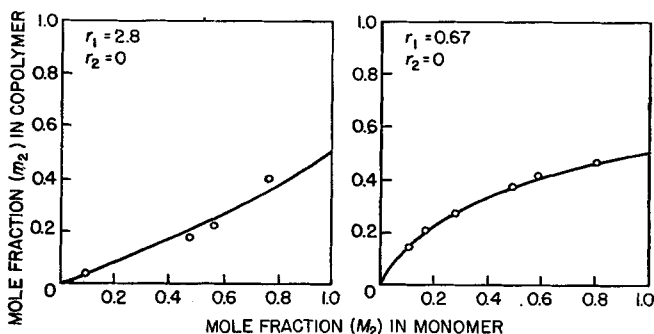


Fig. 1. Copolymer composition curve for the system vinyl acetate (M_1)-*cis*-dichloroethylene (M_2).

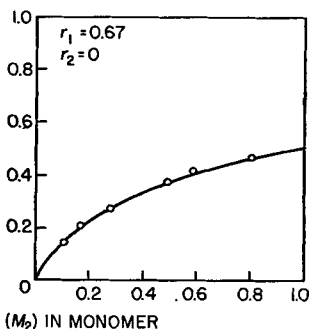


Fig. 2. Copolymer composition curve for the system vinyl acetate (M_1)-trichloroethylene (M_2).

within experimental error. Systems III and IV involve styrene as monomer M_1 . Styrene monomer is so reactive with free radicals that *cis*- and *trans*-dichloroethylenes enter the copolymer only in very small amounts. The reactivity ratios for these two systems are less precisely determined. Reactivity ratios for all five monomer pairs are given in Table I. (Values for vinyl acetate with tetrachloro-

TABLE I
REACTIVITY RATIOS

System No.	M_1	M_2	r_1	r_2
1	Vinyl acetate	<i>trans</i> -Dichloroethylene	0.85	0
2	Vinyl acetate	<i>cis</i> -Dichloroethylene	2.8	0
3	Styrene	<i>trans</i> -Dichloroethylene	~10	0
4	Styrene	<i>cis</i> -Dichloroethylene	50-100	0
5	Vinyl acetate	Trichloroethylene	0.67	0
(Part II-4)	Vinyl acetate	Tetrachloroethylene	5	0
(Part II-1)	Vinyl acetate	Vinyl chloride	0.3	2.1
(Part II-6)	Vinyl acetate	Vinylidene chloride	0.1	6

ethylene, vinyl chloride, and vinylidene chloride from Part II of this series.³) We can summarize our findings as follows:

(1) All six chlorine-substituted ethylenes copolymerize with vinyl acetate. In those cases where both carbon atoms are substituted, the monomer exhibits a specific reluctance for self-propagation. This is true for the unsymmetrical trichloroethylene, as well as the symmetrical compounds.

(2) Vinyl chloride is slightly more reactive than vinyl acetate.

(3) Introduction of a second chlorine atom in the 1 position (to form vinylidene chloride) increases the reactivity about threefold.

(4) *Trans*-dichloroethylene is about four times as reactive with a vinyl acetate radical as the *cis*-isomer, but less than half as reactive as vinyl chloride.

(5) The reactivity of trichloroethylene is slightly greater than that of *trans*-dichloroethylene.

(6) Tetrachloroethylene is about half as reactive as *cis*-dichloroethylene; about $\frac{1}{7}$ as reactive as *trans*-dichloroethylene and trichloroethylene.

(7) The above results are consistent with the hypothesis that further substitution on the carbon atom which is being attacked by a radical *decreases* the rate constant for the addition reaction, but that further substitution of the other carbon atom of the double bond *increases* the rate constant for addition. (We assume here that attacking radicals add preferentially to the *least* substituted carbon atom.)

Synopsis

Experimental results are reported for the copolymerization of *cis*- and *trans*-dichloroethylenes and trichloroethylene with vinyl acetate and styrene. Unsymmetrical as well as symmetrical 1,2 polysubstituted ethylenes exhibit extremely small rate constants for self-propagation, but are easily attacked by vinyl-type radicals such as that formed by vinyl acetate. The attack of such monomers by vinyl "growing chain" radicals is retarded by substitution on the attacked carbon atom, but is favored by substitution on the other carbon atom of the double bond.

Résumé

Les résultats expérimentés sont rapportés pour la copolymérisation de *cis* et *trans* éthylène bichloré et trichlorure d'éthylène avec l'acétate de vinyle et styrène. Des éthylènes 1,2 polysubstitués, symétrique et asymétrique montre une constante de la vitesse très petite pour la autocatalyse, mais sont attaqués facilement par les radicaux du type de vinyle tels que ceux formés par l'acétate de vinyle. L'attaque de ces monomères par la chaîne croissante de radicaux viniliques

est retardée par la substitution sur l'atome de carbone attaqué, mais est favorisée par la substitution sur l'autre atome de carbone de la liaison double.

Zusammenfassung

Es wird über die Kopolymerisation von *cis*- und *trans*-Dichloräthylenen und Trichloräthylenen mit Vinylacetat und Styrol berichtet. Unsymmetrische und symmetrische 1,2 poly-substituierte Äthylene geben äusserst kleine Geschwindigkeitskonstanten für Autokatalyse, werden aber durch Radikale vom Vinyltypus, wie z.B. die von Vinylacetat gebildeten leicht angegriffen. Der Angriff solcher Monomeren durch "wachsende Ketten"-Vinylradikale wird durch Substitution am angegriffenen Kohlenstoffatom gehemmt, wird aber durch Substitution an dem anderen Kohlenstoffatom der Doppelbindung begünstigt.

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