Tetrachlorocyclopropene. Penultimate Effect and Three-Membered Ring Structure in Copolymerizations with Vinyl Acetate and Styrene

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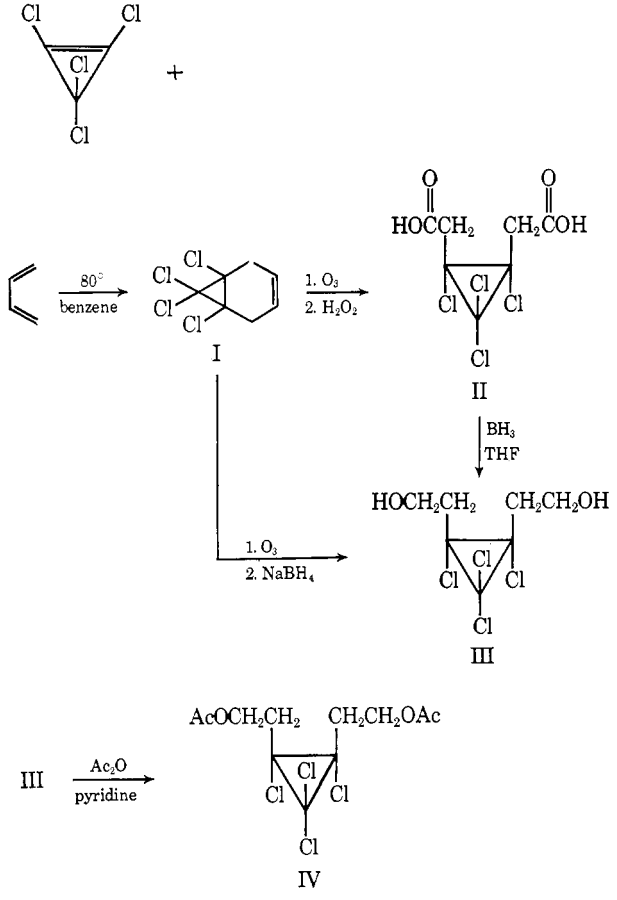
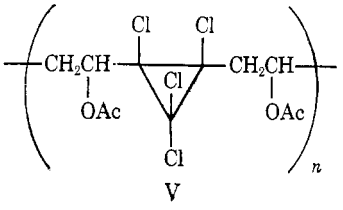
ABSTRACT: The presence of chlorinated three-membered rings in copolymers of tetrachlorocyclopropene has been confirmed by synthesis of the diacetate of 1,2,3,3-tetrachlorocyclopropane-*cis*-1,2-diethanol and comparison of its spectra with those of vinyl acetate copolymers. Analysis of low-conversion data in free-radical copolymerizations with vinyl acetate and styrene indicates that tetrachlorocyclopropene does not add to a growing chain when the penultimate unit is tetrachlorocyclopropene. Assuming that self-addition of tetrachlorocyclopropene is forbidden, reactivity ratios have been calculated for vinyl acetate (0.72 ± 0.02 at 80°) and styrene (5.7 ± 0.4 at 60°).

Although tetrachlorocyclopropene fails to homopolymerize, it enters into copolymerization reactions which have been the subject of an earlier report.[1] In order to learn more about the structure of the polymers and the reactivity of this interesting monomer, we have synthesized a model compound for spectral comparisons with the vinyl acetate copolymers and have studied the kinetics of low-conversion copolymerizations.

SCHEME I



Model Compound Synthesis. A model system close in structure to vinyl acetate–tetrachlorocyclopropene copolymers containing retained three-membered rings is the diacetate of 1,2,3,3-tetrachlorocyclopropane-*cis*-1,2-diethanol. The synthetic mechanism used in the preparation of this compound (IV) is shown in Scheme I. Compound IV is not a perfect model for two reasons. It has the *cis* stereochemistry because of its preparation from Diels–Alder adduct I, whereas the copolymers could have either *cis* or *trans* arrangements of chains joined to the rings. Furthermore, the acetoxyethyl side chains are attached to the ring by the β-carbon atom (tail) while vinyl acetate copolymers should have the head-to-tail structure (V). The similarity of the infrared spectra of the model and the copolymer (Figures 1 and 2), however, leaves little doubt of the predominance of units such as V in the polymers.



The ultraviolet spectrum of compound IV in acetonitrile shows a weak extinction (ε 300) at a maximum of 228 mμ. Now that the nature of the repeating unit in the vinyl acetate copolymers is known, the extinction of the copolymers can be calculated using wt 350 (structure V) for those polymers where the mole fraction of C_3Cl_4 units is 0.33. Such a polymer (mol wt 2200 from vapor pressure osmometry) has ε 1600 in acetonitrile at 227 mμ. Because a polymer of this size should contain an average of 6.3 units of structure V, and a chlorinated double bond should have ε 10,000,[2a] the presence of an

(1) J. K. Hecht, *J. Polym. Sci., Part B*, **6**, 395 (1968).

(2) (a) J. D. Idol, Jr., C. W. Roberts, and E. T. McBee, *J. Org. Chem.*, **20**, 1743 (1955); (b) the ultraviolet extinction calculations are not intended to give a precise determination of olefinic content of the copolymers. What is shown here is that the absorption is much too strong to be accounted for by only cyclopropane rings but not strong enough for more then one double bond per chain. Thus the termination step involving ring opening is suggested.

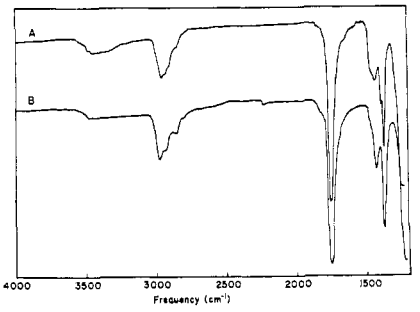


Figure 1. Infrared spectra of model compound IV (A) and a copolymer with structure V (B); frequency 1500–4000 cm^{-1}.

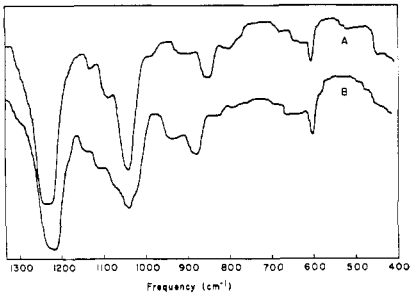
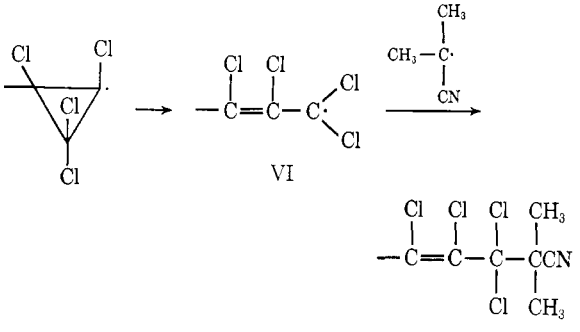


Figure 2. Infrared spectra of model compound IV (A) and a copolymer with structure V (B); frequency 400–1300 cm^{-1}.

average of one double bond per chain is indicated. This is strongly suggestive of a termination step involving allylic species such as VI.[2b]



Copolymerization Parameters of Tetrachlorocyclopropene. Low-conversion free-radical copolymerizations of tetrachlorocyclopropene were carried out in bulk with vinyl acetate and styrene. The monomer ratios in the copolymers were determined by chlorine analysis. Attempted fitting of data to a Fineman–Ross plot[3] produced a considerable amount of scatter and negative reactivity ratios for tetrachlorocyclopropene.

Examination of the composition curves (Figures 3 and 4) shows that as the mole fraction of tetrachlorocyclopropene was increased in the monomer mixtures its mole fraction in the copolymers reached approximately 0.33 as a limiting value. This is strongly indicative of a penultimate effect in which tetrachlorocyclopropene refuses to add to a growing chain unless it is terminated by at least two vinyl acetate or styrene units, or the addition is rapidly reversed by depolymerization.

The equation of Merz, Alfrey, and Goldfinger[4] taking into account the effect of penultimate groups reduces to $f - 2 = rF$ if the rates of addition of tetrachlorocyclopropene are set to zero when tetrachlorocyclopropene is the penultimate or end group in the growing chain. Here $f = [m_1]/[m_2]$ in the copolymer and $F = [M_1]/[M_2]$ in the monomer mixture, M_2 = tetrachlorocyclopropene (where brackets indicate mole fraction). Then $r = k_{111}/k_{112}$ and is the slope of a linear plot of $f - 2$ against

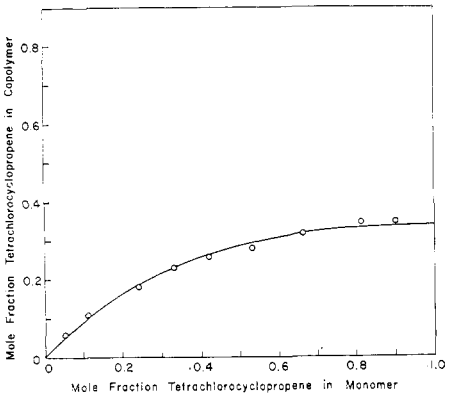


Figure 3. Copolymerization composition curve for vinyl acetate and tetrachlorocyclopropene.

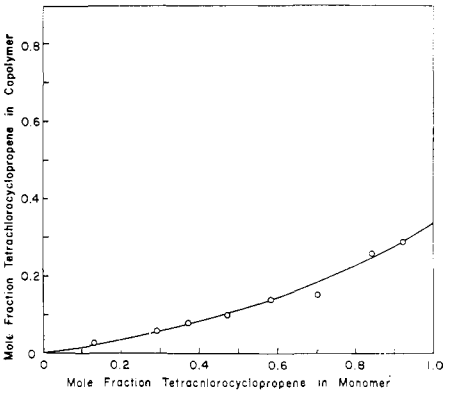


Figure 4. Copolymerization composition curve for styrene and tetrachlorocyclopropene.

F. Such plots are shown for vinyl acetate–tetrachlorocyclopropene (Figure 5) and styrene–tetrachlorocyclopropene (Figure 6). The higher reactivity ratio for styrene (5.7 ± 0.4) than that for vinyl acetate (0.72 ± 0.02) was the expected result.

The penultimate effect observed here is probably due to steric interference between chlorine atoms on a tetrachlorocyclopropene monomer and a corresponding unit already incorporated into a polymer chain. Examination of molecular models shows severe interactions between tetrachlorocyclopropane units when they are separated by only one vinyl acetate or styrene unit. Steric factors are significant in free-radical polymerization of 1,1-disubstituted monomers (low ceiling temper-

(3) M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
(4) E. Merz, T. Alfrey, and G. Goldfinger, *ibid.*, **1**, 75 (1946). This equation is discussed thoroughly by G. E. Ham in "Copolymerization," G. E. Ham, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter 1.

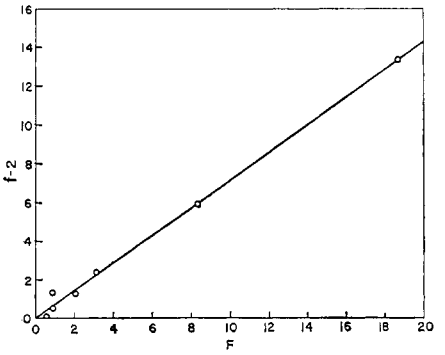


Figure 5. Reactivity ratio for vinyl acetate: r = slope = 0.72 ± 0.02 at 80°.

atures) and 1,2-disubstituted olefins (reluctance to homopolymerize). Because tetrachlorocyclopropene is tetrasubstituted, its polymerization behavior should be expected to be subject to steric effects as we have observed. Penultimate effects have been discussed for fumaronitrile and other monomers by Ham,[5,6] Barb,[7] Kreisel, Garbatski and Kohn,[8] and Sumitomo and Azuma.[9]

Experimental Section[10]

1,6,7,7-Tetrachloro-*cis*-bicyclo[4.1.0]hept-3-ene (I).[11] Two capped polymer pressure tubes were each charged with a solution of 20 g (0.11 mol) of tetrachlorocyclopropene, 20 ml of butadiene, and 0.4 g of 2,6-di-*t*-butyl-*p*-cresol in 30 ml of benzene and heated in an oil bath at 80° for 118 hr. The tubes were cooled until frozen solid, opened, combined, and concentrated under reduced pressure. The crude product was recrystallized from petroleum ether (bp 30–60°) yielding 38 g (82%) of adduct, mp 51–52°.

1,2,3,3-Tetrachlorocyclopropane-*cis*-1,2-diacetic acid (II).[12] A solution of 2.32 g (0.01 mol) of 1,6,7,7-tetrachloro-*cis*-bicyclo[4.1.0]hept-3-ene in 30 ml of acetic acid and 15 ml of acetic anhydride was ozonized at 0° for 30 min. After the solution was flushed with nitrogen to remove dissolved ozone, a solution of 7 ml of 30% hydrogen peroxide in 50 ml of water was added. The clear mixture was heated on a steam bath for 75 min and then refluxed for 19 hr.[13] Distillation at atmospheric pressure gave a residue which was dissolved in ether. The ether solution was dried over magnesium sulfate and concentrated under reduced pressure. From 1.86 g of crude acid there was crystallized 0.86 g (29%) of material, mp 201–202°, by addition of chloroform. Small additional amounts of product continued to crystallize slowly from the chloroform solution.

Anal. Calcd for $C_7H_6Cl_4O_4$: C, 28.41; H, 2.04; Cl, 47.92. Found: C, 28.27; H, 1.87; Cl, 47.90.

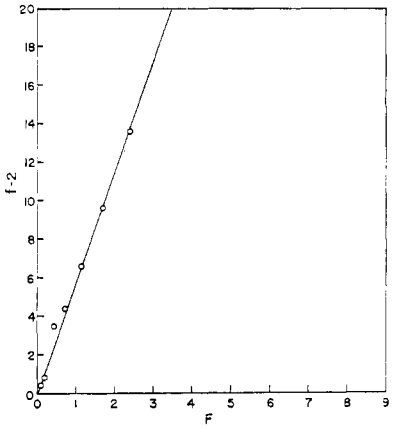


Figure 6. Reactivity ratio for styrene: r = slope = 5.7 ± 0.4 at 60°.

1,2,3,3-Tetrachlorocyclopropane-*cis*-1,2-diethanol (III) by Borane Reduction of 1,2,3,3-Tetrachlorocyclopropane-*cis*-1,2-diacetic Acid.[14] A solution of 0.50 g (0.0017 mol) of the diacid in 10 ml of dry tetrahydrofuran was cooled to 10° in a nitrogen atmosphere. A 1 *M* solution of borane (10 ml) in tetrahydrofuran (obtained from Ventron Corp.) was added dropwise over a 15-min period. The mixture was stirred for 2 hr as the temperature rose slowly to 26°. A solution of 5 ml of methanol in 10 ml of tetrahydrofuran was added dropwise to decompose excess borane. After the solvents were removed under reduced pressure, the residue (0.54 g) was dissolved in ether and 6 *N* hydrochloric acid. The ether solution was washed with saturated aqueous sodium bicarbonate, dried over $MgSO_4$, and concentrated yielding 0.32 g (71%) of crude glycol, mp 100–101°. Recrystallization from a mixture of ethyl acetate and benzene gave an analytical sample, mp 107–108°.

Anal. Calcd for $C_7H_{10}Cl_4O_2$: C, 31.37; H, 3.76; Cl, 52.93. Found: C, 31.45; H, 3.69; Cl, 52.73.

1,2,3,3-Tetrachlorocyclopropane-*cis*-1,2-diethanol (III) by Ozonization of 1,6,7,7-Tetrachloro-*cis*-bicyclo[4.1.0]hept-3-ene Followed by Reduction with Sodium Borohydride. A solution of 2.32 g (0.01 mol) of 1,6,7,7-tetrachloro-*cis*-bicyclo[4.1.0]hept-3-ene and 0.15 g of sodium hydroxide in 50 ml of methanol was ozonized for 20 min at 0°. After the mixture was flushed with nitrogen, a suspension of 3.8 g (0.1 mol) of sodium borohydride and 0.15 g of sodium hydroxide in 50 ml of methanol was added over a 20-min period with cooling in an ice–water bath. After stirring for 15 min at room temperature, the solution was neutralized with 6 *N* sulfuric acid and concentrated under reduced pressure. The residue was extracted with ether and the ether solution was dried over magnesium sulfate. Evaporation of the ether gave 2.19 g of crude glycol, which was recrystallized from a mixture of ethyl acetate and benzene, yielding 1.07 g (40%) of glycol, mp 105–107°.

Acetylation of 1,2,3,3-Tetrachlorocyclopropane-*cis*-1,2-diethanol. A solution of 0.50 g (0.0019 mol) of the glycol in 3 ml of dry pyridine and 3 ml of acetic anhydride was heated for 0.5 hr on a steam bath, allowed to cool to room temperature, and added to 100 ml of cracked ice. The mixture was extracted with ether, and the ether solution was washed with cold 6 *N* hydrochloric acid, saturated aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated, yielding 0.59 g (89%) of light yellow liquid diacetate IV. An analytical sample ($n^{25}D$ 1.4970) was prepared by

(5) G. E. Ham, *J. Polym. Sci.*, **14**, 87 (1954).
(6) G. E. Ham, *ibid.*, **45**, 177 (1960).
(7) W. G. Barb, *ibid.*, **11**, 117 (1953).
(8) M. Kriesel, V. Garbatski, and D. H. Kohn, *ibid., Part A*, **2**, 105 (1964).
(9) H. Sumitomo and K. Azuma, *ibid., Part B*, **4**, 883 (1966).
(10) Infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer and ultraviolet spectra on a Perkin-Elmer Model 202 spectrophotometer. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.
(11) The procedure used here is a modification of that described by D. C. F. Law and S. W. Tobey, *J. Amer. Chem. Soc.*, **90**, 2376 (1968).
(12) Ozone was generated from a Welsbach Model T-23 ozonator using oxygen at about 600 ml/min.
(13) The general procedure used in this preparation was that of S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3235 (1961). Refluxing hydrogen peroxide is necessary to effect complete oxidation (see J. K. Hecht, *Tetrahedron Lett.*, 3503 (1968)).
(14) Borane reduction was adapted from J. K. Hecht and C. S. Marvel, *J. Polym. Sci., Part A-1*, **5**, 685 (1967).

TABLE I[a]
COPOLYMERIZATION OF STYRENE (M_1) AND TETRACHLOROCYCLOPROPENE (M_2) AT 60°

Wt % M_1	Wt % M_2	Mole fractions (of monomers) M	M_2	% Cl in copolymers	Mole fractions (in copolymers) m_1	m_2	Conversion wt %
5	95	0.083	0.92	32.75	0.71	0.29	1.8
10	90	0.16	0.84	30.34	0.74	0.26	3.2
20	80	0.30	0.70	18.83	0.85	0.15	0.2
30	70	0.42	0.58	16.88	0.87	0.14	0.8
40	60	0.53	0.47	13.28	0.90	0.10	0.6
50	50	0.63	0.37	10.24	0.92	0.079	1.0
60	40	0.71	0.29	7.92	0.94	0.060	1.0
80	20	0.87	0.13	4.42	0.97	0.033	1.6

[a] Molecular weights were not determined for the low-conversion experiments. Previous work, however (see ref 1), shows that the molecular weights for these systems range between 2000 and 5000 and decrease with increasing tetrachlorocyclopropene content in the copolymers.

short-path distillation at 2 mm with a pot temperature of 200°.

Anal. Calcd for $C_{11}H_{14}Cl_4O_4$: C, 37.52; H, 4.02; Cl, 40.28. Found: C, 37.89; H, 3.93; Cl, 40.21.

Copolymerizations. Tetrachlorocyclopropene (bp 130–132°), obtained from Dr. S. W. Tobey of this laboratory and from Aldrich Chemical Co., was shown to be homogeneous by gas chromatography on a silicone oil column at 50°. Styrene was Eastman White Label grade, distilled before use. Vinyl acetate was Eastman Practical grade, distilled and passed through silica gel.

Polymerizations were run in bulk in capped polymer tubes in a nitrogen atmosphere. Temperatures were regulated by thermostated oil baths to 60 ± 1° for styrene copolymerizations and to 80 ± 1° for vinyl acetate runs.

TABLE II[a]
COPOLYMERIZATION OF VINYL ACETATE (M_1) AND TETRACHLOROCYCLOPROPENE (M_2) AT 80°

Wt % M_1	Wt % M_2	Mole fractions (of monomers) M_1	M_2	% Cl in copolymers	Mole fractions (in copolymers) m_1	m_2	Conversion, wt %
5	95	0.098	0.90	43.24	0.65	0.35	0.1
10	90	0.19	0.81	42.21	0.65	0.35	0.1
20	80	0.34	0.66	39.76	0.68	0.32	0.6
30	70	0.47	0.53	31.38	0.72	0.28	3.6
40	60	0.58	0.42	33.57	0.74	0.26	3.2
50	50	0.67	0.33	30.82	0.77	0.23	4.2
60	40	0.76	0.24	25.33	0.82	0.18	5.9
80	20	0.89	0.11	16.30	0.89	0.11	16.2
90	10	0.95	0.051	9.45	0.94	0.06	10.0

[a] See Table I, footnote *a*.

Styrene runs were conducted for 1 hr[15] using 0.2% by weight of azobisisobutyronitrile (AIBN) as the initiator (Table I). Conversions were less than 4% under these conditions. The styrene copolymers were precipitated from methanol for purification. Vinyl acetate copolymerizations were run for 15 min[15] with 0.2% AIBN to less than 17% conversion (Table II). The precipitation solvent was petroleum ether, bp 30–60°. All of the polymers were dried in a vacuum oven at 60° for 16–20 hr.

Acknowledgment. The authors are indebted to Dr. Turner Alfrey, Jr., The Dow Chemical Co., Midland, Mich., for generous help in interpretation of our data.

(15) Polymerizations in which the starting mixture of monomers contained more than 0.8 mole fraction of tetrachlorocyclopropene were conducted for 16 hr because of the slow rate of polymer formation at these concentrations.