[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Infrared Spectra and Force Constants of Chloroform and Trichlorosilane[1a,b]

BY T. G. GIBIAN[1c,d] AND D. S. MCKINNEY

The infrared spectra of chloroform and trichlorosilane were obtained with a rock salt spectrometer in the range of 1–15μ in both the liquid and vapor states. The C–H stretching bond of chloroform vapor was resolved into the PQR branch with a high resolution grating spectrometer. A complete assignment of observed bands was made. A simplified potential function is proposed on basis of which the force constants of chloroform and trichlorosilane are obtained. Using these force constants fundamental frequencies are calculated which agree to within 1.5% with the experimental ones.

This paper presents infrared absorption spectra of chloroform and trichlorosilane in the liquid and vapor states from 1 to 15 μ obtained by means of a rock salt spectrometer. The nature of the chloroform spectrum in the 3 μ region has also been investigated under high resolution with the aid of a grating spectrometer.

The hitherto published infrared spectra of chloroform were limited mostly to the liquid or dissolved chloroform in the regions of the fundamentals only,[2,3] whilst the Raman spectrum was obtained by numerous investigators in the liquid[2,4,5] as well as in the vapor states.[6]

In the case of trichlorosilane, only the Raman spectrum of the liquid has been reported so far[7,8] with no infrared data published prior to this investigation.

Consideration of the published Raman and infrared data, together with the data given here, permitted a complete assignment of the observed spectral bands as well as the calculation of the force constants for these compounds on the basis of a simplified potential function. This potential function is particularly suited to the analysis of the spectra of pentaatomic tetrahedral molecules of the type HXY_3, where X = C, Si, Ge and Y = Cl, B, I, utilizing the F and G Matrix method of Wilson.[9]

Experimental

The spectrometers have been described by others.[10,11] The spectra were taken by the usual cell-in, cell-out method, using a rock salt dummy. Readings were usually taken every slit width; sometimes, two per slit width when it seemed advisable.

The chloroform was Merck C.P., further purified by shaking with concentrated sulfuric acid three times, washing with water, and after drying with $CaCl_2$ redistilling from a ground glass equipment using a Widmer column. The middle fraction was taken and stored in a dark bottle. Only small amounts were kept at a time and more chloroform purified as needed.

The trichlorosilane was obtained from the Anderson Laboratories, Adrian, Michigan, and was used without further purification. The manufacturer's analysis for the pure grade was $SiHCl_3 >$ 99.5%, $SiCl_4 <$ 0.5%.

Amalgamated lead washers[12] were used as spacers for the liquid cells. They also served to provide a gas tight joint between the rock salt window and the glass body of the vapor absorption cell. In the cell for the liquid chloroform investigation a narrow strip of lead was drawn tightly over the outside surface and sealed with a film of polyvinyl alcohol from a methyl alcohol solution. This seal remained gas-tight for periods of 24 to 48 hours.

Due to the rapid decomposition of trichlorosilane in air, both the liquid and vapor cells were filled in a dry-box filled with drierite. To ensure perfect sealing, a layer of silicone putty was placed on the outside of the amalgamated lead washer, and the cell brought slowly to 180° and kept at this temperature for 8 hours. The hardened putty was then coated with silicone varnish and further cured at 150°. Both these silicone materials were special samples obtained through the courtesy of the Westinghouse Electric Corporation. With these precautions no decomposition of $SiHCl_3$ took place, and the cells remained gas-tight for several days.

The equilibrium vapor pressure method was used to obtain the desired concentrations of chloroform and trichlorosilane in the vapor cells. The liquid was placed in a small (10 cc.) glass bulb connected to the body of the vapor cell through a ground-glass joint. To obtain chloroform vapor pressures at higher than room temperature, the whole cell assembly was heated electrically, with the temperature of the cell being kept higher than that of the liquid bulb to prevent condensation on the rock salt windows. To reduce the vapor pressure of trichlorosilane (b.p. 318°), cooling mixtures (ice/water, Dry Ice, CO_2/acetone) were placed around the liquid container.

The cell thicknesses and vapor concentrations are indicated on the spectra.

Results

The infrared spectra of chloroform and trichlorosilane in the liquid and vapor are shown in Figs. 1, 2. The observed bands are given in Table I

---

(1) (a) Abstracted from a thesis submitted by T. G. Gibian to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the D.Sc. degree, December, 1948. (b) Presented before the Division of Physical and Inorganic Chemistry at the Meeting of the American Chemical Society, September, 1950, Chicago, Ill. (c) American Chemical Society pre-doctoral fellow, 1946–1948. (d) Atlantic Refining Company, Philadelphia, Pa.

(2) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945.

(3) G. L. Jenkins and J. W. Straley, *Phys. Rev.*, **68**, 99 (1945).

(4) K. W. F. Kohlrausch, "Der Smekal-Raman Effect," J. Springer, Berlin, 1931.

(5) J. H. Hibben, "The Raman Effect and Chemical Applications," Reinhold Publishing Corp., New York, N. Y., 1939.

(6) J. R. Nielsen and N. E. Ward, *J. Chem. Phys.*, **10**, 81 (1942).

(7) C. A. Bradley, *Phys. Rev.*, **40**, 908 (1932).

(8) M. de Hemptienne, *Nature*, **138**, 884 (1936).

(9) E. Bright Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); *ibid.*, **9**, 76 (1941).

(10) D. S. McKinney, C. E. Leberknight and J. C. Warner, THIS JOURNAL, **59**, 481 (1937).

(11) C. E. Leberknight and J. H. Ord, *Phys. Rev.*, **51**, 430 (1937).

(12) L. Gildart and N. Wright, *Rev. Sci. Inst.*, **12**, 204 (1941).

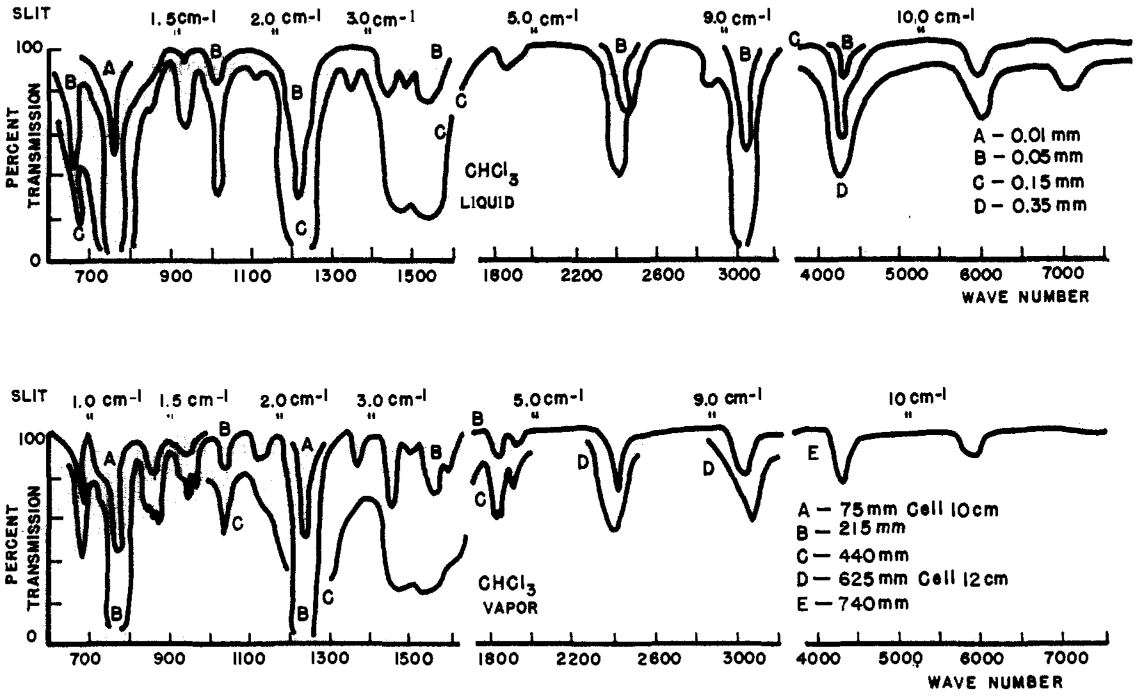

Fig. 1.—Infrared spectrum of chloroform.

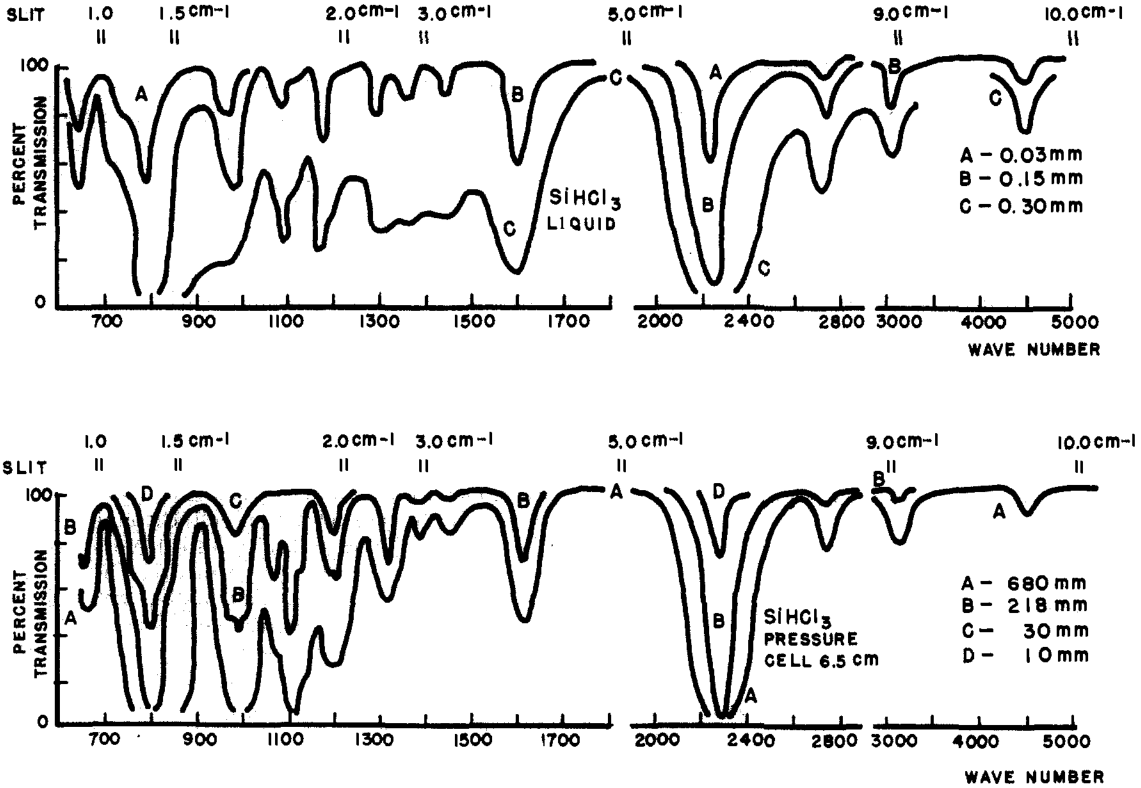

Fig. 2.—Infrared spectrum of trichlorosilane.

together with the complete assignment of the fundamentals, overtones and combination frequencies. The convention used for designating and ordering the frequencies is that adopted by Herzberg.[2] Best values of the fundamental frequencies as determined by Raman spectroscopy are compared with those of the present investigation in Table II.

TABLE I

THE OBSERVED FREQUENCIES AND ASSIGNMENTS OF CHLOROFORM AND TRICHLOROSILANE

Assignment	$CHCl_3$		Assignment	$SiHCl_3$	
	Liquid	Vapor		Liquid	Vapor
ν_2	668(s)	680(s)	$\nu_2 + \nu_6$	654(m)	667(m)
$2\nu_3$	709(sh)	720(sh)	$\nu_5 + \nu_6$	739(sh)	752(sh)
ν_5	759(s)	774(s)	ν_4	798(s)	808(s)
$\nu_4 - \nu_3$	851(w)	843	$\nu_3 + \nu_5$		829(sh)
		852(m)			
		858	$2\nu_2$	978(m)	971
					985(m)
[illegible] $+ \nu_6$	932(m)	924(sh)			991
		932(w)			
		944	$\nu_3 + \nu_4$	1048(sh)	1061(w)
$\nu_5 + \nu_6$	1017(m)	1029(w)	$\nu_2 + \nu_5$	1090(m)	1096(m)
$\nu_3 + \nu_5$	1118(w)	1125(w)	$2\nu_6 + \nu_4$	1111(sh)	1124(w)
ν_4	1218(s)	1221(s)	$2\nu_5$	1182(m)	1196 1204 (m)
$2\nu_2$	1338(w)	1356(w)	$\nu_2 + \nu_4$	1301(m)	1305(m)
$\nu_2 + \nu_5$	1428(m)	1447(m)	$\nu_4 + \nu_5$		1386(w)
$\nu_4 + \nu_6$	1480(m)	1481(w)	$2\nu_2 + \nu_3$	1441(w)	1454(w)
$2\nu_5$	1527(m)	1549(m)	$2\nu_4$	1594(m)	1610(m)
$\nu_3 + \nu_5$	1582(sh)	1580(w)	ν_1	2258(s)	2274(s)
$\nu_1 + \nu$[illegible]		1834 1840 (m)	$\nu_1 + \nu_2$	2734(w)	2751(w)
$\nu_2 + \nu_4$	1886(w)	1894(w)	$\nu_1 + \nu_4$	3059(w)	3090(w)
$2\nu_4$	2420(m)	2424(m)	$2\nu_1$	4514(w)	4526(w)
	2480(sh)				
$2\nu_4 + \nu_3$	2870(w)				
		3028(a)	a—with grating spectrometer		
ν_1	3032(s)	3034(s)	(sh)—shoulder		
		3041	(s)—strong		
$\nu_1 + \nu_4$	4260(m)	4273(m)	(m)—moderate		
$2\nu_2 + \nu_1$	4420(sh)		(w)—weak		
$2\nu_1$	5920(w)	5934(w)			
$2\nu_1 + \nu_5$	7049(w)				

TABLE II

COMPARISON OF FUNDAMENTAL FREQUENCIES OF CHLOROFORM AND TRICHLOROSILANE

Assignment	Chloroform				Trichlorosilane		
	This work		Raman vapor[6]	Infrared[2]	This work		Raman[7]
	Vapor	liquid			Vapor	Liquid	
ν_6	..	..	261	260	..	..	179
ν_3	..	..	363	364	..	..	250
ν_2	680	668	672	667	..	..	489
ν_5	774	759	760	760	..	..	587
ν_4	1221	1218	1217	1205	808	798	799
ν_1	3034	3032	3030	3033	2274	2258	2258

With the aid of the grating spectrometer the C–H stretching band in $CHCl_3$ was resolved into the PQR components in the vapor, but not in the liquid.

Calculation of Force Constants.—The chloroform and trichlorosilane molecules belong to the C_{3v} point group,[2,13] with three non-degenerate symmetrical fundamental vibrations A_1 and three doubly degenerate, anti-symmetrical fundamentals E, active both in the infrared and the Raman. A simplified potential function with six force constants was set up, containing force constants associated with changes in bond length and bond angle, as well as force constants related to the changes in the distances between the non-bonded atoms. The proposed potential function takes into account the interactions between the C–Cl (or Si–Cl) stretching and the various bond bendings, but sets the interactions of the C–H (or Si–H) bond stretchings with the various bendings as well as the interactions between the different bond bendings equal to zero. This is necessary to keep the number of force constants used to six, which is the number of the observed fundamentals.

The assumption that the omitted terms are quite small is reasonable on physical grounds, and is supported by the work of Decius[14] on the systematic halomethane force constants. Further data of Simanouti,[15] published after the completion of the present work, also agree with this postulate. The potential function was written as

$$\begin{aligned}2V = {} & f_d[\Delta d_1{}^2 + \Delta d_2{}^2 + \Delta d_3{}^2] + f_\alpha d^2[\Delta\alpha_{12}{}^2 + \Delta\alpha_{23}{}^2 + \\ & \Delta\alpha_{31}{}^2] + f_D[\Delta D^2] + f_\beta d^2[\Delta\beta_1{}^2 + \Delta\beta_2{}^2 + \Delta\beta_3{}^2] + \\ & 2f_{d\beta}d[(\Delta\beta_1)(\Delta d_1) + (\Delta\beta_2)(\Delta d_2) + (\Delta\beta_3)(\Delta d_3)] + \\ & 2f_{d\alpha}d[\Delta d_1(\Delta\alpha_{12} + \Delta\alpha_{31}) + \Delta d_2(\Delta\alpha_{12} + \Delta\alpha_{23}) + \\ & \Delta d_3(\Delta\alpha_{23} + \Delta\alpha_{31})]\end{aligned}$$

where d = equilibrium distance of C–Cl (or Si–Cl) bond; f_i = force constant associated with change in i's internal coördinate. In $HYCl_3$ molecules the coördinates used are. bond length, H–Y = D; Y–Cl = d_1, d_2, d_3; bond angles, HYCl = β_1, β_2, β_3; ClYCl = α_{12}, α_{31}, α_{23}.

The F matrices of Wilson's method[9] were then calculated from this potential function.

F Matrix for A_1 Type Vibrations

$$\begin{vmatrix} F_{11} & F_{12} & F_{13} \\ F_{21} & F_{22} & F_{23} \\ F_{31} & F_{32} & F_{33} \end{vmatrix} = \begin{vmatrix} f_D & 0 & 0 \\ 0 & f_d & \frac{d}{\sqrt{2}}(2f_{d\alpha} - f_{d\beta}) \\ 0 & \frac{d}{\sqrt{2}}(2f_{d\alpha} - f_{d\beta}) & \frac{d^2}{2}(f_\alpha + f_\beta) \end{vmatrix}$$

Type E Vibrations

$$\begin{vmatrix} F_{11} & F_{12} & F_{13} \\ F_{21} & F_{22} & F_{23} \\ F_{31} & F_{32} & F_{33} \end{vmatrix} = \begin{vmatrix} f_d & df_{d\beta} & -df_{d\alpha} \\ df_{d\beta} & d^2f_{d\beta} & 0 \\ -df_{d\alpha} & 0 & d^2f_\alpha \end{vmatrix}$$

The G matrix related to the kinetic energy was obtained by the method outlined by Wilson.[9] The G matrix depends only on the symmetry of the molecule, the reciprocal masses and interatomic distances, and was worked out for a C_3 type molecule by Wilson[9] for CH_3Cl. Substitution of the proper constants into these G matrix expressions yields the matrices used in these calculations.

Using these F and G matrices, the secular equations for A_1 and E type vibrations were written in expanded form and the coefficients of these cubics equated to the coefficients of similar cubics obtained from the experimental values of the fundamental frequencies. Two sets of three equations containing the six force constants as unknowns are thus obtained and can be solved.

To test the validity of the potential function, the stretching force constants for chloroform, f_d and f_D were transferred from Decius.[14] The remaining four force constants were then calculated and are listed in Table III. It is seen that the agreement with the experimental fundamentals is very good.

The procedure followed in calculating the force constants of trichlorosilane was similar to that outlined above. However, due to the lack of known silicon force constants, only the Si–H stretching constant (f_D = 2.84) was transferred

---

(13) J. E. Rosenthal and G. M. Murphy, *Rev. Mod. Phys.*, **8**, 317 (1936).

(14) J. C. Decius, *J. Chem. Phys.*, **16**, 214 (1948).

(15) T. Simanouti, *ibid.*, **17**, 245 (1949).

from SiH_4,[2] and adjusted slightly to give best agreement. The other five force constants were then calculated and are listed in Table III.

TABLE III

FORCE CONSTANTS AND CALCULATED FREQUENCIES

Force constant × 10^5		Frequency Calcd.	Frequency Obsd.[2]	This work liquid	Deviation, % From ref. 2	Deviation, % From this work
			Chloroform			
f_d	3.38[a]	3034	3033	3032	+0.03	+0.06
f_D	5.04[a]	664	667	668	−0.35	−0.60
f_α	0.59	366	364	..	+0.55	....
f_β	0.21	263	260	..	+1.26	....
$f_{d\alpha}$	0.36	758	760	759	−0.27	−0.13
$f_{d\beta}$	0.48	1207	1205	1218	+0.16	−0.91
			Trichlorosilane[7]			
f_d	2.92[b]	2256	2258	2258	−0.01	0.0
f_D	4.43	486	489	..	−0.6	....
f_α	0.43	253	250	..	+1.2	....
f_β	0.11	802	799	798	+0.38	+0.48
$f_{d\alpha}$	0.67	583	587	..	−0.69	....
$f_{d\beta}$	0.35	181	179	..	+1.1	....

[a] Transferred from ref. 14. [b] Transferred from ref. 2.

The agreement between calculated frequencies from the above force constants and the experimental values is within 1.5%. It should be pointed out that these force constant calculations were based upon the published values of fundamental frequencies obtained by Raman spectroscopy for $SiHCl_3$ and by infrared spectroscopy for $CHCl_3$. This was necessary to ensure a consistent set of values, since for $SiHCl_3$ only two of the six fundamentals are in the 1–15 μ range of our spectrometer, and for $CHCl_3$ only four fundamentals were determinable.

The value of the stretching constant $f_{Si-H} = 2.93$ compares well with the 2.84 value in SiH_4 quoted by Herzberg.[2] Our Si–Cl stretching constant $f_{Si-Cl} = 4.43$ falls between the $SiCl_4$ value of 3.75 of Herzberg[2] and the value of 5.10 obtained by Linnett.[16]

The bending and interaction constants for $SiHCl_3$ agree in relative magnitude with those calculated for $CHCl_3$, but due to the lack of data no further comparison can be made at this time.

Acknowledgments.—The authors wish to thank Professors R. G. Parr and J. S. Koehler for helpful discussions and the American Chemical Society for the grant of a predoctoral fellowship to T. G. Gibian during the tenure of which this research was undertaken.

[16] D. F. Heath and J. W. Linnett, *Trans. Faraday Soc.*, **44**, 561 (1948).

PITTSBURGH, PENNA. RECEIVED SEPTEMBER 5, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Copolymerization of 2-Chloroallyl Linoleate with Styrene[1]

BY ELIZABETH DYER AND WILLIAM C. MEISENHELDER[2]

Studies have been made of the composition, properties and structure of copolymers of 2-chloroallyl linoleate and styrene. These were prepared by bulk polymerization with benzoyl peroxide at 80°, with stannic chloride at room temperature and by emulsion polymerization in the presence of potassium persulfate at 50°. The ester content of the copolymer was dependent on the monomer ratio, the amount of catalyst, and the type of polymerization. Self-polymerization did not occur with benzoyl peroxide as catalyst.

As the ester content of the polymers was increased to 27% (one ester per nine styrene units), the softening temperatures and intrinsic viscosities were lowered. Polymers containing a higher proportion of ester were infusible and largely insoluble.

By analysis of the copolymers after saponification it was shown that approximately 83% of the ester polymerized with styrene through chloroallyl double bonds, and 17% through linoleic double bonds. In the infusible polymers cross-linking had occurred through linoleic side-chains.

There have been several recent papers[3] on the polymerization of vinyl and allyl esters of various fatty acids. In the case of the oleates, Swern, Billen and Knight[3b] showed that the 2-chloroallyl ester had a greater tendency to polymerize than the allyl, methallyl or 3-butene-2-yl esters. It was thought of interest to prepare 2-chloroallyl linoleate and study its copolymerization with styrene.

The 2-chloroallyl ester of linoleic acid is not mentioned in the literature except in a patent by Coleman and Hadler,[4] in which the actual preparation and properties are not described. In the present work the ester was obtained by the acid-catalyzed reaction of 2-chloroallyl alcohol with linoleic acid.

Unlike 2-chloroallyl oleate[3b] and allyl acetate[3e] this ester did not polymerize when heated with benzoyl peroxide (1 or 2% of the quantity of the ester) at 80° for 40 hours under nitrogen.

Copolymers of the ester with styrene were formed by peroxide and stannic chloride-catalyzed reactions in bulk and by emulsion polymerization with a persulfate catalyst. The composition and properties of the copolymers are given in Table I. The unreacted ester recovered from the copolymerization mixtures was practically unchanged in unsaturation except in the case of the stannic chloride reactions, when some evidence of dimer formation was obtained.

It was found that the ester content of the copolymers was increased by increasing the proportion of ester in the monomer mixtures, although this was at the expense of the yield of polymer. This

---

[1] From the Ph.D. Thesis of William C. Meisenhelder, University of Delaware, 1950.

[2] Armstrong Cork Company Research Fellow.

[3] (a) P. O. Powers, *Ind. Eng. Chem.*, **38**, 837 (1946); (b) D. Swern, G. N. Billen and H. B. Knight, THIS JOURNAL, **69**, 2439 (1947); (c) D. Swern and E. F. Jordan, *ibid.*, **70**, 2334 (1948); (d) E. F. Jordan and D. Swern, *ibid.*, **71**, 2377 (1949); (e) P. D. Bartlett and R. Altschul, *ibid.*, **67**, 816 (1945); (f) E. Dyer, T. G. Custer and W. C. Meisenhelder, *ibid.*, **71**, 2728 (1949); (g) S. A. Harrison and D. H. Wheeler, *ibid.*, **73**, 839 (1951).

[4] G. H. Coleman and B. C. Hadler, U. S. Patent 2,127,660 (1938).