[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Acetylenic Ethers. V.[1] The Polymerization of Phenoxyacetylene

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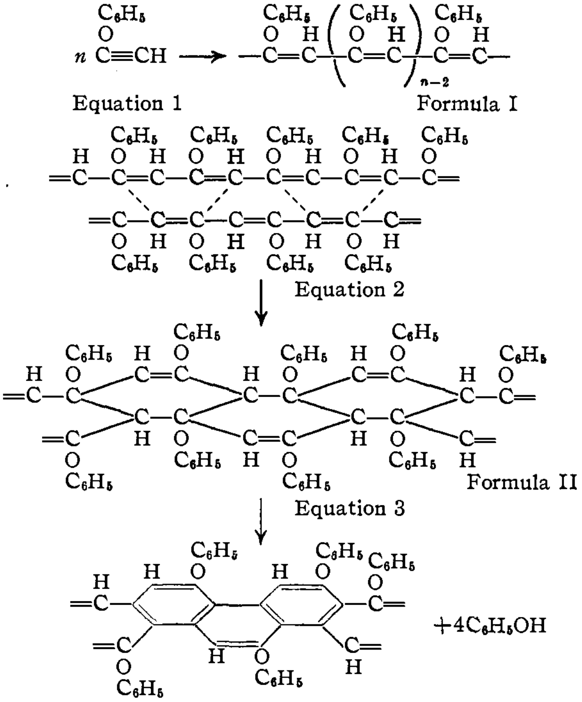
The polymerization of acetylenic compounds other than acetylene itself has been investigated in only a few instances[3] although the literature occasionally contains a reference to the changes which these compounds undergo when heated, and a few substituted acetylenes are known to polymerize readily at room temperature or below.[4,5,6,7] Among the latter, acetylenic ethers of the type $ROC\equiv CH$ appear to offer several advantages for a more careful study of the process.

Phenoxyacetylene polymerizes spontaneously at a moderate rate at room temperature to give first a deep red liquid and finally a hard, shiny, brittle, black solid. The change was shown to be a true polymerization by powdering this solid and extracting it with benzene in which it is partially soluble. The insoluble residue had the same composition as the monomer. The reaction appears to occur in two stages, involving first a chain reaction to give a linear, conjugated polyene and next a cross-linking step in which the conjugation is broken. The second reaction probably begins soon after the first linear chains are formed and insolubility occurs well before all of the monomer is consumed. It is suggested that the cross-linking may occur by a Diels–Alder reaction and that the polymerization may be represented by the equations shown.



The first stage in the polymerization may be followed by observing the rate of disappearance of monomer. Methods of analysis involving the acetylenic hydrogen of phenoxyacetylene or other properties such as ultraviolet absorption were not readily adapted to the problem, and the determination finally was made by finding the molecular weights cryoscopically of samples polymerized under various conditions. This method was used by Taylor and Vernon[8] to follow the photopolymerization of styrene and vinyl acetate in benzene solution. It was found that the polymers themselves as precipitated from benzene by petroleum ether had molecular weights of 3000 to 8000 so that, within the experimental error, the lowering of the freezing point of benzene by a small sample of partly polymerized phenoxyacetylene was due entirely to monomer. Tables I and II record the data obtained at 25 and 40°. The percentage of polymerization of each sample was readily calculated, and also the rate constants for the gross reaction. A first order rate equation fits the data slightly better than a second order one, but the reaction could not be followed much beyond 50% completion due to insolubility of the polymer and no choice between first and second order kinetics could be made (see Fig. 1). The values of the rate constants are

	k at 25°	k at 40°
First order	0.34×10^{-6} sec.$^{-1}$	2.2×10^{-6} sec.$^{-1}$
Second order	0.41×10^{-6} sec.$^{-1}$ wt. fraction^{-1}	2.6×10^{-6} sec.$^{-1}$ wt. fraction^{-1}

From the first order values, the temperature coefficient for the over-all reaction of producing the linear polymer is found to be 4.3 per 10° between 25 and 40° and the total energy of activation is 23 kcal. per mole of monomer. It is interesting that styrene gives a value of 23.5 kcal. from specific rates determined at 100.5° and 132°.[9,10] The

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[1] For the fourth paper of this series see Jacobs and Searles, THIS JOURNAL, **66**, 686 (1944).

[2] Much of this paper is based upon the Ph.D. thesis of William Penn Tuttle, Jr., September, 1943. A preliminary report of the work was given before the Organic Division of the American Chemical Society at the New York Meeting, September, 1942. Dr. Tuttle was killed while hiking in the Sierra Nevada in August, 1946.

[3] The literature to 1941 is summarized by Mark and Raff, "High Polymeric Reactions," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 298-316.

[4] Butadiyne: Mueller, *Helv. Chim. Acta*, **8**, 826 (1925); Straus and Kollek, *Ber.*, **59**, 1664 (1926).

[5] Haloacetylenes: Nef, *Ann.*, **298**, 356 (1897); Lawrie, *Am. Chem. J.*, **36**, 487 (1906); Hofmann and Kirmreuther, *Ber.*, **41**, 314 (1908); **42**, 4232 (1909); Wallach, *Ann.*, **203**, 88 (1880); Ingold, *J. Chem. Soc.*, **125**, 1528 (1924).

[6] Cyanoacetylene: Moureu and Bongrand, *Ann. chim.*, [9] **14**, 47 (1920).

[7] Propargyl aldehyde: Hüttel, *Ber.*, **74**, 1680 (1941).

[8] Taylor and Vernon, THIS JOURNAL, **53**, 2527 (1931).

[9] Schulz and Husemann, *Z. physik. Chem.*, **36B**, 184 (1937).

[10] Walling, Briggs and Mayo, THIS JOURNAL, **68**, 1145 (1946).

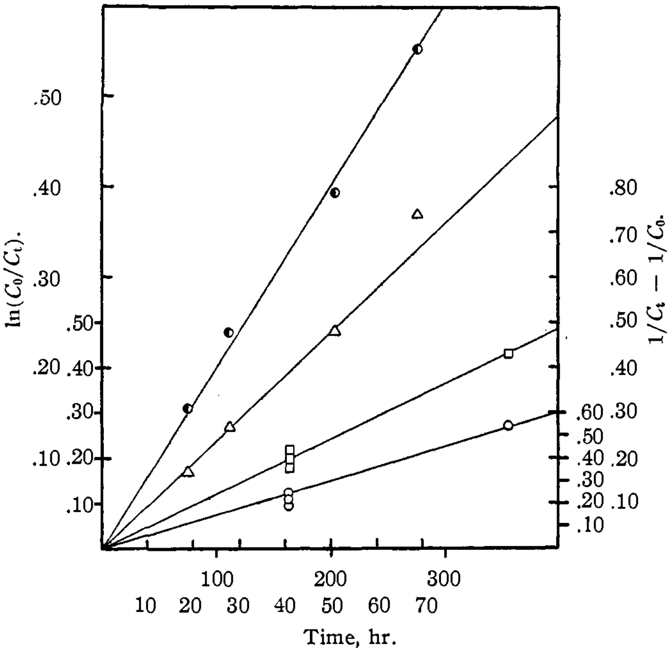

Fig. 1.—Thermal polymerization of phenoxyacetylene at 25.0 and 40.0°: □, first order equation, 25°, inner left-hand scale and inner time scale; O, second order equation, 25°, inner right-hand scale and inner time scale; ◐, first order equation, 40°, outer left-hand scale and outer time scale; △, second order equation, 40°, outer right-hand scale and outer time scale; C_t is wt. fract. of monomer, C_0 is original wt. fract. of monomer = 1.

cross-linking reaction made it difficult to get information about the constancy of chain length.

Although no attempts were made to determine the heat of polymerization of phenoxyacetylene, a considerable amount of heat is evolved in the reaction. Samples of monomer in an air-bath produced heat faster than it was conducted away at temperatures of 55° or above, and sealed samples could seldom be polymerized above 80° without exploding violently. Larger samples exploded as low as 65°.

Tables I and II also contain the results of a preliminary study on the influence on the polymerization of typical catalysts and inhibitors for vinyl monomers. Most of these were ineffective in the concentrations used. Among substances expected to promote ionic polymerization only cadmium iodide produced a change, and even with it the catalysis was erratic in a series of qualitative experiments. The polymer obtained appeared to be different from that formed in the absence of the catalyst. Stannic chloride and aluminum chloride gave no qualitative evidence of catalytic action, but were not tested quantitatively. *p*-Toluenesulfonic acid may have been without effect because it added to the triple bond.

Iodine was tried because it is a powerful catalyst for the polymerization of vinyl ethers.[11] Since it is known to add to phenoxyacetylene,[12] the failure to observe catalysis is not surprising. The experiment with metallic sodium was noteworthy because when care was taken to bring the phenoxyacetylene into contact with the bright metallic surface under an inert atmosphere and with care-

TABLE I

THE RATE OF POLYMERIZATION OF PHENOXYACETYLENE AT 25.0° AND THE EFFECT OF CATALYSTS

Time, hr.	Substance added	Amount added, mole %	Number average mol. wt.	% polymerized $\left(1 - \frac{118}{\text{M. W.}}\right) 100$
0	....	....	117.2 (theoret. 118)	0
164	....	....	142	16.6
164	Iodine	1.4 (as I_2)	141	
164	....	....	146	19.0
164	Cadmium chloride	2.8	145	
164	....	....	144	17.9
164	Metallic sodium	11.8	147	
164	Cadmium chloride	2.2	144	
164	Cadmium iodide	2.3	665	
356	....	....	182	35.1
356	Benzoyl peroxide	0.20	181	
288[a]	....	....	165[a]	28.5[a]

[a] This experiment was run at 23–24°.

TABLE II

RATE OF POLYMERIZATION OF PHENOXYACETYLENE AT 40.0° AND THE EFFECT OF CATALYSTS AND INHIBITORS

Time, hr.	Substance added	Amount added, mole %	Number average mol. wt.	% polymerized $\left(1 - \frac{118}{\text{M. W.}}\right) 100$
19	....	...	138	14.6
19	Phenylazotriphenylmethane	0.29	141	
28	....	...	150	21.4
33[a]	....	...	163[a]	27.3[a]
33[a]	Powdered cupric acetate	Trace	162[a]	
51	....	...	175.0	32.5
51	Phenyl α-naphthyl amine	Trace	175.6	
69	....	...	205	42.2
69	*p*-Toluenesulfonic acid	0.05	203	
114	....	...	(283)[b]	(58.3)[b]

[a] The thermostat was raised to 45° during the last hour.

[b] This sample dissolved extremely slowly in benzene; the freezing point lowering was determined after standing two months.

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(11) Chalmers, *Can. J. Research*, **7**, 472 (1932).

(12) Jacobs, Cramer and Weiss, THIS JOURNAL, **62**, 1849 (1940).

ful exclusion of moisture, even the expected reaction of the acetylenic hydrogen with the metal failed to occur and the surface remained clean and bright throughout the experiment. In other experiments when a piece of sodium was mashed under phenoxyacetylene, the metal dissolved but there was no evidence that the polymerization was catalyzed.

The experiments with benzoyl peroxide and phenylazotriphenylmethane give very little evidence about the influence of free radicals on the polymerization because, at the temperature used, the rate of production of radicals was probably so small that it was negligible. If one assumes that the rate of decomposition of benzoyl peroxide in phenoxyacetylene is about the same as in benzene, styrene, phenetole, and diphenyl ether, and calculates the rate of formation of radicals by the first order process,[13] it is found that at 25° with the concentration used, no more than one or two chains in a thousand could be started by radicals resulting from the decomposition of benzoyl peroxide even if these were 100% effective. The rate of radical formation in phenylazotriphenylmethane is not known, but the compound is an effective catalyst for styrene polymerization at 50°[14] although the evolution of nitrogen is not observed below 55°.[15] Since the rate of thermal chain initiation appears to be about 10,000 times greater for phenoxyacetylene than for styrene at 25 or 40°, it is not surprising that most of the catalysts which are commonly used with the latter are ineffective with the former. Phenyl α-naphthylamine which merely destroys peroxides should be without action on the polymerization as was observed. Cupric acetate, commonly used to inhibit the polymerization of vinyl acetate, is quite insoluble in phenoxyacetylene which may account for its lack of inhibiting action. Further experiments are planned on the effect of more powerful inhibitors and of compounds that decompose to give radicals at lower temperatures.

Absorption spectra give considerable information on the structure of the polymer and the course of the polymerization. Studies were made on samples polymerized for various periods and on polymers isolated by precipitation Typical curves are shown in Figs. 2 and 3. Phenoxyacetylene does not absorb above 3000 Å. (Fig. 4) and the absorption by the polymers at longer wave lengths is believed to be due to a conjugated system of double bonds as suggested above. It is somewhat surprising to find a maximum in the absorption curve of a polymer only once reprecipitated (A, Fig. 2). A number of reprecipitations produced only slight sharpening of this maximum (A, Fig. 3). This may indicate that the conjugated chains are somewhat uniform in length, but in the absence of suitable model systems the evidence is uncertain. If one assumes that a straight line represents the plot of the squares of the wave lengths of the absorption maxima of a series of compounds indicated by Formula I against the number of double bonds (n), that the slope is the same as for the corresponding plot for the α,ω-diphenylpolyenes,[16] and that the value of the 2250 Å. band of phenyl vinyl ether (B, Fig. 4) may be taken for $n = 1$, then the 4600 Å. maximum in Curve A, Fig. 3 corresponds to about 10 conjugated double bonds. The effect of phenoxyl groups placed either alternately along the chain as shown in Formula I, or at random, cannot be predicted quantitatively, but such groups would be expected to increase the wave length ab-

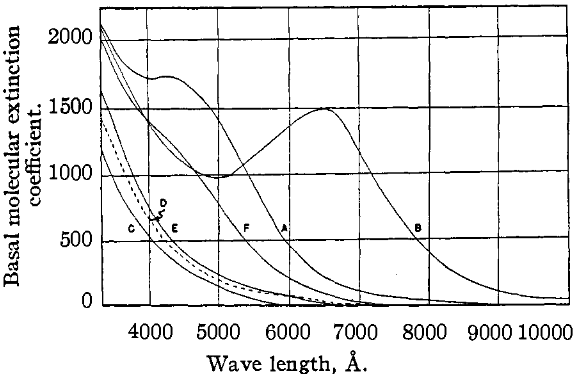

Fig. 2.—Absorption spectra of polyphenoxyacetylene in benzene: A, polymer 2, 0.029 g./l.; B, solution used for A plus 40.0 g. trichloroacetic acid/l.; C, solution used for A after standing 62 days at 25°; D, solution used for C plus 40.0 g. trichloroacetic acid/l.; E, solution used for B after standing 62 days at 25°; F, polymer 4.

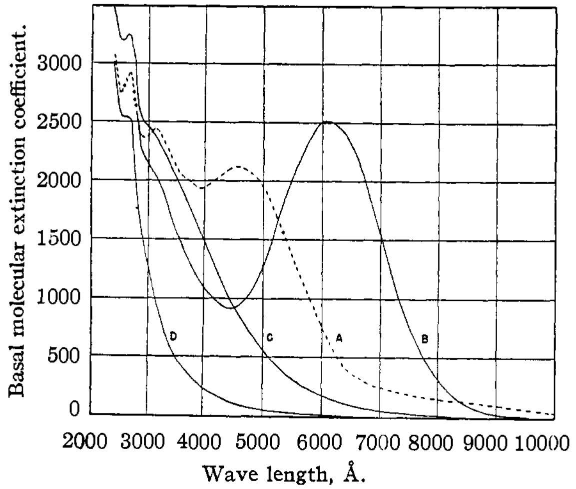

Fig. 3.—Absorption spectra of polyphenoxyacetylene in chloroform: A, polymer 3, 0.0166 g./l.; B, solution used for A plus 1.76 g. antimony trichloride/l.; C, polymer 5, 0.0166 g./l.; D, polymer 6.

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(13) Bartlett and Nozaki, THIS JOURNAL, **68**, 1686 (1946); **69**, 2299 (1947).

(14) Schulz, *Z. Elektrochem.*, **47**, 265 (1941).

(15) Wieland, *Ann.*, **514**, 145 (1934).

(16) Lewis and Calvin, *Chem. Rev.*, **25**, 290 (1939).

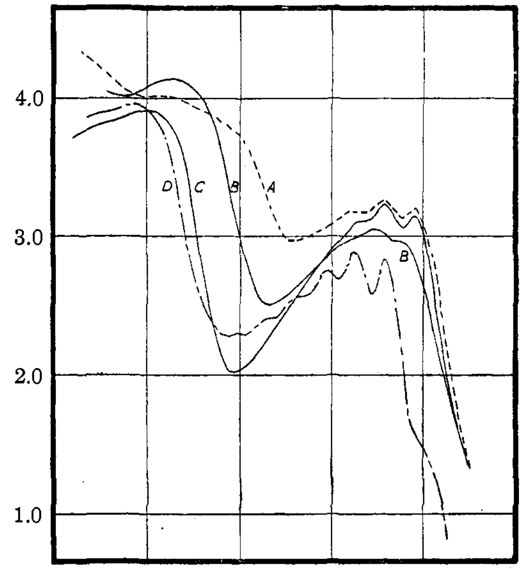
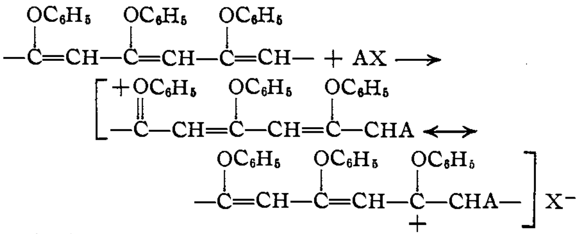


Fig. 4.—Absorption spectra in 96% ethanol: A, diphenyl ether; B, phenyl vinyl ether; C, phenetole; D, phenoxyacetylene.

sorbed.[17] Further uncertainty arises from lack of knowledge of the steric arrangement of the chain.[18] However, the value of 10 is not unreasonable. If the degree of polymerization were 40 corresponding to a molecular weight of 4700, it would take only one cross link per molecule to reduce the conjugation on the average to 10 double bonds, since each cross link that breaks the conjugation effects the absorbing system by a factor 4. Lack of material prevented determination of the molecular weight of the five-hour polymer, but a six-day polymer gave a cryoscopic molecular weight of 8100 and it is probable that considerable cross linking had already occurred in this sample. The polymers show some absorption out to 9000 Å. and beyond, which corresponds to 46 or more conjugated double bonds on the assumptions indicated.

It was found that polymers isolated after brief polymerization absorbed at longer wave lengths than later polymers and that the absorption in the visible of the early polymers decreased greatly when their solutions were allowed to stand for long periods. This change is represented by the difference between Curves A and C in Fig. 2 and indicates clearly that a secondary reaction involving decrease in conjugation has occurred. In ether solution the decrease was even more marked. The absorption at 4300 and 3850 Å. of an ether solution containing 1.49×10^{-4} basal moles of polymer 4 per liter changed from basal molecular extinction coefficients of 2060 and 1900 to 30 and 152, respectively, on standing at room temperature in the dark for 202 days. At the end of this experiment the solution appeared visually to be completely colorless.

The early polymers behaved like linear, conjugated systems, giving a deep blue color with antimony trichloride in chloroform (Curve B, Fig. 3), bromine (violet) and stannic chloride (violet). This behavior is similar to that of positive ethylenes[19,20] such as 1,1-di-(p-dimethylaminophenyl)-ethylene, and can be interpreted similarly as due to the formation of a resonating positive ion in which the positive charge is distributed among the oxygens of the phenoxyl groups and the alternate carbons along the chain.



$$-\overset{OC_6H_5}{\overset{|}{C}}{=}CH-\overset{OC_6H_5}{\overset{|}{C}}{=}CH-\overset{OC_6H_5}{\overset{|}{C}}{=}CH- + AX \longrightarrow$$

$$\left[-\overset{+OC_6H_5}{\overset{\|}{C}}-CH{=}\overset{OC_6H_5}{\overset{|}{C}}-CH{=}\overset{OC_6H_5}{\overset{|}{C}}-CHA \longleftrightarrow -\overset{OC_6H_5}{\overset{|}{C}}{=}CH-\overset{OC_6H_5}{\overset{|}{C}}{=}CH-\underset{+}{\overset{OC_6H_5}{\overset{|}{C}}}-CHA-\right]X^-$$

and other resonance forms.

These formulas are drawn with the monomer units arranged head-to-tail, which permits the maximum participation of the oxygen atoms in the resonance, but there is as yet no evidence for such arrangement in these polymers and the participation of part of the oxygens, which could occur in random or other arrangements, might account for the colors produced. As with the positive ethylenes, highly colored solids could be obtained in certain instances (bromine or stannic chloride) by adding the reagent to the polymer in a non-polar solvent such as carbon tetrachloride. The solid could be redissolved by adding ethanol to the reaction mixture, although this solvent would not dissolve the original polymer. This behavior would be expected of a polar salt of the type suggested.

The color produced by acids was readily discharged by even such weakly basic compounds as diethyl ether. Relatively large amounts of less basic compounds like phenyl vinyl ether or phenetole were required to discharge the color and diphenyl ether had no influence on the phenomenon. Pyridine discharged the color instantly and an insoluble pyridinium salt soon precipitated. Further evidence that the color produced by acids was due to transfer of a proton to the polymer, was obtained by studying the color change with a number of acids. The intensity of the color produced (as determined visually) was greater, the greater the dissociation of the acid, as indicated in Table III. Acetic acid not only failed to alter the color of the polymer solution, but in large amounts discharged the color produced by stronger acids.

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(17) Bowden, Braude and Jones, *J. Chem. Soc.*, 948 (1946). In this paper it is shown that the effect of alkoxyl and similar groups is less when placed in cross-conjugation, but that it is in the same direction. Additional unpublished results from the same group on alkoxy and aryloxy dienoic and trienoic acids support this generalization. We wish to thank Dr. Ernest A. Braude for his assistance and suggestions in the interpretation of the absorption spectra of the polymers.

(18) Zechmeister, Le Rosen, Schroeder, Polgar and Pauling, THIS JOURNAL, **65**, 1940 (1943).

(19) Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928).

(20) Wizinger and Fontaine, *Ber.*, **60**, 1377 (1927).

TABLE III

Acid	Dissociation constant in water at 25°	Color produced on polymer in chloroform or benzene
Trichlorcacetic	Strong acid	Bright blue
Maleic	1.5×10^{-2}	Bluish green
Malonic	1.61×10^{-3}	Olive
Chloroacetic	1.55×10^{-3}	Olive
dl-Malic	4×10^{-4}	Slight darkening (in chloroform)
α-Naphthoic	2×10^{-4}	Reddish color of polymer unchanged
Benzoic	6.6×10^{-5}	
Acetic	1.86×10^{-5}	

The maximum in the absorption spectrum of the colored solution produced with antimony trichloride (Curve B, Fig. 3) is at nearly the same wave length as that produced similarly with Vitamin A (617 mm.).[21] This corresponds to five double bonds in the absorbing ion,[22] but since the carotenoids with larger conjugated chains absorb at lower wave lengths,[21] possibly due to coördination with more than one molecule of antimony trichloride,[22] and since no information on the effect of phenoxyl groups is available, it is not possible to correlate the maximum with chain length in our system. The maximum is surprisingly distinct for a polymer system, however, and again suggests some uniformity in the chain length of the absorbing system.

The secondary reaction of cross-linking must involve the double bonds of the polyene polymer, and results in loss of the conjugation. The cross-linked material no longer gives colors with acids, antimony trichloride, etc., as is shown in Curve D, Fig. 2. The colors produced by these reagents on the early polymers fade fairly quickly and cannot be restored by more reagent. This fading occurs much more rapidly than the simple solutions of polymer lose their power to give the colors, which suggests that these reagents catalyze the cross-linking reaction.

Further evidence for the cross-linking reaction is obtained by chromatography. A sample of phenoxyacetylene polymerized for six days at 25° could be separated by adsorption from benzene solution onto magnesium oxide into a strongly held, dark red material and a weakly held, yellow substance. Complete separation of these bands was attained by elution of the yellow material with benzene and of the red with alcohol–benzene. Absorption curves showed that the latter absorbed more strongly, but insufficient material was at hand for isolation of the polymers and the value of the extinction coefficients were therefore not known. It was found that the precipitated, early polymer was absorbed strongly like the dark red material and could be eluted similarly. Its absorption spectrum (Curve A, Fig. 2) was only slightly changed by the adsorption.

The physical properties of the polymers gave evidence that the secondary reaction was a true cross-linking. Early, precipitated polymers had sintering points as low as 90° while late polymers obtained by bulk polymerization at 65–75° did not sinter at 400°. Intermediate polymers sintered at intermediate temperatures. These polymers were thermosetting, and could not be remelted after heating. Under controlled conditions the thermosetting did not involve decomposition, and the products were very brittle. The thermosetting polymers were poor cements, having low adhesive and cohesive strengths. Attempts to draw threads from the "melts" led only to exceedingly brittle fibers. All of these properties are consistent with a structure made up of cross-linked relatively short chains.

It was found that the cross-linked polymers lost phenol when heated under reduced pressure to 200°. The amount of phenol liberated corresponded to 46% of the phenoxyl groups present, and no more was obtained by heating to above 400°. The polymerization probably did not involve substitution in the ring of the remaining phenoxyl groups, since fusion of the dephenolated polymer with alkali gave a moderate yield of phenol based on phenoxyls still remaining. It was found that the soluble polymers also lost phenol when heated in benzene solution. The ready loss of phenol is easily interpreted if the cross-linking is assumed to occur by a Diels–Alder reaction (Equation 2). The product of such a cross-linking would be a hydroaromatic compound that could aromatize by losing phenol (Equation 3). In bulk or precipitated polymers the cross-linking would be expected to occur at random, leaving considerable portions of the linear, conjugated system unchanged. In solution the cross-linking might occur in a more regular fashion to produce a polycyclic hydroaromatic compound such as is shown in Formula II. Such a change requires the loss of just 50% of the phenoxyl groups. These polymers would absorb much less at the longer wave lengths than would a cross-linked polymer produced by bulk polymerization. The absorption spectra are in agreement with this interpretation.

The primary polymerization to form the linear, conjugated polyene appears on the basis of absorption spectra to be a chain reaction, and this may involve a free radical mechanism. The failure of the usual free radical catalysts to influence the polymerization is explained by the high rate of thermal initiation relative to the rates of production of free radicals by the catalysts. Solvents slow down the polymerization very markedly, and long exposure of an ether solution of phenoxyacetylene to sunlight gave a polymer that appeared to contain fragments of the ether molecule. This is most readily interpreted on the basis of a free radical mechanism. It seems clear that an ionic mechanism is also possible for the polymerization since cadmium iodide acts as a catalyst.

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(21) "The Application of Absorption Spectra to the Study of Vitamins, Hormones and Coenzymes," by R. A. Morton, Adam Hilger Ltd., 1942, p. 95.

(22) Meunier, *Compt. rend.*, **221**, 64 (1945); *Bull. soc. chim.*, **13**, 73 (1946).

The investigation is being extended to establish the course of the reaction more exactly.

The polymerization of acetylenic compounds in general is relatively complex, and on the basis of the extensive work on acetylene itself probably takes place in several ways.[3] It has been suggested[23] that conversion of acetylene to cuprene occurs by primary formation of a conjugated linear polyene which cross links at once. Cuprene is believed to have an aromatic or partially aromatic structure,[24,25] and analyses indicate that some hydrogen has been lost during the reaction. This suggests that under these special conditions acetylene may behave like phenoxyacetylene. Other readily polymerized acetylenes are now being investigated to determine how general this mode of reaction may be.

Experimental Part

Phenoxyacetylene was prepared as described earlier[12] and was redistilled at least twice before use. Care was taken to exclude moisture at all times; the distillate was collected in a receiver cooled in solid carbon dioxide, and the samples sealed off under reduced pressure and stored without allowing them to warm up. The following physical constants are more accurate than those reported earlier[12]: b. p. 61.5–61.8° (25 mm.); d^{20}_4 1.0114; n^{20}_D 1.5171 MR_D obsd. 35.34, calcd. 35.12; d^{25}_4 1.0088; n^{25}_D 1.5143. The density and refractive index did not change perceptibly in the course of an hour although the samples darkened markedly.

The rate of polymerization and the effect of catalysts were found by polymerizing 0.3-g. samples in thin-walled bulbs of 0.5 to 1 ml. capacity. Carefully cleaned, dry Pyrex glass tubing which had been rinsed with ammonia and repeatedly with distilled water was used in making the bulbs and care was taken to exclude moisture. However, soft glass bulbs or less carefully cleaned Pyrex gave the same results. The purified phenoxyacetylene sample was allowed to warm up to room temperature before opening, and the liquid transferred to the bulbs with a micropipet. The bulbs were then cooled in solid carbon dioxide and sealed. Catalysts were added to the bulb before the acetylene was introduced. The sealed bulbs were weighed to determine the exact amount of phenoxyacetylene and the samples polymerized by immersion in a thermostatted bath at 25 or 40°.

The depression of the freezing point of pure benzene by the samples was determined in the usual Beckmann apparatus modified to exclude moisture and using a carefully standardized rate of cooling which gave reproducible values. In each case the freezing point of the pure benzene was determined, the bulb carefully dried and broken in the benzene and the freezing point depression determined at once. The results are summarized in Tables I and II.

Cross-linked Polyphenoxyacetylene Polymer 1.—Phenoxyacetylene (8 g.) was sealed in glass under 20 mm. pressure and polymerized at 40° for forty-eight hours to a thick red fluid. The temperature was then increased to 60° for twenty-one hours, slowly raised to 75° during five hours and maintained at 75° for nineteen hours longer. After cooling, the glass was broken away leaving a hard, brittle, shiny, ebony-black solid which had a faint odor of phenoxyacetylene. The mass was homogeneous and contained no bubbles. It broke with conchoidal fracture. Pieces barely floated in carbon disulfide, indicating a density of about 1.26. Chips of the material colored chloroform and carbon disulfide, but otherwise were unaltered even on prolonged standing, remaining hard and brittle. Carbon tetrachloride, alcohol, 15% aqueous sodium hydroxide and 10% sulfuric acid exerted no visible effect over a long period of time. Concd. sulfuric acid attacked the solid only slowly. The polymer was ground in a mortar, giving a dark brown powder.

Anal. Calcd. for $(C_8H_6O)_x$: C, 81.35; H, 5.08. Found: C, 81.61; H, 4.83.

The powder was exhaustively extracted with benzene in a Soxhlet extractor. The soluble portion, 39%, was almost entirely polymer; a trace of phenoxyacetylene (odor) was recovered by heating under reduced pressure, and as the temperature was raised to 370° at 1 mm. a crystalline material (35% of the weight of the soluble portion) was collected in a receiver cooled in Dry Ice. Phenol was separated from this distillate by extraction with 5% sodium hydroxide, and determined as usual.[26] It made up 85% of the weight of the distillate, and was identified by conversion to tribromophenol, m. p. and mixed m. p. 93.0–93.5° The neutral material (50 mg.) in the distillate was a dark oil with a faint odor of phenoxyacetylene. It was not identified.

The insoluble portion from the benzene extraction of the original polymer had the composition of phenoxyacetylene.

Anal. Found: C, 81.31; H, 5.38.

It was heated at 1 mm. in an all-glass apparatus with a U-tube receiver cooled in solid carbon dioxide; at 200° a distillate collected, and no further change was observed as the temperature was raised to 400° and maintained there for some time. The total distillate amounted to 44% of the initial weight of polymer (1 g.) and 84% of the distillate was phenol (by titration[26]) which corresponds to 46.4% of the phenoxyls present in the polymer. The rest of the distillate was an oil with a pleasant, fruity (almost cinnamon-like) odor which was a mixture and could not be identified.

The powder remaining in the flask was dark brown and inert to reheating to 400°. It absorbed air readily and was burned with difficulty.

To show that the phenoxyl groups remaining in the polymer were unsubstituted, 0.21 g. of the dephenolated powder was added to 14 g. of molten potassium hydroxide (C. P. 85% alkali plus 0.6 ml. of water) at 250°. The fusion was continued for fifteen minutes at 300–350° which gave a homogeneous melt. It was poured onto ice and phenol isolated and determined as usual. The yield was 0.04 g. which corresponds to 25% of the phenoxyls which should still remain on the dephenolated polymer. The rest of the fusion product was an alkali soluble, dark brown resin which may have resulted in part from phenol. Although the yield of phenol was not high, it is as good as could be expected under the conditions of the experiment and furnishes some evidence that the original polymerization did not involve substitution of the phenoxyl groups.

Early Polyphenoxyacetylene.—Quantitative precipitation of the polymers could not be achieved due to their solubility in phenoxyacetylene or in the large amounts of solvent required to remove the monomer, and to their tarry nature while even traces of the monomer remained. Petroleum ether (b. p. 30–60°) was the most effective precipitating solvent and in reprecipitations and fractionation the polymer was dissolved in a little benzene and 4 to 8 volumes of petroleum ether added. Due to the tendency of the powders to acquire an electric charge, it was necessary to avoid rubbing or scratching of vessel walls, and a centrifuge technique proved far superior to filtration, which was used at first.

Polymer 2.—Only 20 mg. of a reddish brown powder was obtained after a single precipitation from 25.6 g. of phenoxyacetylene allowed to polymerize for five hours at 25°. The first order rate constant shows that 160 mg. should have been obtained. Losses were due to solubility and to mechanical difficulties in the filtration technique used. The polymer had sintering point 90° m. p. 110–115°.

Polymer 3 was obtained from 45.3 g. of phenoxyacetylene which was allowed to polymerize for five hours at 25°

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[23] Staudinger, *Z. angew. Chem.*, **42**, 37, 67 (1929).

[24] Herzog, *Kunststoffe*, **21**, 49 (1931).

[25] Kaufmann and Schneider, *Ber.*, **55**, 267 (1922).

[26] Redman, Weith and Brock, *Ind. Eng. Chem.*, **5**, 389 (1913).

and reprecipitated eight times using a centrifuge technique. The yield was 80 mg. or 30% of the weight calculated to have been formed (from the first order rate constant, the polymerization should be 0.61% complete); sintering point, 86–87°, m. p. 103–107°. No molecular weight determinations were carried out because of the small amounts of material available.

Polymer 4 was prepared from 19.2 g. of phenoxyacetylene by polymerization at 25° for six days and reprecipitated once (filtration technique); yield, 2.05 g.; sintering point, 113°; mol. wt. 8100 (cryoscopic determination in benzene).

Anal.[27] Calcd. for $(C_8H_6O)_x$: C, 81.35; H, 5.08; C/H ratio, 16.0. Found: C, 78.30, 78.07; H, 4.83, 4.95; C/H ratio 16.0.

The low values are believed to be due to adsorption of air by the powder. The combustion left no residue, and the polymer contained no halogen. When the polymer was placed under dibutyl ether, in which it was insoluble, or dissolved in benzene, a continuous stream of bubbles was produced. No bubbles could be obtained similarly from polymer 1.

A micro Zerewitinoff determination[27] on the polymer gave 1 active H for 17 phenoxyacetylene units and 1 mole of methylmagnesium iodide adding for 2.5 moles of phenoxyacetylene. The presence of adsorbed air accounts for much of the Grignard reagent addition and may have vitiated the active hydrogen determination as well.

Polymer 5 was obtained from 12.3 g. of phenoxyacetylene by polymerization at 40° for seventy-four hours. After 1 reprecipitation the yield was 3.75 g.; sintering point, 125°, mol. wt. 2900 (cryoscopic determination in benzene).

Absorption Spectra.—An older Beckmann Photoelectric Spectrophotometer, Model D, was used to determine the curves given in Fig. 2 while the newer model DV equipped with fused silica cells was employed for all other curves given. The polymers were insoluble in ethanol or hexane; benzene was used when working with the older instrument and chloroform or ether with the new. All solvents were redistilled through a 2-ft. column packed with helices. When carefully purified chloroform free from alcohol was stored, it decomposed even when under nitrogen in the dark and soon produced a slight acid color reaction with the early polymers. This purified chloroform was therefore used only to make up a standard antimony trichloride solution. For other spectra a redistilled chloroform containing a little alcohol was employed; it did not give an acid reaction with the early polymers even after standing for some time in the dark. Chloroform is opaque to ultraviolet light below 2420 Å., but was used because it is the most suitable solvent for the antimony trichloride color reaction.

The antimony trichloride solution was made up with freshly purified chloroform and kept under nitrogen in the dark. Its concentration was 17.6 g./l. and exactly 1 ml. was added to the dilute polymer solution in chloroform in making up the final 10 ml. dilution for the spectrophotometer. This amount of antimony trichloride was approximately twice that needed to give a strong blue color with polymer 4. The intense blue color (Curve B, Fig. 3) did not fade perceptibly in one or two hours, but the solution was nearly colorless in one or two days. The stock solution did not absorb in the range 3350–12000 Å., but below 3300 Å. absorption increased and the solution was opaque at 2810 Å. In the curves with antimony trichloride present, the stock solution was used in the reference cell of the spectrophotometer.

ϵ, the basal molecular extinction coefficient, is obtained as usual except that concentration is expressed in basal moles (weight of polymer per liter divided by the molecular weight of the monomer, 118).

It was shown with polymer 3 in benzene that Beer's law is closely obeyed over a three-fold change in concentrations. Thus with concentrations of 0.720×10^{-4}, 1.44×10^{-4} and 2.16×10^{-4} basal moles/l. ϵ at 4400 Å. was 2180, 2190 and 2170, respectively, and at 3850 Å. ϵ was 2010, 2040, and 2010, respectively.

The absorption spectra of phenoxyacetylene and phenyl vinyl ether were of interest for study of the polymer absorptions. Phenetole and diphenyl ether were also measured for comparison. Ethanol (96%) was used as the solvent because in general it is more satisfactory than chloroform. The curve for phenetole in methanol or hexane is very similar[28] but was not extended to show the maximum at 2205 Å. Our curve for diphenyl ether agrees with spectra in the literature.[29,30,31]

The phenoxyacetylene used for the measurement was a carefully purified sample which was dissolved very quickly in the solvent and contained so little polymer that there was no measurable absorption at 4000 Å. The phenetole, phenyl vinyl ether and diphenyl ether were purified by distillation under reduced pressure through a 30-cm. Podbielniak-type column and had the following physical properties.

Diphenyl ether: b. p. 114° (8 mm.), m. p. 27–27.4°. Values from 26 to 29° are recorded in the literature.

Phenyl vinyl ether: b. p. 112° (200 mm.), $n^{15}D$ 1.5255, $n^{20}D$ 1.5226, $n^{25}D$ 1.5198. Chalmers[32] found $n^{20}D$ 1.5226.

Phenetole: b. p. 105° (100 mm.), $n^{18.8}D$ 1.5087. The literature[33] records $n^{18.8}D$ 1.5084.

Polymerization in Solution: Polymer 6.—Eight grams of phenoxyacetylene in 75 ml. of anhydrous ether was sealed in Pyrex glass under reduced pressure and allowed to polymerize for seven months in the open air exposed to sunlight. The resulting solution was reddish yellow and contained a small amount of a light colored, flocculent precipitate. A control sample kept in the dark was similar in color but homogeneous. The main sample contained 0.0072 g. of phenol per g. of phenoxyacetylene, the control only 0.002 g. Ether was removed under reduced pressure and phenoxyacetylene recovered from the main sample by distillation in a molecular still at room temperature with pressures finally as low as 5×10^{-4} mm. The recovery of phenoxyacetylene was 61%; after extraction of phenol and redistillation, this phenoxyacetylene polymerized at the usual rate. The dark red sirup in the molecular still was dissolved in benzene and precipitated with petroleum ether as a very light, buff-colored powder. Two reprecipitations left 0.22 g. of polymer, sintering point 115–120°, m. p. 145–210° with thermosetting at 210°.

Anal. Calcd. for $(C_8H_6O)_x$: C, 81.35; H, 5.08. Found: C, 77.24, 77.06; H, 6.33, 6.36; ethoxyl, 5.11, 5.20.

The material was not hygroscopic and burned smoothly. Its absorption in chloroform was lower than any of the cross-linked polymers (Curve D, Fig. 3, in which it was assumed to have the composition of polyphenoxyacetylene for the purposes of calculating the extinction coefficients). It gave no color reactions with antimony trichloride, bromine or trichloroacetic acid.

The mother liquors from the precipitation contained more distillable by-products than could be obtained from the products of ordinary polymerization. These were oils that could not be purified or identified.

Summary

Phenoxyacetylene polymerizes spontaneously at room temperature and above by a two stage process. The first step is a chain reaction believed to yield a linear, conjugated polyene which then undergoes cross-linking. The rate of disappearance of monomer could not be followed beyond

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[27] Microchemical Laboratories, California Institute of Technology

[28] Wolf and Herold, *Z. physik. Chem.*, **13B**, 201 (1931).

[29] Ley and Specker, *Z. wiss. Phot.*, **38**, 13 (1939).

[30] Ramart-Lucas and Hoch, *Compt. rend.*, **194**, 96 (1932).

[31] Marenzi and Vilallonga, *Rev. soc. Argentina biol.*, **17**, 262 (1941).

[32] Chalmers, *Can. J. Research*, **7**, 464 (1932).

[33] Cotton and Mouton, *Ann. chim.*, [8] **28**, 214 (1913).

50% reaction and no choice between first and second order kinetics could be made. A preliminary study of the effect on the reaction, of several of the common catalysts and inhibitors for vinyl polymerization showed that only cadmium iodide was effective. Thermal initiation appears to be so rapid that the usual free radical catalysts have negligible effect, and the question of free radical initiations can be answered only by examining more active radical-producing substances. Early polymers isolated by precipitation have absorption spectra indicating a conjugated, polyene structure, and give color reactions with strong acids, metallic salts and bromine easily explained on this basis. Cross-linking involves breaking of the conjugation of the chain as indicated by decreased absorption, and the cross-linked polymers readily lose up to 46% of their phenoxyl content on heating. This suggests that the cross-linking may occur by a Diels–Alder reaction and that the hydroaromatic structure so produced is aromatized by loss of phenol. The early polymers are thermosetting and can be separated from later, cross-linked polymers chromatographically. Solvents greatly retard the polymerization and some indication that the primary reaction may involve free radicals was obtained by carrying out the reaction in ether which produced a polymer containing fragments of the ether molecule.

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Raman Frequencies of *n*-Paraffin Molecules

BY SAN-ICHIRO MIZUSHIMA AND TAKEHIKO SIMANOUTI

I. Intramolecular Rotation

The experimental results of Raman effect, infrared absorption, dipole moment and electron diffraction made for ethylene dihalides by Mizushima, Morino, Watanabe, Simanouti, and others in our Laboratory[1] has shown that there are three potential minima in one complete rotation about a carbon single bond as axis (Fig. 1). These three potential minima correspond to one *trans* form (T) in which two halogen atoms are at the farthest distance apart and two *gauche* forms (G and G′) obtainable from the *trans* form by internal rotation of ±120° (see Fig. 2). The energy difference between the *trans* and the *gauche* minima amounts to 1 kcal./mole (1.2 kcal. for ethylene dichloride and 1.3 kcal. for ethylene dibromide), from which the equilibrium isomeric ratio in the gaseous state can readily be calculated, but this ratio becomes naturally different in the liquid state owing to the intermolecular effect. In the solid state the intermolecular force (*i. e.*, crystal force) plays such a predominant role as to make only the *trans* form stable, which is most clearly seen from the disappearance of Raman lines assigned to *gauche* form on solidification.[2]

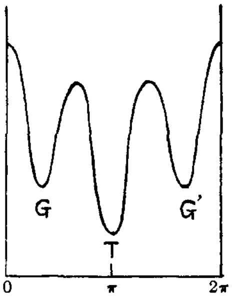

Fig. 1.—Intramolecular potential curve of ethylene dihalides XH_2C–CH_2X.

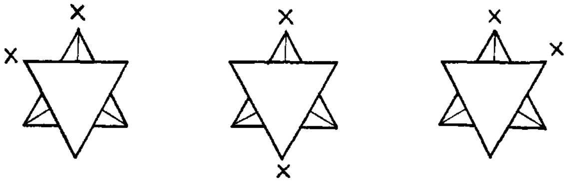

Fig. 2.—Molecular forms corresponding to the three potential minima.

II. Raman Spectra of *n*-Paraffins in the Liquid and Solid States

The change of Raman spectra of *n*-paraffins on solidification observed by Mizushima, Okazaki, Morino, Takeda and Nakamura in our Laboratory (see Table I) can readily be explained, if we assume quite similarly the existence of only one molecular form in the solid state and of several forms in the liquid state. It is seen from the calculation of normal frequency similar to that made for ethylene dihalide that the only one molecular form realized in solid butane is the *trans* form.[3] It is, therefore, quite reasonable to assume that the molecular form of *n*-paraffin in general is the extended zigzag configuration in which four consecutive CH_2-groups form the *trans* configuration. This is also compatible with the results of X-ray investigation made by Müller[4] and Bunn[5] for long chain paraffins. Let us explain in the following the Raman frequencies observed for solid paraffins on the basis of this molecular model.

In Table I we see that in the lower frequency region there was observed only one Raman line for each solid paraffin and its frequency is inversely

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(1) Mizushima, Morino and others, *Physik. Z.*, **35**, 905 (1934); **38**, 459 (1937); *J. Chem. Phys.*, **9**, 826 (1941); Mizushima, Morino, Watanabe, Simanouti and others, *Sci. Pap. I. P. C. R.* (*Tokyo*), **39**, 396, 401 (1942); **40**, 87, 100, 417, 425 (1942); **42**, *Chem.* 1, 5, 27, 51 (1944).

(2) Mizushima and Morino, *Physik. Z.*, **38**, 459 (1937); Mizushima, Morino and Takeda, *J. Chem. Phys.*, **9**, 826 (1941).

(3) Mizushima, Morino and Simanouti, *Sci. Pap. I. P. C. R.* (*Tokyo*), **40**, 87 (1942).

(4) Müller, *Proc. Roy. Soc.* (*London*), **A120**, 437 (1928); **124**, 317 (1929); **127**, 417 (1930).

(5) Bunn, *Trans. Farad. Soc.*, **35**, 482 (1939).