

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

The Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. II. Polyacrylic Anhydride and the Derived Polyacrylic Acid^{1,2}

BY ALLAN CRAWSHAW AND GEORGE B. BUTLER

RECEIVED MAY 7, 1958

Acrylic anhydride has been polymerized in solution to afford a series of saturated, linear polymers. Values of molecular weight from a few thousand up to 95,000 were recorded for the various products. The properties of the polymers showed that polymerization had occurred by the alternating intramolecular-intermolecular mechanism, in this case leading to a poly-3(5)-methyleneglutaric anhydride structure. The polyacrylic acid obtained by hydrolysis of a polyacrylic anhydride has been shown to have a much more regular structure than normal polyacrylic acid, as reflected in their relative degrees of crystallinity.

Certain monomers containing a 1,6-diene system can, on polymerization, undergo an alternating intramolecular-intermolecular chain propagation or cyclization, leading to the formation of saturated, linear polymers.³⁻⁶ Such polymers have a structure consisting of a linear chain of six-membered rings alternating with methylene groups along the chain. In the first paper of this series,⁶ the proof of the structure in the case of the poly-(diallyl-ammonium halides) was given.

Acrylic anhydride is particularly suited to undergo this type of polymerization, having two highly-reactive ethylenic double bonds in correct positions for the formation of six-membered rings in the intramolecular step. Also, the opening of the resultant anhydride rings in the polymer would afford products with interesting stereospecific possibilities.

The homopolymerization of this monomer has apparently not been studied previously. Polyacrylic anhydride having the proposed poly-3(5)-methyleneglutaric anhydride structure has undoubtedly been prepared,⁷ but the nature and structure of the polymer were not investigated. In the polymer field, acrylic anhydride has found its main use as a cross-linking agent for other vinyl monomers.

Results and Discussion

Organic peroxides were found to initiate the polymerization of acrylic anhydride very readily and other initiating systems were not studied to any extent. On mass polymerization, brittle white polymers were obtained which swelled considerably in dimethylformamide and dimethyl sulfoxide, dissolving completely, however, on standing for several hours. This behavior, along with the observation of a definite softening range, suggested that these polymers were linear and of high molecular weight. Benzene, toluene and dioxane were effective solvents for solution polymerization and

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract number AF18(603)-116. Reproduction in whole or in part is permitted for any purpose of the United States government.

(2) This paper was presented before the Division of Polymer Chemistry, American Chemical Society, San Francisco, Calif., April, 1958.

(3) George B. Butler and Rudolph J. Angelo, *THIS JOURNAL*, **79**, 3128 (1957).

(4) C. S. Marvel and R. D. Vest, *ibid.*, **79**, 5771 (1957).

(5) C. S. Marvel and J. K. Stille, *ibid.*, **80**, 1740 (1958).

(6) George B. Butler, Allan Crawshaw and W. Lamar Miller, *ibid.*, **80**, 3615 (1958).

(7) L. M. Minsk and J. J. Chechak, Eastman Kodak Co., U. S. Patent 2,632,004; *C. A.*, **47**, 12071h (1953).

by varying the solvent and the concentration of monomer in the solution a series of polymers of different molecular weights was obtained.

The intrinsic viscosities of the polyanhydrides were measured in dimethylformamide solution, but no data exist to correlate these values directly with molecular weights. These were calculated from determinations of intrinsic viscosities $[\eta]$ in 2 *N* sodium hydroxide solution, the equation⁸

$$[\eta] = 4.27 \times 10^{-3} P^{0.69}$$

for polyacrylic acid under these conditions being used to calculate the values for degree of polymerization *P*. These values for the polyacids corresponded to molecular weights for the polyacrylic anhydrides of from 95,000 to < 5,000 depending on the particular polymerizing conditions used.

All the polyacrylic anhydrides were white powders, thermoplastic, fairly hygroscopic and soluble in some organic solvent; the lower molecular weight products were soluble in acetone, dioxane and ethyl acetate, and the higher molecular weight polymers in dimethylformamide and dimethyl sulfoxide. The solubility in organic solvents and the thermoplasticity of the polymers demonstrates their linear nature. The higher molecular weight polymers were unchanged by solution in dimethylformamide and dimethyl sulfoxide, the recovered polymers being free of nitrogen and sulfur, respectively, and having identical solubility and infrared absorption characteristics to the original polymers.

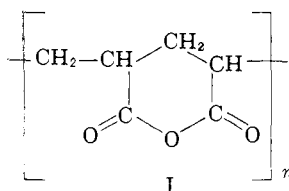
The infrared spectrum of the polymers showed almost negligible absorption in the C=C stretching region, along with strong absorption bands at 5.5 and 5.65 μ , characteristic of the carbonyl absorption of an anhydride group. A sample of glutaric anhydride prepared for comparison showed similar bands at 5.5 and 5.65 μ and a very small absorption at 6.0-6.15 μ (C=C). The latter suggests that the trace of residual ethylenic unsaturation in the polymers is caused by a small contribution from enol forms rather than by the presence of unsaturated end-groups. The failure of the polymers to react with bromine in solution confirmed the negligible nature of the unsaturation.

Treatment with water hydrolyzed polyacrylic anhydride to polyacrylic acid having an identical infrared spectrum to normal polyacrylic acid, prepared from acrylic acid. Allowing the polyanhydride to stand open to the atmosphere eventually achieved the same result.

From these results it is evident that acrylic an-

(8) Kagawa and Fuoss, *J. Polymer Sci.*, **18**, 535 (1955).

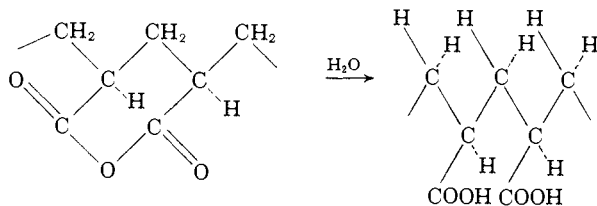
hydride polymerizes in solution exclusively by the alternating intramolecular-intermolecular route, the structure of the products being I.



Other results, typical of anhydride groups, provided further confirmation of this structure. For example, these groups were titrated potentiometrically by allowing the polymer to react with an excess of standard sodium hydroxide solution and back titrating with acid; 90% of the anhydride groups react. The failure of some of the groups to react is typical of polymer titrations and in this case is probably a result of the accumulating negative charge on the polymer chains as the reaction progresses, which prevents the approach of the hydroxide ions to the last few anhydride units. Coiling of the polymer chains may also contribute some steric hindrance which would have the same effect.

Efforts to prepare a corresponding polyacrylimide by dissolving a polyacrylic anhydride in concentrated ammonium hydroxide solution, removing the water and heating the residue at 200° *in vacuo*, resulted in a cross-linked polymer, presumably because some intermolecular imide formation had occurred.

The presence of anhydride rings in the polymer structure means that, on hydrolysis to polyacrylic acid, the configuration of the carboxylic acid group and the hydrogen atom on two newly-formed adjacent asymmetric carbon atoms, arising from the same ring, should be identical.



If the conformation of all the anhydride rings was the same, then completely stereospecific polyacrylic acid should be obtained on hydrolysis. When compared to normal polyacrylic acid, further regularity of structure should be apparent because of the absence of any head-to-head units. To investigate this point, X-ray diffraction measurements were made on polyacrylic acid from the polyanhydride and on normal polyacrylic acid. Efforts were made during the hydrolysis of the polyanhydride to prevent, if possible, any racemization.

Cold water was used for the hydrolysis and the product was freeze-dried. The X-ray diffraction patterns of the two polyacids (Fig. 1) show a substantial degree of crystallinity, indicated by the size and sharpness of the peak, in the polyacrylic acid from polyacrylic anhydride, whereas normal polyacrylic acid shows little, if any, crystallinity.

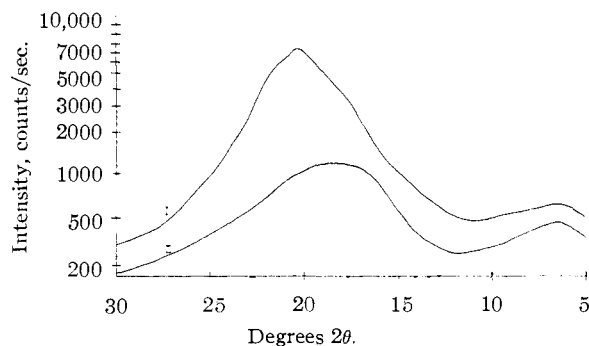


Fig. 1.—Polyacrylic acid: I, from polyacrylic anhydride; II, from acrylic acid.

Experimental

Polymerization of Acrylic Anhydride.—The monomer was freshly distilled under partial vacuum through a short column immediately before use. The general method was to dissolve the monomer and the initiator in the dry solvent in a screw-capped tube or pressure bottle, replace the air with dry nitrogen, seal, and place in an oven at 65° for the requisite time. The details of representative experiments are given in Table I. Polymer A was precipitated from solution by the addition of dry ether; polymers B and C precipitated out during the polymerization.

TABLE I

Monomer concn., %	Benzoyl peroxide as % of monomer	Solvent	Reacn. time, hr.	Conversion to polymer, %	Polymer soluble in	$[\eta]$ in dimethylformamide
2.5	0.25	Dioxane	116	50 (A)	Acetone dioxane ethyl acetate, etc.	Almost negl.
10	1.0	Benzene	10	90 (B)	D.M.F. D.M.S.	0.52
50	1.0	Benzene	2	85 (C)	D.M.F. D.M.S.	1.95

General properties of the polymers were: (a) Infrared spectrum showed strong bands at 5.5 and 5.65 μ (carbonyl groups of anhydride) and a small shoulder at 6–6.15 μ (trace of double bond); spectrum of glutaric anhydride has similar strong bands at 5.5 and 5.65 μ and the shoulder at 6–6.1 μ ; (b) They do not react with bromine in solution. (c) The softening points were approximately: A, 70°; B, 145°; C, 220°.

The polymers were precipitated from solutions in dimethylformamide and dimethyl sulfoxide by the addition of dry ether. After vacuum drying, the polymers were shown to be unchanged by this treatment.

Mass Polymerization.—The redistilled monomer (1 g.), mixed with benzoyl peroxide (0.005 g.), was sealed under dry nitrogen and placed in an oven at 60°. After one hour, rapid polymerization occurred, the polymer being a brittle white solid (1 g.), soluble in dimethylformamide and dimethyl sulfoxide on standing overnight, but insoluble in all other solvents; softening point approximately 235°.

Determination of Molecular Weights.—Viscosities were determined in 2 *N* sodium hydroxide solution using a calibrated Ubbelohde viscometer in a constant temperature bath at 30.0°. The concentration of polymer in the solution was between 0.2 and 0.9%. Intrinsic viscosities $[\eta]$ were calculated in the usual way from the viscosity at three different concentrations. With the equation given previously, these values were used to calculate the degree of polymerization *P* of the polyacids and these in turn were correlated with the molecular weights of the polyanhydrides. The results are given in Table II.

TABLE II

Polymer	$[\eta]$	<i>P</i> of polyacid	Mol. wt. of polyanhydride
A	Very small (0.045)	Small	<5,000
B	0.31	498	31,500
C	0.67	1520	94,500

Potentiometric Titration.—Polyacrylic anhydride (B) (0.1838 g.) was allowed to dissolve in carbonate-free sodium hydroxide solution (0.338 *N*, 100 ml.) over a period of two days, carbon dioxide-free nitrogen being bubbled slowly through the solution during this time. The excess sodium hydroxide was then estimated by potentiometric titration (glass and calomel electrodes) with hydrochloric acid solution (0.05 *N*). The sodium hydroxide solution consumed in the reaction (77.0 ml.) represents reaction with 90% of the anhydride units. Direct potentiometric titration of a solution of polyacrylic anhydride with sodium hydroxide solution was less efficient, reaction occurring with only 80% of the anhydride units in this case.

Determination of X-Ray Diffraction Patterns.—For this work polyacrylic anhydride (B) was hydrolyzed to polyacrylic acid by allowing it to dissolve in water at 5° and removing the excess water by freeze-drying. The polyacid was ground to <200 mesh particle size and redried. Normal

polyacrylic acid was prepared by a potassium persulfate-initiated polymerization of acrylic acid in aqueous solution, and ground and dried as above. The two polyacrylic acid samples had identical infrared spectra. The X-ray diffraction patterns were run on a General Electric XRD-5 diffractometer, using copper $K\alpha$ radiation at 50 KVP and 16 MA. A 1° beam slit and a 0.2° detector slit were used, with a 3° beam slit positioned in the Soller slit position preceding the detector slit. Figure 1 shows the diffraction patterns obtained.

Acknowledgment.—We wish to thank Dr. W. F. Loranger, of this department, and the X-ray diffraction laboratory of General Electric Co., for the determination and interpretation of the X-ray diffraction patterns.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

The Spontaneous Polymerization of Phenylacetaldehyde¹

By J. L. E. ERICKSON AND G. N. GRAMMER

RECEIVED APRIL 29, 1958

Phenylacetaldehyde polymerizes slowly to yield a crystalline trimer, which has been identified as a sesquiacetal, 2,4-dibenzyl-5-phenyl-6-hydroxy-1,3-dioxane (I).

When phenylacetaldehyde is allowed to stand for several weeks it undergoes a gradual but noticeable change as evidenced by increased viscosity and other changes in physical properties. Over a longer period of time, apparently as the result of a spontaneous polymerization process, phenylacetaldehyde yields a very viscous oil from which a crystalline substance is continuously separating. Measurements^{2,3} involving rates of change in physical properties appear to have been of little value in determining the nature of this process. Stobbe and Lippold² and later Treibs and Krumbholz⁴ treated phenylacetaldehyde with alkali and obtained a number of viscous oils and resins, but efforts to identify them failed, and suggestions as to the structure of these substances are not convincing. Pound³ observed that a very old sample of phenylacetaldehyde contained a crystalline substance which melted at 104°, and had a molecular weight corresponding to that of a trimer, but no further investigation was made of this product.

The stabilization of phenylacetaldehyde against polymerization has been a problem of much concern to manufacturers and users of this substance, and our investigation has been directed toward the identification of the crystalline substance and the nature of the process by which it is formed. We have found that phenylacetaldehyde upon storage for a period of 8 to 10 months becomes very viscous, and there is deposited a solid which may be collected by filtration and purified to yield 20 to 30% of a well-defined crystalline substance melting at 114.5–115°. The filtrate continues to yield these crystals and, if they are removed periodically,

yields higher than 50% may be obtained at the end of 12 to 14 months. It was found that the rate of formation of this substance may be catalyzed by bases, and that potassium hydroxide at the rather critical concentration of 0.03% in phenylacetaldehyde increases the rate about fifty-fold, so that uniform yields of 25 to 30% may be obtained within 5 to 7 days, and much larger yields result over a longer period of time. Manifestly, this polymer is not identical with the paraldehyde-type trimer, 2,4,6-tribenzyl-*s*-trioxane (Ia), m.p. 155–156°, obtained by Stobbe and Lippold² from phenylacetaldehyde by an acid-catalyzed process.

The carbon-hydrogen analysis and molecular weight of the crystalline substance, m.p. 114.5–115°, require that its structure correspond to that of a trimer of phenylacetaldehyde. It yields a monoacetate and a monobenzoate, and its infrared spectrum shows strong absorption bands at 2.98 and 8.74 μ , suggesting structural features such as a hydroxyl group and an ether linkage. The formation of this substance from phenylacetaldehyde by a base-catalyzed process suggests that an aldol condensation may have taken place to yield phenylacetal-dol (II), which then combined with another molecule of phenylacetaldehyde to yield the sesquiacetal I. A cyclic compound of this type would be, in fact, the cyclic acetal of phenylacetaldehyde and the hemiacetal of phenylacetal-dol. Sesquiacetals of this type have been obtained as liquids by a number of workers^{5,6} from acetaldehyde, propionaldehyde, butyraldehyde and isobutyraldehyde.

The proposed structure (I) for the trimer of phenylacetaldehyde was confirmed by reducing the

(1) Taken from a part of the dissertation submitted by G. N. Grammer in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Louisiana State University, June, 1958.

(2) H. Stobbe and A. Lippold, *J. prakt. Chem.*, **90**, 277 (1914).

(3) J. R. Pound, *J. Phys. Chem.*, **35**, 1174 (1931).

(4) W. Treibs and K. Krumbholz, *Chem. Ber.*, **85**, 1116 (1952).

(5) E. Spath, R. Lonrenz and E. Freund, *Ber.*, **76**, 57, 1196 (1943); E. Hanschke, *ibid.*, **76**, 180 (1943).

(6) R. H. Saunders, M. J. Murray, *et al.*, *THIS JOURNAL*, **65**, 1309, 1714 (1943); **66**, 206 (1944).