

LETTERS TO THE EDITORS

The mixture of the two components of the catalyst placed in a crown-cap bottle was heated in hydrocarbon under nitrogen atmosphere at 80°C. for 1 hour. At early stage evolution of gas was observed. Then liquid monomer was added to this mixture at about 0°C. After polymerization, polymer was isolated by reprecipitation procedure.

Table I shows the results of the polymerization of propylene oxide. Polypropylene oxide was extracted with the mixture of acetone and methanol, and precipitated in water.

The polymers obtained by alumina alone were tacky solids, while those by the mixed catalyst were nontacky elastic materials.

A mixed catalyst of silica-alumina (SiO₂ 87%, Al₂O₃ 13%) and zinc diethyl also gave solid polymer of high molecular weight, although silica-alumina alone gave liquid polymer. The results are shown in Table II.

The mixed catalyst was also effective in the polymerization of ethylene oxide. The results are shown in Table III. Polyethylene oxide was purified by precipitation from a benzene solution with petroleum ether and dried *in vacuo* at room temperature.

Details and further development will appear elsewhere.

Reference

1. M. E. Pruitt, L. Jackson, and J. M. Baggett, U. S. Pats. 2,706,181, 2,706,182.
2. C. C. Price, M. Osgan, R. E. Hughes, and C. Shambelan, *J. Am. Chem. Soc.*, **78**, 690 (1956).
3. L. E. St. Pierre and C. C. Price, *J. Am. Chem. Soc.*, **78**, 3432 (1956).
4. C. C. Price and M. Osgan, *J. Am. Chem. Soc.*, **78**, 4787 (1956).
5. S. Kambara and M. Hatano, *J. Polymer Sci.*, **27**, 584 (1958).
6. G. Natta, P. Corradini, and G. Dall'Asta, *C.A.*, **50**, 16270 (1956).
7. F. N. Hill, F. E. Bailey, and J. T. Fitzpatrick, *Ind. Eng. Chem.*, **50**, 5 (1958).
8. *Chem. Eng. News*, **35**, 24 (July 8, 1957).
9. E. T. Borrows and D. G. Stewart, Brit. Pat. 785,053 (1957).
10. W. Münster, German Pat. 821,349 (1951).

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Detection of Crystallinity Changes in Copolymers of Vinylidene Chloride and Alkyl Acrylates by Torsional Modulus Measurements*

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Changes in the value of the torsional modulus of amorphous samples of elastomers were shown by Gehman and co-workers¹ to correlate with an increase in the density of these polymers thus demonstrating crystallization. An apparatus similar to Gehman's, the Williamson² torsional wire apparatus, has been used to observe changes in the crystallinity of copolymers of vinylidene chloride and alkyl acrylates. The sensitivity of this apparatus has permitted (a) the detection of the onset of rapid crystallization, (b) the

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estimation of the temperature of the maximum rate of crystallization, and (c) determination of changes of the amount of crystallinity with temperature.

Copolymers of vinylidene chloride containing 10 mole-% of, respectively, butyl, octyl, and octadecyl acrylate were prepared by the method previously described.³ Test specimens were molded at 120°C. and 6000 psi without stabilizers. Amorphous materials were obtained by heating the samples of 170°C. for 10 min. and quenching in a mixture of alcohol and solid carbon dioxide (-60°C.) and were maintained at this temperature until used. Torsional modulus measurements were made at five degree intervals from -50°C. until the temperature at which viscous flow of the specimen began.

Figure 1 shows the change in modulus of the copolymers as a function of temperature as the latter was increased at the rate of 1°/min. Above the approximate second-order transition temperature (taken as the temperature at which the modulus is 1.35×10^5 psi⁴), the magnitude of the modulus declined in a narrow temperature range to a minimum

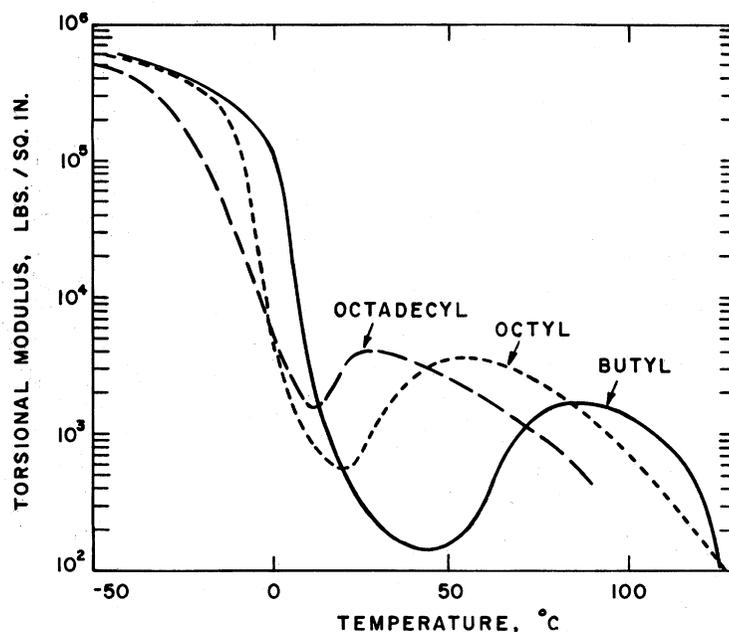


Fig. 1. Effect of temperature on the torsional modulus of amorphous vinylidene chloride copolymers containing 10 mole-% alkyl acrylates demonstrating onset of crystallization.

value, then rose to a maximum through a greater temperature interval and, finally, declined slowly until viscous flow was experienced. The temperatures at which the minimum modulus occurred were in the order octadecyl (11°C.), octyl (19°C.), butyl (43°C.). The temperature at which the maxima occurred also increased in the same order: octadecyl (26°C.), octyl (55°C.), butyl (85°C.). The magnitude of the minimum modulus was significantly affected by an increase in the chain length of the alkyl acrylate; the magnitude of the maximum modulus varied slightly.

The temperature dependence of the torsional modulus of these copolymers at temperatures between those of the approximate second-order transition and of the minimum modulus of Figure 1 is characteristic of many amorphous polymers and represents the effect of temperature on increasing the mobility of amorphous polymer segments. However, the increase in the modulus at temperatures above the minima was manifestly not

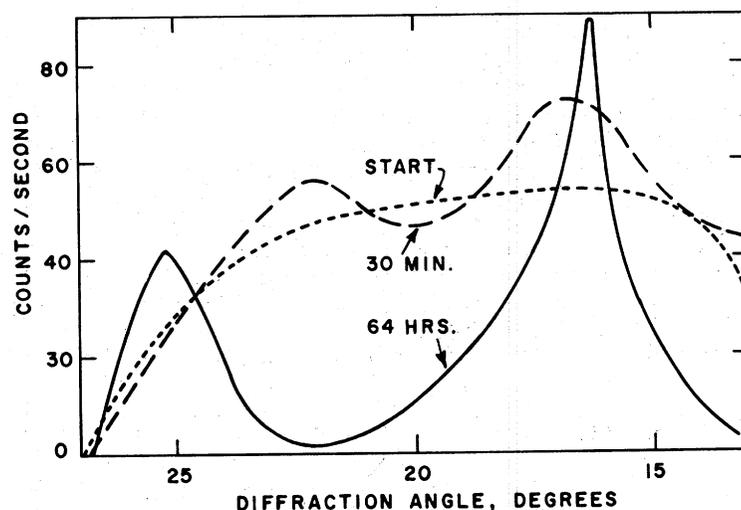


Fig. 2. Isothermal crystallization at 22°C. of a copolymer of vinylidene chloride containing 10 mole-% octyl acrylate demonstrated by x-ray diffraction.

in accord with the expected behavior of amorphous polymers. If rapid crystallization had set in, however, the rise in the modulus could be accounted for.

X-ray diffraction studies gave support to the hypothesis of crystallization. Figure 2 shows the change at representative times in the diffraction pattern (smoothed out) of an amorphous sample of a copolymer of vinylidene chloride and octyl acrylate at 22°C. Initially, the pattern was the typically diffuse one of an amorphous polymer. By the end of 30 min., weak peaks had developed, and after 64 hr., sharp diffraction peaks characteristic of crystalline poly(vinylidene chloride) had developed. In a subsequent report, it will be shown that in 30 min. about 20% of the crystallization of this copolymer had occurred. Although crystallization as indicated by x-ray diffraction is barely detectable in this interval, it is plainly evident from torsional modulus measurements. It is believed, therefore, that this method is potentially a more sensitive procedure for detection and estimation of crystallinity.

Results of isothermal studies and estimations of the extent of crystallization as a function of temperature will be published later.

References

1. S. D. Gehman, P. J. Jones, C. S. Wilkinson, Jr., and D. E. Woodford, *Ind. Eng. Chem.*, **42**, 475 (1950).
2. I. Williamson, *Brit. Plastics*, **23**, 87 (1950).
3. E. F. Jordan, Jr., W. E. Palm, L. P. Witnauer, and W. S. Port, *Ind. Eng. Chem.*, **49**, 1695 (1957).
4. R. F. Clash, Jr., and R. M. Berg, *Modern Plastics*, **21**, No. 11, 119 (1944).

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High Polymerization of Acetaldehyde by Alumina—A New Method of Preparation of Polyether

Since 1936 it has been known that acetaldehyde is polymerized when its vapor is condensed at a temperature below the melting point ($-123.3^{\circ}\text{C}.$) or when it is frozen.^{1,2} The solidification of acetaldehyde was reported to be an indispensable process for polymerization.³⁻⁵

We have now found a new method to polymerize acetaldehyde without solidification. By using alumina as the polymerization catalyst, acetaldehyde was converted into a high polymer at a temperature above its melting point. The polyacetaldehyde thus obtained was a white, nontacky, highly elastic material which may be a polyether having the structure $[-\text{CH}(\text{CH}_3)\text{O}-]_n$.⁶

Under reduced pressure (3 mm. Hg) 15 ml. of acetaldehyde prepared by decomposing paraldehyde was distilled for 1.5 hr. onto 5 g. of alumina granules (8 to 14 mesh) which was cooled at -70 to $-68^{\circ}\text{C}.$ by a Dry Ice-alcohol bath. Alumina was calcinated at 500 to $600^{\circ}\text{C}.$ for 15 hr. prior to use. The mixture of monomer and alumina was kept at -70 to $-68^{\circ}\text{C}.$ Liquid acetaldehyde soon became viscous and after 30 to 40 hr. it jellified. After 65 hr. the polymer was extracted with acetone and precipitated in water from acetone solution. On drying *in vacuo* at room temperature, 7.3 g. of white elastomeric material was obtained (conversion 66%) whose intrinsic viscosity in methyl ethyl ketone at $27.6^{\circ}\text{C}.$ was 2.4 (dl./g.). By using the constants of the modified Staudinger equation,⁷ $[\eta] = KM^{\alpha}$ ($\alpha = 0.65$, $K = 3.36 \times 10^{-4}$), the molecular weight of this polyacetaldehyde is estimated as 4.1×10^5 .

By using a similar method at -15 to $-10^{\circ}\text{C}.$, little solid polymer was obtained. When liquid acetaldehyde was added to alumina at -70 to $-68^{\circ}\text{C}.$, the yield and the degree of polymerization were very low.

Details and further developments will be published elsewhere.

References

1. M. W. Travers, *Trans. Faraday Soc.*, **32**, 249 (1936).
2. M. Letort, *Compt. rend.*, **202**, 767 (1936).
3. M. Letort et al., *Compt. rend.*, **216**, 58, 608 (1943); **224**, 50 (1947); **231**, 519 (1950); **240**, 86 (1955); **241**, 651, 1765 (1955); **242**, 371 (1956), *J. chim. phys.*, **48**, 594 (1951).
4. J. C. Bevington and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A196**, 363 (1949).
5. H. A. Rigby, C. J. Danby, and C. N. Hinshelwood, *J. Chem. Soc.*, **1948**, 234.
6. G. B. B. M. Sutherland, A. R. Philpotts, and G. H. Twigg, *Nature*, **157**, 267 (1946).
7. F. A. Bovey and R. C. Wands, *J. Polymer Sci.*, **14**, 113 (1954).

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