The rates of polymerization and effects of catalysts were studied by cryoscopic (*9, 18*) and gravimetric methods. Samples of monomer were polymerized in thin-walled soft-glass bulbs (volume ~0.5 ml.) whose inner surfaces had been cleaned, neutralized, and dried. The bulbs were filled with nitrogen, catalysts or inhibitors were added if such were to be used, monomer was added under nitrogen, and the bulbs were sealed. The amounts of materials were determined by weight, and the samples were polymerized in constant temperature baths. Polymerization in vacuo gave the same results as under nitrogen. Freezing point depressions were determined in dioxane or cyclohexane in the usual Beckman apparatus. Corrections were made for the presence of acetone, alcohol, and dimer (amounts determined in larger runs after vacuum train separation); the average molecular weight of the polymer was taken into account in calculation of the amount of unreacted monomer from the observed freezing point depression. A standard cooling rate was used in each case.

Gravimetric determinations employed a thick-walled borosilicate glass tube which could be weighed accurately, in which the bulbs could be broken conveniently and which could be evacuated on a vacuum train. Volatile material was removed under reduced pressure at room temperature and collected for determination of by-products. Data from the two methods are summarized in Table I; agreement was ± 10%.

LITERATURE CITED

(1) Arens, J.F., private communication.
(2) Arens, J.F., Modderman, P., *Proc. Koninkl. Nederland. Akad. Wetenschap.* **53**, 1163 (1950).
(3) Belash, P.M., Smol'kov, N.A., Belov, V.F., Muratov, U.G., Nechushkin, A.M., Paushkin, Ya.M., Nizova, S.A., *Radiospektrosk. Tverd. Tela* **1967**, 411-14; *CA* **68**, 105625 (1968).
(4) Bellamy, L.J., "Infrared Spectra of Complex Molecules," 2nd ed., Wiley, New York, 1958.
(5) Belov, V.F., Oganesov, S.S., *Tr. Mosk. Inst. Neftekim. i. Gaz Prom.*, No. **58**, 136 (1965); *CA* **65**, 3988 (1966).
(6) Eglinton, G., Jones, E.R.H., Shaw, B.L., Whiting, M.C., *J. Chem. Soc.* **1954**, 1860; *Org. Syn.* **34**, 46 (1954).
(7) Ficini, J., *Bull. Soc. Chim. France* **21** [5], 1367 (1954).
(8) Jacobs, T.L., Cramer, R., Hanson, J.E., *J. Am. Chem. Soc.* **64**, 223 (1942).
(9) Jacobs, T.L., Tuttle, W.P., Jr., *Ibid.*, **71**, 1313 (1949).
(10) Jacobs, T.L., Whitcher, W.J., *Ibid.*, **64**, 2635 (1942).
(11) Juettner, B., Smith, R.C., Howard, H.C., *Ibid.*, **59**, 236 (1937).
(12) Juster, Norman, Ph.D. thesis, University of California, Los Angeles, Calif., 1956.
(13) Murahashi, S., Ketsuki, H. (to Mitsubishi Chemical Industries Co.), Japan. Patent **3713** (March 3, 1966); Appl. Sept. 17, 1963; *CA* **65**, 828 (1966).
(14) Nieuwenhuis, J., Arens, J.F., *Rec. Trav. Chim.* **77**, 761 (1958).
(15) Nizova, S.A., Patalakh, I.I., Paushkin, Ya.M., *Dokl. Akad. Nauk SSSR* **153**, 144 (1963).
(16) Pfister Chemical Works, Ridgefield, N.J., Tech. Bull.
(17) Pregl, F., "Quantitative Organic Microanalysis," revised and edited by J. Grant, 4th English ed., pp. 134-42, Blakiston, New York, 1946.
(18) Taylor, H.S., Vernon, A.A., *J. Am. Chem. Soc.* **53**, 2527 (1931).

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Crystalline Propylene Glycol

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Crystals of propylene glycol were induced in the *d*-isomer and used to seed the crystallization of the racemic mixture, m.p. −31.5° to −29.3° C. The *d*-isomer has two melting points, −35.5° to −33° C. and −31.6° to −29.6° C. Solubilities in acetone at −35°, −40°, and −78° C. are approximately 30, 10, and 2 grams per 100 ml., respectively. Suitable recrystallization solvents are acetone, *n*-propyl and *sec*-butyl alcohols, acetone and ethyl acetate or ethyl ether, and ethanol and ethyl ether; methanol and ethanol alone fail. Crystals can be induced at −78° C. in propylene glycol containing up to about 10% water.

PROPYLENE glycol has been known for over 100 years, but it has only now been obtained in the crystalline state. Crystallization was induced by ordinary scratching of a very pure sample of either the *d*- or the *l*-isomer. Seed crystals of either isomer would sometimes induce crystallization in the racemic mixture, but this was best done by crushing together crystals of the two isomers and using the mixture of crystals for seeds. Racemic crystals seeded either optical isomer. The glycol could be crystallized neat or from solution, but crystallization of only one isomer from the racemic mixture has not yet been achieved.

The melting point of racemic propylene glycol (The Dow Chemical Co., USP grade) was −31.5° to −29.3° C. Partial melting occurred in the *d*-isomer from −35.5° to about −33° C. where the mass completely solidified, to remelt from −31.6° to −29.6° C., suggesting the existence of at least two allotropic forms. The samples used for determination of the melting points contained about 0.02% water.

Unseeded supersaturated solutions of racemic propylene glycol of 50% and greater in acetone will exist indefinitely at Dry Ice temperature, but in the presence of crystals the solubility in acetone at −78° C. was 1.4 grams per 100 ml. At −40° and −35° C., the solubilities in acetone were 10 and 30 grams per 100 ml., respectively.

Acetone is the most convenient solvent found so far for the recrystallization of propylene glycol. Other suitable solvents are *n*-propyl and *sec*-butyl alcohols, mixtures of acetone with either *n*-propyl alcohol, ethyl acetate, or ethyl ether, and mixtures of ethanol with ethyl acetate or ethyl ether. Methanol and ethanol alone failed. Crystals could be induced at −78° C. in propylene glycol containing up to about 10% water.

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