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Abstract

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ON THE RADIATION POLYMERIZATION OF VINYL CHLORIDE IN SOLID SOLUTIONS AT LOW TEMPERATURES

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It had previously been established ([1]) that pure vinyl chloride does not polymerize in the solid state under the action of γ-radiation. Of all the greater interest is the recently published communication ([2]) on the radiation polymerization of vinyl chloride at −78° in solid glassy solutions of the monomer in vaseline oil (a mixture of long-chain hydrocarbons of various structures). It was found that the rate of polymerization increases sharply as the monomer concentration decreases and reaches a maximum for very dilute solutions containing a few weight percent of monomer ([2]). The polymerization described earlier of solid amorphous solutions of vinyl acetate, methyl methacrylate, and styrene in vaseline oil ([2]) proceeds analogously. Inhibition of the polymerization by benzoquinone and iodine ([3]) and data on the copolymerization of styrene with methyl methacrylate ([4]) indicate that the reaction in these systems proceeds by a radical mechanism.

We have studied the radiation polymerization of vinyl chloride in vaseline oil at a dose rate of 70 rad/sec and at temperatures of −78 and −196°. Thus, in contrast to the cited works, the reaction was carried out at temperatures above and below the melting point of vinyl chloride. The purified vaseline oil was dried in vacuum at 100°. The monomer was distilled on a column with 20 theoretical plates and dried over barium oxide. The filling of ampoules with monomer was carried out in a special apparatus under conditions excluding contact with the atmosphere. The reaction ampoules were made of molybdenum glass, with an internal diameter of 8 mm (except in specially noted experiments). Co^{60} was used as the radiation source.*

The mixture of vinyl chloride with vaseline oil, both before and after irradiation, was externally a transparent homogeneous glass. After irradiation the ampoules were warmed to room temperature, opened, and the reaction mixture was treated with an excess of *n*-heptane. The precipitated polymer was washed many times with heptane and dried in vacuum at room temperature to constant weight. The yield of polymer depends strongly on the time of thawing of the irradiated mixture: in a 6% (wt.) solution at −196° the yield in 7 hours is

Fig. 1

Figure 1: Fig. 1

18.1% after thawing in less than 30 sec, and 49% after thawing in a cryostat at a constant rate over 4 hours. These data indicate significant post-polymerization occurring during thawing of the solutions. The kinetic data given below were obtained with rapid thawing of the irradiated solutions under identical conditions.

Figure 1 gives the kinetic curves of polymerization at −78 and −196° and a monomer content of 6%. At −196° the reaction rate decreases sharply already at the initial stage, so that polymerization practically ceases at a conversion of 15-20%. The polymer yield decreases sharply when the vinyl chloride content is increased from 6 to 15% (Fig. 2).

* For the construction of the source see ([5]).

At −78°, at first a sharp acceleration of the reaction is observed; then the polymerization rate reaches a maximum and, at conversions of 50-60%, rapidly decreases (Fig. 1). In this respect, the polymerization of vinyl chloride differs from the polymerization of methyl methacrylate, which under analogous conditions proceeds at a constant rate up to a conversion of 40% ([2]).

Fig. 1. Dependence of polymer yield on time. Vinyl chloride content—6 wt.%. The numbers on the curves indicate the irradiation temperature, °C.

Special experiments showed that changing the thickness of the solution layer from 8 to 0.15-0.30 mm does not affect the polymer yield under identical irradiation and thawing conditions for the solid solutions, although the thawing rate increases sharply with such a decrease in the thickness of the solution layer. It is therefore quite likely that the kinetic curves obtained correspond to a reaction occurring directly during irradiation of the solid solutions. After irradiation of vinyl chloride solutions in vaseline oil at −78°, a considerable dark reaction is observed; the polymer yield in a 10% solution after 3 h of irradiation at −78° is 50% 30 min after the end of irradiation and 62% after 15 h. At −196°, postpolymerization does not occur.

The polymers formed upon irradiation of the solid solutions are of low molecular weight. For example, the polymer obtained in a 10% solution at −78° after 3 h of irradiation has an intrinsic viscosity of 0.15 (in cyclohexanone at 30°). The products obtained contain less chlorine and more hydrogen and carbon than pure polyvinyl chloride. The elemental composition of the polymer formed in a 6% solution at −196° after 4 h of irradiation is: C 41.8%; Cl 50%; H 6.4% (total 98.2%); for pure polyvinyl chloride: C 38.4%; Cl 56.8% and H 4.8%. Apparently, hydrocarbon molecules of the vaseline oil enter into the polymer chains.

Fig. 2. Dependence of polymer yield on vinyl chloride content. Irradiation temperature −196°; irradiation time 4 h.

Fig. 2

Figure 2: Fig. 2

Among the kinetic data obtained, attention is drawn above all to the sharp decrease (almost to zero) in the reaction rate upon attainment of a certain conversion. Such a phenomenon is characteristic of low-temperature polymerization of crystalline monomers directly under irradiation ([1,2]). It is believed that the decrease in rate is connected with destruction of the crystal in the course of polymerization ([2]). Thus, already on the basis of the kinetic data one may suppose that the polymerization of vinyl chloride in solid solutions in vaseline oil is due to a certain ordered arrangement of the vinyl chloride molecules. It should be especially emphasized that in solid amorphous solutions (glasses) of vinyl chloride in low-molecular paraffins (a mixture of *n*-pentane and 2,2-dimethylbutane), polymerization, as we have established, does not proceed. Polymerization also does not proceed in frozen vinyl chloride–*n*-heptane systems. The fact that vinyl chloride polymerizes in a mixture with low-molecular paraffins indicates the determining influence of the structure of the frozen systems on the polymerization process. It is known that in solutions containing chain molecules of different sizes, in the vicinity of long chains, the usual arrangement is disrupted—

···the arrangement of small molecules characteristic of the low-molecular-weight substance taken separately [6]. An example is mixtures of *n*-alkanes of different lengths, where the "geometric" factor in the formation of solutions plays a decisive role. Since the distance between units in a paraffin chain is considerably smaller than the average intermolecular distances in a liquid, compression of the low-molecular-weight substance will occur near a long-chain molecule. This compression accounts for the observed decrease in volume upon mixing liquid paraffins of different lengths [6]. It is not excluded that an analogous process occurs in the formation of a solution of vinyl chloride in vaseline oil. It is quite probable that near the paraffin chains, where the vinyl chloride molecules are brought closer to one another, favorable conditions for polymerization are created.

In contrast to amorphous solutions of vinyl chloride in low-molecular-weight paraffins, the solid vinyl chloride—vaseline oil system is microheterogeneous. In the presence of microheterogeneity, significant kinetic effects may arise.

The question of the structure of frozen solutions of vinyl chloride in vaseline oil deserves special attention. The study of the structure of these systems, which we are carrying out at present, will make it possible to clarify more fully the causes of the observed kinetic regularities.

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CITED LITERATURE

[1] M. Magat, *Polymer* (London), **3**, 449 (1962).
[2] A. Chapiro, Materials of the Conference on High-Molecular-Weight Compounds, Paris, June 1963. *Chemistry and Technology of Polymers*, No. 4, 1964.
[3] Y. Amagi, A. Chapiro, *J. chim. phys.*, **59**, 537 (1962).
[4] A. Chapiro, M. Pertessis, *J. chim. phys.*, **61**, 991 (1964).
[5] A. Kh. Breger, V. A. Belinskii et al., article in the collection *The Action of Radiations on Inorganic and Organic Systems*, Publishing House of the USSR Academy of Sciences, 1958, p. 379.
[6] J. D. Gomez-Ibañez, Chia-Tsun Lin, *J. Phys. Chem.*, **67**, 1388 (1963).

Note: Figure translations are in progress. See original paper for figures.