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Polymerization of Nitroethylene under the Action of γ-Radiation

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Unsaturated nitro compounds are of interest because of the possibility of converting them into polymeric materials resistant to the action of various solvents and possessing satisfactory thermal stability. Polymerization of the simplest nitroalkene—nitroethylene—under the influence of water ([1,8]), aqueous solutions of carbonates of alkali and alkaline-earth metals ([2,3]), and inorganic and organic bases, proceeding by an ionic mechanism ([4]), leads to the formation of a powdery low-molecular-weight polymer (molecular weight up to 2000). Some physical properties of such a polymer have been studied (heat of explosion, impact sensitivity, work of explosion) ([8]).

By polymerization in solvents that dissolve both nitroethylene and its polymer (N,N-dimethylformamide, tetrahydrofuran), high-molecular-weight products were obtained ([5]), which, however, were powdery polymers.

From the literature data cited it follows that, in the polymerization of nitroethylene in the presence of an initiator in a solvent medium, powdery products are obtained that are contaminated with the initiator and the solvent. It is known that, when polymerization is carried out under the action of ionizing radiation, the purity of the polymer corresponds to the purity of the initial monomer. In addition, radiation polymerization can readily be carried out in the absence of a solvent, since it is possible to regulate the polymerization rate precisely by changing the radiation intensity.

In connection with the above, we set ourselves the task of determining the possibility and developing the conditions for obtaining high-molecular-weight polynitroethylene by bulk polymerization under the action of γ-radiation.

The radiation source was radioactive Co^{60}. The design of the radiation apparatus used in this work was described by Breger et al. ([9]). The activity of the source, equal to 1450 g-equiv Ra, provided a dose rate from 0.28 to 0.72 million r per hour. For polymerization, nitroethylene obtained by dehydration of 1-nitroethanol-2 with phthalic anhydride was used ([6,7]). The monomer was subjected to repeated fractional distillation, and fractions with b.p. 36°/100

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

mm were collected. Glass ampoules, preliminarily purged with hot nitrogen, were weighed and filled with freshly distilled nitroethylene. To remove occluded atmospheric oxygen, the usual freezing and melting operations were carried out. The ampoules sealed under vacuum were placed in the working chamber of the radiation apparatus. Irradiation was carried out at 20°. After irradiation the ampoules were opened and the monomer was distilled off under vacuum. The polymer yield was determined gravimetrically.

Figure 1 shows the dependence of the degree of conversion of the monomer on the integral radiation dose at dose rates of 0.28 (1) and 0.49 (2) Mr/hour.

In the initial period of irradiation ($1 \cdot 10^6$ r), the transparent monomer becomes cloudy, and then a white precipitate ($5 \cdot 10^6$ r), identical to the polymer obtained under the influence of organic bases, separates out ([4]).

Upon further irradiation, the resulting paste-like mixture of polymer and monomer is transformed into a transparent pale-yellow block of polymer. The formation of the block polymer is apparently associated with the occurrence of secondary reactions of addition of growing polymer chains to the previously···

to the polymer formed and is accompanied by an increase in its molecular weight. It is interesting to note that the formation of block polynitroethylene does not occur at dose rates > 0.3 Mr/hour. In this case, up to 100% conversion, the polymer remains powdery, and its color changes from white to light brown. It should be noted that the formation of transparent block polynitroethylene is a very complex physicochemical process, depending on many factors; therefore, sometimes at 100% conversion a partially powdery polymer is also formed.

It was established that partially polymerized nitroethylene samples continue to polymerize even after irradiation has ceased. This makes it possible to conclude that, under the action of γ-radiation, relatively long-lived polymer radicals are formed.

Fig. 1

Fig. 2

The character of post-radiation polymerization at initial conversions of 50% (1) and 20% (2) is shown in Fig. 2.

During post-radiation polymerization, the formation of block polynitroethylene also takes place.

The polymerization process of nitroethylene under the action of γ-radiation is inhibited by hydroquinone and oxygen, which also indicates its radical character. The radiation polynitroethylene obtained is insoluble in ordinary solvents, but readily soluble in N,N-dimethylformamide; its intrinsic viscosity in this solvent is 0.38, which corresponds [5] to a molecular weight of 38,000. The density of block polynitroethylene is d_{20} 1.535, m.p. 150°.

Elemental analysis of the polymer indicates the absence of a denitration reaction during irradiation: $(\text{—CH}_2\text{—CHNO}_2)_n$. Calculated: N 19.2%. Found: N 19.19%.

X-ray analysis of the polymer showed that no crystalline phase is present in it. The intense narrow halo and weak broad halo correspond to short-range order parameters of 5.15 Å and 3.73 Å* (see Fig. 3 in the inset).

It was also established that nitroethylene under the action of γ-radiation readily copolymerizes with other unsaturated nitro compounds, for example 1,4-dinitrobutadiene-1,3.

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* The X-ray structural analysis of the polymer was carried out by S. G. Strunskii.

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