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ON THE INFLUENCE OF ADDITIVES OF SEMICONDUCTOR NATURE ON THE RADIATION POLYMERIZATION OF ACRYLONITRILE AND METHYL METHACRYLATE

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Previously ([1,2]), in the low-temperature radiation polymerization of isobutylene, significant kinetic effects were found in the presence of additives of zinc oxide, magnesium oxide, and others. It was also shown that, when the surface area of the reaction vessel (glass) is increased, the rate of polymerization of isobutylene and styrene increases ([3]). As is known, both of these monomers polymerize under the indicated conditions by a carbonium mechanism.

The influence of oxide additives on the radiation polymerization of monomers prone to anionic polymerization has not been described in the literature. We investigated the polymerization of acrylonitrile and methyl methacrylate under the action of γ-rays at low temperatures in the presence of semiconductor oxides of various natures. The experiments were carried out using a Co^{60} γ-radiation source with an activity of 20,000 g-equiv. radium. The purification of the monomers and solvents, as well as the procedure for carrying out the experiments, were described previously ([4,5]). Zinc oxide, titanium oxide, chromium oxide, magnesium oxide, cuprous oxide, nickelous oxide, and lithium-doped nickelous oxide were used in the work. The oxides employed were heated, before loading the monomers, in the reaction ampoules under vacuum at 100° for 6 hours. Zinc oxide and magnesium oxide were preheated at 300 and 150°, respectively. Solid additives were introduced in an amount necessary to fill the entire volume of the monomer. We established that, in contrast to isobutylene, increasing the surface area of the reaction zone by means of glass powder not only does not cause an increase in the rate of polymerization of acrylonitrile at −78°, but, on the contrary, leads to a certain decrease in the rate of the process (when the surface area is increased 20-fold, the polymerization rate decreases by a factor of 2). It was also shown that no increase in the rate of polymerization of acrylonitrile at low temperatures is observed when the reaction is carried out in the presence of additives of zinc oxide, titanium oxide, and chromium oxide. As is known, these oxides are n-type semiconductors. However, when n-type additives were replaced by p-type additives (cuprous oxide, nickelous oxide, and

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

lithium-doped nickelous oxide), we found a sharp increase in the rate of polymerization of acrylonitrile at −78° (melting point −81.7°) under the action of γ-radiation. An analogous effect is also observed in the presence of magnesium oxide. It is of considerable importance that the significant kinetic effects observed in the presence of the indicated additives are accompanied by a sharp increase in the molecular weight of the polymer (Table 1, Fig. 1). An increase in rate (Table 1) is also observed in the polymerization of acrylonitrile in a solution of triethylamine in the presence of p-type oxides at −78°.

It is significant that the increase in the rate of polymerization of acrylonitrile occurs only at low temperatures. At 0°, as is seen from Fig. 2, no accelerating effect due to the introduction of magnesium oxide is observed.

is observed. In the polymerization of acrylonitrile in triethylamine at 0°, only a weak kinetic effect is observed.

The rate of polymerization of acrylonitrile in the solid state at −196° in the presence of magnesium oxide or cuprous oxide increases by more than a factor of two in comparison with the rate in the absence of additives.

Fig. 1. Polymerization of acrylonitrile in bulk in the presence of oxide additives. $t = -78°$, intensity 15 r/sec; a—without additive, —in the presence of titanium oxide, —in the presence of zinc oxide, —in the presence of magnesium oxide

Fig. 2. Polymerization of acrylonitrile in bulk at various temperatures. Intensity 15 r/sec. 1, 2—temperature −78°: 1—without additive, 2—in the presence of magnesium oxide; 3, 4—temperature 0°: 3—without additive, 4—in the presence of magnesium oxide

Table 1

Polymerization of acrylonitrile in the presence of oxide additives at −78°C, intensity 80 r/sec

Additive	In bulk: rate, mol/l·sec·10^5	In bulk: *M*	In triethylamine solution: rate, mol/l·sec·10^5	In triethylamine solution: *M*	Additive	In bulk: rate, mol/l·sec·10^5	In bulk: *M*	In triethylamine solution: rate, mol/l·sec·10^5	In triethylamine solution: *M*
—	1.05	—	3.5	—	MgO	10.1	51 500	11.9	117 000
—	0.9	8000	3.33	10 000	Cu_2O	13.3	206 000	5.9	—
ZnO	1.12	—	3.4	—	Ni_2O	11.9	—	5.9	—
Cr_2O_3	1.01	—	2.6	—	$Ni_2O \cdot Li_2O$	9.8	—	4.95	—
TiO_2	0.98	—	3.5	—					

It is known that the radiation polymerization of acrylonitrile at 0° and above proceeds by a radical mechanism. The data obtained on significant kinetic effects during the polymerization of acrylonitrile under the action of γ-rays in the presence of the corresponding solid additives in the low-temperature region may indicate an ionic (anionic) mechanism of the polymerization of acrylonitrile in bulk under the action of γ-rays at low temperatures. By the method of IR spectroscopy it was shown that in polymers obtained in the presence of oxide additives, absorption is observed in the region of 1675 cm^{-1}, which indicates that polymerization proceeds not only through the —C=C—bond, but also through the —C N bond.

We also established that significant kinetic effects are observed in the polymerization of methyl methacrylate (melting point —52.5°) in the presence of magnesium oxide at low temperatures—both below and somewhat above the melting point (approximately by a factor of 30-35). At the same time, polymethyl methacrylate obtained at —56° possesses

high density, which indicates its stereoregular nature. Thus, the results obtained convincingly demonstrate the exceptional role of solid additives in the development of the polymerization reaction under the action of ionizing radiation.

In the present work, the selective effect of various semiconductor additives on radiation polymerization at low temperatures is considered for the first time, depending on their nature and on the chemical structure of the monomer. Thus, semiconductors of electronic nature cause significant kinetic effects, as was shown earlier ([1], [2]) in the polymerization of isobutylene—a monomer that polymerizes by a cationic mechanism. However, additives of this nature do not alter the polymerization rates of monomers prone to the formation of chains of anionic nature, for example, acrylonitrile. The positive effects observed in the presence of magnesium oxide in the case of monomers of different nature are apparently explained by its dual nature under radiation conditions. It is possible that this is connected with the presence of impurities in magnesium oxide.

At present it is impossible to propose a mechanism for the action of the indicated additives on radiation polymerization. There is no doubt that in these cases the polymerization reaction proceeds with the participation of the surface of the solid additives. In this connection, the role of the solid additives may be expressed both in increasing the yield of initiating centers of polymerization and in suppressing the termination reaction as a result of fixation of the corresponding counterion on the surface. Further investigations should clarify this question.

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