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Fig. 2. Dependence of the copolymer composition on the composition of the initial mixture during the joint polymerization of acrylonitrile and methyl methacrylate. 1, 2, 3, 4—as in Fig. 1; 5, 6—at −50°; 7, 8—at 0°. 5, 7—with glass powder, 6, 8—with ZnO

Figure 2: Fig. 2. Dependence of the copolymer composition on the composition of the initial mixture during the joint polymerization of acrylonitrile and methyl methacrylate. 1, 2, 3, 4—as in Fig. 1; 5, 6—at −50°; 7, 8—at 0°. 5, 7—with glass powder, 6, 8—with ZnO

Abstract

Full Text

Physical Chemistry

L. P. MEZHIROVA, A. P. SHEINKER, A. D. ABKIN

ON THE MECHANISM OF THE RADIATION POLYMERIZATION OF ACRYLONITRILE AND METHYL METHACRYLATE IN THE PRESENCE OF SOLID ADDITIVES

(Presented by Academician S. S. Medvedev on May 9, 1964)

Earlier [1] we showed that the rate of polymerization of acrylonitrile under the action of gamma radiation at low temperatures increases sharply in the presence of *p*-type semiconductor oxides (cuprous oxide, nickel oxide, lithiated nickel oxide). An analogous effect is also observed in the presence of magnesium oxide. A considerable increase in the rate is observed

also in the polymerization of methyl methacrylate in the presence of magnesium oxide at temperatures both above and somewhat below the melting point.

The present work was undertaken in order to elucidate the mechanism of polymerization (radical or ionic) of acrylonitrile and methyl methacrylate in the presence of solid additives. To investigate the mechanism, the method of joint polymerization was used.

The experiments were carried out using a Co^{60} gamma-radiation source with an activity of 20,000 g-eq of radium, at a radiation intensity of 45 r/sec. The purification of the monomers, as well as the procedure for carrying out the experiments, were described earlier [1,2]. It was

it has been established that the rates of separate and joint polymerization of acrylonitrile (1) with methyl methacrylate (2) in bulk at −50° in the presence of magnesium oxide are approximately an order of magnitude higher than without magnesium oxide. At 0° the kinetic effects are small—1.5-2-fold (Fig. 1).

From Fig. 2 it is evident that the copolymers obtained in the presence of magnesium oxide, both at 0° and at −50°, are enriched in the acrylonitrile component.

Table 1

Copolymerization of acrylonitrile and methyl methacrylate

Experimental conditions	Temp., °C	Additive	r_1	r_2
γ-Rays, in bulk	−50	MgO	4.5	0.2
γ-Rays, in bulk	−50	ZnO	0.42	1.65
γ-Rays, in bulk	−50	Glass powder	0.42	1.65
γ-Rays, in bulk	−50	–	0.42	1.65
γ-Rays, in bulk	0	MgO	2.8	0.15
γ-Rays, in bulk	0	ZnO	0.14	1.65
γ-Rays, in bulk	0	Glass powder	0.14	1.83
γ-Rays, in bulk	0	–	0.14	1.83
γ-Rays, in a solution of triethylamine ([2])	−78	–	7.0	0.05
Catalyst nBuLi in bulk ([3])	−8	–	7.0	0.39

Fig. 3. Kinetics of polymerization of (1) acrylonitrile (−196°) and (2) methyl methacrylate (−78°) in the solid state

Figure 3: Fig. 3. Kinetics of polymerization of (1) acrylonitrile (−196°) and (2) methyl methacrylate (−78°) in the solid state

Experimental conditions	Temp., °C	Additive	r_1	r_2
Catalyst—benzoyl peroxide (4)	+60	–	0.18	1.35

Conversely, copolymers obtained without magnesium oxide, and also in the presence of glass powder and zinc oxide, contain more methyl methacrylate than the initial mixture. The values of r_1 and r_2 calculated for these cases are given in Table 1.

From the data of Table 1 it is evident that r_1 and r_2 for copolymers obtained in the presence of magnesium oxide at −50° and at 0° under the action of gamma rays differ from the corresponding constants for copolymers obtained at these temperatures without magnesium oxide, or, in the case of peroxide initiation, approach in their values the constants for the anionic mechanism.

These data indicate that in the presence of magnesium oxide the reaction proceeds mainly by an anionic mechanism. It is significant that anionic polymerization takes place not only at −50°, but also at 0°.

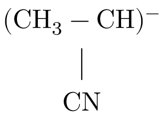
Earlier (1) we showed that the rate of polymerization of acrylonitrile and methyl methacrylate increases in the presence of solid additives not only in the liquid, but also in the solid state. It is known (5,6) that during the polymerization of acrylonitrile in the solid state (−196°) termination of the polymerization process is observed when the polymer yield is ∼ 5%. Our data, as is evident from Fig. 3, show that in the presence of magnesium oxide this "inhibition" occurs no earlier than 25% conversion. The rate of polymerization of methyl methacrylate in the solid state (−196, −78°) is extremely low (5,6). In the presence of magnesium oxide at −78°, a sharp increase in the rate is observed; moreover, in the dose range studied, polymerization proceeds with acceleration over time.

Fig. 3. Kinetics of polymerization of (1) acrylonitrile (−196°) and (2) methyl methacrylate (−78°) in the solid state.

Thus, in the present work it has been shown for the first time that the mechanism of radiation polymerization of acrylonitrile and methyl methacrylate changes from radical in the absence of magnesium oxide to anionic in the presence of additions of this oxide. At the same time, the yield of ionic reactions increases on going from 0° to −50° (the rates of copolymerization and the compositions of the copolymers). This result confirms the idea expressed earlier (7) concerning the exclusive role

surface in the growth of chains of an ionic nature during polymerization under the action of high-energy radiation. However, the results of the present work, as well as those obtained earlier (1), lead to the conclusion that the nature of the solid additives influences the development of polymerization by one mechanism or another. This is clearly illustrated by the data of the work on the different mechanisms of copolymerization of acrylonitrile and methyl methacrylate (at 0 and −50°) in the presence of magnesium oxide and zinc oxide or glass powder, and also by the data (1) on significant kinetic effects in the polymerization of acrylonitrile (−78°) in the presence of cuprous oxide, nickelous oxide, and lithium-doped nickelous oxide (p-type semiconductors), as well as magnesium oxide. The semiconductor properties of magnesium oxide are discussed in (8). Conversely, no increase in the polymerization rate is observed either in the case of the nitrile or of methyl methacrylate when zinc oxide, titanium oxide, or chromium oxide—n-type semiconductor additives—are introduced into the system. These and other studies of ours (9), as well as works (10,11), leave no doubt that polymerization in the presence of solid oxides proceeds in the chemisorbed layer on the surface of these additives. In this case, the appearance of active centers of polymerization of cationic or anionic nature on the surface is due to the transfer of an electron from the adsorbed particle to the solid additive in the first case (isobutylene—electron additives) and, conversely, to the capture of an electron by adsorbed particles from the solid additive in the second case (acrylonitrile, methyl methacrylate—hole additives). On the basis of works (1,2,3), it may be accepted with sufficient probability that the initial center of the cationic polymerization of isobutylene under the action of ionizing radiation is H^+, formed in the chemisorbed layer as a result of the transfer of an electron by a hydrogen atom to the solid additive (ZnO).

It may be thought that, in the case of acrylonitrile, the initial center of anionic polymerization is the carbanion



$$(\mathrm{CH_3} - \underset{\displaystyle \mathrm{CN}}{\underset{|}{\mathrm{CH}}})^-$$

formed as a result of addition of an electron from the additive to the radical $CH_3\dot{C}HCN$. The formation of this radical is connected with the interaction of atomic hydrogen with an acrylonitrile molecule chemisorbed on the surface of the solid additive. The presence of the radical $\dot{C}H_3CHCN$ in the solid-phase polymerization of acrylonitrile was shown in (6). Other possibilities for the formation of the carbanion are also not excluded.

We are inclined to think that the effect we have found of magnesium oxide on the solid-phase polymerization of acrylonitrile and methyl methacrylate may also be connected with the participation of holes and electrons.

According to the data of work (14), the probability of an ionic mechanism under conditions of solid-phase polymerization is very high.

Further studies in this direction will clarify the question under investigation.

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