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ON THE SPECIFIC NATURE OF RADIATION-INDUCED SOLID-PHASE POLYMERIZATION DURING IRRADIATION

The problem of radiation-induced polymerization in the solid phase has now attracted considerable interest both from the standpoint of possible practical applications and for the development of general theoretical ideas in chemical kinetics. The usual method for studying the kinetics of radiation-induced solid-phase polymerization is based on the fact that, after irradiation of a solid monomer, it is thawed (with melting) and the monomer is separated from the polymer, with determination of the yield of the latter. Thus, the polymer yield and the rate of polymerization are determined after completion not only of the irradiation itself, but also of the subsequent strong heating, accompanied by melting and often also by phase transitions (before melting of the irradiated system). As a result, the information obtained proves to be very uncertain, since it remains unclear whether polymerization of the given monomer occurs in the solid phase (and, if so, when exactly—during irradiation or due to post-effects) or during thawing, for example at phase-transition points, the special role of which was demonstrated in interesting works by V. A. Kargin and co-workers ([1], [2]), or at the moment of melting ([3], [4]). Meanwhile, in order to establish the mechanism of the polymerization process for each given monomer, the question of when exactly it occurs is of decisive importance.

In this connection, we undertook a detailed study of the radiation-induced solid-phase polymerization of acrylonitrile (AN) and vinyl acetate (VA), with calorimetric measurements of heat evolution (absorption) during thawing of the irradiated monomers and with observation of ESR signals (under the beam and after the end of irradiation).

The monomers studied were irradiated with electrons of energy 1.6 MeV on the electron accelerator of the Institute of Chemical Physics, Academy of Sciences

Fig. 1

Figure 1: Fig. 1

of the USSR. Irradiation was carried out in an automatic cassette (for 8 cuvettes), which made it possible to move the cuvettes remotely under the beam (without switching the latter on). A description of the methods for purification of the monomers, thermostating, dosimetry, and analysis of the irradiation results is given in detailed communications (5). To determine when exactly the polymerization reaction effectively proceeds—in the solid phase or during thawing—a diathermic calorimeter was constructed and used, the principle of which was proposed in (6). The design of the calorimeter allowed irradiation of the monomer directly in the calorimetric cell. During uniform thawing of the sample on an EPP-09 recorder, the temperature of the sample and the temperature difference on the inner and outer sides of the diathermic jacket (by means of a battery of differential thermocouples), which is proportional to the heat flux, were recorded simultaneously. The described apparatus made it possible to determine thermal effects (of both signs) of 10-40 cal/g with an accuracy of $±1cal/g.BytheESRmethod—ontheapparatusdescribedin(^{7}$) —the accumulation of active centers during irradiation of AN and VA at various temperatures, as well as their disappearance after the end of irradiation, was observed. V. N. Shamshev took part in these experiments, to whom the authors express their sincere gratitude.

To study the kinetics of post-polymerization, the irradiated samples were kept in a cryostat (thermostating accuracy $±$2°), after which they were rapidly thawed and analyzed.

The main experimental results are given below.

Acrylonitrile (AN) CH_2 = CH–CN, m.p. −82°; b.p. +78.5°. The kinetic curves obtained at different temperatures (from −196 to 0°) and different dose rates I (0.3 Mrad/min in the solid phase and 0.75 Mrad/min in the liquid phase) are shown in Fig. 1. The activation energy of the reaction in the liquid phase, in agreement with (8), is $E_\ell \approx 3$ kcal/mol; in the solid phase $E_s \approx 0$. In both the solid and the liquid (8) phases, the initial polymerization rate $W_{\text{init}} \sim I^{0.8}$. At temperatures below $\sim -140°$, a "limiting" polymer yield is observed at high radiation doses, expressed especially clearly at −196°. Under repeated irradiation with large doses (8 Mrad each), with thawing of the sample (to melting) and refreezing after each irradiation, the limiting polymer yield increased proportionally to the number of irradiations. The molecular weight of the resulting polymer (at −196°) decreased with increasing dose—from $\overline{M} \approx 3.5 \cdot 10^5$ to $\overline{M} \approx 7 \cdot 10^4$ (at $D = 8$–20 Mrad).

Fig. 1. Kinetic curves of radiation polymerization of AN. 1—at 0°, 2—at −30°, 3—at −75° (all at $I = 0.75$ Mrad/min); 4—at −90°, 5—at −100°, 6—at −150°, 7 —at −170°, 8—at −196° (all at $I = 0.3$ Mrad/min)

Fig. 2

Figure 2: Fig. 2

The presence of post-polymerization at −140, −120, and −90° was established, with its absence in the region of lower temperatures. The kinetic curve of post-polymerization in the solid phase at −90° (for a sample irradiated at −196°, $I = 0.3$ Mrad/min, $D = 2.4$ Mrad) is presented in Fig. 2, where the absence of an aftereffect at −196° is also illustrated. During post-polymerization, a strong increase in the molecular weight of the polymer is observed (up to $\overline{M} \approx 10^6$ in 10 hours at −90°), followed by the formation of a protective polymer. The activation energy for post-polymerization in the solid phase was found, in agreement with (^{9}), to be 3 kcal/mol, i.e., the same as for liquid-phase radiation polymerization. It may therefore be assumed that the nature of the active centers and the mechanism of chain propagation in the radiation polymerization of AN in the liquid phase and its post-polymerization in the solid phase are similar.

Measurements of the EPR spectra of solid AN showed that the appearance of the signals under the beam and after the end of irradiation is the same. When the irradiated sample was kept at −172° for 30 min, the signal intensity did not decrease. The heat of fusion of AN, according to our calorimetric measurements, is 35 ± 1 cal/g, which is almost an order of magnitude less than the heat of polymerization (327 cal/g (^{10})). Meanwhile, in measuring the heats of fusion of AN samples irradiated at low temperatures (polymer yield up to 12%) no changes in the measured heat of fusion were observed within the stated error (±1 cal/g), which corresponds to the formation of less than 2.7% polymer (of the observed yield) at the melting point. From the data given above on the rate of post-polymerization it is clear that appreciable formation of polymer could not occur during the rapid thawing of the irradiated samples either. Thus, we arrive at the conclusion that polymerization of AN at $t^0 < -140^\circ$ occurs entirely, and at $t^0 > -140^\circ$—after subtracting the negligible contribution of slow aftereffects—occurs in the solid phase during irradiation.

Fig. 2. Kinetic curve of post-polymerization of AN in the solid phase: 1—at −90°, 2—at −196° (samples were irradiated with $D = 2.5$ Mrad)

Vinyl acetate (VA): $CH_2{=}CH{-}O{-}C({=}O)CH_3$, m.p. −93°, b.p. +72.5°. Kinetic curves for the polymerization of VA were obtained at seven temperatures (from −196 to 0°). At $t^0 < -129^\circ$ (the glass-crystal phase-transition point), the kinetics of solid-phase polymerization of glassy (unstable in this temperature region) and crystalline VA were studied separately; moreover, the polymerization rate of glassy VA proved to be approximately an order of magnitude higher. The temperature dependence of the initial rate of radiation polymerization of VA (at $I = 5$ Mrad/min) is shown in Fig. 3. In the liquid phase $E_\ell \approx 3.7$ kcal/mol, in the solid phase $E_t \approx 0$. In the solid phase $W_{\text{initial}} \sim I$, whereas

Fig. 3. Temperature dependence of the initial polymerization rate of VA
($I = 5$ Mrad/min)

Figure 3: Fig. 3. Temperature dependence of the initial polymerization rate of VA ($I = 5$ Mrad/min)

in the liquid phase (11) $W_{\text{initial}} \sim I^{0.5}$. In contrast to AN, no “limit” on the polymer yield is observed for VA. The molecular weight of polyvinyl acetate (for the glassy monomer at $-150°$) decreases with increasing dose—from $\overline{M} \approx 3 \cdot 10^4$ to $\overline{M} \approx 7 \cdot 10^3$ at $D = 150$ Mrad); in the polymerization of crystalline VA the value of $\overline{M}$ is several times smaller.

Fig. 3. Temperature dependence of the initial polymerization rate of VA ($I = 5$ Mrad/min)

Another essential difference between VA and AN is the complete absence of any post-polymerization in the solid phase. The form of the EPR signals during irradiation and after its termination is also the same for VA. Upon thawing of the irradiated glassy VA, the intensity of the EPR signal remained practically unchanged up to the phase-transition point ($-129°$), after which the signal disappeared.

Calorimetric measurements during thawing of VA very clearly demonstrate heat evolution at the phase transition (34 ± 1 cal/g) and heat absorption (33 ± 2 cal/g) at the melting point (Fig. 4). Comparison of calorimetric data for unirradiated and irradiated VA samples leads, as in the case of AN, to the conclusion that the entire polymerization reaction, to an accuracy of several percent of the observed polymer yield, takes place in the solid phase during irradiation. It is known that polymerization of VA in the liquid phase is a typical radical reaction (12). Therefore, the absence of post-polymerization of VA in the solid phase, despite preservation of the same form and intensity of the EPR signal as under the beam, serves as a demonstration of the absence of radical polymerization in the unirradiated solid phase.

In the present brief communication we are unable to interpret in detail all the results obtained and therefore shall dwell here only briefly on one conclusion following from the results set forth above. The sharp difference between the rapid polymerization of solid AN during irradiation and its slow post-polymerization in the solid phase, and the rapid polymerization of solid VA under the beam with complete absence of aftereffects in the solid phase

testify to the specificity of radiation solid-phase polymerization during irradiation. It is possible that the main reason for the effective course of solid-phase polymerization specifically during irradiation is the formation of short-lived excited molecules, which, naturally, rapidly perish after the beam is switched off in the solid phase, while in the liquid phase they accumulate under the beam only to much lower stationary concentrations because of the increased rate of “quenching.”

Fig. 4. Thermographic curve of thawing of VA

Figure 4: Fig. 4. Thermographic curve of thawing of VA

Fig. 4. Thermographic curve of thawing of VA

Such active centers may prove to be far more effective than ions or radicals for carrying out the mechanism of solid-phase polymerization considered by N. N. Semenov [13,14] through the development of energy chains (see also [15]). A second possible reason for the acceleration of radiation solid-phase polymerization under the beam is the change in the state of the solid substance during irradiation. As is known, irradiation with heavy particles produces rather strong local heating along tracks with high specific ionization [16,17]. For electrons, however, such heating, as can be shown on the basis of [16], does not exceed several degrees and therefore does not play a noticeable role. Much more significant may be the "loosening" of the substance along the tracks of primary particles and δ-electrons, apparently responsible also for the phenomenon of radiation enhancement of diffusion [18,19]. The possibility of molecular displacements in a solid under the action of electron impact, short-term unfreezing of internal rotation, and excitation of all possible vibrations brings the properties of the irradiated solid closer to those observed near phase-transition or melting points and, as is known, promotes effective polymerization [13,14,1,2].

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