M. A. BRUK, A. D. ABKIN, P. M. KHOMIKOVSKII, G. A. GOL' DER, CHU SYAN-LIN

1964

SovietRxiv

Abstract

Full Text

M. A. BRUK, A. D. ABKIN, P. M. KHOMIKOVSKII, G. A. GOL' DER, CHU SYAN-LIN

ON CERTAIN QUESTIONS OF RADIATION POLYMERIZATION AND COPOLYMERIZATION OF TETRAFLUOROETHYLENE IN THE SOLID STATE

(Presented by Academician V. A. Kargin, 3 IV 1964)

In connection with the broad development in recent years of research in the field of solid-phase polymerization, particular interest attaches to the study of the character of the molecular motions of a monomer in a crystal lattice, and also of the behavior of the active particles arising in the system during the initiation of polymerization.

Earlier (^{1}) we showed that tetrafluoroethylene (TFE) polymerizes in the crystalline state under the action of γ-rays and fast electrons, the activation energy of the process being very small, while the dependence of the initial polymerization rate on temperature is characterized by a curve with a maximum in the solid state near the melting temperature of the monomer (−131°). In the course of further investigation it was established that on the curve of the dependence of the initial polymerization rate on temperature there is an additional maximum (or a sharp inflection, depending on the radiation intensity) in the temperature region from −160 to −165° (Fig. 1). In this same temperature region the death of radicals stabilized in the solid monomer at lower temperatures begins, and luminescence also appears in the study of the thermoluminescence of irradiated specimens (Fig. 2)*. Some differences are also observed in the course of the kinetic polymerization curves above and below this temperature region. We found an effect of a rather sharp decrease in the initial polymerization rate in the solid state at a small depth of the process. The stationary polymerization rate established after this proves to be 2–4 times (depending on the irradiation temperature) lower than the initial rate. In the temperature region below −165° this effect is observed at a conversion depth of 0.5%; in the region of higher temperatures, at a conversion depth of about 2%.

(Figure: Fig. 1)

Fig. 1. Temperature dependence of the initial rate V_0 of TFE polymerization under γ-irradiation. $I = 220$ rad/sec, $D = 0.2$ Mrad. The point at −138° refers to a supercooled liquid; —in the course of irradiation, partial melting and crystallization of the specimen took place.

To clarify the question of the nature of the changes occurring in crystalline TFE at a temperature of about −165°, we carried out an X-ray investigation of the phase state of the monomer at temperatures above and below this temperature region. Table 1 gives the results of X-ray photography at temperatures −196 and −155°, which—

* The thermoluminescence curve was obtained by V. A. Tochin at the Institute of Chemical Physics, Academy of Sciences of the USSR.

···indicate the absence of a structural transition in this temperature region.

The totality of the experimental data listed above leads to the conclusion that the effects observed at a temperature of about −165° are associated with the unfreezing of molecular motions in the crystal lattice of irradiated TFE, leading to a sharp increase in the interaction between particles.

Fig. 2. Temperature dependence of radical decay R (1), the postpolymerization rate V_{pp} (2), and the thermoluminescence intensity I_l (3) in TFE irradiated at low temperature.

It is seen from Fig. 2 that, at temperatures approximately 10° below the melting temperature, postpolymerization begins in the solid monomer irradiated at low temperature. In this same temperature region there is a sharp weakening of the intensity of X-ray scattering. When an attempt was made to record an X-ray diffraction pattern at $-140 \div -145°$, it was not possible to obtain even a single clearly expressed interference line. All this is apparently associated with a sharp intensification of the vibrational motions of monomer molecules in the lattice at these temperatures. From comparison of the temperature course of the radical-decay curves and the luminescence intensity it follows that the luminescent glow is not a consequence of the act of radical decay. This conclusion is consistent with the results obtained in work (2) for hydrocarbon systems.

To elucidate the mechanism of polymerization processes of various monomers in the solid state, the method of solid-phase copolymerization may be of very considerable interest. It is known that, depending on the mechanism of the process (radical, ionic), the copolymerization constants of monomers usually differ sharply.

We investigated the copolymerization of tetrafluoroethylene and trifluorochloroethylene (TFChE). In the copolymerization of these monomers at temperatures close to room temperature under the action of radical initiators (3), the composition of the copolymers at various monomer ratios is equal to the composition of the initial mixture (the copolymerization constants are equal to unity).

We carried out copolymerization of these monomers in the gas (+62°) and liquid (0°) phases under the action of γ-rays. The dependence of the copolymer composition on the composition of the initial mixture is presented in Fig. 3 (curve 1). This dependence also corresponds to copolymerization constants close to 1, i.e., to the radical mechanism of copolymerization.

Fig. 3. Dependence of the copolymer composition on the composition of the initial mixture in the system C_2F_4—C_2F_3Cl: a −gas phase (62°), $I \cong 220$

rad/sec, $D \cong 2$ Mrad, conversion 16%; b –liquid (0°), $I \cong 220$ rad/sec, $D \cong 2$ Mrad, conversion from 5 to 87%; v –solid solution (−170°); g –solid solution (−145°); $I = 130$ rad/sec, $D = 3.3$ Mrad, conversion 1-4%. Curve 2 –calculated for $r_{\text{TFE}} = 25$, $r_{\text{TFChE}} = 0.04$.

Since, for the study of copolymerization in the solid phase···

the question of the distribution of monomers in the system is decisive, the mutual solubility of TFE and TFCE in the solid state was studied. From analysis of the phase diagram we obtained, composition–melting temperature, it was concluded that TFE (m.p. = −131°) and TFCE (m.p. = −158°), in the region of TFCE concentrations up to approximately 60%, form a continuous series of single-phase solid solutions stable at temperatures of −170° and above. Copolymerization in the solid state was studied in this concentration range. At higher TFE concentrations the solid systems are not single-phase. From curve 2 of Fig. 3 it is seen that at −145 and −170°, for all the studied compositions of the initial monomer mixture (up to 50% TFCE), the copolymers are very strongly enriched in TFE. The copolymerization constants are: r_1 (TFE) = 25, r_2 (TFCE) = 0.04.

The data obtained indicate that radiation copolymerization of TFE and TFCE in the solid state proceeds by a mechanism substantially different from the radical mechanism that occurs in the gas and liquid phases at temperatures close to room temperature, i.e., probably by an ionic mechanism. This fact is an important argument in favor of an ionic mechanism of separate polymerization of TFE in the solid state.

It was established by us that pure TFCE does not polymerize under the action of radiation (dose ~ 3 Mrad) either in the solid phase (crystalline and amorphous states) or in the liquid at low temperature (−120°).

(Figure: Fig. 4. Dependence of copolymer yield in the C2F4–C2F3Cl system on the composition of the initial mixture. A–D = 3.3 Mrad, I = 130 rad/sec, samples were melted in air without inhibition of postpolymerization; B–D = 2 Mrad, I = 130 rad/sec. Samples were melted with simultaneous inhibition of postpolymerization; a–tirr = −170°; b–tirr = −140°)

Fig. 4. Dependence of copolymer yield in the system C_2F_4—C_2F_3Cl on the composition of the initial mixture. A–$D = 3.3$ Mrad, $I = 130$ rad/sec, samples were melted in air without inhibition of postpolymerization; B–$D = 2$ Mrad, $I = 130$ rad/sec. Samples were melted with simultaneous inhibition of postpolymerization; a–$t_{\text{irr}} = -170°$; b–$t_{\text{irr}} = -140°$.

From Fig. 4 it is seen that, in solid-phase copolymerization, the addition of small amounts (up to 1%) of TFCE to TFE sharply decreases the polymer yield. The established inhibition by small additions is associated with the participation of TFCE in copolymerization.

Experimental procedure. Purification of TFE, thermostating of samples at low temperatures, and irradiation have been described in (1). The polymer yield in the study of the kinetics of polymerization of TFE in the solid state was determined gravimetrically after thawing of the irradiated samples.

Table 1

Calculation of rotation powder roentgenograms for crystalline C_2F_4, taken at temperatures of −196 and −155° ($\vartheta°$—reflection angles; d—interplanar spacings)

No.	$t =$ −196°	$t =$ −155°	No.	$t =$ −196°	$t =$ −155°				
	$\vartheta°$	d, Å	$\vartheta°$	d, Å		$\vartheta°$	d, Å	$\vartheta°$	d, Å
1	10.48	4.23	–	–	6	20.15	2.23	20.13	2.23
2	12.26	3.62	12.15	3.65	7	22.25	2.03	22.10	2.04
3	14.30	3.11	14.18	3.14	8	30.00	1.54	0.300	1.52
4	16.04	2.78	16.00	2.79	9	33.50	1.39	33.30	1.40
5	17.70	2.53	17.85	2.51					

with simultaneous treatment with an inhibitor solution (a solution of triethylamine in Freon-12) under conditions that practically exclude the formation of a postpolymer. Powder rotation X-ray patterns for TFE at low temperatures in CuK_α radiation were taken in an RKB-type camera according to the procedure described in (^{4}). The samples for photography were prepared in Pyrex glass capillaries 1 mm in diameter with a wall thickness of 0.05 mm. HFP was purified analogously to TFE. The purified monomer had a melting point of −158°. The phase diagram of composition—melting temperature for the TFE—HFP system was constructed on the basis of data on the melting-temperature intervals of solid mixtures of various compositions and data on the temperature dependence of the melting kinetics of each solution within its own melting-temperature interval.

Received
2 III 1964

REFERENCES

1. M. A. Bruk, A. D. Abkin, P. M. Khomikovskii, DAN, **149**, No. 6 (1963).
2. V. G. Nikol' skii, V. A. Tochin, N. Ya. Buben, *Fiz. tverd. tela*, **5**, 8, 2248 (1963).
3. British Patent 593605, 1947; U.S. Patent 2662072, 1953.
4. G. A. Gol'der, in: *X-ray Methods of Investigation in the Chemical Industry*, 1953, p. 139.

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