Kinetics and mechanism of thermal polymerization of hexafluoropropylene under high pressures

A. A. Zharov and I. A. Guzyaeva*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. E-mail: zharov@ioc.ac.ru

The basic kinetic parameters of thermal polymerization of hexafluoropropylene, namely, general rate constants, degree of polymerization, and their temperature and pressure dependences in the range of 230—290 °C and 2—12 kbar (200—1200 MPa) were determined. The activation energy (E_{act} = 132±4 kJ mol^{-1}) and activation volume ($\Delta V_0^{\neq}$ = −27±1 cm^3 mol^{-1}) were calculated. The activation energy of thermal initiation of polymerization was estimated. The reaction scheme based on the assumption about a biradical mechanism of polymerization initiation was proposed.

Key words: hexafluoropropylene, polymerization, thermal polymerization, polyhexafluoropropylene, high pressure, thermal initiation, polymerization mechanism, activation energy, activation volume, NMR spectroscopy, IR spectroscopy, X-ray spectroscopy.

Among fluorinated compounds there is a group of monomers, which are not polymerized at all or are hardly polymerized. This group includes some perfluorinated monomers, for instance, perfluoropropylene, perfluorobutene, perfluorobutadiene, and perfluoroalkyl vinyl esters.[1,2]

The use of high pressures in a range of 2—15 kbar (200—1500 MPa) allows one to synthesize new fluorine-containing polymers.

In 1960—1970s a series of works was performed on studying the possibility of application of high pressures for the preparation of new fluorine-containing polymers, in particular, polyhexafluoropropylene. Polymerization was initiated by ionizing radiation[3,4] or by radical initiators.[5]

The synthesis of polymer from hexafluoropropylene (HFP), which is not polymerized under normal conditions, under a pressure of 4000—12 000 atm, at 100—230 °C, and with the initiation of polymerization by γ-radiation has been described.[3] Depending on the experimental conditions, the HFP polymer had the molecular weight from $3 \cdot 10^3$ to $6 \cdot 10^6$ at. units. The reaction rate was proportional to the radiation dose in the power of 0.5. The activation energy of polymerization (E_{act} = 10 kcal mol^{-1}) and the volume of the activated complex ($\Delta V^{\pm}$ = = −10 cm^3 mol^{-1}) were estimated.

Studies in this area were not further developed, probably, because of experimental difficulties. During the next years no publications devoted to the study of regularities of polymerization of fluoromonomers under high pressures appeared.

It has recently been shown[6] that under a pressure of 3—12 kbar (300—1200 MPa) and at the temperature of 240—300 °C HFP can be polymerized thermally, *i.e.*, without adding initiator to the reaction mixture.

In this work, we report on the study of the kinetic regularities and on the mechanism of thermal polymerization of hexafluoropropylene under high pressures.

Experimental

Experiments were carried out with a Barostat setup (Fig. 1), which made it possible to study chemical reactions under

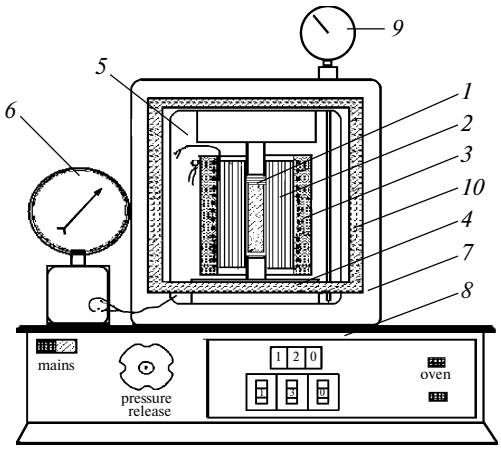

Fig. 1. Barostat setup for studying chemical reactions under high pressures: *1*, fluoroplastic tube with the reaction mixture; *2*, high-pressure unit with inserted rods; *3*, electric oven; *4*, press piston; *5*, thermocouple; *6*, reference manometer; *7*, barostat frame; *8*, electronic temperature-controlling unit; *9*, micrometer for measuring rod motion with an accuracy of ±0.01 mm; *10*, protective organic glass screen 25 mm thick.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1199—1205, June, 2010.

pressures lower than 18 kbar (1800 MPa) and temperatures below 350 °C.

The Barostat setup is a compact assembly consisting of a 40-ton press and a small pump placed inside the setup (working pressure up to 100 MPa) supplying compressed oil to the cylinder of the press.

The reaction was carried out in 1.5- or 20-cm^3 fluoroplastic tubes, which were inserted in the high-pressure unit. An electric oven was put on the high-pressure unit, and the regime of oven heating was controlled by an electronic thermoregulator, whose temperature sensor was a chromel—constantan thermocouple. The reaction volume was sealed due to the packing consisting of an antiextrusive steel ring with a triangular cross-section, a red copper disc, and a disc of Fluoroplastic-4. When the pressure increased, the condensing discs alternately deformed, providing impermeability of the reaction volume.

In setups of the cylinder—piston type (Barostat is among them), errors caused by friction in packings results in a difference between the real pressure P_{rel} inside the high-pressure unit and the pressure calculated by formula (1)

$$P_{calc} = P_{man} \cdot S_{pist}/S_{rod}, \quad (1)$$

where P_{man} and P_{calc} are the pressures in the press cylinder and high-pressure unit, respectively; S_{pist} and S_{rod} are the surface areas of the press piston and high-pressure rod, respectively. In this case, P_{rel} is lower when the rod moves inside the unit, whereas it is higher than the calculated pressure for the backward movement (pressure discharge). The regime of piston motion inside the reaction vessel was always used in the present work.

To determine the real pressure, the setup was calibrated by the phase transitions liquid—solid of toluene (P_{l-s} = 843 MPa) and acetone (P_{l-s} = 880 MPa) at 22 °C (see Ref. 7). The point of phase transition was detected by the break in the P_{man}—H curve, where H is the piston displacement.

The temperature of the reaction tube (T_{rel}) did not correspond to the temperature specified on the external heater of the high-pressure unit because of heat leakages. Corrections related to the difference in temperatures of the heating oven (T_{oven}) and the inner part of the high-pressure unit were determined by a thermocouple placed at the center of the reaction vessel. The following equations were found for the determination of the pressure and temperature inside the reactor

$$P_{rel} = 0.88P_{calc},$$

$$T_{rel} = 0.95T_{oven}.$$

The error of pressure reproduction in the reaction vessel was ±0.2 kbar at 10 kbar and ±0.1 kbar at 4 kbar. The temperature in the reactor was reproduced with an accuracy of ±1.5 °C at 200 °C and ±1 °C at 100 °C.

When calculating the polymerization rate and rate constant, a correction to the change in the concentration of the reaction mixture due to its compressibility was introduced. To determine the HFP concentrations, the published data[3] were used, which were extrapolated by the Tait equation to the temperature and pressure in experiments (Fig. 2). Each point in the curve (see Fig. 2) consists of closely lying and confluent points, which correspond to the HFP concentrations at the temperatures 240—290 °C. Since the temperature effect on the HFP concentration is insignificant, the HFP concentration was accepted to be equal to 12.9 mol L^{-1}, which corresponds to 265 °C, when processing the results of experiments performed at different temperatures and a fixed pressure of 8.8 kbar.

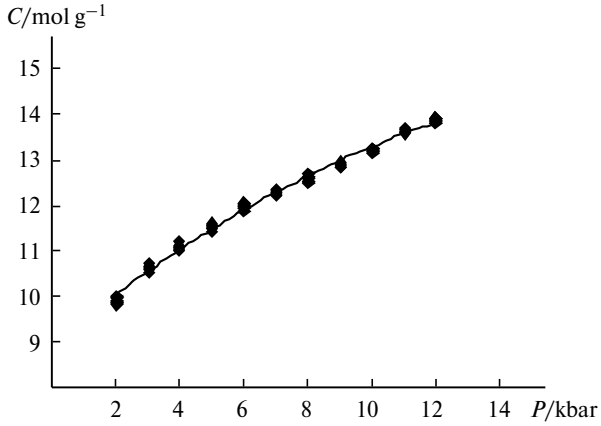

Fig. 2. Pressure dependence of the HFP concentration (C).

Hexafluoropropylene (Public Corporation Kirovo-Chepetsk Chemical Industrial Complex, sort I) and solvent FC-75 (a mixture of cyclic perfluoro esters, 3M Fluorinert) were used as received. Prior to use perfluorobenzene (P&M) was distilled on a fractionator. ^{19}F NMR spectra were recorded on a Bruker AC-200 instrument (190 MHz) in a perfluorobenzene solution, and chemical shifts were determined relative to $CFCl_3$ (external standard).

IR spectra were obtained on a Bruker IFS 113v instrument. The polymer film was obtained by evaporating solution of the HFP polymer in FC-75 solvent on a KBr crystal window. The volatile parts of reaction mixtures were analyzed by gas-liquid chromatography (GLC) on a Khrom-4 chromatograph (column with SE-30 phase, column length 3 m) and on a VG 7070E chromatograph coupled with a mass spectrometer (capillary column with SE-30 phase, column length 25 m).

Experiments were carried out under pressures of 2—12 kbar and at temperatures of 230—300 °C. Hexafluoropropylene was fed from a steel cylinder to the vacuum setup and degassed by multiple freezing and evacuation, after which HFP was overflowed to the calibrated glass cylinder, from which necessary amounts were frozen into glass tubes. The monomer dosage was controlled by a vacuum meter (accuracy class 0.35).

The monomer from the glass tube was fed under argon to the Fluoroplastic-4 reactor placed in the high-pressure unit and cooled to −60 °C. The unit with the inserted pistons, packings, and put-on oven was mounted in the Barostat setup (see Fig. 1). The rods were pressed in the unit under the action of the press of the Barostat setup, thus creating the required pressure in the reaction volume.

The duration of experiments was varied from 1 to 24 h. The reaction kinetics was monitored by measuring the displacement of the piston with an accuracy of 0.01 mm, which correlated with the polymerization depth of HFP.

Then unit was cooled down, and the reaction mixture was unloaded from the unit and placed in the vacuum setup. During evacuation, the volatile fraction of the reaction mixture was trapped, and the polymer was kept at 100 °C in a vacuum of 10^{-3}—10^{-4} Torr until attaining a constant weight. The polymer obtained and volatile products were analyzed by

GLC, ^{19}F NMR spectroscopy, IR spectroscopy, and X-ray photoelectron spectroscopy.

The intrinsic viscosity of the polymer obtained was measured at 30 °C in an FC-75 solution using the Ubellohde viscosimeter. The molecular weight of the polymers was calculated from the intrinsic viscosities[3] by the following formula:

$$[\eta] = 3.8 \cdot 10^{-4}(150DP_v)^{0.55}, \quad (2)$$

where [η] is the intrinsic viscosity, and DP_v is the mean-viscosity degree of polymerization.

The polymer obtained thermally at 7 kbar and 265 °C was used for spectral studies. The polymer was reprecipitated with carbon tetrachloride from a solution in perfluorobenzene.

The ^{19}F NMR spectrum of polyhexafluoropropylene (PHFP) exhibits signals at δ −73, −102, and −179, which were assigned to the fluorine atoms of CF_3, CF_2, and CF groups, respectively. The peak areas in these regions are in the ratio of 3 : 2 : 1, which corresponds to the formula of monomer unit [—CF_2—CF(CF_3)—]. The shoulder observed in the δ_F region from −105 to −110 ppm can be ascribed to the signal of the fluorine atoms of the CF_2 group in the —CF(CF_3)—C$\underline{F}_2$—C$\underline{F}_2$—CF(CF_3)— fragment[8] suggesting that the monomer adds to the polymer radical according to the "head-to-head"—"tail-to-tail" type.

The IR spectrum of PHFP exhibits the absorption band at 1200—1350 cm^{-1} (maximum at 1241 cm^{-1}), which can be attributed to stretching vibrations of the CF_2 and CF_3 groups, and the band at 1000—1100 cm^{-1} can be assigned to vibrations of the CF group. In addition, there are bands at 983, 932, 912, 864, 743, 732, 710, 691, and 537 cm^{-1} in the IR spectrum.

A weak band at 1780 cm^{-1} characteristic of the CF_2=CF group was observed in the spectrum of the polymer synthesized at 2 kbar and 290 °C. This band decreases with increasing pressure and finally disappears.

The spectra of PHFP have no bands in the UV, visible, and IR regions, *i.e.*, this polymer is transparent for the light with the wavelengths 200—2000 nm.

The X-ray spectrum of PHFP exhibits three highly diffuse peaks indicating the presence of small ordered regions. The size of these regions does not exceed the level of the lower limit of coherent X-ray scattering, *i.e.*, it is within tens of angström. Thus, the X-ray diffraction data indicate that the structure of PHFP is amorphous for X-rays.

It is worthy to note some characteristic features of the polymer obtained. The PHFP plate is transparent and resembles a poly(methyl methacrylate) film. However, unlike the latter, PHFP is transparent in a broader spectral range (200—2000 nm). Polyhexafluoropropylene is insoluble in ketones and halide-containing and aromatic solvents. It is soluble in some perfluorinated solvents, for example, perfluorotoluene, perfluoromethylcyclohexane, and perfluorodecalin. The refractive index of PHFP is n_D^{20} = 1.3334, and its glass transition temperature is T_g = 162 °C. Since the polymer molecule of HFP contains many CF_3 groups, the HFP polymer possesses pronounced antiadhesive properties (the wetting angle with water is 117°), but it is not wetted with mineral oils and even with petroleum. In its chemical stability and electric properties, the polymer is analogous to Fluoroplastic-4, being inferior to it only in thermal stability (the operating temperature of PHFP is 160—170 °C).

The kinetic studies of the thermal polymerization of HFP were carried out under the pressure from 3 to 12 kbar at 230—290 °C. Some selected results are presented in Table 1. It is seen from the tabulated data that the yields of PHFP can reach 90%, and the intrinsic viscosity values are as high as 1.5 dl g^{-1}.

Table 1. Yields and intrinsic viscosities [η] of polyhexafluoropropylene obtained at different temperatures and pressures

T/°C	*P*/kbar	*t*/h	Yield (%)	[η]/dl g^{-1}
266	3.52	14.5	73.5	0.35
266	4.84	9.5	78.0	0.50
266	5.28	10.7	87.0	0.57
266	6.16	6.9	82.0	0.72
266	7.92	9.3	89.0	0.83
266	8.80	6.7	87.0	1.08
266	10.56	6.4	86.0	1.51
237.5	8.80	24.0	61.1	1.26
247	8.80	12.8	89.7	1.30
256	8.80	8.8	91.0	1.19
266	8.80	6.6	88.6	1.00
275.5	8.80	5.0	90.0	1.00

It was found that the formation of the cyclic dimer of HFP occurred along with polymerization. The dimer was isolated from the volatile fraction by chromatography and identified by ^{19}F NMR and IR spectroscopies. The amount of the dimer formed usually did not exceed 3% of the polymer weight and was ignored in the calculations of the kinetic parameters.

Examples of the kinetic curves of thermal polymerization of HFP are shown in Fig. 3.

The reaction order is temperature-dependent: at ~235 °C it is close to zero (Fig. 3, *a*, curve *1*), at ~265 °C it is close to the first order (Fig. 3, *a*, curve *2*), and at ~290 °C it is close to the second order (Fig. 3, *a*, curve *3*).

One of the main parameters that characterize the kinetic regularities of thermal polymerization is the initial polymerization rate (W_0), which is determined as a slope of the tangent to the kinetic curve at the zero time. Since the graphical method for W_0 determination is subjective, the W_0 value was determined from the value of the second-power polynomial derivative describing experimental data by the least-squares method (Exel software).

The pressure effect on the polymerization rate and mean-viscosity molecular weight of PHFP are shown in Figs 4 and 5. The mean-viscosity molecular weight was calculated from the intrinsic viscosity values [η] using Eq. (2).

The data of Fig. 4 show that the polymerization rate increases by 1.6—1.7 times with the pressure increase by 1 kbar.

The temperature dependences of the polymerization rate and intrinsic viscosity of PHFP are shown in Figs 6 and 7. Using the data of Fig. 6, one can estimate the temperature coefficient of the polymerization rate: the polymerization rate increases twofold with the temperature rise of every 10 °C.

The decrease in the intrinsic viscosity ([η]) with increasing temperature indicates the decrease in the molecular weight of the polymer (see Fig. 7).

To determine the order of the polymerization reaction with respect to the monomer, we performed experiments on measuring the dependence of the initial polymerization rate *vs* initial

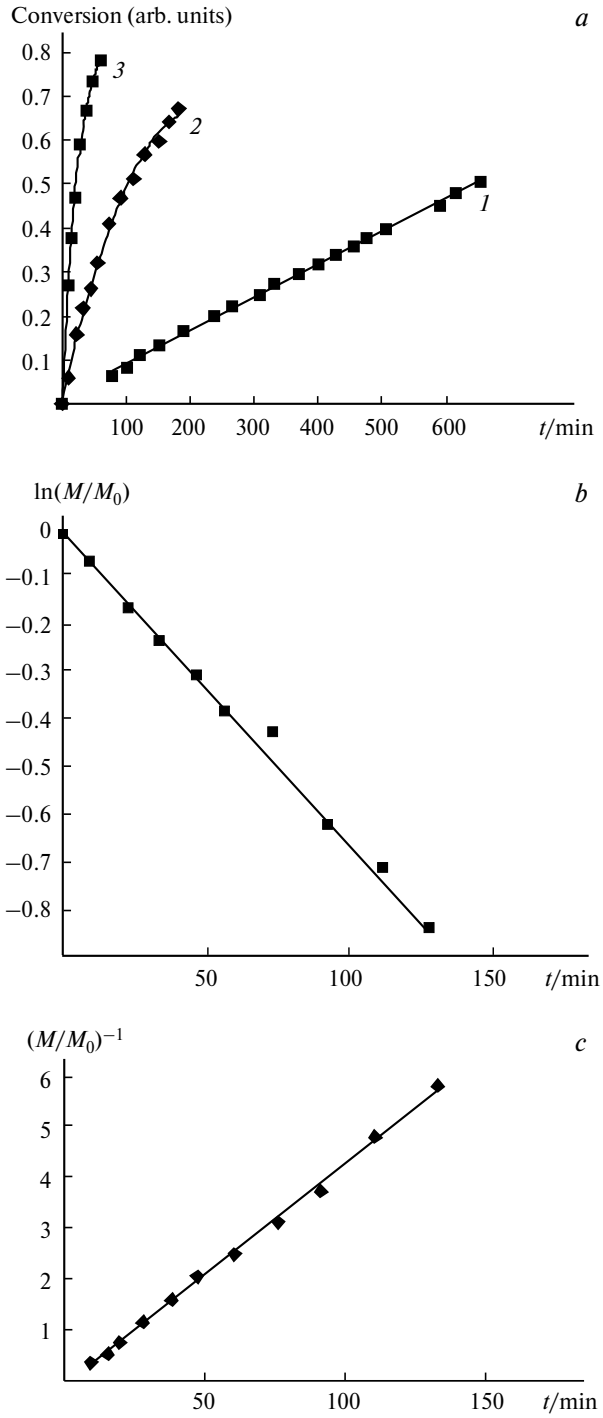

Fig. 3. Kinetic curves (*a*) under a pressure of 8.8 kbar at 235 (*1*), 265 (*2*), and 290 °C (*3*); linear tranformations of curves *2* (*b*) and *3* (*c*).

concentration of the monomer. The reaction order was determined by the equation

$$\ln W_0 = \ln k + n \ln M_0,$$

where M_0 is the initial concentration of the monomer, k is the rate constant of polymerization, and n is the reaction order with respect to the monomer (Fig. 8). The reaction order with respect to the monomer is 2.

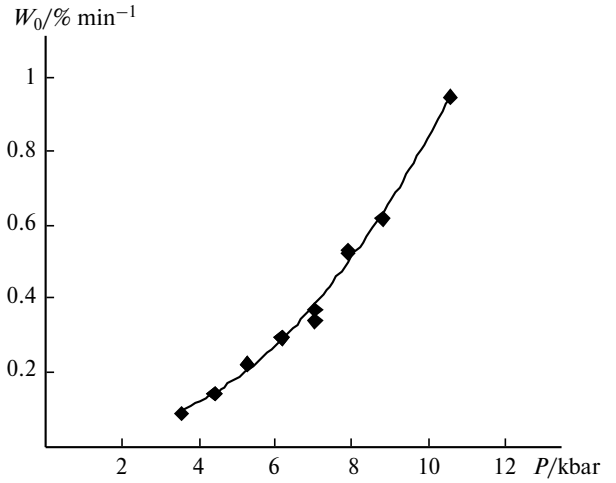

Fig. 4. Pressure dependence of the initial polymerization rate (W_0) at 265 °C.

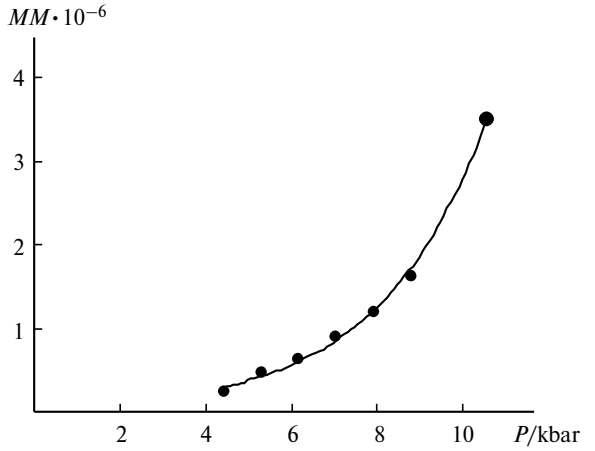

Fig. 5. Pressure dependence of the mean-viscosity molecular weight of PHFP (*MM*) at 265 °C.

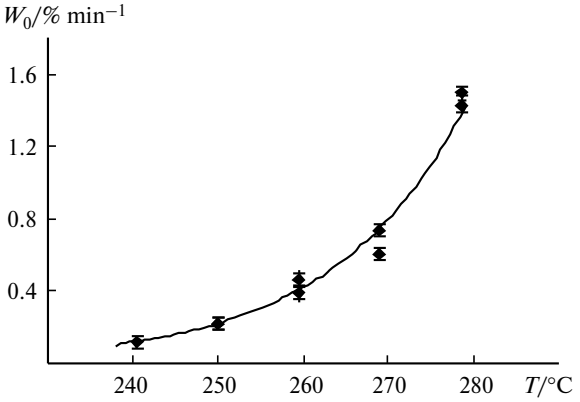

Fig. 6. Temperature dependence of the initial polymerization rate (W_0) under a pressure of 8.8 kbar.

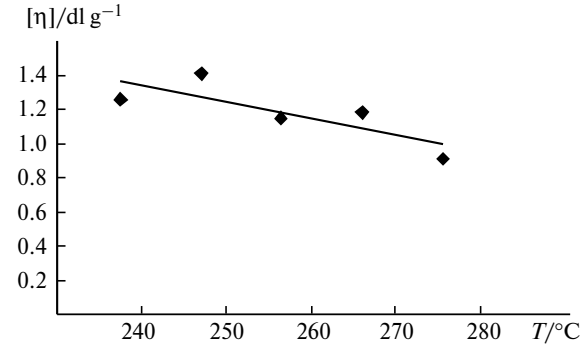

Fig. 7. Dependence of the intrinsic viscosity ([η]) of PHFP on the temperature of the polymerization reaction (P = 8.8 kbar).

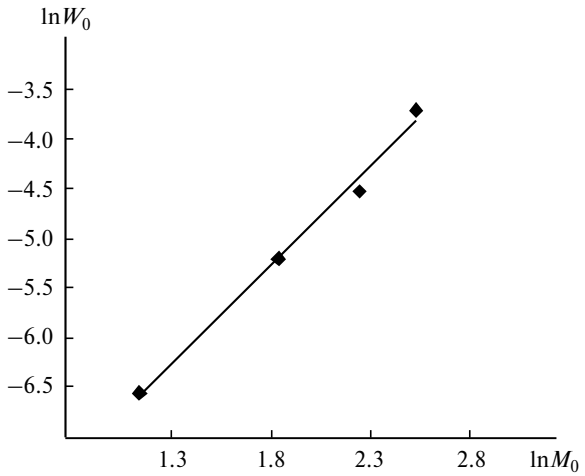

Fig. 8. Dependence of the initial polymerization rate (W_0) on the initial concentration of the monomer (M_0) under a pressure of 6.2 kbar at 266 °C.

Results and Discussion

According to the literature data,[3] the γ-ray initiated polymerization of HFP under high pressures occurs by a radical mechanism. Based on the results on the initiation of polymerization by radical initiators, other authors[5,9] also proved the radical mechanism. In addition, it was found that the ^{19}F NMR spectra of the polymers obtained in Ref. 9 and those synthesized by thermal polymerization were almost identical evidencing the similarity of the mechanisms of polymer chain formation.

Thus, it can be concluded that the thermal polymerization of HFP also proceeds by the radical polymerization mechanism.

As mentioned above, the appearance of the kinetic curves changes with temperature. This can be related to the gel-effect phenomenon: the chain termination reaction is controlled by the diffusion of polymer radicals and depends on the viscosity of the medium. At low temperatures diffusion control starts already at small depths of conversion and manifests itself as a linear dependence of the polymer yield on time (zero order). The viscosity of the reaction medium decreases with temperature, diffusional control of the polymer chain termination takes place at greater depths of conversion, and the kinetic curves begin to obey equations close to the first-order law and then to the second-order law.

The data in Fig. 8 indicate that at the initial stages polymerization is described by the equation

$$W_0 = kM_0^2, \qquad (3)$$

where M_0 is the initial concentration of the monomer, and k is the general rate constant of polymerization.

The results obtained allow one to assume that the initiators of thermal polymerization of HFP are biradicals formed upon the interaction of two HFP molecules. Arguments in favor of the biradical mechanism of initiation of thermal polymerization of HFP are the dependence of W_0 on the squared concentration of the monomer and the parallel reaction of cyclic dimer formation, which follows the mechanism of [2+2] addition and proceeds *via* the stage of dimeric biradical formation.[10]

The thermal polymerization of HFP can be presented by the following sequence of reactions (Scheme 1).

Scheme 1

Initiation

$$M + M \xrightarrow{k_i} {}^{\bullet}R_1{}^{\bullet},$$

dimerization

$${}^{\bullet}R_1{}^{\bullet} \xrightarrow{k_d} D,$$

chain propagation

$${}^{\bullet}R_1{}^{\bullet} + nM \xrightarrow{k_p} {}^{\bullet}R_{n+1}{}^{\bullet},$$

$$R_n{}^{\bullet} + mM \xrightarrow{k_p} R_{m+n}{}^{\bullet},$$

transfer to monomer

$${}^{\bullet}R^{\bullet} + M \xrightarrow{k_{tr}} R^{\bullet} + R_1{}^{\bullet},$$

tranfer to impurity

$${}^{\bullet}R^{\bullet} + X \xrightarrow{k_{xtr}} R^{\bullet} + X^{\bullet},$$

kinetic chain termination by recombination

$${}^{\bullet}R_p{}^{\bullet} + {}^{\bullet}R_q{}^{\bullet} \xrightarrow{k_{t_1}} {}^{\bullet}R_{p+q}{}^{\bullet},$$

chain termination by recombination

$$R_p{}^{\bullet} + R_q{}^{\bullet} \xrightarrow{k_{t_1}} P_{p+q},$$

kinetic chain termination by disproportionation

$${}^{\bullet}R_p{}^{\bullet} + {}^{\bullet}R_q{}^{\bullet} \xrightarrow{k_{t_2}} {}^{\bullet}R_p + R_q{}^{\bullet},$$

chain termination by disproportionation

$$R_p{}^{\bullet} + R_q{}^{\bullet} \xrightarrow{k_{t_2}} R_p + R_q$$

For the thermal polymerization of HFP, solutions of the corresponding differential equations, using the stationarity principle with allowance for Eq. (3) and assuming that the biradicals are transformed into monoradicals already at the initial stage due to the transfer to the monomer or impurities, result in Eq. (4)

$$W = -(\mathrm{d}M/\mathrm{d}t) = k_p[k_i/k_t]^{1/2}M^2, \quad (4)$$

where M is the monomer concentration; k_i, k_p, and k_t are the rate constants for initiation, propagation, and termination of polymer chains, respectively.

It is known that this equation is often used for the description of the kinetics of thermal polymerization of monomers with the double bond.[11]

The pressure effect on the general rate constant of polymerization k is shown in Fig. 9.

To compare the pressure effects on chemical reaction rates and to evaluate the structure of the activated reaction complex, the activation volume of the reaction $\Delta V^{\neq} = V_{act} - V_r$ is usually used, where V_r and V_{act} are the volumes of reactants in the initial and activated states at $P = 0$, respectively.

The activation volume ($\Delta V^{\neq}$) is calculated by the equation

$$\mathrm{d}\ln k/\mathrm{d}P = -\Delta V^{\neq}/RT, \quad (5)$$

where k is the reaction rate constant, P is pressure, T is the absolute temperature, and R is the gas constant.

Since the $\Delta V^{\neq}$ value is pressure-dependent, the plot $\ln k$—P should be extrapolated to zero pressure in order to find the $\Delta V^{\neq}$ value. For this purpose, various empirical formulas[12] are usually used, and the calculated $\Delta V^{\neq}$ value depends on the equation used for experimental data processing.

To estimate the $\Delta V^{\neq}$ value, we chose Eq. (6) (see Ref. 13), which, as it was shown by the processing of the data on methyl methacrylate polymerization under high pressures,[14] describes well the pressure effect on the polymerization rate, if one accepts that β equals 0.065 kbar^{-1}

$$\ln[k_p/k_0] = (-\Delta V^{\neq}P)/RT(1 + \beta P), \quad (6)$$

where k_p and k_0 the general polymerization rate constants under high and low (usually atmospheric) pressures, respectively.

From the slope of the straight line in Fig. 10, which, according to formula (6) is equal to $-\Delta V_0^{\neq}/RT$, we find that the activation volume $\Delta V_0^{\neq}$ is -27.4 ± 1 cm^3 mol^{-1}.

The derivative of Eq. (6) $\mathrm{d}(\ln k)/\mathrm{d}P = \Delta V_0^{\neq}/RT(1 + \beta P)^2$ makes it possible to calculate the $\Delta V^{\neq}$ value under different pressures using Eq. (5) (Fig. 9, *b*). It is seen that the decrease in $\Delta V^{\neq}$ with increasing pressure occurs in the same manner as the change in compressibility of the monomer, which can be deduced from the data presented in Fig. 3.

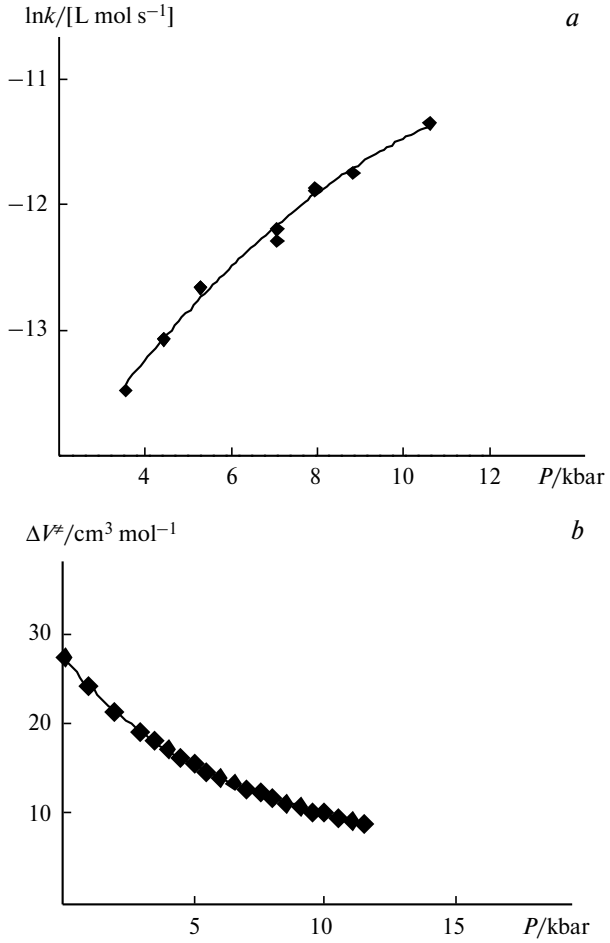

Fig. 9. Pressure dependences of the logarithm of the general rate constant of HFP thermal polymerization ($\ln k$) (*a*) and the activation polymerization volume ($\Delta V^{\neq}$) (*b*) at 559 K.

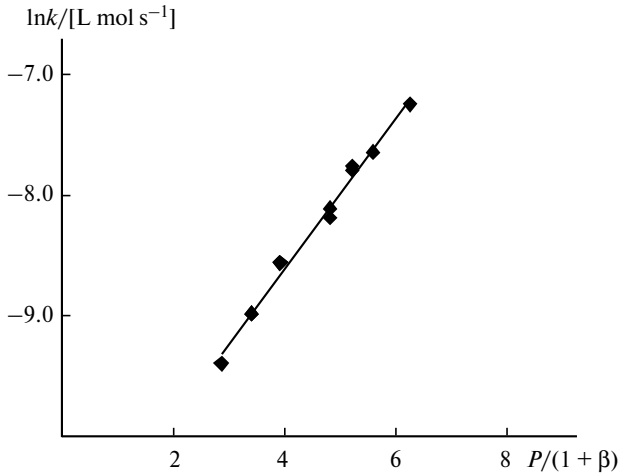

Fig. 10. Dependence of the logarithm of the general polymerization constant of HFP ($\ln k$) on $P/(1 + \beta P)$ ($\beta = 0.065$ kbar^{-1}) at 539 K.

The temperature dependence of the logarithm of the HFP polymerization rate constant is presented in Fig. 11 in the form of the Arrhenius equation

$$\ln k = \ln A - (E_{act}/RT).$$

According to the data in Fig. 11, the activation energy and pre-exponential factor were calculated for a pressure of 8.8 kbar: $E_{act} = 132.3 \pm 4$ kJ mol^{-1} (31 600±1000 cal mol^{-1}), $\ln A = 17.88$. Thus, the general polymerization rate constant is $k = 5.8 \cdot 10^7 \exp(-132/RT)$ L (mol s)$^{-1}$. Taking into account the published results[3] (Fig. 12), we can estimate the activation energy of thermal initiation. After taking the logarithm and differentiation of Eq. (4), we obtain

$$d\ln W/dT = d\ln k_p/dT + 0.5(d\ln k_i/dT) - 0.5(d\ln k_t/dT)$$

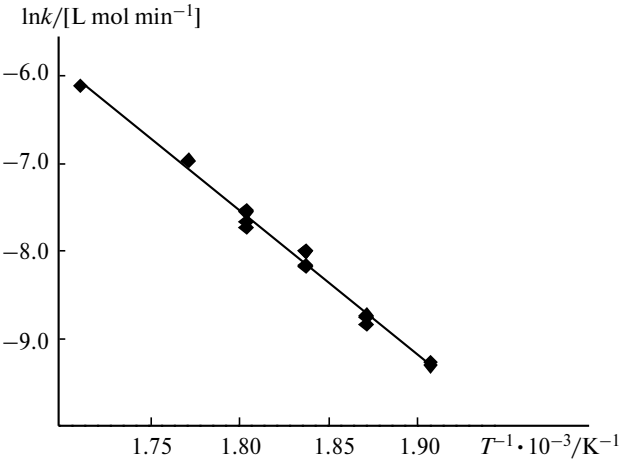

Fig. 11. Plot of the logarithm of the HFP polymerization rate constant (ln*k*) *vs* inverse temperature under a pressure of 8.8 kbar (880 MPa).

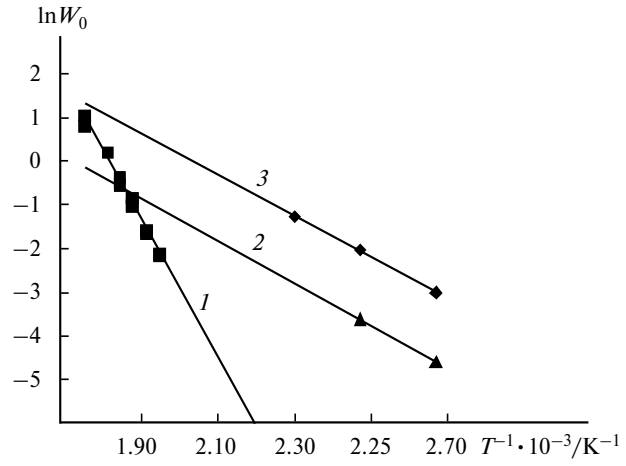

Fig. 12. Plots of the HFP polymerization rate *vs* inverse temperature: *1*, thermal polymerization under 8.8 kbar (880 MPa), E_{act} = 31.6 kcal mol^{-1}; *2* and *3*, polymerization initiated by γ-radiation, under 10 kbar, E_{act} = 9.6 kcal mol^{-1} (*2*) and 15 kbar, E_{act} = 9.3 kcal mol^{-1} (*3*). Lines *2* and *3* were plotted according to the literature data.[3]

and

$$E_W = E_p + 0.5E_i - 0.5E_t.$$

Since $0.5E_i = E_W - (E_p - 0.5E_t) = 31.6 - 9.6 = 22$ kcal mol^{-1}, the activation energy of thermal initiation is E_i = 184 kJ mol^{-1} (44 kcal mol^{-1}).

The above values of the activation energy of HFP thermal polymerization, pre-exponential factor, and activation volume are characteristic of the thermal polymerization of compounds with a double bond.[15,16] The calculated activation energy of thermal initiation is high and goes beyond the typical values.

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Received October 16, 2009;
in revised form February 2, 2010