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Abstract

Full Text

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Radiation Polymerization of Hexamethylcyclotrisiloxane in the Solid Phase

In our works ([1–3]) we investigated the kinetic regularities of the polymerization of certain vinyl compounds in the solid phase under the action of accelerated electrons. Subsequently we turned to the solid-phase polymerization of cyclic monomers, choosing as the first example hexamethylcyclotrisiloxane (HMCTS).

Fig. 1. Kinetic curves of HMCTS polymerization at various temperatures (in °C). In the liquid phase: a +66, b +82. In the solid phase: v +55, g +35, d +0, e −50, zh −90, z −120, and i −196 (all curves $I = 2$ Mrad/min)

The solid-phase polymerization of HMCTS had been reported earlier ([4,5]); however, no detailed kinetic analysis of it had been made.

Experimental procedure. HMCTS was obtained by pyrolysis of dimethylsiloxane rubber. The product obtained was distilled twice, collecting fractions with b.p. 135–140° and m.p. 64°. HMCTS pellets 15 mm in diameter and 1.5 mm high were irradiated in air with an electron beam of energy 1.6 MeV. The procedure for irradiation, thermostating, and dosimetry was described earlier ([1–3]). The polymer yield was determined gravimetrically. The viscosity of the polymers obtained was measured in benzene solution at 25°, and the molecular weights were calculated by the formula ([5]):

$$\overline{M}_w = [\eta] \cdot 1.17 \cdot 10^4.$$

The procedure for calorimetric measurements had also been described earlier ([1–3]); however, for HMCTS a more sensitive calorimeter was used, which made it possible to determine thermal effects with an accuracy of up to 0.1 cal/g.

Fig. 2. Temperature dependence of the initial polymerization rate in the liquid phase of HMCTS at $I = 2$ Mrad/min. a—large crystal, b—small crystal

Figure 2: Fig. 2. Temperature dependence of the initial polymerization rate in the liquid phase of HMCTS at $I = 2$ Mrad/min. a—large crystal, b—small crystal

Experimental Results

Thermographic analysis of HMCTS showed that in the temperature range from $-196°$ to $+64°$ there is a phase transition at approximately $-10°$. As can be seen from Fig. 1, the kinetics of polymerization in the solid phase above and below the phase transition differ substantially. The influence of defectiveness and crystal size on the rate of HMCTS polymerization was studied. Large HMCTS crystals were obtained by holding the monomer for a period of

2–3 days at a temperature of 55°. Fine-crystalline and highly defective HMCTS was obtained by pouring the melt into liquid nitrogen.

In the temperature region from -196 to $-10°$, independently of the size of the monomer crystals, the initial rate w_0 is constant over the entire temperature interval, and the polymer yield rapidly reaches a limiting value, moreover at small degrees of conversion (not more than 5%). The magnitude of the limiting yield decreases with increasing temperature (see Fig. 1). The initial rate w_0 is proportional to the dose rate to the power 1.2 (measured at $-196°$). The molecular weights of the polymers obtained in this region do not exceed 1000–3000 (measured cryoscopically). In the temperature region from 0° up to the melting temperature, the degree of crystallinity of the monomer has a large influence on the polymerization kinetics. In fine-crystalline HMCTS, polymerization proceeds at a lower rate than in large crystals, and its rate depends more weakly on temperature. The polymer yield in this region increases proportionally to the dose (see Fig. 1) up to high degrees of conversion, and the polymerization rate increases with temperature. The polymers obtained in this temperature region are only partially soluble. The initial rate of polymerization of HMCTS in this region (measured at $+30°$) is also proportional to the irradiation intensity to the power 1.2. The temperature dependence of the initial rate of polymerization of HMCTS is presented in Fig. 2.

Fig. 2. Temperature dependence of the initial polymerization rate in the liquid phase of HMCTS at $I = 2$ Mrad/min. a—large crystal, b—small crystal

The temperature dependence is absent in the interval from -196 to 0°: $E_{\text{act}} = 0$, while in the interval from 0° to the melting point, $E_{\text{act}} = 8.5$ kcal/mol for a large crystal and 3.9 kcal/mol for a highly defective crystal. It should be noted that the temperature dependence of the initial rate of polymerization of HMCTS in different crystalline modifications was obtained by us for the first time. The IR spectra of the polymers obtained in different temperature regions are completely identical.

We were unable to observe post-polymerization of HMCTS even at temperatures close to melting (+55°). This conclusion is also confirmed by calorimetric measurements during thawing of irradiated HMCTS. Nor was it possible to observe anomalous accelerations of polymerization at the phase-transition point or upon melting of the irradiated monomer.

Discussion of the results. For the solid-phase polymerization of HMCTS, apparently, two types of processes are characteristic, realized in two different crystalline modifications. In the low-temperature region ($-196 \div 0°$), a fast activationless reaction takes place, which is not affected by the size or defectiveness of the HMCTS crystals. It is possible that the low-temperature modification of HMCTS has a structure similar to that of the polymer chain, i.e., it contains "templates" along which polymerization proceeds at a high rate by the mechanism of energy chains, i.e., without activation. Since the molecular weights of the polymers obtained in this region are small (degree of polymerization 5-15), and, consequently, the "templates" have a small extent, the defectiveness of the crystal has little effect on this process. A very

An interesting result is also the "limiting" of the polymer yield in the low-temperature region. This phenomenon is apparently quite common for solid-phase polymerization ([1,2,6]). However, unlike acrylonitrile ([2]), in the case of HMCTS the value of the limiting yield decreases with increasing temperature. We are now carrying out a more detailed study of this interesting phenomenon, to which a separate communication will be devoted.

In the temperature range from $-10°$ up to the melting point, polymerization proceeds in a crystal lattice of another type. The polymer yield increases proportionally to the dose up to high degrees of conversion; the polymerization rate increases with increasing temperature, and markedly faster for more perfect crystals. In ([7]) we analyzed the main kinetic regularities of polymerization of monomers in the solid phase. The mechanism proposed there, with certain modifications, is also suitable for describing the solid-phase polymerization of HMCTS in this temperature range. The scheme assumes initiation not in the primary, but in the secondary act, with possible destruction of the intermediate product

$$\mathrm{M} \rightsquigarrow A_{k_1} \xrightarrow{k} R \xrightarrow[k_p]{+M} \text{chain growth.}$$

$$\downarrow$$

destruction

Such a scheme quite realistically represents the process that may take place during radiolysis. The particle A, formed as a result of the primary act, may either, after overcoming certain steric hindrances, initiate polymerization, or be destroyed in some other process (for example, by transferring its energy to

another particle). Chain growth continues up to a defect in the crystal lattice, where polymerization ceases. Irradiation creates an additional probability of termination at defects formed by the radiation. On the basis of the proposed scheme, the process of radiation polymerization of HMCTS can be described by the following system of equations:

$$\frac{dA}{dt} = gI - (k\ + k_1)A,$$

$$\frac{dR}{dt} = k\,A - k_p(\alpha_0 + gIt)R,$$

$$w = \frac{d\Pi}{dt} = k_{pR},$$

where g is the radiation-chemical yield of A, k_1 is the constant of monomolecular destruction of A, I is the irradiation intensity, k is the initiation constant, k_p is the constant of chain growth and also of destruction of R, α_0 is the probability of encountering a defect in an unirradiated crystal, and g is the probability of radiation formation of a defect per unit dose.

For the stationary case, the concentration of active centers is characterized by the expression:

$$R = \frac{k}{k\ + k_1}\,gI\,\frac{1}{k_p(\alpha_0 + gIt)}. \tag{1}$$

Hence,

$$w_0 = \frac{k}{k_1 + k}\,\frac{gI}{\alpha_0}. \tag{2}$$

It is of interest to compare the pre-exponential factors z of the polymerization rate constants of HMCTS in different structural modifications. The pre-exponential factors calculated from kinetic data at $I = 2$ Mrad/min are, respectively: for the low-temperature crystalline modification, $z_1 = 4 \cdot 10^{-3}$ sec^{-1}; for finely crystalline HMCTS in the high-temperature region (from -10 to

i.e., $z_2 = 1.2$ sec^{-1}, and for coarse-crystalline HMCTS in the same region $z_3 = 5 \cdot 10^3$ sec^{-1}. Such a sharp decrease (by a factor of 10^6) in the pre-exponential factor on going from the high-temperature to the low-temperature crystalline modification is apparently associated with a change in the mutual orientation of the monomer units in the specimen.

As follows from equation (2), within one crystalline modification the magnitude of the pre-exponential factor of the polymerization-rate constant should decrease

with increasing defectiveness of the structure (with increasing a_0). However, the decrease by a factor of $4 \cdot 10^3$ in the pre-exponential factor on going from coarse-crystalline to fine-crystalline HMCTS (the molecular weights of the polymer here fall by only a factor of 2–3) cannot be associated with changes in the structure of the specimen.

In addition, in the high-temperature region phenomena of the compensation-effect type ([8,9]) are observed: the decrease in the activation energy of polymerization in fine-crystalline HMCTS (in comparison with coarse-crystalline HMCTS) is compensated by a decrease in the pre-exponential factor, so that the polymerization rates at $+5^\circ$ become equal in both forms. The decrease in the activation energy and the pre-exponential factor in fine-crystalline HMCTS may be caused by the fact that, in preparing this modification (pouring an HMCTS solution into liquid nitrogen), partial stabilization of the low-temperature crystalline form is possible. Thus, fine-crystalline HMCTS is a highly defective high-temperature crystalline form with a small admixture ($\sim 10^{-5}\%$) of the low-temperature crystalline modification, the transition of which into the high-temperature modification is kinetically hindered. Since for the low-temperature modification the magnitude of the pre-exponential factor is very low, while the activation energy is altogether absent, the decrease in the pre-exponential factor and in the activation energy in fine-crystalline HMCTS in comparison with coarse-crystalline HMCTS becomes understandable.

The available experimental data are still insufficient to make a definite judgment about the nature of the active centers that cause the polymerization of HMCTS. We note only that the conclusion about the ionic nature of solid-phase polymerization of HMCTS ([4,5]), drawn on the basis of the fact that this monomer in the liquid phase polymerizes only by an ionic mechanism, seems to us insufficiently reliable. Determining the nature of the active centers is very important, since independent observation of the kinetics of formation of these centers during irradiation would make it possible to establish whether the activation energy of 8.5 kcal/mol is inherent in the initiation process or whether it also includes the activation energy of chain growth.

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