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Abstract

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THE EFFECT OF PRESSURE ON THE RATE CONSTANTS OF SOME CHAIN-TRANSFER REACTIONS IN THE RADICAL POLYMERIZATION OF STYRENE

(Presented by Academician B. A. Kazanskii, January 18, 1965)

The study of the polymerization of various monomers at high pressures makes it possible to obtain important information about the mechanism of the course of this entire process, as well as of its individual stages. Recently, in particular, several works have been published devoted to investigation of the effect of pressure on the ratio of the rate constants of chain transfer and chain growth. Walling and Pellon (^{1}) investigated the polymerization of styrene in the presence of CCl_4 and established that the rate constant of chain transfer through CCl_4 increases with increasing pressure approximately in the same way as does the rate constant of chain growth. The same authors (^{2}) found that the ratio of the rate constants of transfer and chain growth in the polymerization of allyl acetate changes little with increasing pressure. An analogous conclusion was also drawn in work (^{3}) in the study of the polymerization of vinyl acetate and its telomerization with CCl_4. However, during the performance of the present investigation, Tsuki and Uil (^{4}) published data on a significant decrease in the ratio of the rate constants of chain transfer and chain growth with increasing pressure during the polymerization of styrene in the presence of triethylamine.

On the basis of general considerations, one could expect that, in the processes of polymerization of vinyl monomers, the ratio of the rate constants of transfer and chain growth with increasing pressure may change in different ways, depending chiefly on the mechanism and structure of the transition state in the chain-transfer reaction. This assumption was based on the fact that chain-growth processes are reactions of one type—addition of a polymer radical to the double bond of the monomer—whereas the mechanisms of chain-transfer reactions may differ substantially. In order to test the above assumption, we investigated the radical polymerization of styrene, initiated by azoisobutyronitrile (AIBN), in the presence of butyraldehyde and isobutyraldehyde, as well as CCl_4 (as chain-transfer agents), at pressures up to 4000 kg/cm^2. In the present case, the quantity reciprocal to the average degree of polymerization ($1/\bar{P}_n$) can be expressed as follows (neglecting chain transfer through the initiator and monomer):

$$\frac{1}{\bar{P}_n} = \frac{(1+\lambda)W_{\text{in}}^{1/2}(k_o + k_o')^{1/2}}{2k_p[\mathrm{M}]} + \frac{k_{\mathrm{p}}}{k_p}\frac{[\mathrm{S}]}{[\mathrm{M}]} + \frac{k_{\mathrm{p}}'}{k_p}\frac{[\mathrm{S}']}{[\mathrm{M}]}. \qquad (1)$$

Here $k_p, k_o, k_o', k_{\mathrm{p}}$, and k_{p}' are, respectively, the rate constants of chain growth, termination by recombination of radicals, termination by disproportionation of radicals, chain transfer through butyraldehyde or isobutyraldehyde, and chain transfer through CCl_4; λ is the fraction of radicals terminating the chain by disproportionation; [S], [S′], and [M] are the molar concentrations of aldehyde, CCl_4, and styrene; W_{in} is the initiation rate.

If the first term on the right-hand side of equation (1) depends little on the ratio [S]/[M] or is small in comparison with the second term,

and $[S'] = 0$, then, plotting $1/\overline{P}_n$ against $[S]/[M]$, we obtain a straight line whose slope is equal to $k_{\mathrm{p}} : k_{\mathrm{p}}$. For $[S'] \neq 0$ and a constant ratio $[S]/[M]$, the slope of the straight-line dependence of $1/\overline{P}_n$ on $[S']/[M]$ gives the value $k_{\mathrm{p}}' : k_{\mathrm{p}}$.

The polymerization reaction was carried out in a solution of parabutyraldehyde, chain transfer through which is negligibly small in comparison with chain transfer through the aldehydes used and CCl_4. In order to keep the concentrations of styrene and AIBN constant, when the chain-transfer agent was added, part of the solvent was replaced by an equal volume of the added substance.

Experimental Part

Purification of the starting substances. Styrene was washed several times with 5% KOH and then with water to neutral reaction, dried over $CaCl_2$, and distilled in vacuum in a stream of nitrogen purified from oxygen and moisture. The middle fraction of styrene was stored in a refrigerator and, before the experiment, was again distilled under the same conditions. Butyraldehyde was distilled on a column in a nitrogen atmosphere; the fraction with b.p. 74.6°/760 mm, n_D^{20} 1.3794 (lit. (^{5}): b.p. 74.8°/760 mm, n_D^{20} 1.3792) was collected. Isobutyraldehyde was purified in an analogous manner: b.p. 64.4°/756 mm, n_D^{20} 1.3730. Butyraldehyde and isobutyraldehyde were used freshly distilled on a column in a nitrogen atmosphere. Parabutyraldehyde was obtained from butyraldehyde (^{6}) and, after drying over $CaCl_2$, was twice distilled in vacuum in a stream of nitrogen. Parabutyraldehyde was stored in a refrigerator and, before the experiment, was distilled once more under the same conditions; b.p. 127—127.5°/25 mm, n_D^{20} 1.4262, d_4^{25} 0.914, d_4^{50} 0.891, freezing point −11.7°. Carbon tetrachloride was purified by the procedure described in ([3],[7]). Azobisisobutyronitrile was purified and stored as described previously ([8]).

Procedure for carrying out the experiments and processing the polymers. Polymerization was carried out in lead ampoules to polymer yields not exceeding 10%. The scheme of the high-pressure apparatus and the procedure for carrying out the experiments were, in their main features, analogous to those described previously ([8]). After the experiment, the ampoules were opened and the polymer was precipitated in a tenfold (by volume) amount of methyl alcohol. The polymer was filtered off, dissolved in methyl ethyl ketone, and reprecipitated. After reprecipitation the polymer was dissolved in benzene (0.2 g in 10–15 ml), the solution was frozen, and then evacuated in vacuum (0.1 mm Hg) at room temperature to constant weight. The specific viscosities η_{sp} of benzene solutions of the polymers were determined in an Ubbelohde viscometer with a "suspended level" at 25°. The intrinsic viscosity $[\eta]$ was determined by extrapolation of the straight line drawn through four values of η_{sp}/C to zero concentration (C is the concentration of polymer in g per 100 ml). The molecular weight was calculated by the formula ([9]):

$$\overline{M}_n = 178\,000\,[\eta]^{1.37}.$$

Discussion of Results

Figure 1 presents the data obtained by us on the dependence of $1/\overline{P}_n$ on the molar ratio aldehyde : styrene in a solution of parabutyraldehyde at various pressures. As can be seen, the indicated dependence, within the limits of accuracy of the determinations, is expressed by a straight line, the angle of inclination of which to the abscissa axis decreases as the pressure increases. The values of $k_{\mathrm{p}} : k_p$ found from Fig. 1 by formula (1) are given below:

Pressure, kg/cm^2	Atmospheric	1000	2000	3000	4000
$(k_{\mathrm{p}} : k_p) \times 10^5$: butyraldehyde	143	80	47	37	27
$(k_{\mathrm{p}} : k_p) \times 10^5$: isobutyraldehyde	210		130		82

As is evident from the data presented, in the polymerization of styrene over the

Figure 1

Figure 1: Figure 1

pressure interval from atmospheric to 4000 kg/cm^2, the ratio $k_{\mathrm{p}} : k_{\mathrm{r}}$ for chain transfer through butyraldehyde decreases by a factor of 5.3, whereas through isobutyraldehyde it decreases only by a factor of 2.6. From the data we obtained on the effect of pressure on the ratio $k_{\mathrm{p}} : k_{\mathrm{r}}$, one can determine

Fig. 1. Polymerization of styrene at 50°; at atmospheric pressure $[M] = 2.56$ mol/l, [ADN] = 0.0185 mol/l. Dependence of the quantity reciprocal to the degree of polymerization on the molar ratio aldehyde : styrene $[S] : [M]$ at different pressures.
a –S –butyraldehyde, **1** –atm. pressure, **2** –1000 kg/cm^2, **3** –2000 kg/cm^2, **4** –3000 kg/cm^2, **5** –4000 kg/cm^2; **b** –S –isobutyraldehyde, **1** –atm. pressure, **2** –2000 kg/cm^2, **3** –4000 kg/cm^2.

(see (1)) the difference between the activation volume effects of the chain-transfer and chain-growth reactions ($\Delta V_{\mathrm{p}}^{\neq} - V_{\mathrm{r}}^{\neq}$); this difference proves to be equal to 15.5 cm^3/mol for butyraldehyde and 6.5 cm^3/mol for isobutyraldehyde (both figures refer to the pressure interval from atmospheric to 2000 kg/cm^2). The quantity $\Delta V_{\mathrm{p}}^{\neq}$ in both cases represents the volume change upon formation of the transition state in the chain-growth reaction during styrene polymerization. It could be assumed that this quantity changes little on passing from butyraldehyde to isobutyraldehyde; then the different change in $k_{\mathrm{p}} : k_{\mathrm{r}}$ with increasing pressure is due to different activation volume effects in the chain-transfer reactions. To confirm this, it seemed advisable to check whether the presence of butyraldehyde would affect the change in the ratio $k_{\mathrm{p}} : k_{\mathrm{r}}$ with increasing pressure for another chain-transfer agent, for example CCl_4. We carried out experiments at atmospheric pressure and 4000 kg/cm^2 at a constant molar ratio butyraldehyde : styrene equal to 1.0; the amount of added CCl_4 was 0.1-0.3 M/M styrene. The concentrations of styrene, butyraldehyde, and initiator were kept constant by a corresponding change in the amount of "inert" solvent (parabutyraldehyde). The results of the experiments are shown in Fig. 2. According to these data, the value of $k_{\mathrm{p}} : k_{\mathrm{r}}$ is, at 50° and atmospheric pressure, 100×10^{-4}, and at 4000 kg/cm^2 -80×10^{-4}.

In their study of the radical polymerization of styrene, Walling and Pellon obtained for CCl_4 $k_{\mathrm{p}} : k_{\mathrm{r}} = 93 \times 10^{-4}$ (60°). According to the data of work (10), $E_{\mathrm{p}} - E_{\mathrm{r}} = 4.5$ kcal/mol; consequently, at 50° $k_{\mathrm{p}} : k_{\mathrm{r}} = 76 \times 10^{-4}$. The latter value is only slightly lower than the value of $k_{\mathrm{p}} : k_{\mathrm{r}}$ for CCl_4 obtained in the present work in the presence of a considerable amount of bu—

···butyraldehyde. The effect of pressure on the ratio $k'_{\mathrm{p}} : k_{\mathrm{p}}$ is very small, i.e., the rate constants of propagation and chain transfer increase to approximately the same extent with increasing pressure ($\Delta V_{\mathrm{p}}^{\neq} \approx \Delta V_{\mathrm{r}}^{\neq}$). These data are in complete agreement with the results obtained in the absence of butyraldehyde

Figure 2

Figure 2: Figure 2

(1). Consequently, our data confirm the assumption that $\Delta V_{\mathrm{p}}^{\neq}$ is constant under the conditions studied. If $\Delta V_{\mathrm{p}}^{\neq} = -20$ cm^3/mol is adopted (11), then the values of $\Delta V_{\mathrm{tr}}^{\neq}$ for CCl_4, isobutyraldehyde, and butyraldehyde are, respectively, -19, -13.5, and -4.5 cm^3/mol.

It may be assumed that the substantial difference between the values of $\Delta V_{\mathrm{tr}}^{\neq}$ and $\Delta V_{\mathrm{p}}^{\neq}$ in the polymerization of styrene in the presence of butyraldehyde and isobutyraldehyde is due to the different nature of the propagation and chain-transfer reactions: in propagation, the polymer radical adds to the carbon atom of the monomer double bond, whereas in transfer it abstracts a hydrogen atom from the aldehyde molecule. The question of the reasons for the considerable difference in the values of $\Delta V_{\mathrm{tr}}^{\neq}$ in chain transfer through butyraldehyde and isobutyraldehyde is more complicated. As is known (12,13), in a number of cases the possibility of charge separation during formation of the activated complex in chain-transfer reactions is admitted, in particular through CCl_4 in the polymerization of styrene. If this is so, then the volume effect of activation must include an additional negative term due to solvation of the activated complex. The small value of $\Delta V_{\mathrm{tr}}^{\neq}$ for butyraldehyde could be explained by the fact that, in this case, unlike isobutyraldehyde, no appreciable charge separation occurs in the activated complex. This question requires further study.

Fig. 2. Polymerization of styrene at 50°; at atmospheric pressure $[M] = 4.14$ mol/l, $[ADH] = 0.0185$ mol/l. Dependence of the reciprocal of the average degree of polymerization on the molar ratio CCl_4 : styrene ($[S] : [M]$) in the presence of butyraldehyde (4.14 mol/l) at different pressures: **1** –atmospheric; **2** –4000 kg/cm^2.

The data obtained in the present work indicate that the ratio of the rate constants of transfer and chain propagation in radical polymerization may depend on pressure in different ways. The character of this dependence is determined mainly by the features of the mechanism and structure of the activated complex in the chain-transfer reaction.

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