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Effect of Pressure on Free-Radical Copolymerization Kinetics. I. A Concept of Additivity of Partial Molar Volumes of Activation

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Synopsis

A short review of the effect of pressure on copolymerization kinetics shows the necessity of simple models for a better understanding of activation volumes. Therefore, a simple concept, possibly generally valid for free-radical polymerization, is proposed, based on the assumption that molar volumes of activation can be expressed as an addition of a characteristic radical and a monomer contribution, regardless of the combination involved. The scheme may facilitate the visualization of the transition state and contribute to the understanding of reaction mechanisms of radical polymerizations. Ethylene-vinyl acetate copolymerization at 62°C with *tert*-butyl alcohol as solvent agrees with the proposed scheme, appearing from the pressure independence of the product of reactivity ratios at the different levels (35, 600, and 1200 kg/cm²). Implicitly it can be shown that an ethylene monomer contributes about 2 cm³/mole more to the activation volumes of the propagation reactions than does the vinyl acetate monomer, whereas for the radicals the difference of the respective contributions to the activation volumes is opposite in sign.

INTRODUCTION

The aspects relevant to polymerization under the condition of high pressure include effects of pressure on concentration, viscosity, phase condition, and reaction rate constants. Here, we will focus on the pressure dependence of reaction rate constants, which can be derived¹ from the transition state theory:

$$(\partial \ln k / \partial p)_T = -\Delta V^\ddagger / RT$$

where the volume of activation ΔV^\ddagger is the excess of the molar volume of the transition state over the sum of the molar volumes of the reactants. Thus, the effect of pressure on rate constants depends on the sign and magnitude of ΔV^\ddagger . Volumes of activation are somewhat pressure-dependent, and their numerical value tends to decrease as pressure increases. In many cases the activation volume has been used in probing reaction mechanisms.¹⁻³

RADICAL POLYMERIZATION

In free-radical polymerization, reaction rate and average degree of polymerization \overline{DP} may be given (under simplified conditions) by the well-known equations:

$$\text{rate} = k_p (fk_d[I]/k_t)^{0.5} [M]$$

and

$$\overline{DP} = k_p [M] / (fk_d[I]k_t)^{0.5}$$

where k_d is the initiator decomposition rate constant, k_p is the chain propagation rate constant, k_t is the chain termination rate constant; f is initiator efficiency, $[I]$ is initiator concentration, and $[M]$ is monomer concentration. The effect of pressure on polymerization rate and \overline{DP} can be formally expressed in terms of overall volumes of activation:

$$\begin{aligned} \Delta V_{\text{pol}}^\ddagger &= \Delta V_p^\ddagger + \frac{1}{2}\Delta V_d^\ddagger - \frac{1}{2}\Delta V_t^\ddagger \\ -16 &= -12 + \frac{1}{2}(+4) - \frac{1}{2}(+12) \end{aligned}$$

and

$$\begin{aligned} \Delta V_{\text{DP}}^\ddagger &= \Delta V_p^\ddagger - \frac{1}{2}\Delta V_d^\ddagger - \frac{1}{2}\Delta V_t^\ddagger \\ -20 &= -12 - \frac{1}{2}(+4) - \frac{1}{2}(+12) \end{aligned}$$

As a typical example, the approximate values (cm^3/mole) for styrene polymerization are given.^{1,4} That the composite quantities $\Delta V_{\text{pol}}^\ddagger$ and $\Delta V_{\text{DP}}^\ddagger$ are both negative indicates a simultaneous increase of polymerization rate and degree of polymerization with pressure. Although the parameters $\Delta V_{\text{pol}}^\ddagger$ and $\Delta V_{\text{DP}}^\ddagger$ can be determined experimentally with a fair degree of accuracy, there is much uncertainty about the values of the activation volumes of the separate rate-determining steps.

On the one hand, a possible complication is that often these simplified relations for polymerization rate and degree of polymerization do not apply. On the other hand, separating the effects of pressure on k_p and k_t requires application of an intricate technique, viz., the sector method (intermittent illumination), under the condition of high pressure.⁴ As a consequence, the effect of pressure has been examined in detail for only a few polymerizations.⁴⁻⁶ It will be shown that copolymerization immediately leads to the (relative) effect of pressure on propagation constants.

COPOLYMERIZATION

Under certain conditions, free-radical copolymerization can be described by the well-known copolymer equation:^{7,8}

$$\frac{dn_a}{dn_b} = \frac{r_a(n_a/n_b) + 1}{r_b(n_b/n_a) + 1} \quad (1)$$

where $r_a = k_{aa}/k_{ab}$ and $r_b = k_{bb}/k_{ba}$, the monomer reactivity ratios, are ratios of the chain propagation constants involved; n_a and n_b are numbers of moles of monomers in the reactor, and dn_a/dn_b is the composition of the instantaneously formed copolymer.

The main theoretical interest of copolymerization is that the r values provide information on the relative reactivities of different monomers with regard to a given radical, and consequently on the relation between reactivity and structure.

It can be seen from eq. (1) that in copolymerization, the effect of pressure shows

up in a changing relation of feed versus product composition. Although the latter relation is determined by four rate constants, the advantage is here that only one type of constant is involved, viz., propagation rate constants.

The effect of pressure on the r values can be separated in the contributions from both propagation rate constants, e.g.:

$$\frac{\partial \ln r_a}{\partial p} = \frac{\partial \ln k_{aa}}{\partial p} - \frac{\partial \ln k_{ab}}{\partial p} = - \frac{\Delta V_{aa}^\ddagger - \Delta V_{ab}^\ddagger}{RT} \quad (2)$$

and is consequently governed by the difference of the two pertaining volumes of activation.

CONCEPT OF ADDITIVITY

Although, according to eq. (2) the effect of pressure on the r values may yield an estimation of $\Delta V_{aa}^\ddagger - \Delta V_{ab}^\ddagger$, this does not contribute considerably to a better understanding of activation volumes and their correlation with structure and reaction mechanism.

In an attempt to achieve this purpose, a simple concept has been adopted. An activation volume can always be expressed as an addition of two volumetric contributions, viz., the partial activation volumes of a radical and a monomer. Then, at the risk of oversimplification, it is assumed that these partial activation volumes are characteristic of the monomers and the radicals, regardless of the combination involved. Hence:

$$\begin{aligned} \Delta V_{aa}^\ddagger &= \Delta V_{a^\cdot}^\ddagger + \Delta V_a^\ddagger \\ \Delta V_{bb}^\ddagger &= \Delta V_{b^\cdot}^\ddagger + \Delta V_b^\ddagger \\ \Delta V_{ab}^\ddagger &= \Delta V_{a^\cdot}^\ddagger + \Delta V_b^\ddagger \\ \Delta V_{ba}^\ddagger &= \Delta V_{b^\cdot}^\ddagger + \Delta V_a^\ddagger \end{aligned}$$

Combination with eq. (2) yields:

$$\begin{aligned} \partial \ln r_a / \partial p &= -(\Delta V_{aa}^\ddagger - \Delta V_{ab}^\ddagger) / RT \\ &= -(\Delta V_{a^\cdot}^\ddagger - \Delta V_b^\ddagger) / RT \end{aligned} \quad (3)$$

and analogously:

$$\begin{aligned} \partial \ln r_b / \partial p &= -(\Delta V_{bb}^\ddagger - \Delta V_{ba}^\ddagger) / RT \\ &= -(\Delta V_{b^\cdot}^\ddagger - \Delta V_a^\ddagger) / RT \\ &= -\partial \ln r_a / \partial p \end{aligned} \quad (4)$$

Since the radical contributions cancel out, the effect of pressure on both r values may be described by the difference of partial monomer activation volumes, and consequently:

$$\partial \ln (r_a r_b) / \partial p = 0$$

If this concept is valid, the r values will change with increasing pressure in opposite directions with $r_a r_b = \text{constant}$. In case the activation volume cannot be described as the sum of independent partial volumes, it may at least be expected that $\partial \ln r_a / \partial p$ and $\partial \ln r_b / \partial p$ are opposite in sign.

The validity of the proposed scheme and its limitations should be examined by determining the effect of pressure on the reactivity ratios for a great number of copolymerizations. In the first instance the ethylene-vinyl acetate copolymerization has been studied; the results are given in the present paper.

EXPERIMENTAL

Ethylene and vinyl acetate were copolymerized in *tert*-butyl alcohol with a radical initiator (α, α' -azobisisobutyronitrile) at 62°C. Series of kinetic experiments were carried out at three different pressure levels: 35, 600, and 1200 kg/cm². The monomer feed composition of the high-pressure experiments (600 and 1200 kg/cm²) was measured prior to the reaction and after termination of the copolymerization by quantitative gas-chromatographic analysis. In the case of the low-pressure experiments (35 kg/cm²), monomer consumption was measured during the entire course of the copolymerization reaction, as reported elsewhere.^{9,10} A computational method has been developed, enabling the evaluation of more accurate reactivity ratios than did our¹¹ and other¹²⁻¹⁴ methods reported previously. This new method, based on the integrated copolymerization equation, considers errors both in the monomer feed composition q and the conversion f , whereas our preceding method,¹¹ for example, considered only errors in one of these dependent variables, i.e., the degree of conversion. The two variables q and f directly result from the gas-chromatographic analysis data. Mathematics and computational procedure will be published separately.

RESULTS AND DISCUSSION

It has been proved^{9,15} that under the pertinent conditions the copolymerization of ethylene and vinyl acetate can be accurately and adequately described by the usual model [eq. (1)]. The calculated reactivity ratios, summarized in Table I, reveal a decreasing difference between the reactivity of ethylene and vinyl acetate with respect to both radicals with increasing pressure.

According to eqs. (3) and (4), the results in Table I allow calculation of the activation volume differences from the various pressure intervals. These results are summarized in Table II.

The pressure dependences of r_e and r_v are given in Figures 1 and 2. For computational purposes, the measured points have been connected by straight lines, the activation volumes being assumed to be independent of pressure within

TABLE I
Reactivity Ratios, Product of Reactivity Ratios, and Standard Deviations at Different Pressure Levels for the Copolymerization of Ethylene (e) and Vinyl Acetate (v)

Reaction pressure, kg/cm ²	r_e	r_v	$r_e r_v$
35	0.740 ± 0.007 ^a	1.504 ± 0.008 ^a	1.11 ± 0.02 ^a
600	0.782 ± 0.010	1.421 ± 0.013	1.11 ± 0.03
1200	0.802 ± 0.011	1.366 ± 0.014	1.10 ± 0.03

^a Calculated standard deviations.

TABLE II
Differences of Volumes of Activation Calculated from Various Pressure Intervals

Pressure range, kg/cm ²	$\Delta V_{ee}^\ddagger - \Delta V_{ev}^\ddagger$, cm ³ /mole	$\Delta V_{vv}^\ddagger - \Delta V_{ve}^\ddagger$, cm ³ /mole
35-600	-2.8	+2.8
35-1200	-2.0	+2.3
35-1200 ^a	-2.0 ± 0.3^b	$+2.3 \pm 0.3^b$

^a All reactivity ratios are considered, assuming a linear course of $\ln r_e$ and $\ln r_v$ vs. pressure.

^b Estimated standard deviation.

the pertaining pressure interval(s). The latter assumption is in accordance with the fact¹ that, in general, the pressure dependence of activation volumes is negligible in the range from 1 to 1000 kg/cm². Also, for various homopolymerizations, the propagation constants turn out to be linearly dependent on the pressure within the given range.^{4,5,16,17} A pressure independence of activation volumes, however, is not a necessary condition for the proposed concept of additivity of activation volumes.

From Table II it appears that $\Delta V_{ee}^\ddagger - \Delta V_{ev}^\ddagger$ and $\Delta V_{vv}^\ddagger - \Delta V_{ve}^\ddagger$ are opposite in sign and equal within experimental error, which also appears from the pressure

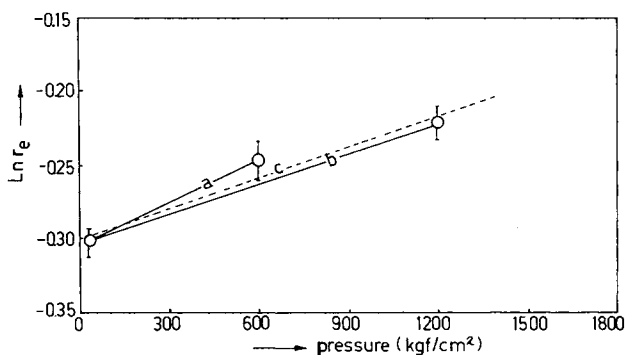


Fig. 1. Plots of $\ln r_e$ as a function of pressure for the copolymerization of ethylene (e) and vinyl acetate (v): (a) 35-600 kg/cm²; (b) 35-1200 kg/cm²; (c) best fitting curve for all three points.

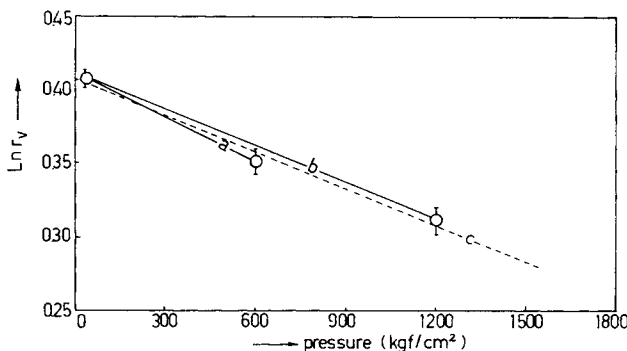


Fig. 2. Plots of $\ln r_v$ as a function of pressure for the copolymerization of ethylene (e) and vinyl acetate (v): (a) 35-600 kg/cm²; (b) 35-1200 kg/cm²; (c) best fitting curve for all three points.

independence of the product of reactivity ratios within the experimental error. Consequently, it follows that for this copolymerization under the given conditions the proposed concept seems to be valid, and

$$\Delta V_e^\ddagger - \Delta V_v^\ddagger = -2.2 \pm 0.3 \text{ cm}^3/\text{mole} \quad (5)$$

This means that the ethylene monomer undergoes some more contraction than does the vinyl acetate monomer when participating in a transition state with either radical. Since quantum chemical calculations have indicated that monomers add to a radical from a direction perpendicular to the last C—C bond of the radical chain end,¹⁸⁻²⁰ it seems quite possible that a larger overlap of the σ -orbital of the radical with the π -orbitals of the ethylene monomer, i.e., a larger penetration of the free radical into the ethylene monomer, will be necessary to disturb the symmetric double bond. In VAc, however, the presence of an electron-withdrawing side group yields a dipole momentum on the double bond,²¹ which in turn may facilitate the formation of the transition state.

Combination of our results with values reported in literature for activation volumes of homopolymerizations of ethylene and vinyl acetate allows a few more, though preliminary, conclusions to be drawn. Unfortunately, the scarce literature values turn out to be very scattered. The values $\Delta V_{ee}^\ddagger = -15.6 \text{ cm}^3/\text{mole}$ up to about 2000 kg/cm² (reported by Luft²²) and for $\Delta V_{vv}^\ddagger = -23.3 \text{ cm}^3/\text{mole}$ at 30°C up to about 1000 kg/cm² (reported by Yokawa et al.^{16,17}) seem to be the most reliable choice. According to eqs. (3), (4), and (5), the difference of the partial radical activation volumes can then be calculated.

$$\Delta V_{e^\cdot}^\ddagger - \Delta V_{v^\cdot}^\ddagger = +9 \text{ cm}^3/\text{mole}$$

In contrast to the relation found for the monomers [eq. (5)], this indicates that the vinyl acetate radical undergoes a larger contraction than does the ethylene radical when participating in a transition state with either monomer.

In the vinyl acetate radical, the acetate group is bonded to the carbon atom that also carries the free radical. The mobility of this side group will be reduced in the transition state, since the barrier for free rotation is much higher in this state. Moreover, the approach of a monomer may be sterically hindered when a vinyl acetate radical is involved in the formation of the transition state, and consequently the acetate group should be compressed. Also, the inductive effect of the acetate side group may cause this radical to become more attached to the nucleus, and consequently be less accessible than the ethylene radical.

Finally, the combination of the present experimental results with literature data allows calculation of the activation volumes of all four propagation steps:

$$\Delta V_{ev}^\ddagger = -14 \text{ cm}^3/\text{mole}$$

$$\Delta V_{vv}^\ddagger = -23 \text{ cm}^3/\text{mole}$$

$$\Delta V_{ee}^\ddagger = -16 \text{ cm}^3/\text{mole}$$

$$\Delta V_{ve}^\ddagger = -25 \text{ cm}^3/\text{mole}$$

Apparently, the “ev” cross-propagation is less accelerated by pressure than the “ve” cross-propagation, whereas both homopropagations take intermediate positions.

CONCLUSIONS

It has been shown that by means of a simple concept of additivity of partial activation volumes, we may arrive at important conclusions concerning the various propagation steps in copolymerization.

Moreover, if the present concept turns out to be valid more generally, it becomes possible to predict the effect of pressure on copolymerization. Since the effect of pressure on the copolymerization of monomer a with monomer b is given by $A = \Delta V_a^\ddagger - \Delta V_b^\ddagger$ and that of monomer a with monomer c is given by $B = \Delta V_a^\ddagger - \Delta V_c^\ddagger$, the effect of pressure on the copolymerization of monomer b with monomer c is given by $B - A$, and can be predicted if A and B have been determined experimentally.

The present results are limited to the ethylene-vinyl acetate copolymerization, and it is debatable if this scheme applies to the same extent to other systems. However, it seems worthwhile to study the effect of pressure on other copolymerizations on the basis of this simple scheme. For this purpose a number of binary copolymerization experiments under pressure are in progress. As soon as the nature and magnitude of any possible deviations are known, correction terms may have to be added to the present scheme.

In addition, it may be inferred that the concept of (partial) activation volumes is simple and much easier to visualize than free energy, entropy, and enthalpy of activation, since it is primarily determined by the nuclear positions. In that way, activation volumes will yield information on reaction mechanisms, structures, and reactivities concerning radical polymerization but also, and possibly in particular, ionic polymerization and other chemical reactions.

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