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DILATOMETRIC STUDY OF THE SOLUTION COPOLYMERIZATION OF 1,1,5-TRIHYDROPERFLUOROAMYL ACRYLATE AND METHACRYLONITRILE *

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The additivity of polymer volumes and densities in a monomer or solvent has to be taken into account in any strict determination of the contraction factors (K_{11} , K_{22} , K_{12} and K'_{12}) when kinetic studies of radical copolymerization processes employ dilatometric analysis. This paper relates to our comparative analysis of equations proposed by Wittner and Bevington, and to their validity as a means of calculating contraction factors in copolymerization processes. As an example we take the case where there are marked differences in the relative reactivities of the comonomers, and in their contraction factors.

INTERPRETATION of the dilatometric data in cases where copolymerization kinetics are investigated dilatometrically involves use of the relation [1-3]

$$q = \frac{\Delta V \times 100}{K_{12} V}, \quad (1)$$

where q is the monomer conversion, %; ΔV is the volume change in a system at the reaction temperature, cm^3 , V is the original volume of the monomers at the reaction temperature, cm^3 ; K_{12} is the overall contraction factor during copolymerization.

However, it should be noted that each composition of a monomer mixture in the copolymerization process has a different numerical value for contraction factor K_{12} . Bevington and coworkers [4] used the relation

$$K_{12} = K_{11}m_1 + K_{22}m_2, \quad (2)$$

which is a linear interpolation between homopolymerization contraction factors K_{11} and K_{22} , and the mole fractions m_1 and m_2 of the respective monomer units in the copolymer. Later

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on, experimental results published in papers [5-7] showed that equation (2) is not in keeping with many actual conditions. It was then that Wittmer [5] proposed an equation that takes account of the composition of the monomer mixture and compositional distribution probabilities for the copolymer

$$K_{12} = K_{11}B_{11} + K_{22}B_{22} + K'_{12}B_{12}, \quad (3)$$

where B_{ij} are coefficients of probabilities of appearance of the M_i-M_j bond in the copolymer. These were obtained from the copolymerization constants r_1 and r_2 and the composition of the monomer mixture ($x = [M_1]/[M_2]$)

$$B_{11} = \frac{r_1 x}{2 + r_1 x + r_2/x}; \quad B_{22} = \frac{r_2/x}{2 + r_1 x + r_2/x}; \quad B_{12} = \frac{2}{2 + r_1 x + r_2/x}, \quad (4)$$

where K'_{12} is the contraction factor for the alternating step in the propagation process

$$K'_{12} = \frac{K_{12} - (K_{11}B_{11} + K_{22}B_{22})}{B_{12}} \quad (5)$$

With the exception of K'_{12} , all the quantities in equation (3) may readily be determined. Assuming that K'_{12} is constant, it will in that case be possible to predict the behaviour of any composition of the monomer mixture after measuring the contraction, during copolymerization, of one composition, followed by calculation of K_{12} , using equations (1) and (3).

It has been shown [5-7] that equation (3) is applicable for cases of copolymerization solely when the relative reactivities and contraction factors of the monomers differ only insignificantly. It was desired to determine the validity of the above equations for copolymerization systems where r_1 and r_2 and K_{11} and K_{22} differ quite markedly.

To do so we carried out a dilatometric study of the copolymerization kinetics, taking as an example 1,1,5-trihydroperfluorooamyl acrylate (M_1) and methacrylonitrile (M_2) in DMSO medium ($r_1 = 0.14 \pm 0.07$, $r_2 = 1.03 \pm 0.08$).

Methacrylonitrile (MAN) used for the investigation was purified as follows: 500 cm³ of MAN and 1000 cm³ of a 10% solution of NaOH containing 120 g of $\text{NH}_4\text{OH} \cdot \text{HCl}$ were boiled for 6 hr in a flask fitted with a reflux condenser. The mixture was decanted into a separating funnel, and washed with distilled water to neutral reaction. Monomer was separated, dried over CaCl_2 and distilled on a fractionating column; the fraction with b.p. 363-364 K, n_D^{20} 1.3975, ρ_4^{20} 805.1 kg/m³ was collected. 1,1,5-Tri-hydroperfluorooamyl acrylate (FAA) was twice distilled under vacuum; the fraction collected had b.p. 342-343 K/2.8 kPa, n_D^{20} 1.3431, ρ_4^{20} 1481.2 kg/m³. Azobisisobutyronitrile (ABN) was twice recrystallized from ethyl alcohol, m.p. 374-375 K. DMSO was dried over CaCl_2 , and vacuum distilled; the fraction collected had b.p. 323-326 K/0.4 kPa, n_D^{20} 1.4783, ρ_4^{20} 1101.4 kg/m³.

The synthesis of homo- and copolymers of FAA and MAN in DMSO was performed with the starting concentration of monomers at 3 kmole/m³ in the presence of 1.5×10^{-3} kmole/m³ of ABN at 343 ± 0.05 K. The concentration and volume of the monomers was determined from the results obtained on weighing the dilatometer before and after it had been filled with the reaction system of a known composition. Oxygen was removed from the system by fivefold freezing and evacuation, after which the dilatometer was filled with He or Ar. Polymerization was continued to a conversion not exceeding 5-7 mole %. Changes in the position of the meniscus in the dilatometer capillary during polymerization were measured with a KM-8 type cathetometer, accurate to $\pm 1.0 \times 10^{-3}$ mm. The copolymer composition was determined from the nitrogen concentration, using the Kjeldahl method. The effective copolymerization constants were calculated by the analytical method used by Yezrielev, Brokhina and Roskin.

TABLE 1. DENSITY VALUES OF POLY-FAA AND POLY-MAN IN DMSO ASSUMING ADDITIVITY OF VOLUMES ρ_p^v AND ADDITIVITY OF DENSITIES ρ_p^d AT 343 K

W_p , p.b.w.	Poly-FAA			Poly-MAN		
	ρ_{ps}	ρ_p^v	ρ_p^d	ρ_{ps}	ρ_p^v	ρ_p^d
0.10	1.086	1.481	1.379	1.046	0.972	0.965
0.15	1.102	1.470	1.389	1.048	1.007	1.005
0.20	1.119	1.479	1.355	1.052	1.012	1.010
0.25	1.137	1.482	1.395	1.055	1.014	1.012
0.30	1.155	1.481	1.397	1.057	1.015	1.014
0.40	1.194	1.479	1.391	1.058	1.016	1.015

Note. Average values of ρ_p^v and ρ_p^d for poly-FAA are 1.479 and 1.384, and for poly-MAN, 1.005 and 1.010; the respective values of K_{11} are 0.048 and -0.023; 0.254 and 0.252.

Contraction factors in the homopolymerization of FAA and MAN were calculated from the results of measuring the densities of solutions of poly-FAA and poly-MAN in DMSO, and from the dilatometric data. The authors of [8] considered a number of conditions that influence the contraction factor, one being the assumption that solutions of a polymer in the monomer or in a solvent are ideal solutions. Those authors [8] also took the view that volumes and densities of a polymer or monomer in a solvent are additive; now the specific volume of a polymer in the monomer or in a solvent is

$$V_{sp} = \frac{w_p \cdot V_p}{w_m + w_p} + \frac{w_m V_m}{w_m + w_p}, \quad (6)$$

or, if one considers that the specific weights of the components are additive, then the density of a solution of the polymer

$$\rho_{ps} = \frac{w_p}{(w_m + w_p)\rho_p} + \frac{w_m}{(w_m + w_p)\rho_m}, \quad (7)$$

where w is the weight fraction of a component; V is the specific volume; the meanings of the subscript letters are: ps solution of polymer in monomer or solvent, p —polymer, m —monomer, ρ —density.

For a hypothetical system with $\rho_p=1060$ and $\rho_m=907$ kg/m³, e.g. a styrene system, it was shown in [8] that, on recalculating for conversion, there is a discrepancy of 10% in eqns. (6) and (7).

Assuming that the densities are additive, we found that in the case of MAN polymerization the results differ slightly from the dilatometric data, while in the case of PhAA we even obtained negative values for the contraction factor (Table 1). This means that in the case of homopolymerization of FAA in DMSO it is not the densities, but volumes of the components that are additive.

The average values of the contraction factors, based on the dilatometric data and on equation (1), are in this case $K_{11}=0.0443$ for FAA, and $K_{11}=0.2606$ for MAN.

In further calculations we used contraction factors based on the dilatometric data, since contraction is a linear function of conversion in the homopolymerization of FAA and MAN.

To determine the contraction factor for the copolymerization alternating step K'_{11} , one needs to know the values of B_{11} , B_{22} , B_{12} and K_{12} . To calculate the overall contraction factor K_{12} we have equation (1). Figure 2 shows the probability coefficients B_{ij} in relation

to the composition of the initial monomer mixture. As the amount of FAA in the mixture increases the probability coefficient B_{12} increased during copolymerization, reaching a maximum at FAA ~ 0.7 mole fraction (Fig. 2, curve 1). Coefficients B_{11} (curve 3) and B_{22} (curve 2) are at this point equal, and small compared with B_{12} . It follows that in calculations of K'_{12} errors will be smallest at the maximum point for B_{12} . On the other hand, when B_{12} values are small, slight errors in determination of the overall contraction factor K_{12} may lead to large errors in determination of K'_{12} . This must be borne in mind when calculating K'_{12} .

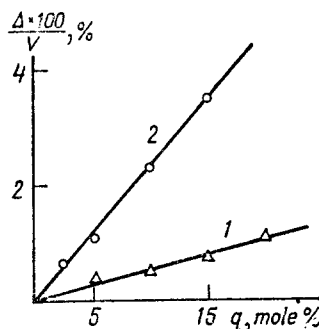


FIG. 1. Contraction versus conversion in the homopolymerization of FAA. (1) and MAN (2) in DMSO medium at 343 K.

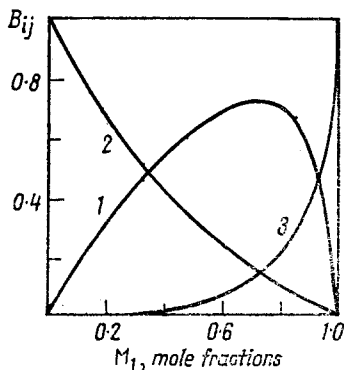


FIG. 2

FIG. 2. Probability coefficients B_{ij} vs. composition of initial monomer mixture in FAA-MAN copolymerization in DMSO: 1— B_{12} ; 2— B_{22} , 3— B_{11} .

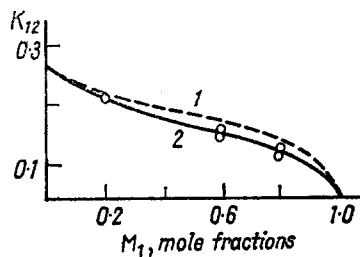


FIG. 3

FIG. 3. Over-all contraction factor K_{12} vs. composition of the monomer mixture in FAA-MAN copolymerization (calculated by eqns. (2) (1) and (3) (2)).

It is seen from the results of determination of the copolymerization contraction factors K_{12} and K'_{12} (Table 2) that the overall contraction factor depends on the composition of the obtained polymer, and hence on the composition of the monomer mixture. If the MAN concentration in the initial mixture is increased, coefficient B_{22} is higher (Fig. 2) and, since $K_{22} \geq K_{11}$, the value of K_{12} is also increased.

TABLE 2. INFLUENCE OF THE COMPOSITION OF THE INITIAL MONOMER MIXTURE ON CONTRACTION FACTORS K_{11} AND K'_{11} IN THE COPOLYMERIZATION OF FAA (M_1) AND MAN (M_2)

$[M_1] : [M_2]$, mole %	Concentration $\frac{\Delta V \times 100}{V}$, %	q , mole %	K_{11}	K'_{11}
80 : 20	0.9458	7.548	0.1253	0.1290
60 : 40	1.2851	7.982	0.1610	0.1386
20 : 80	1.2470	5.781	0.2157	0.1489
10 : 90	1.1033	4.387	0.2515	0.1600

Figure 3 shows the theoretical plot of the contraction factor K_{11} vs. composition of the initial monomer mixture, based on equation (2) (fractured line) and (3) (solid line). The points denote experimental results. Thus it appears that the theoretical curve based on equation (3) is more in line with experimental findings.

To investigate conditions under which there is agreement between theoretical curves proposed in papers by Wittmer and Bevington we set equal eqns. (2) and (3) and obtained $K'_{11} = (K_{11} + K_{12})/2$. This means that the absolute value of $K'_{11} - (K_{11} + K_{12})/2$ may serve as a measure of the degree of divergence of theoretical curves, while equation (2) is but a special case of equation (3). We deduce from the total of these considerations that it is sensible to compare the results of a dilatometric study of the copolymerization with the results of calculations based on equation (2), if only to get an approximate estimate of the value of K'_{11} .

The investigations described here show that the Wittmer equation [5] does satisfactorily describe the dilatometrically analysed kinetics of radical copolymerization, even in cases where the copolymerization constants and the comonomer contraction factors are by no means in agreement.

Translated by R. J. A. HENDRY

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