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Kinetics of copolymerizations: 1. Dilatometric investigation of the copolymerizations of benzyl methacrylate, styrene and methyl methacrylate

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INTRODUCTION

Dilatometry is a well known method for determination of conversions and polymerization rates. The necessary condition is a volume change during the polymerization and a correlation between shrinkage and conversion (U) yields the equation[1]:

$$U = \frac{1}{K} \times \frac{\Delta V}{V} \times 100 \qquad (1)$$

where V is the initial volume, ΔV is the decrease in volume and K the so-called conversion factor. K can be evaluated from equation (1) by direct gravimetric determination of the conversion for a polymerization of known shrinkage.

A second method is based on the densities of monomer (ρ_m) and polymer (ρ_p):

$$K = \frac{\rho_p - \rho_m}{\rho_p} \qquad (2)$$

The two equations are valid for homo- as well as copolymerizations, although it must be noted that for any particular composition of monomers there must be a corresponding conversion factor Bevington *et al.*[2] used the relation:

$$K = K_1x_1 + K_2x_2 \qquad (3)$$

which is a linear interpolation between the conversion factors K_1 and K_2 of the two homopolymerizations x_1 and x_2 are the mole fractions of the two components in the copolymer. Most experimental data[3,4] do not obey equation (3) and Wittmer[4] suggested that:

$$K = K_{11}B_{11} + K_{22}B_{22} + K_{12}B_{12} \quad (4)$$

involving binary bonding frequencies B_{ij} and conversion factors. The B_{ij} values can be easily calculated[4] from the reactivity ratios of a binary system and the composition of the actual monomer mixture. K_{11} and K_{22} are the conversion factors of the respective homopolymerizations and K_{12} that of the alternating copolymerization step. Apart from K_{12}, all quantities in equation (4) are easily accessible.

For the system ethyl acrylate/styrene, Wittmer confirmed the constancy of K_{12}. Accordingly it is possible to predict the behaviour of any possible monomer mixture of a copolymerization system by measuring the shrinkage for only one monomer mixture and hence calculating K_{12}.

The purpose of the present investigation was to test Wittmer's theory for the three binary copolymerizations of benzyl methacrylate (BMA), styrene and methyl methacrylate (MMA). Discussion of the kinetics of the copolymerizations will be given in another paper. The volume changes during polymerization have been followed in a specially designed dilatometer which has the advantage over others described in the literature[5–7] in that it is of relatively large volume, and allows the reaction mixture to be stirred vigorously; a temperature gradient in the vessel can thus be avoided and the large volume can lead to substantial yields of polymer even for low conversions. The second and greater advantage of the dilatometer is the possibility of regulating and recording the temperature of the polymerizing mixture. The heat of polymerization can be dissipated so that the reaction proceeds isothermally. A temperature rise due to the Trommsdorff-effect at higher conversions cannot be controlled because of the inertia of the cooling system.

EXPERIMENTAL

Materials

Benzyl methacrylate was prepared by esterification of methacrylic acid with benzyl alcohol. Immediately before use, it was vacuum distilled under nitrogen and run over a basic aluminium oxide column. Boiling point: 85°C/1.7 Torr.

Styrene and methyl methacrylate was distilled under nitrogen after removing the stabilizer.

Azoisobutyronitrile (AIBN) was recrystallized twice from ethanol.

Polymerizations

Polymerizations were carried out in bulk at 60°C with AIBN as initiator.

For determining reactivity ratios, monomer mixtures were polymerized under nitrogen. The resulting polymers were precipitated in methanol and dried *in vacuo* at 50°C to constant weight for determination of conversion. The compositions were found by n.m.r.-spectroscopy and elemental analysis.

The polymerizations for kinetic measurements were followed dilatometrically. Because of the complicated design of the dilatometer these experiments could not be carried out in the absence of oxygen. The polymer samples have been treated as described above.

Methods

Dilatometric measurements. The principle of the recording dilatometer, kindly placed at our disposal by BASF Aktiengesellschaft, has been described elsewhere[8]. The capacity of the glass reaction vessel is about 50 ml (*Figure 1*) and the reaction mixture can be stirred turbulently; it is surrounded by a tempering mantle. Temperature control by an external thermostat was not good enough and for this reason a twofold thermocouple has been inserted into the reaction vessel, allowing independent regulation and recording of the temperature. A temperature of 60.0° ± 0.1°C could be maintained in the reaction mixture. To enable rapid heating and cooling, the flow of the cooling water is controlled by a magnetic valve.

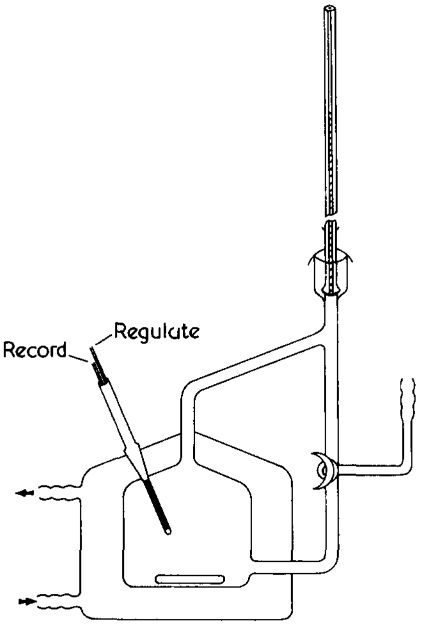

Figure 1 Principle features of the dilatometer vessel

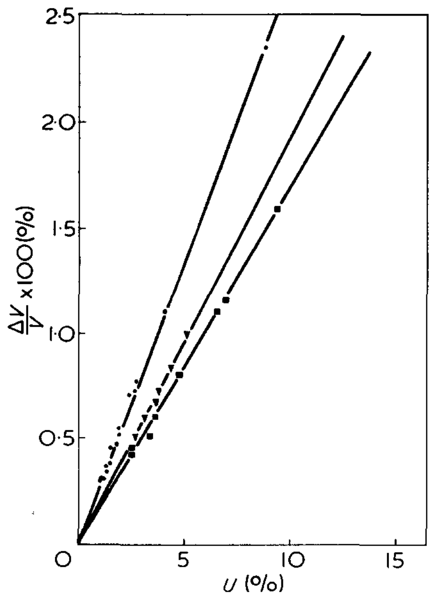

Figure 2 Relative volume change *versus* conversion for the homopolymerizations of BMA (▼), styrene (■) and MMA (●) at 60°C

Table 1 Comparison of conversion factors K from dilatometric and density measurements for the homopolymerizations of BMA, styrene and MMA at 60°C

	K calculated from equation (1)	Densities		K calculated from equation (2)
		ρ_m (g/cm^3)	ρ_p (g/cm^3)	
BMA	0.192	1.004	1.240	0.190
styrene	0.170	0.871	1.050	0.170
MMA	0.267	0.897	1.208	0.257

Table 2 Bulk copolymerization of BMA and styrene at 60°C with 0.05 mol % AIBN as initiator. Polymerization time: 60 min

	$\frac{M_1}{M_1+M_2}$	Conversion (%)	Carbon content in the copolymer (%)	$\frac{m_1}{m_1+m_2}$
BS 1	0.08	2.3	87.42	0.188
BS 2	0.18	2.5	84.95	0.304
BS 3	0.31	2.8	83.08	0.403
BS 4	0.40	3.1	81.67	0.485
BS 5	0.48	3.4	81.12	0.519
BS 6	0.58	4.3	79.92	0.598
BS 7	0.67	4.7	79.33	0.639
BS 8	0.72	5.4	78.64	0.690
BS 9	0.80	6.4	77.87	0.748
BS 10	0.87	7.6	77.50	0.777

M_i = moles of component i in the monomer mixture; m_i = moles of component i in the copolymer

Table 3 Bulk copolymerization of BMA and MMA at 60°C with 0.05 mol % AIBN as initiator

	$\frac{M_1}{M_1+M_3}$	Polymerization time (min)	Conversion (%)	N.m.r. peak areas (arbitrary units)			$\frac{m_1}{m_1+m_3}$
				$-C_6H_5$	$-OCH_2-$	$-OCH_3$	
BM 1	0.11	30	5.8	–	10.00	120.00	0.111
BM 2	0.20	30	6.6	–	28.67	139.33	0.236
BM 3	0.29	30	7.3	187.33	91.33	156.66	0.324
BM 4	0.39	30	5.8	110.33	35.50	80.66	0.425
BM 5	0.51	30	7.4	188.66	75.00	93.33	0.547
BM 6	0.61	30	8.1	129.66	65.66	50.66	0.635
BM 7	0.72	30	9.7	131.00	51.98	28.33	0.735
BM 8	0.81	20	9.2	321.30	137.30	48.30	0.810
BM 9	0.93	20	14.0	140.00	46.33	5.50	0.930

M_i = moles of component i in the monomer mixture; m_i = moles of component i in the copolymer

At the end of the polymerization, the reaction mixture was cooled by pumping ice water through the cooling tubes. The densitometric investigations have been carried out with a digital apparatus for density measurements[9] (DMA 02/C, Paar KG, Graz, Austria). Polymer densities were determined from measurements on solutions of the homopolymers in the corresponding monomer and of the copolymers in the corresponding initial monomer mixtures. Use was made of the relation:

$$\rho_{\text{polymer}} = \frac{p \times \rho_{\text{solvent}} \times \rho_{\text{solution}}}{\rho_{\text{solvent}} - (1-p) \times \rho_{\text{solution}}} \quad (5)$$

where ρ = densities; p = weight fraction of the polymer in solution.

The n.m.r. spectra were taken with a 100 MHz n.m.r. spectrometer (VARIAN HA 100) using about 10 wt % solutions of the polymers in CCl_4 or $CDCl_3$. Analyses of the copolymers were based on the peaks due to the:

$-OCH_2-$	group for BMA
$-C_6H_5$	group for styrene
$-OCH_3$	group for MMA

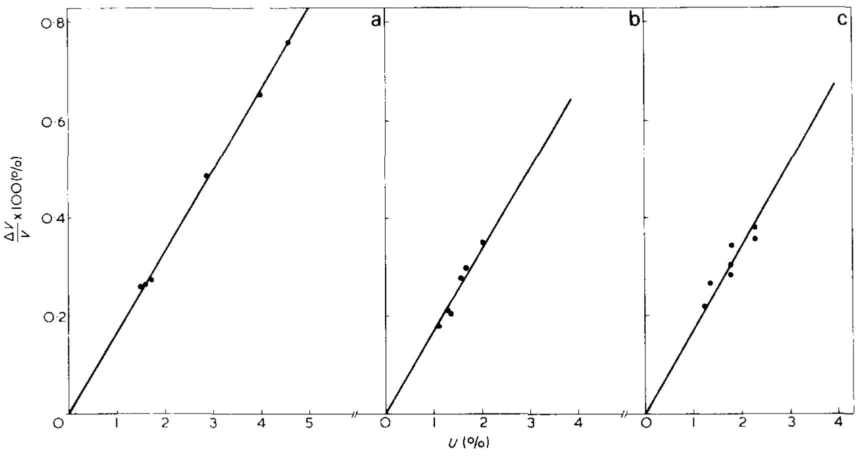

Figure 3 Relative volume change *versus* conversion for the copolymerization of BMA and styrene at 60°C. (a) $K = 0.165$, $M_1/(M_1 + M_2) = 0.18$; (b) $K = 0.165$, $M_1/(M_1 + M_2) = 0.59$; (c) $K = 0.173$, $M_1/(M_1 + M_2) = 0.77$

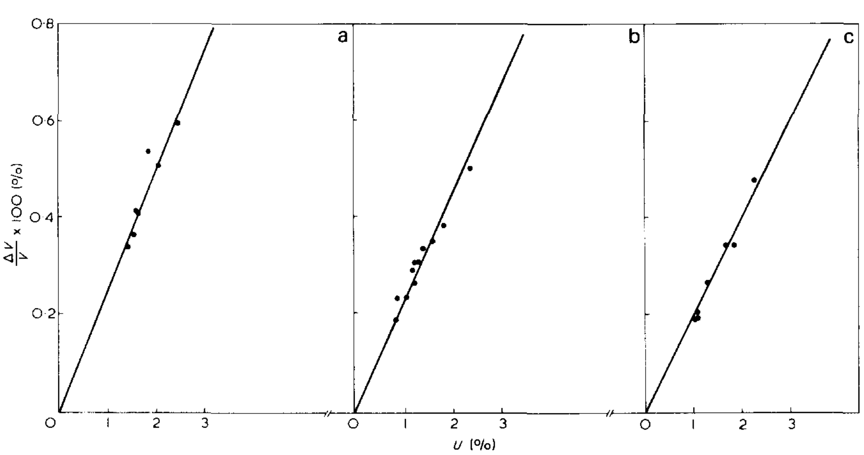

Figure 4 Relative volume change *versus* conversion for the copolymerization of BMA and MMA at 60°C. (a) $K = 0.248$, $M_1/(M_1 + M_3) = 0.11$; (b) $K = 0.220$, $M_1/M_1 + M_3) = 0.39$; (c) $K = 0.198$, $M_1/(M_1 + M_3) = 0.76$

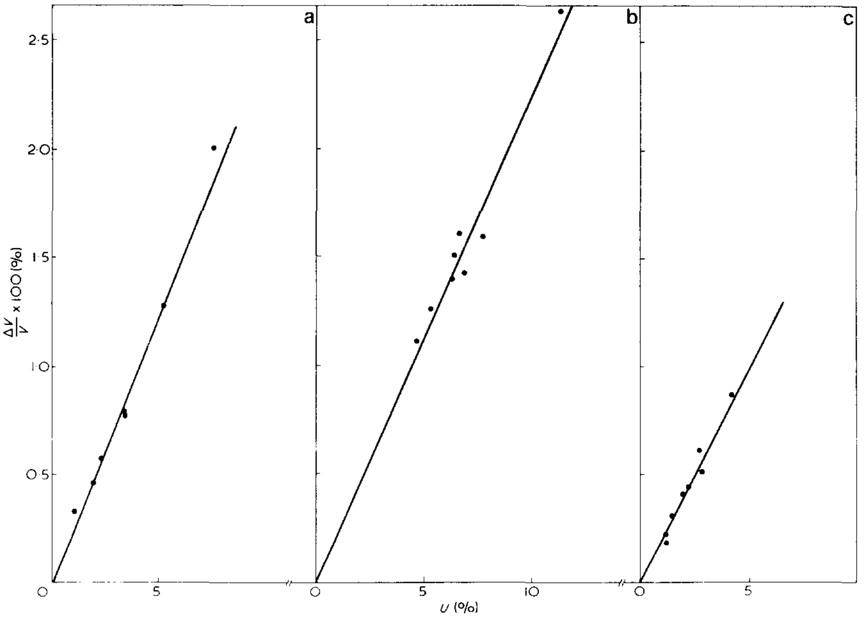

Figure 5 Relative volume change *versus* conversion for the copolymerization of styrene and MMA at 60°C. (a) $K = 0.234$, $M_2/(M_2 + M_3) = 0.22$; (b) $K = 0.227$, $M_2/(M_2 + M_3) = 0.44$; (c) $K = 0.203$; $M_2/(M_2 + M_3) = 0.76$

RESULTS AND DISCUSSIONS*

Homopolymerizations

The dilatometric results are represented graphically in *Figure 2* and conversion factors are summarized in *Table 1.* The greatest shrinkage occurs for MMA (about 27%) followed by BMA (about 19%) and styrene (17%).

The conversion factors have been checked by density measurements (see *Table 1*). Good agreement is found for BMA and styrene but the values differ slightly for MMA. The reason is discussed below. Further calculations have involved dilatometrically evaluated *K*-values.

Copolymerizations

Determinations of the reactivity ratios. The reactivity ratios have been determined for the systems BMA/styrene and BMA/MMA; those for the system styrene/MMA have been taken from the literature[10]. *Tables 2* and *3* show the experimental data for the two systems under investigation.

The reactivity ratios have been calculated by a method of Braun *et al.*[11]:

$r_{12} = 0.53 \quad r_{21} = 0.34$ for BMA/styrene

$r_{13} = 1.06 \quad r_{31} = 0.83$ for BMA/MMA

For BMA/styrene, Otsu *et al.*[12] reported:

$r_{12} = 0.51 \quad r_{21} = 0.44$

for bulk copolymerization at 60°C with AIBN as initiator; they were based upon elemental analyses and the method of Fineman–Ross[13] was used. For the bulk copolymerization of BMA/MMA at 60°C with AIBN as initiator the values:

$r_{13} = 1.05 \quad r_{31} = 0.93$

have been published[14], based upon analysis of the copolymers by a tracer method and application of the method of Fineman–Ross[13].

Reactivity ratios for the system styrene/MMA have been given[10] as:

$r_{23} = 0.52 \quad r_{32} = 0.46$

Conversions in the copolymerizations were kept quite low in order to satisfy the differential copolymerization equation[15]. The experimentally found reactivity ratios have been used to check monomer composition as a function of conversion by numerical integration of the copolymerization equation. It was confirmed that there

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* For simplification the monomers BMA have been indexed with 1, styrene with 2 and MMA with 3 in the following.

Table 4 Overall conversion factors K calculated from equation (2) from monomer and copolymer densities for the copolymerizations of BMA/styrene, BMA/MMA and styrene/MMA

BMA/styrene				BMA/MMA				Styrene/MMA			
	Densities				Densities				Densities		
$\frac{M_1}{M_1+M_2}$	ρ_m (g/cm^3)	ρ_p (g/cm^3)	K	$\frac{M_1}{M_1+M_3}$	ρ_m (g/cm^3)	ρ_p (g/cm^3)	K	$\frac{M_2}{M_2+M_3}$	ρ_m (g/cm^3)	ρ_p (g/cm^3)	K
0.18	0.906	1.088	0.167	0.11	0.916	1.239	0.261	0.22	0.891	1.182	0.246
0.59	0.959	1.146	0.163	0.39	0.953	1.224	0.221	0.44	0.885	1.147	0.228
0.77	0.979	1.180	0.170	0.76	0.987	1.220	0.191	0.76	0.877	1.096	0.119

M_i = moles of component i in the monomer mixture

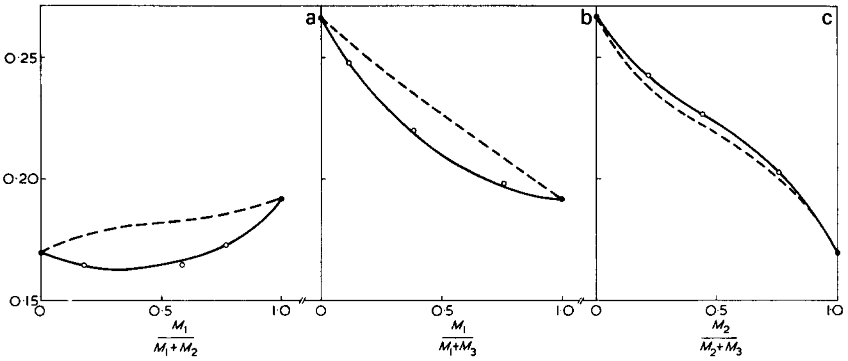

Figure 6 Overall conversion factors K *versus* monomer composition for (a) BMA/styrene, K_{12} = 0.157; (b) BMA/MMA, K_{13} = 0.195; (c) styrene/MMA, K_{23} = 0.227. ○, Experimental points; ——, calculated according to equation (4); – – – –, calculated according to equation (3)

is no appreciable change in monomer composition up to about 10% conversion for the systems under investigation. There is an azeotropic point for the system BMA/styrene but not for BMA/MMA. In both cases, random copolymers may be expected, the second system approaching an ideal azeotropic copolymerization.

Dilatometry

The results of the dilatometric studies of the three binary copolymerizations are represented in *Figures 3* to *5*. There is a linear dependence of the volume change on the conversion. The evaluated overall conversion factors K are plotted in *Figure 6 versus* the corresponding monomer compositions. Depending on the system, there is a relatively strong deviation from the linear interpolation† (equation (3), broken line) between the K-values of the homopolymerizations.

Calculation of the conversion factors K_{ij} for the alternating polymerization step according to equation (4) for the various monomer mixtures leads to values which can be considered constant within experimental error. The mean values are: $K_{12} = 0.157$; $K_{13} = 0.195$; $K_{23} = 0.227$.

The curves for the overall conversion factors K calculated by equation (4) and the K_{ij} values are plotted in *Figure 6* and show excellent agreement between the experimental and calculated data.

The present investigation supports Wittmer's treatment for all three systems and thus from a knowledge of the conversion factors for the homopolymerizations and that of the alternating polymerization step as well as the reactivity ratios, the conversion and the rate of polymerization can be determined according to equation (1) from the volume change for any monomer mixture.

Density measurements

It is necessary now to consider, whether in copolymerizations, as in homopolymerizations, the overall conversion factor K can be calculated using equation (2) from the densities of copolymers and monomer mixtures. The densities of monomers and polymers – estimated from equation (5) – are summarized in *Table 4* together with the corresponding K-values. Comparison with the values in *Figures 3* to *6* shows relatively good agreement. Some deviation, however, is understandable in regarding the equation for calculation of polymer densities. It is a question of division by a very small quantity so that a small change in the denominator produces a large effect in the overall expression.

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† In this case it is not a straight line, as the linear interpolation according to equation (3) is carried out for the polymer mole fractions, whilst in Figure 6 the monomer composition is plotted as abscissa.

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