Table 1 Styrene composition of polymers formed by reacting equimolar mixtures of styrene and methyl methacrylate with a lithium dispersion in various reaction media[11]

Solvent	Styrene (%)
Bulk	28
Heptane	15
THF	7
$(C_2H_5)_3N$	3
$(C_2H_5)_2NH$	1
NH_3	0

Tobolsky and coworkers[12–14] originally proposed that lithium initiated by a one electron transfer to monomer to produce a radical anion species of type I, and that this propagated anionically at one end and by a free radical mechanism at the other until termination occurred. The anionic mechanism propagates methyl methacrylate exclusively whereas free radical propagation in equimolar styrene–methacrylate mixtures yields a 50/50 random copolymer. Segments of the latter composition should therefore appear in the product from lithium dispersion initiation if such a mechanism were to hold. This process was, however, later disproved by Overberger and Yamamoto[15] who showed by ^1H n.m.r. examination that the styrene component of these polymers was present as homopolymer sequences and that there was no evidence of random sequences of both monomers. They proposed that styrene was adsorbed on to the surface in preference to methyl methacrylate and homopropagated anionically until the oligomer detached itself and reacted with methyl methacrylate in the monomer mixture.

Work carried out in these laboratories confirms the hypothesis that the adsorptive power of styrene is greatly superior to that of methyl methacrylate

on lithium metal. Under conditions which, with styrene alkyl halide and lithium metal in THF, yield significant quantities of the dimer adduct, methyl methacrylate and the same reagents form a carbinol almost exclusively (90%)[16,17]. The reaction has been shown to proceed by initial reaction of alkyl halide with lithium metal to generate alkyl lithium [first equation (6)] which then attacks methyl methacrylate in the manner of a Grignard reagent to yields first the ketone and then the carbinol. Thus the adsorption of methyl methacrylate on to lithium metal must be very small compared with that of styrene, and this adds support to Overberger's theory.

It is interesting to note from *Table 1* that the amount of styrene incorporated decreases as the solvating power of the solvent and its ability to interact directly with the metal increases. The concept that the dimer dianion is desorbed on its formation need apply only in the presence of a good solvating solvent like THF; in bulk or in inert solvents like heptane the free energy gain due to solvation on desorption is largely lost, and so the probability of further propagation on the surface with adsorbed styrene monomer is increased. Eventually the polystyrene oligomer grows to a chain length sufficient to create a favourable free energy change on desorption, and passes into solution where it subsequently reacts exclusively with methyl methacrylate. With the amine Lewis bases, their strong cation solvating powers support early desorption of oligomers and introduce direct competition by these solvents for the available adsorption sites. Furthermore, direct reaction with alkali metal yields

lithium amides which initiate homogeneously and so polymerize methyl methacrylate exclusively.

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Dilatometric investigations of the terpolymerization of benzyl methacrylate, styrene and methyl methacrylate

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(Received 15 June 1977)

INTRODUCTION

Investigations on the terpolymerization field are mainly dealing with the examination of the validity of the well

known Alfrey—Goldfinger equation[1]:

$$d[M_1] : d[M_2] : d[M_3] =$$

$$m_1 : m_2 : m_3$$

$$= M_1 \left[\frac{M_1}{r_{31} r_{21}} + \frac{M_2}{r_{21} r_{32}} + \frac{M_3}{r_{31} r_{23}} \right] \times$$

$$\left[M_1 + \frac{M_2}{r_{12}} + \frac{M_3}{r_{13}} \right]$$

$$: M_2 \left[\frac{M_1}{r_{12} r_{31}} + \frac{M_2}{r_{12} r_{32}} + \frac{M_3}{r_{32} r_{13}} \right] \times$$

$$\left[M_2 + \frac{M_1}{r_{21}} + \frac{M_3}{r_{23}} \right]$$

$$: M_3 \left[\frac{M_1}{r_{13}\,r_{21}} + \frac{M_2}{r_{23}\,r_{12}} + \frac{M_3}{r_{13}\,r_{23}} \right] \times$$

$$\left[M_3 + \frac{M_1}{r_{31}} + \frac{M_2}{r_{32}} \right] \qquad (1)$$

Here

$$r_{ij} = \frac{k_{ii}}{k_{ij}} \qquad (i,j = 1,2,3; \quad i \neq j) \quad (2)$$

are the binary reactivity ratios and M_i and m_i are the mole fractions of monomer i in the monomer mixture and the terpolymer.

Rates of terpolymerization have up to now — because of the complexity of the reaction — very rarely been investigated[2]. A possibility to approach to the problem is the inspection of the dilatometric behaviour of ternary systems.

The correlation between shrinkage and conversion in a polymerization reaction is given by[3]:

$$U = \frac{1}{K} \times \frac{\Delta V}{V} \times 100 \qquad (3)$$

where U signifies the conversion, V the initial volume, ΔV 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):

$$K = \frac{\rho_P - \rho_M}{\rho_P} \qquad (4)$$

The two equations are valid for homo- as well as multicomponent polymerizations, though in the latter case K is dependent on the compositions of the monomer mixture. For binary copolymerizations Wittmer[4] developed the equation:

$$K = K_{11}B_{11} + K_{22}B_{22} +$$
$$K_{12}B_{12} \qquad (5)$$

and proved its validity for the system ethyl acrylate/styrene. Braun *et al.*[5], too, could describe the dilatometric behaviour of the three binary copolymerizations of the monomers benzyl methacrylate, styrene and methyl methacrylate by this relation.

In a ternary system of monomers M_1, M_2 and M_3 there may result bonds of the type $-M_1M_1-$, $-M_2M_2-$ and $-M_3M_3-$ as well as $-M_1M_2-$, $-M_1M_3-$ and $-M_2M_3-$ or *vice versa*.
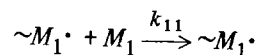
According to Wittmer's theory[4] the ii steps ($i = 1, 2, 3$) are associated with the conversion factors of the homopolymerizations K_{ii} and the ij steps ($i, j = 1, 2, 3; i \neq j$) with the alternating conversion factors K_{ij} which can be evaluated from the three binary copolymerizations by equation (5).

The overall conversion factor in a terpolymerization will thus be combined from six increments:
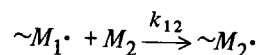
$$K = K_{11}B_{11} + K_{22}B_{22} + K_{33}B_{33} +$$
$$K_{12}B_{12} + K_{13}B_{13} + K_{23}B_{23} \qquad (6)$$

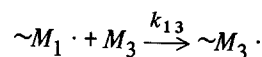The B_{ii} and B_{ij} values are the frequencies of the single bonding types in the terpolymer. These bonding frequencies can be evaluated from the following considerations. In a terpolymerization of the monomers M_1, M_2 and M_3 there exist 9 possible binary reactions of the type[6]:

$$\sim M_1^{\bullet} + M_1 \xrightarrow{k_{11}} \sim M_1^{\bullet}$$

$$v_{11} = k_{11} [\sim M_1^{\bullet}] [M_1] \qquad (7a)$$

$$\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim M_2^{\bullet}$$

$$v_{12} = k_{12} [\sim M_1^{\bullet}] [M_2] \qquad (7b)$$

$$\sim M_1^{\bullet} + M_3 \xrightarrow{k_{13}} \sim M_3^{\bullet}$$

$$v_{13} = k_{13} [\sim M_1^{\bullet}] [M_3] \qquad (7c)$$

where v_{ij} are the rates of the elementary reactions. The same is valid for the active chain ends $\sim M_2^{\bullet}$ and $\sim M_3^{\bullet}$. With respect to equation (2) the corresponding probabilities W_{ij} for the formation of a certain bond are (representative for all W_{ij}'s).

$$W_{11} = \frac{v_{11}}{\displaystyle\sum_{i=1}^{3} v_{1i}} = \frac{[M_1]}{[M_1] + \dfrac{[M_2]}{r_{12}} + \dfrac{[M_3]}{r_{13}}} \qquad (8a)$$

$$W_{12} = \frac{v_{12}}{\displaystyle\sum_{i=1}^{3} v_{1i}} = \frac{\dfrac{[M_2]}{r_{12}}}{[M_1] + \dfrac{[M_2]}{r_{12}} + \dfrac{[M_3]}{r_{13}}} \qquad (8b)$$

Table 2 Conversion factors K for the terpolymerization of BMA, styrene and MMA

M_1 $\dfrac{}{\sum_{i=1}^{3} M_i}$	M_2 $\dfrac{}{\sum_{i=1}^{3} M_i}$	M_3 $\dfrac{}{\sum_{i=1}^{3} M_i}$	ρ_P	ρ_M [g/cm^3]	K_{dens} (equation 4)	K_{dil} (equation 3)	K_{calc} (equation 6)
T_1 0.764	0.114	0.122	1.195	0.983	0.177	0.205	0.184
T_2 0.479	0.303	0.218	1.165	0.954	0.181	0.180	0.183
T_3 0.182	0.625	0.193	1.104	0.909	0.177	0.189	0.185
T_4 0.113	0.166	0.720	1.175	0.911	0.225	0.234	0.230

M_i = moles of monomer i in the monomer mixture

Table 1 Terpolymerization of BMA, styrene and MMA in bulk at 60°C with 0.5 mol % azoisobutyronitrile as initiator

	M_1 $\dfrac{}{\sum_{i=1}^{3} M_i}$	M_2 $\dfrac{}{\sum_{i=1}^{3} M_i}$	M_3 $\dfrac{}{\sum_{i=1}^{3} M_i}$	Polymerization time (min)	Conversion (%)	N.m.r. peak areas (arbitrary units) $-C_6H_5$	$-OCH_2-$	$-OCH_3$	m_1 $\dfrac{}{\sum_{i=1}^{3} m_i}$ Exp.	Calc.	m_2 $\dfrac{}{\sum_{i=1}^{3} m_i}$ Exp.	Calc.	m_3 $\dfrac{}{\sum_{i=1}^{3} m_i}$ Exp.	Calc.
BSM 1	0.148	0.568	0.284	40	5.2	355.66	35.33	77.33	0.18	0.197	0.55	0.535	0.27	0.268
BSM 2	0.424	0.125	0.451	25	7.7	291.66	84.33	101.00	0.46	0.432	0.17	0.187	0.37	0.381
BSM 3	0.622	0.229	0.149	25	6.5	358.33	99.66	26.66	0.62	0.598	0.27	0.285	0.11	0.117

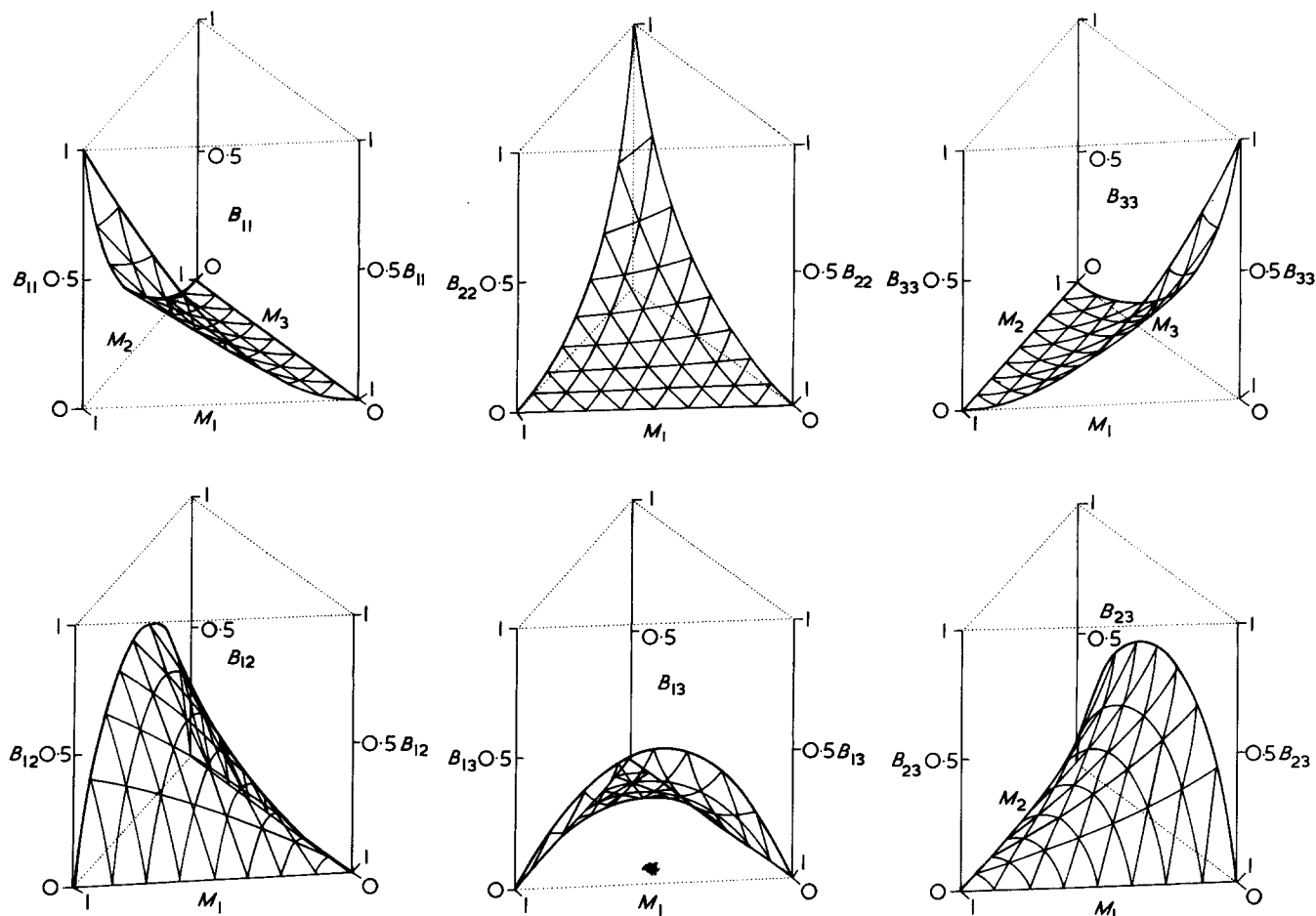M_i = moles of monomer i in the monomer mixture, m_i = moles of monomer i in the terpolymer

Figure 1 Binary bonding frequencies in terpolymerization *versus* monomer composition for the system BMA/styrene/MMA

$$W_{13} = \frac{\nu_{13}}{\sum_{i=1}^{3} \nu_{1i}} = \frac{\dfrac{[M_3]}{r_{13}}}{[M_1] + \dfrac{[M_2]}{r_{12}} + \dfrac{[M_3]}{r_{13}}}$$

(8c)

where

$$\sum_{i=1}^{3} W_{1i} = 1$$

The binary bonding frequencies in a terpolymerization can be calculated by the relations:

$B_{11} = m_1 W_{11}$ (9a)
$B_{22} = m_2 W_{22}$ (9b)
$B_{33} = m_3 W_{33}$ (9c)
$B_{12} = m_1 W_{12} + m_2 W_{21}$ (9d)
$B_{13} = m_1 W_{13} + m_3 W_{31}$ (9e)
$B_{23} = m_2 W_{23} + m_3 W_{32}$ (9f)

The m_i values are known from equation (1) — provided it is valid — and the

relation $\sum_{i=1}^{3} m_i = 1$.

Thus, by knowing the conversion factors K_{ii} of the homopolymerizations, K_{ij} of the binary copolymerizations and the B values from equations (9a)—(9f) and equation (1) the overall conversion factor of the terpolymerization can be calculated by equation (6).

In this paper experimental and theoretical conversion factors for the ternary system benzyl methacrylate (BMA), styrene and methyl methacrylate (MMA) are compared.

EXPERIMENTAL

The experimental part is described in detail in an earlier paper[5]. Terpolymers were prepared in the same way as the copolymers described, their compositions were found by n.m.r. spectroscopy. Polymer densities were determined from measurements on solutions of the terpolymers in the corresponding monomer mixtures.

RESULTS AND DISCUSSION*

Proof of the validity of Alfrey—Goldfinger's equation[1]

For this reason three different monomer mixtures have been polymerized. *Table 1* shows the experimental data as well as the theoretical composition of the terpolymers calculated from equation (1) with the reactivity ratios[5]:

r_{12}	= 0.53	r_{21}	= 0.34
r_{13}	= 1.06	r_{31}	= 0.83
r_{23}	= 0.52	r_{32}	= 0.46

The experimental and calculated values show a very good agreement and, thus, verify the applicability of equation (1).

Bonding frequencies in terpolymerization

With the aid of equations (1) and (8) the binary bonding frequencies can be calculated according to equations (9a)—(9f) for different monomer mixtures.

* For simplification the monomers BMA have been indexed with 1, styrene with 2 and MMA with 3 in the following.
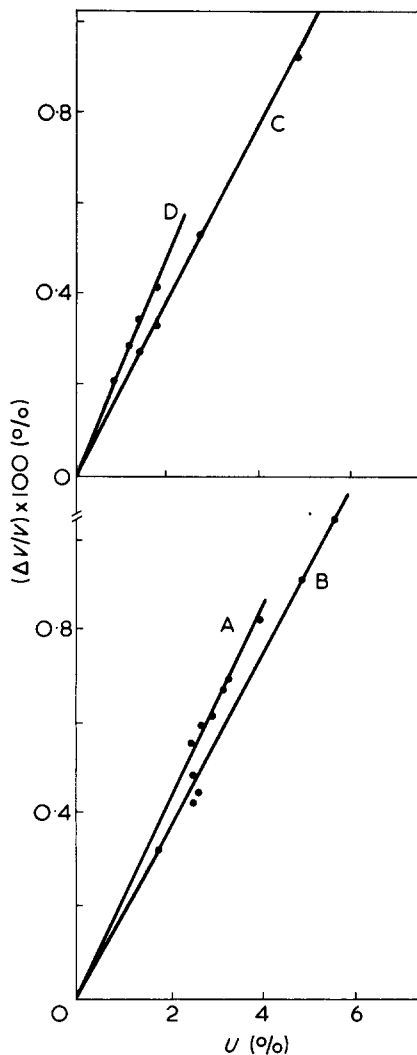
Figure 2 Relative volume change *versus* conversion for the terpolymerization of the system BMA/styrene/MMA at 60°C. A, T_1, $K = 0.205$; B, T_2, $K = 0.180$; C, T_3, $K = 0.189$; D, T_4, $K = 0.234$. Various monomer mixtures, compositions, see *Table 1*

The three dimensional graphical representation of the bonding frequencies as a function of the composition of the monomer mixture (see *Figure 1*) was carried out by a computer and gives a clear idea of the behaviour of the bonding frequencies.

Dilatometry

The results of the dilatometric studies of four different compositions of the terpolymer system BMA/styrene/MMA are represented in *Figure 2*. There is a linear dependence of the volume change on the conversion. The composition of the monomer mixtures and the evaluated conversion factors are summarized in *Table 2* together with the conversion factors calculated from density measurements of the polymers (equation 4) and the theoretical values calculated from equation (6). The K_{ii} values of the homopolymerizations and the K_{ij} values of the alternating steps in the copolymerizations, necessary for the calculation, are as follows[5]:

$$K_{11} = 0.192 \quad K_{22} = 0.170 \quad K_{33} = 0.267$$
$$K_{12} = 0.157 \quad K_{13} = 0.195 \quad K_{23} = 0.227$$

A comparison of the K values for the terpolymerization shows — except in the case of T_1 — a close agreement between the dilatometric and theoretical values. As pointed out in an earlier paper[5], K values from density measurements may show some deviation from the dilatometric values, nevertheless

in this case there is a good correspondence.

Therefore, as a conclusion it can be established that the dilatometric behaviour of the terpolymerization of the system BMA/styrene/MMA can theoretically be predicted by equation (6) developed in this work. Furthermore, as in the case of homo- and copolymerizations, the conversion factors can be confirmed by density measurements of the polymers.

ACKNOWLEDGEMENTS

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