Kinetic study of free radical bulk copolymerization of styrene–methyl methacrylate

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In an attempt to reveal the kinetic mechanism of free radical bulk copolymerization of styrene–methyl methacrylate (SMMA), experiments were conducted in sealed glass ampules at constant temperature using benzoyl peroxide as catalyst. The analysis of the various experimental data for rate of polymerization and other parameters indicate that: (a) the rate of copolymerization is lower than the homopolymerization of pure styrene and methyl methacrylate (MMA), separately and decreases gradually with increasing styrene content from ~0.2 to 0.9 mol fraction in the feed; (b) the termination mechanism in SMMA copolymerization is controlled by diffusion.

INTRODUCTION

In free radical copolymerization the instantaneous composition of the resulting copolymer is related to the monomer feed composition in terms of the rate constants for the possible propagation steps and is given by the equation known as the copolymer composition equation (1)

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{1}$$

where F_1 and f_1 represent mol fraction of monomer 1 (styrene) in the copolymer and in the feed. r_1 and r_2 are the reactivity ratios of monomer 1 (styrene) and 2 (MMA) and are given by:

$$r_1 = \frac{k_{11}}{k_{12}}, \qquad r_2 = \frac{k_{22}}{k_{21}}$$

With the exception of the particular case when $F_1 = f_1$ both the composition of the copolymer and the monomer change with time as the individual monomers will enter into the chain at different rates as the batch copolymerization reaction takes place. The change in composition with conversion can be calculated[2,3].

Two rate expressions for copolymerization are found in the literature.

$$R_P = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)R_i^{1/2}}{(r_1^2 \sigma 1^2 [M_1]^2 + 2\varphi r_1 r_2 \sigma_1 \sigma_2 [M_1][M_2] + r_2^2 \sigma 2^2 [M_2]^2)^{1/2}} \tag{2}$$

$$R_P = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)R_i^{1/2}}{k_t^{1/2}(12)(r_1[M_1]/k_{11} + r_2[M_2]/k_{22})} \tag{3}$$

where $[M_i]$ represents concentration of monomer i (in mol l^{-1}) and

$$\sigma i^2 = 2k_{tii}/K_{ii}^2$$

$$\varphi = \frac{k_{t12}}{2(k_{t11}k_{t22})^{1/2}}$$

$$R_i = 2 f k_d [I]$$

$[I]$, represents initiator concentration (in mol l^{-1}); k_{tii} and k_{ii} are termination and propagation reaction rate constants for monomer i; and $f(k_d)$ is the effective initiator decomposition rate constant. Equation 2 is based upon a chemically controlled termination mechanism. The termination mechanism in binary copolymerization is well documented in the literature, in general.

For a number of specific systems like styrene–acrylonitrile (SAN), vinyl acetate–MMA and MMA–maleic anhydride etc., kinetics have been studied. While for SAN it has been reported[4] that termination mechanism is partially diffusion controlled and partially chemically controlled, for vinyl acetate–MMA[5] and MMA–maleic anhydride[6], the termination has been reported to be diffusion controlled. However, for the system SMMA, the termination mechanism has not been established.

Our object in this work was to obtain a quantitative description of the rate of copolymerization of styrene–/MMA (in terms of the monomer reactivity ratios, monomer mixture composition and rate of copolymerization), calculation of termination rate constants $k_{t(12)}$ and value of φ in order to predict the termination mechanism in SMMA copolymerization, i.e. to measure φ and $k_{t(12)}$ and to compare the usefulness of equations (2) and (3) in describing the rate of copolymerization of styrene–methyl methacrylate.

EXPERIMENTAL

High purity monomers were obtained by deinhibiting the monomers by three shakings with 10% caustic soda solutions followed by three washings with distilled water. The monomers were kept over fused calcium chloride to remove all traces of water. The monomers were then vacuum distilled at pressure less than 100 mmHg.

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Table 1

Sample no.	Mol fraction of styrene in monomers mixture (f_1)	Mol fraction of styrene in the copolymer (F_1)	Mol fraction of styrene in the copolymer as calculated from copolymer equation[1] (F_1)	% drift
1	0.2913	0.365	0.364	0.3
2	0.4900	0.490	0.500	2.04
3	0.6916	0.653	0.643	1.53
4	0.897	0.871	0.848	2.65

Table 2 Initial rate of copolymerization at 60°C for different St-MMA mixture with Bz_2O_2 as initiator

Sample no.	Mole fraction styrene in monomer mixture	Mol fraction styrene in SMMA copolymer	Bz_2O_2 conc. [I] in mol l^{-1} x 10^3	Initial rate of copolymerization $R_p \times 10^5$ mol l^{-1} s^{-1}
1	1.0	1.0	7.6	5.0
2	1.0	1.0	15.2	7.81
3	0.897	0.871	7.6	1.6
4	0.897	0.871	15.2	2.3
5	0.6916	0.653	7.6	2.2
6	0.6916	0.653	15.2	3.19
7	0.490	0.490	7.6	2.80
8	0.490	0.490	15.2	4.23
9	0.2913	0.365	7.6	3.51
10	0.2913	0.365	15.2	5.15
11	0	0	7.6	15.04
12	0	0	15.2	26.27

Monomer mixture with four different styrene:MMA ratios ($f_1 = 0.2913, f_1 = 0.4900, f_1 = 0.6916$ and $f_1 = 0.8971$) were copolymerized in sealed glass ampules (capacity 20 ml and diameter 2 cm) using benzoyl peroxide (BDH) as the initiator. Nitrogen was bubbled inside the ampules at slow rate to remove oxygen before sealing them. Ten ampules of each ratio were polymerized for different length of time at a temperature of 60±0.1°C. Two different concentrations of benzoyl peroxide were used in the above ampules, 5 ampules with each concentration. The overall rate of polymerization was determined from the polymer yield for each ampule. The above rate determination procedure was also repeated for pure styrene and MMA, separately.

The polymers were recovered by precipitation with cold methanol. The volume of the methanol used for each precipitation was 3–4 times the volume of the reaction mixture. The polymers were then redissolved in MEK, filtered and reprecipitated in methanol. The samples were dried to constant weight in a vacuum oven at 60°C.

RESULTS AND DISCUSSION

Conversion of monomers to copolymer was limited to a maximum of 7% such that calculated[1] and experimentally obtained values for coppolymer composition may not have much drift. Braun *et al.*[7] have reported that up to ~10% conversion for system SMMA copolymerization, no appreciable change in monomer composition was found. In our case the drift has been found to be less than 3% and copolymer of relatively uniform composition (*Table 1*) were produced. Our results agree with the published data. In case of homopolymerization of styrene and MMA, the conversion was limited to a maximum of 10% and the homopolymerization rates were calculated from the yield of the polymer and are given in *Table 2*.

For all experiments plots of monomers remaining vs. time of copolymerization were made fitting the data of least squares assuming the function to be linear. Initial rate of copolymerization values were calculated from extrapolation to zero time. Data are shown in *Table 2*. Compositions of the copolymer were checked by Pregl's[8] method for elemental oxygen determination and by i.r. The data of *Table 2* are given in *Figure 1*. Using these experimental rates of copolymerization in equations (2) and (3), values of the kinetically controlled termination rate parameter φ and diffusion controlled termination rate parameter $k_{t(12)}$ for each of the two initiator concentrations were calculated and are shown in *Table 3*. The values of $k_{t(12)}$ in *Table 3* shows that they are independent of the monomer composition but show slight variation with initiator concentration.

The parameter φ compares the cross termination rate constant to the geometric mean of the termination rate constant for like pairs of radicals. A value of φ greater than 1, means that cross termination is favoured and the value of φ less than 1 is indicative of favoured homopolymerization. *Table 3* shows that φ depends upon the particular copolymer composition as well as on initiator concentration. It is known that difference in polarity is responsible for the preference for cross termination as well as for deviation from ideal copolymerization. The copolymerization of pairs of monomers of quite different polarity

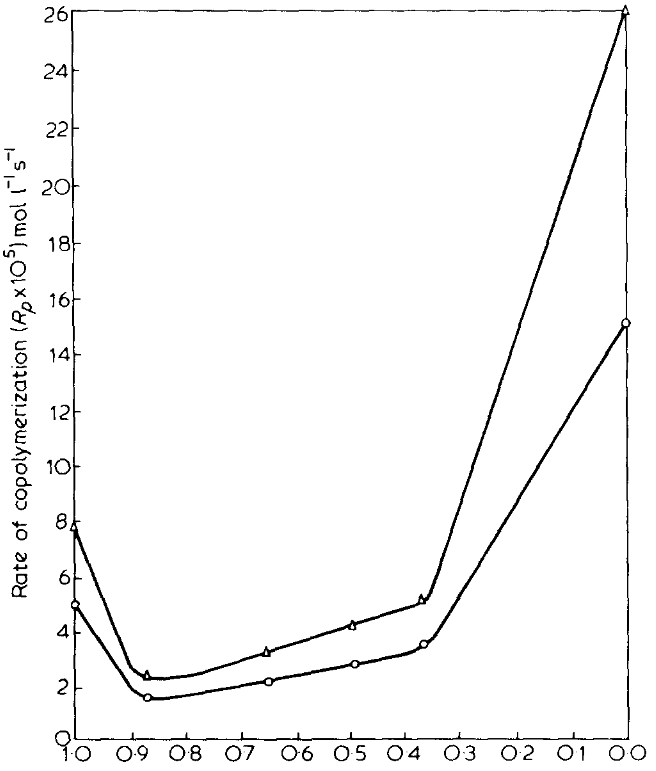

Figure 1 Variation in initial rate of copolymerization with mol fraction of styrene in feed at different initiator concentration at 60°C ○, [I] = 0.0076 mol l^{-1}; △, [I] = 0.0152 mol l^{-1}

Table 3 Termination parameter for free radical SMMA copolymerization with Bz_2O_2 at 60°C

		ϕ		$k_{t(12)} \times 10^{-8}$ in $l\ mol^{-1}\ s^{-1}$	
Sample no.	Mol fraction styrene in copolymerization	$[I] = 7.6 \times 10^{-3}$ mol l^{-1}	$[I] = 15.2 \times 10^{-3}$ mol l^{-1}	$[I] = 7.6 \times 10^{-3}$ mol l^{-1}	$[I] = 15.2 \times 10^{-3}$ mol l^{-1}
1	0.871	127.7	122.3	5.81	5.51
2	0.653	41.6	39.98	5.95	5.56
3	0.490	26.7	22.80	5.86	5.62
4	0.365	20.0	20.24	5.79	5.62
				Av 5.85	Av 5.58

Table 4 Monomers and homopolymers kinetic parameters $k_d = 2.56 \times 10^{-6}\ s^{-1}$ [a]

Monomer	$k_p = 10^{-3}$ $l\ mol^{-1}\ s^{-1}$	$k_t \times 10^{-7}$ $l\ mol^{-1}\ s^{-1}$	r_1	r_2	Ref
Styrene (M_1)	0.176	7.2			13
			0.52	0.46	14
MMA (M_2)	0.573	1.19			15

[a] The value of k_d was calculated from half life period of Bz_2O_2

is likely to be slower than the mean of the rates for the separate homopolymerization[9]. The *e*-values which are a measure of polarity, for styrene and MMA are −1 and 0 respectively[10]. So the rate of the SMMA copolymerization should be lower than that of the homopolymerization of styrene and MMA separately. This is experimentally verified as shown in *Table 2* and *Figure 1*. From *Figure 1*, it is observed that addition of small amounts of styrene (region styrene mol fraction 0 to 0.2) depresses the reaction rate markedly but after a relatively rapid drop up to styrene content 0.2 mol fraction, the copolymerization rate decreases slowly up to styrene mol fraction 0.9 and then again the rate increases sharply in the region styrene mol fraction 0.9 to 1.0 as compared to the region styrene content 0.2 to 0.9 mol fraction. The dramatic +ve and −ve slope in the region 0 to 0.2 and in 0.9 to 1.0 mol fraction of styrene respectively may be attributed to more homopolymerization in these regions. It is also reported[11] that large values of φ are obtained when the termination is diffusion controlled. This has been observed experimentally. The average percentage variation between calculated and experimental values of rate R_p using the average $k_{t(12)}$ values from *Table 3* was 3.15% at $[I] = 0.0076$ mol l^{-1} and 1.75% at $[I] = 0.0152$ mol l^{-1}. The value of parameter φ (*Table 3*) varies from 127.7 to 20.0 for $[I] = 0.0076$ mol l^{-1} and from 122.3 to 20.24 for $[I] = 0.0152$ when mol fraction of styrene decreases from 0.871 to 0.365. *Table 1* shows all values of constants for monomer or homopolymer used in this work.

North and coworkers[5,6] have pointed out that the parameter φ varies with copolymer composition in several systems. For SMMA system, Walling[9] has reported that with increasing methyl methacrylate content in the feed, the value of φ decreases. Whereas Suzuki[12] also calculated the values of the parameter φ from Walling's equation and found it to be between 9 and 23 as the mol fraction of MMA decreases from 0.8 to 0.2.

On the basis of experimentally obtained values of φ and $k_{t(12)}$ which are reported in *Table 3*, and on the basis of the literature available on the termination mechanism of SMMA copolymerization, it can be concluded that the kinetic mechanism in SMMA copolymerization is governed by diffusion controlled termination rather than chemically controlled, even at low viscosity of the reaction mass.

Finally it should be noted that whereas a simple one parameter copolymerization rate equation, such as equations (2) or (3), is convenient and easy to use, a more complex equation with 2 or more parameters might be required to describe the true physical phenomenon. Apart from this single value (unity) which has been taken as initiator efficiency it is probably dependent upon monomer composition and in reality is a variable.

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