A kinetic study on copolymerization of styrene with methyl methacrylate in the presence of zinc chloride

A. K. Srivastava and G. N. Mathur
Department of Plastics Technology, Harcourt Butler Technological Institute, Kanpur-208002, India

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The kinetics of copolymerization of styrene with methyl methacrylate in the presence of zinc chloride as a complexing agent at 50, 60 and 70°C and azobis-isobutyronitrile (AIBN) as an initiator was investigated by use of a dilatometer, modified to carry out reaction in an inert atmosphere. A 'master graph' has been prepared by which any volume contraction data could be converted into percentage conversion and the results used to calculate the rate of copolymerization (*Rp*). It has been observed that *Rp* is directly proportional to the concentration of initiator and methyl methacrylate but is inversely affected by the styrene concentration. Zinc chloride does not initiate the copolymerization reaction but increases *Rp* by increasing the rate of propagation (*Rp'*). It does not affect either the rate of initiation (*Ri*) or the rate of termination (*Rt*) since the system attains a steady state. The rate constants and activation energy have also been calculated.

INTRODUCTION

Copolymerization of a polar vinyl monomer with an electron donating monomer in the presence of a metal halide yields an equimolar alternating copolymer[1,2]. The effect of various initiators, lithium[3], styrene–maleic anhydride charge transfer complex[4] and complexing agents like diethylaluminium chloride[5] and stannic chloride[1], on the kinetics and mechanism of copolymerization of styrene(s) with methyl methacrylate (MMA) has been studied. However, there has been no detailed study in the case of zinc chloride.

In the present paper a modified dilatometric technique has been used to evaluate various kinetic parameters such as rate constants and activation energy of styrene(S) methyl methacrylate (MMA) copolymerization in presence of zinc chloride.

EXPERIMENTAL

Materials

Reagent grade monomers were purified according to the method given by Overberger[3] and were stored under nitrogen atmosphere in the presence of silica gel. Benzene was washed with sulphuric acid and water, dried over calcium chloride and sodium wire, and distilled before use. The initiator azobis-isobutyronitrile (AIBN) was recrystallized twice from alcohol before use[6]. Zinc chloride was used as such without further purification and kept in a desiccator containing anhydrous calcium chloride.

Apparatus

The dilatometer was modified in order to carry out the reaction in an inert atmosphere. The modified dilatometer consists of three parts, A, B and C. Part A is the usual glass dilatometer (bulb 3 cm long with a 6 cm long capillary of 2 mm diameter) and is attached to B which has two high vacuum stop cocks, one connected with a nitrogen line and the other to C which consists of a trap having an 8 ml capacity bulb containing ethylene glycol.

Copolymerization procedure

MMA–$ZnCl_2$ complex was prepared according to the method given by Okuzawa[7]. The initiator (AIBN) was added to the complex. This complex, followed by styrene, was injected into the dilatometer under nitrogen atmosphere. The dilatometer (total volume of reactants, 4.5 ml) was held in a water bath maintained at a particular temperature and the progress of reaction was monitored by measuring the change in level of the capillary tube of the dilatometer with a cathetometer. The contents of the dilatometer were removed after two hours and the copolymer precipitated with acidified methanol. The copolymer was washed with acrylonitrile and cyclohexane to remove polymethyl methacrylate and polystyrene, respectively, and then dried to constant weight.

The rate of copolymerization (*Rp*) was calculated by the following equation:

$$Rp(\text{mol l}^{-1}\,\text{s}^{-1}) = \frac{m \times 100}{204.2 \times 60 \times t} \qquad (1)$$

(204.2 represents combined *MWs* of methyl methacrylate and styrene monomers).

$$Rp = \frac{WU \times 1000}{100 \times 204.2 \times 60 \times t\ (\text{min})} \qquad (2)$$

$$\frac{0.9208 \times U \times 1000}{100 \times 204.2 \times 60 \times t} \qquad (3)$$

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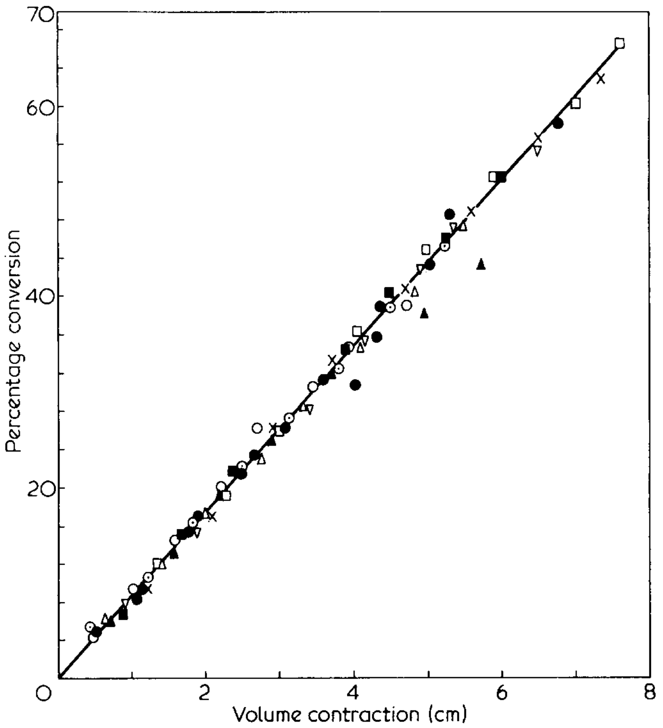

Figure 1 Master graph showing relationship between volume contraction (cm) and percentage conversion at 70°C. MMA = 0.1 mol l^{-1}: styrene = 0.1 mol l^{-1}; AIBN = 2 x 10^{-4} mol l^{-1}; $ZnCl_2$ conc. (mol l^{-1}) = ○, zero; ●, 1 x 10^{-4}; ⊙, 2 x 10^{-4}; △, 3 x 10^{-4}; ▲, 4 x 10^{-4}; ■, 5 x 10^{-4}; △, 6 x 10^{-4}; ●, 7 x 10^{-4}; X, 8 x 10^{-4}; □, 9 x 10^{-4}

$$=0.75150\times10^{-3}\times\frac{U}{t} \qquad (4)$$

where W= sum of weight of monomers per one ml = 0.9208 in the case of an equimolecular ratio of S-MMA; m = weight of copolymer per ml of reactants; U = percentage conversion per ml; and t = polymerization time in min. The intrinsic viscosity (η) of the copolymer was determined in toluene at 30°C by Ubbelohde viscometer and converted to average degree of polymerization ($\bar{P}_n$) by using the equation (5)[1]

$$\eta=5.76\times10^{-3}\times\bar{p}_n^{0.746} \qquad (5)$$

The MW of the copolymer was determined by viscometry using equation (6)

$$\eta=K[M]^{\alpha} \qquad (6)$$

where the values of K and α were taken as 13.2×10^{-5} 0.71 (ref 8).

RESULTS AND DISCUSSION

The copolymerization reaction was carried out at 50, 60 and 70°C and the volume contraction (in cms) was converted into percentage conversion by means of a 'master graph' shown in *Figure 1* (giving the data obtained at 70°C). The effect of concentration of initiator (AIBN) on Rp has been studied by varying the concentration of AIBN from zero to 4×10^{-4} mol l^{-1}. It has been observed that as the concentration of AIBN increases as the Rp increases. A graph (*Figure 2*) between log concentration of initiator and log Rp gave a straight line, the slope of which indicated the relationship between 50 and 70°C.

$$Rp\propto[\mathrm{AIBN}]^{1.6\pm0.4} \qquad (7)$$

The effect of AIBN on Rp can be explained on the basis that with increase of concentration of AIBN, the number of free radicals obtained from dissociation of AIBN increases, resulting in an increase of Rp.

The effect of styrene concentration on the Rp was studied by varying the concentration of styrene from 0.01 to 0.05 mol l^{-1} whereas the concentrations of MMA, AIBN, and $ZnCl_2$ were kept constant. It has been observed that styrene has an inverse effect on Rp. A graph between log concentration of styrene and log Rp was plotted (*Figure 3*). A straight line was obtained, the slope of which gave the relationship from 50 to 70°C.

$$\frac{1}{Rp}\propto[\mathrm{Sty}]^{1.25\pm0.75} \qquad (8)$$

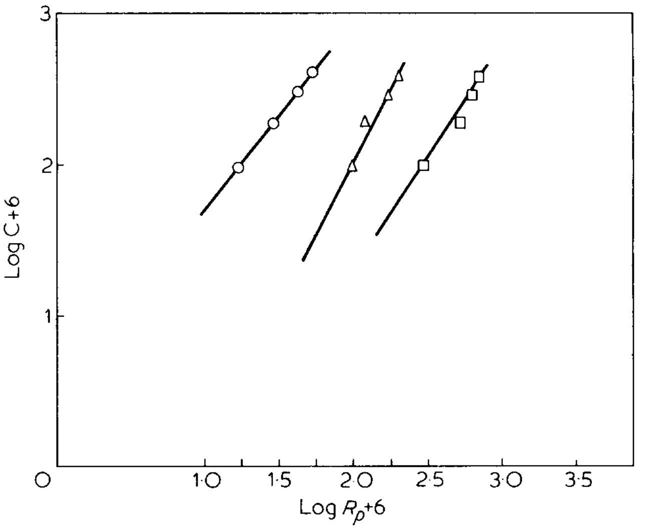

Figure 2 Graph between log concentration of AIBN and log rate of polymerization. Styrene = 0.1 mol l^{-1}; $ZnCl_2$ = 1.5 x 10^{-4} mol l^{-1}; AIBN = 2 x 10^{-4} mol l^{-1}; polymerization time = 120 min; temperature = ○, 50°C; △, 60°C; □, 70°C

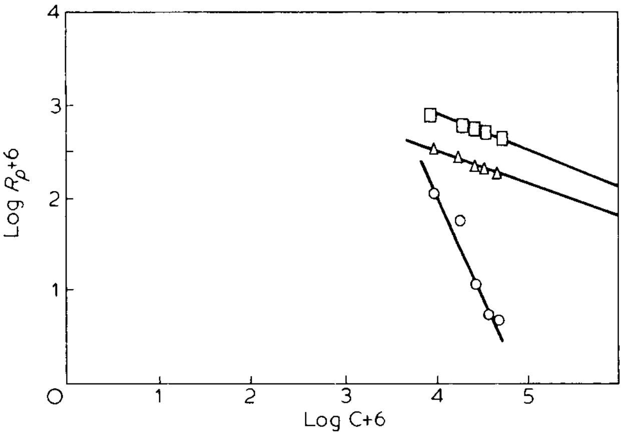

Figure 3 Graph between log concentration of styrene and log rate of polymerization. MMA = 0.1 mol l^{-1}; $ZnCl_2$ = 1.5 x 10^{-4} mol l^{-1}; AIBN = 2 x 10^{-4} mol l^{-1}; polymerization time = 120 min; temperature = ○, 50°C; △, 60°C; □, 70°C

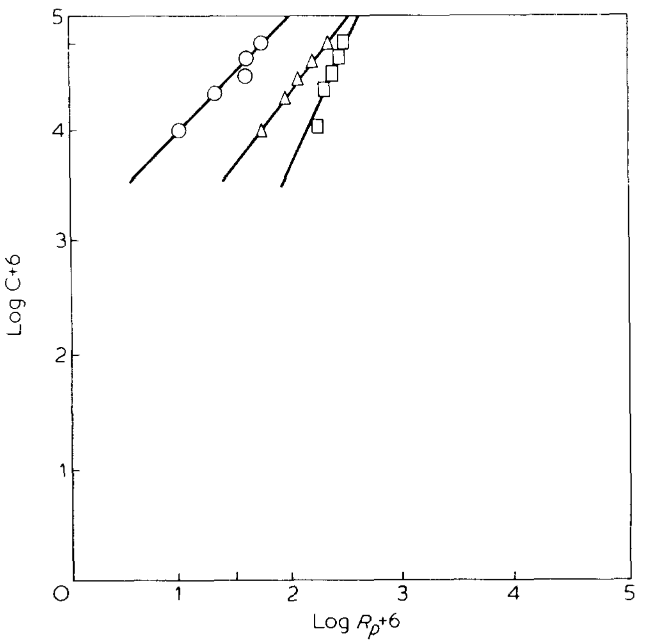

Figure 4 Graph between log concentration of methyl methacrylate and log rate of polymerization. Styrene = 0.1 mol l^{-1}; $ZnCl_2$ = 1.5×10^{-4} mol l^{-1}; AIBN = 2×10^{-4} mol l^{-1}; polymerization time = 120 min; temperature = ○, 50°C; △, 60°C; □, 70°C

The inverse effect of styrene on rate of copolymerization can be explained in that the styryl radical is stabilized due to resonance and hence is less reactive. Therefore, the Rp decreases with increase of styrene concentration.

The effect of MMA on the rate of copolymerization was studied by keeping the concentration of styrene, zinc chloride and AIBN constant and varying the concentration of MMA from 0.01 to 0.05 mol l^{-1}. It was found that the rate of copolymerization was a direct function of concentration of MMA.

A graph between $\log Rp$ and log concentration of MMA gave a straight line (*Figure 4*), the slope of which gave the relationship between 50 and 70°C.

$$Rp \propto [\mathrm{MMA}]^{1.7 \pm 0.7} \tag{9}$$

This effect of MMA on Rp can be explained by the greater reactivity of methyl methacrylate radical due to the lower resonance stabilization of the radical. As the concentration of methyl methacrylate increases, the radical concentration also increases resulting in the increase of copolymerization rate.

The effect of concentration of $ZnCl_2$ on the rate of copolymerization of styrene with MMA was studied by varying the concentration of $ZnCl_2$ from zero to 9×10^{-4} mol l^{-1} but keeping the concentration of monomers and the initiator constant.

No copolymer formed when the system lacked initiator even if concentration of $ZnCl_2$ was increased to 9×10^{-4} mol l^{-1} at 50, 60 and 70°C. This shows that this complexing agent cannot act as an initiator for copolymerization of styrene with methyl methacrylate. It has been observed that as the concentration of $ZnCl_2$ increases, the Rp also increases. *Figure 5* shows a linear relationship when log concentration of $ZnCl_2$ was plotted against log Rp, the slope of which gave following relationship between 50 and 70°C.

$$Rp \propto [\mathrm{ZnCl_2}]^{2.6 + 0.6} \tag{10}$$

Three possible explanations may be offered for increase of Rp due to $ZnCl_2$:

(1) Effect of $ZnCl_2$ on rate of decomposition of AIBN

(2) Increase in rate of propagation (Rp') due to formation of a complex between the MMA and $ZnCl_2$

(3) Decrease in rate of termination (Rt) due to an increase in viscosity of polymerization system

It has been observed[5] that a complexing agent does not accelerate the decomposition of the initiator (AIBN). Therefore $ZnCl_2$ does not affect the rate of initiation (Ri) In order to study effect of $ZnCl_2$ on the rate of termination (Rt) a graph between Rp/Rp^0 and the square root of viscosity of the system was plotted (where Rp is the rate of polymerization in presence of $ZnCl_2$ and Rp^0 is the rate of polymerization in the absence of $ZnCl_2$). A linear relationship was not obtained, showing that the termination step was not diffusion controlled and hence the rate of termination was not reduced. The above conclusions are supported further by the fact that the system attained the steady state because percentage conversion increases with polymerization time but average degree of polymerization ($\bar{p}_n$) remained constant (*Figure 6*).

Therefore, it is concluded that the acceleration effect of $ZnCl_2$ is due to increase in the rate of propagation (Rp') due to the formation of a complex between MMA and $ZnCl_2$ which lowers the activation energy. The activation energy of the system has been calculated by plotting a graph of $\log Rp$ *versus* $1/T$. When there was no $ZnCl_2$ in the system, the activation energy of the system was found to be 14.3 kcal mol^{-1}. If 1×10^{-4} mol of $ZnCl_2$ were added to the system, the activation energy decreased to 3.14 kcal mol^{-1}. If concentration of $ZnCl_2$ was increased to 9×10^{-4} mol l^{-1}, the activation energy was reduced to 2.56 kcal mol^{-1}.

The rate constant Kp has been estimated by plotting initial rate of copolymerization *versus* initial ratio of concentration of monomers. The value of slope of the graph gave the value of rate constant. The average value

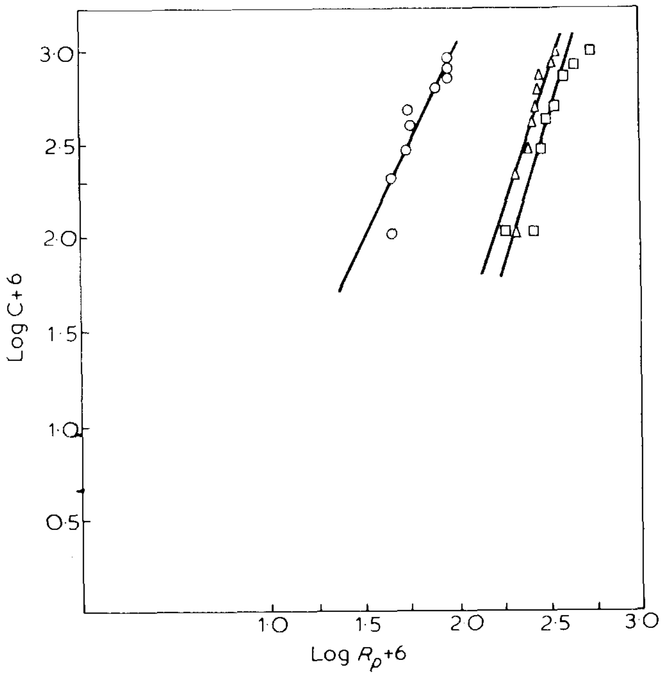

Figure 5 Graph between log concentration of zinc chloride and log rate of polymerization. MMA = 0.1 mol l^{-1}; styrene = 0.1 mol l^{-1}; AIBN = 2×10^{-4} mol l^{-1}; polymerization time = 120 min; temperature = ○, 50°C; △, 60°C; □, 70°C

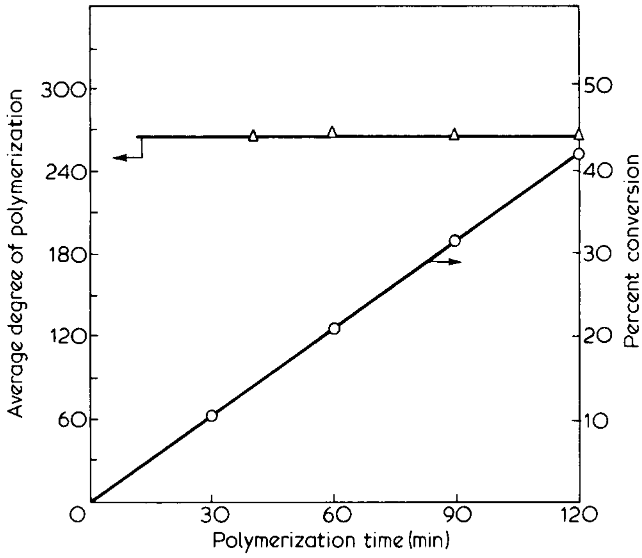

Figure 6 Relationship between polymerization time and percent conversion and average degree of polymerization. Styrene = 0.1 mol l^{-1}; MMA = 0.1 mol l^{-1}; $ZnCl_2$ = 5 x 10^{-4} mol l^{-1}; AIBN = 2 x 10^{-4} mol l^{-1}; temperature = 60°C

of rate constants has been found to be $5.5 \times 10^{-6} \pm 0.33$ $l\,mol^{-1}\,s^{-1}$ at 50°C, $3.5 \times 10^{-6} \pm 0.8$ at 60°C and 2×10^{-6} ± 0.2 at 70°C. It has also been observed that *MW* of copolymer is not a function of concentration of $ZnCl_2$. $ZnCl_2$ does not, therefore, act as a chain transfer agent.

It is concluded that $ZnCl_2$ cannot initiate copolymerization of styrene with methyl methylacrylate. It acts as an accelerator by increasing rate of propagation due to complex formation which results in the decrease of the energy of activation.

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