Bulk copolymerization of methyl methacrylate and styrene in presence of an acrylic elastomer: 1. Kinetic investigations

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(Received 11 October 1983)

The bulk copolymerization rates of methyl methacrylate and styrene in the presence and absence of an acrylic elastomer are investigated. The observed kinetic differences in systems with and without the rubber are explained in terms of the considerable influence of the elastomer macromolecules. The latter are active transfer agents in the kinetic chain propagation and they directly effect the copolymerization process. On the other hand these molecules increase the viscosity of the reaction medium and enhance the dominant influence of the diffusion factor.

(Keywords: acrylic elastomer; bulk-copolymerization; graft-copolymerization; kinetics; methyl methacrylate; styrene; energy–activation)

INTRODUCTION

The radical initiated bulk compolymerization of vinyl monomers in the presence of elastomers is well known[1-5], and is frequently used for the preparation of graft copolymers. Such copolymerization involves two simultaneous reactions: (a) formation of reactive centres on the elastomer macromolecules followed by copolymerization with the monomers, to give a graft copolymer; (b) simple polymerization or copolymerization of the monomers without participation of the rubber. The process leads to a mixture of two products, poly(methyl methacrylate-co-styrene) (MS) and poly(acrylic elastomer-g-methyl methacrylate-co-styrene) (MARS).

In the present work the conditions under which methyl methacrylate (MMA) and styrene (St) copolymerize in the presence and absence of acrylic rubber (AR), are compared.

EXPERIMENTAL

MMA and St were purified by conventional methods. The AR, based on butyl acrylate was a commercial product 'Teison gum' (Nippon Oil Seal—Japan). The benzoyl-peroxide (BDH—England) was used as initiator (0.35 wt% of the total weight of the monomers).

The kinetic investigations were carried out using dilatometric methods, and the temperature was maintained within ±0.05 deg. The reaction was interrupted when the contraction of the polymerization system became constant with the time. The polymer formed was dissolved in acetone, precipitated with heptane, and dried at 60°C for 24 h under vacuum.

RESULTS AND DISCUSSION

Temperature influence on the copolymerization rate

The copolymerizations of MMA with St in the presence and absence of AR were carried out at 70, 80 and 90°C. The rates of the processes[6], cal. are presented in *Figure 1*.

It is obvious that the rate of 'pure' (MMA/St) copolymerization (R_0) is higher than MMA/St copolymerized in the presence of AR (R_p). This is also evident from *Figure 2* which shows the temperature dependence of the copolymerization rates. The factors which influence the character of the above plots are:

(1) The elimination of a hydrogen atom at the tertiary carbon, requiring an activation energy higher than that for the opening of the double bond of a vinyl monomer[7].

(2) Not all active centres, generated on the AR, are able to initiate graft copolymerization. This is due to the steric effects of the elastomer segments or the chains still grafted onto AR. Significance of this factor increases rapidly with the reaction time.

(3) The disproportionation termination is more favourable than the recombination at high temperatures. For styrene this temperature is 80°C and under the same conditions, disproportionation termination for MMA is about 10 times higher than recombination termination.

Hence, an appreciable change in chain termination takes place and as a result the number of active centres increases. This leads to an increase of the copolymerization rate as the temperature increases.

When we compare the plots in *Figure 2* it can be seen that the temperature dependences of the copolymerization rates have decreasing differences with the reaction time. Such behaviour of the systems can be achieved by the levelling of the polymerization conditions. In the begining, the two systems (with and without AR) have different viscosities because of the influence of the dissolved AR polymer. Further, the polymer formed increases with the reaction time and simultaneously increases the viscosity. The relative difference between viscosity in these systems decreases

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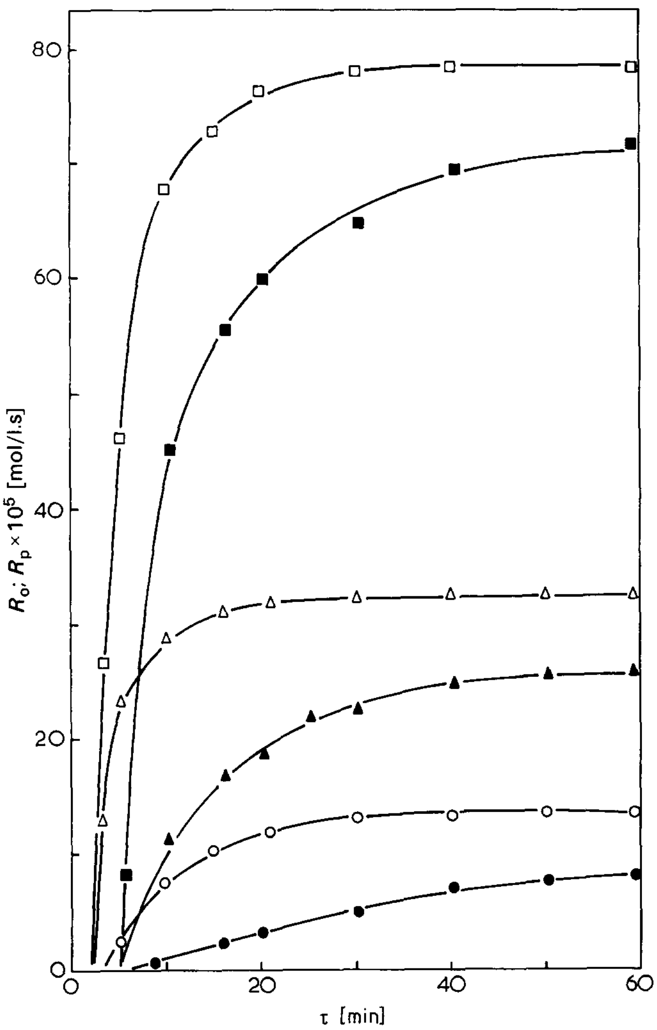

Figure 1 Rate of copolymerization of MMA with styrene (0.35 wt% benzoylperoxide-BPO); in the absence of AR, (○) 70°C, (△) 80°C, (□) 90°C; in the presence of 5 wt% AR, (●) 70°C, (▲) 80°C, (■) 90°C

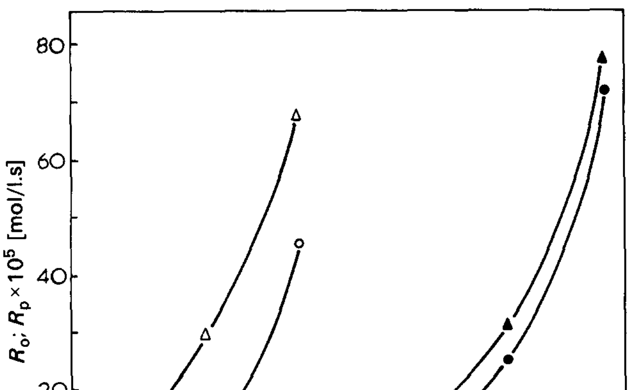

Figure 2 Rate of copolymerization *versus* temperature (0.35 wt% BPO); in the absence of AR, (△) 10th minute, (▲) 60th minute; in the presence of AR, (○) 10th minute, (●) 60th minute

even if the absolute difference remains constant. This is the meaning of the term 'levelling of the copolymerization conditions'.

Influence of rubber concentration on the copolymerization rate

The copolymerization of MMA with St was carried out in presence of different amount of AR—1 to 7 wt%. We used narrow concentration limits of AR because of its high molecular weight. High rubber concentrations (more than 7 wt%) lead to considerable enhancement of the viscosity.

The results are shown in *Figures 3*, *4* and *5*.

Figure 3 shows that two effects arise by increasing the amount of AR. These are:

(1) The retarding effect of AR on the copolymerization rate.

(2) The dependence of the maximum rate of copolymerization and the time to reach the maximum. This time increases as the elastomer concentration is increased.

Figure 4 shows a linear decrease in the copolymerization rate with increases of the rubber concentration.

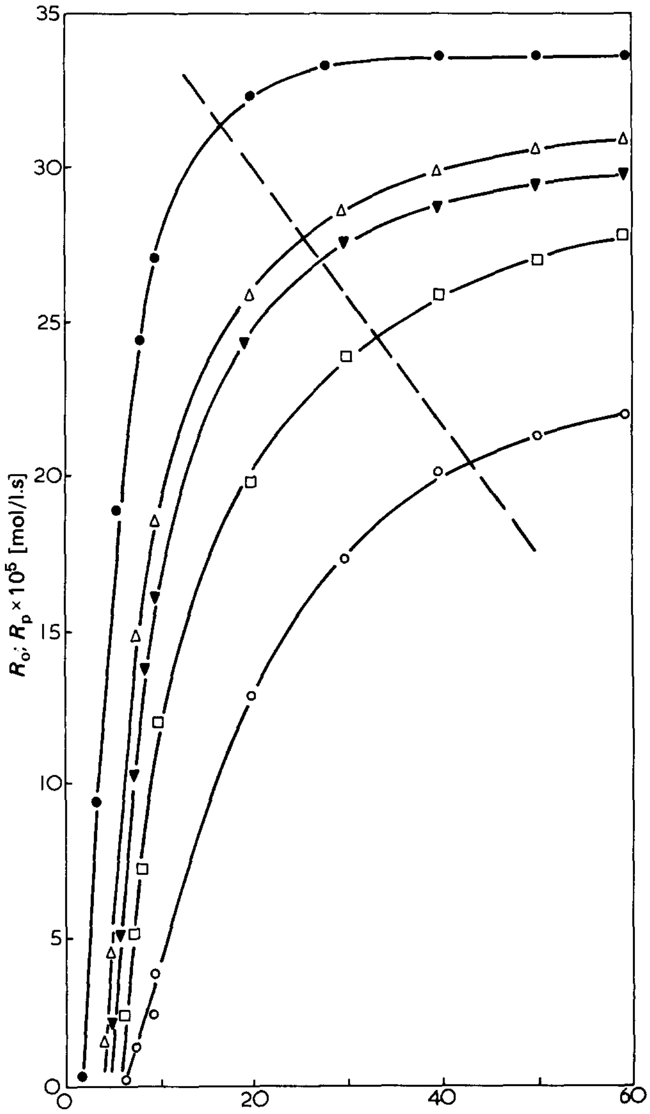

Figure 3 Rate of copolymerization for different wt% AR *versus* reaction time at 80°C and 0.35 wt% BPO: (●) 0 wt% AR; (△) 1 wt%; (▲) 3 wt%; (□) 5 wt%; (○) 7 wt%

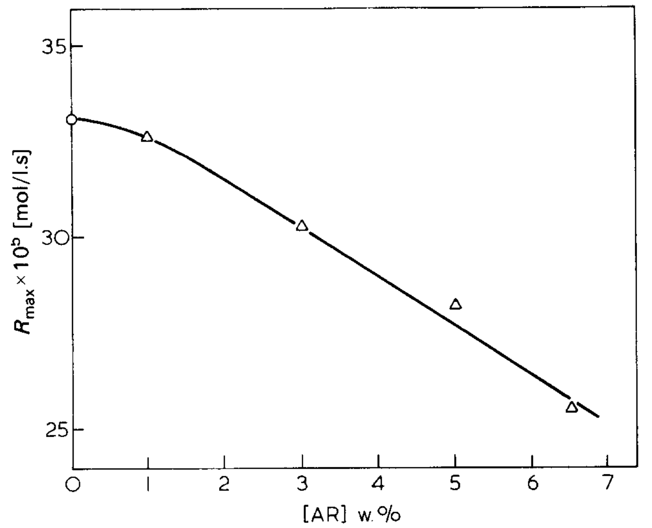

Figure 4 Dependence of maximum rate (R_{max}) of copolymerization on rubber concentration

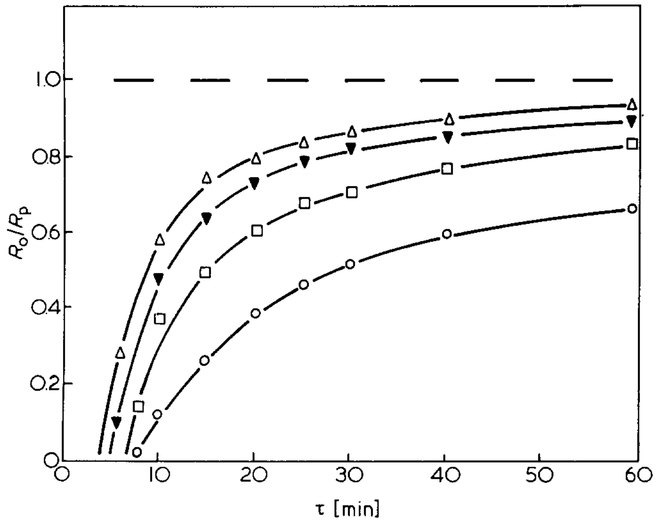

Figure 5 Change of relative velocity with the time; (△) 1 wt%; (▲) 3 wt%; (□) 5 wt%; (○) 7 wt%

In the initial phases *Figure 3* shows that the curve describing the copolymerization rate is noticably displaced from the curve without rubber, indicating that the small additions of AR effect the rate relatively stronger than the higher one. This conclusion is well illustrated in *Figure 5*, which shows that the rubber influence is strongest initially and also explains the dependences, shown on *Figure 2*.

The ability of the dissolved polymer to increase the viscosity of the reaction medium leads to a change in the factors controlling the rate, and it is established[8] that under similar conditions the diffusion has a determining role. Hence, the polymerization rate is diffusion controlled at the very beginning of the reaction, and this is the reason why the rate is retarded. In the case of copolymerization without elastomer, the influence of the diffusion factor appears later and only when the polymer is formed. The rate in the 10th minute is about 1.5 to 8.0 times lower when compared with the rate of 'pure' copolymerization. In the 60th minute, the differences are only 7% to 35%. From the plot on *Figure 5* it can be seen that the relative copolymerization rates tend to the value '1' with time, indicating once more the levelling of the copolymerization conditions in systems with and without AR.

Reaction order and total activation energy

In determining the reaction order, the results from corresponding values are given in *Figure 6*. The analysis and selection of the coordinates of the graph was done with *a priori* acceptance of the first order reaction with regard to the monomers. The evidence for the correctness of the assumption is shown by linear dependence $\log C_\tau = f(\tau)^9$. The difference between the straight line slopes is connected with the values of the rate constants—the higher value of the rate corresponding to a more rapid change of the dependence.

The change of the activation energy for different amounts of AR is presented in *Figure 7*.

The number of the potential active centres, generated on the AR, increases when the concentration of the elastomer is increased and hence, the parts of the growing

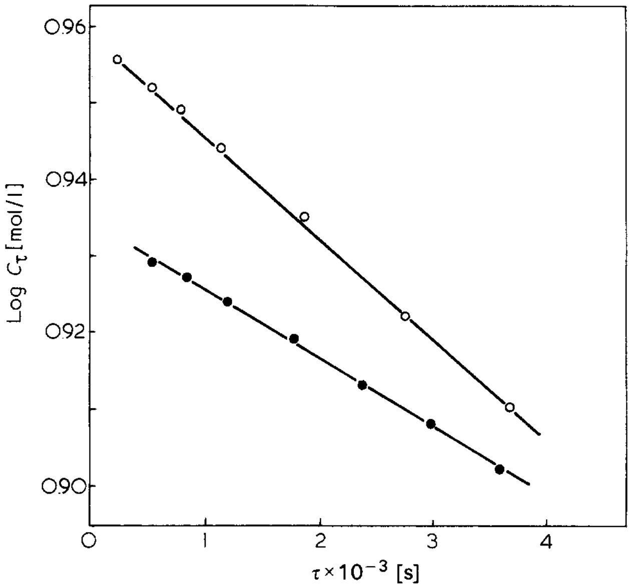

Figure 6 Log C_τ dependence on time for a first reaction order

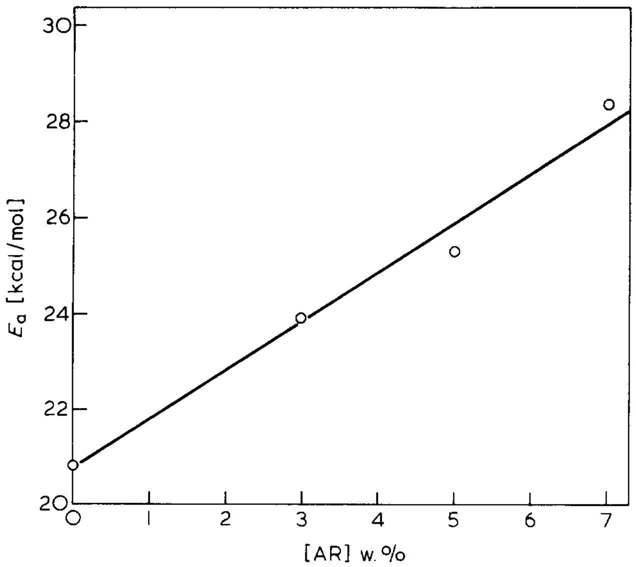

Figure 7 Total activation energy dependence on the elastomer concentration

chains, supporting such generation increases also. To explain the dependence shown in *Figure 7* it is necessary to remember that the elimination of hydrogen atom at tertiary carbon, mentioned above, requires a higher E_a. The enhanced viscosity of the reaction medium leads to diffusion control of the rate, and thus the larger amount of AR corresponds a higher value of the activation energy.

On the other hand the high value of the E_a, for the systems with AR, gives a slower reaction velocity, but a sharper acceleration of the rate with rises in temperature. That fact supports the observed dependences shown in *Figure 2*.

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