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Donor-Acceptor Complexes in Copolymerization. IX. Kinetic Features of Copolymerization of Styrene and Methyl Methacrylate. . . $Al(C_2H_5)_{1.5}Cl_{1.5}$

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SUMMARY

The kinetic features of the copolymerization of styrene and methyl methacrylate in the presence of ethylaluminum sesquichloride in toluene do not unequivocally distinguish between first- and second-order reactions. The reaction does not attain steady-state conditions. The course of the reaction is apparently influenced by many factors including the dissociation of the polymerizable complex into unreactive monomeric species and physical phenomena such as diffusion and dilution effects as well as matrix formation. The use of azobisisobutyronitrile as an initiator indicates apparent bimolecular termination but the kinetic curves show deviation from linearity.

INTRODUCTION

Completely alternating copolymers are formed when the copolymerization of styrene and methyl methacrylate is carried out in the presence of relatively large quantities of ethylaluminum sesquichloride [1]. It has been postulated that the aluminum sesquichloride-complexed methyl methacrylate reacts with styrene to form a charge transfer complex which undergoes homopolymerization

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[2, 3]. The polymerization reaction is characterized by an increase in the molecular weight of the alternating copolymer with conversion [4] and with an increase in the concentration of ethylaluminum sesquichloride [5]. The polymerization proceeds through a rapid initial stage and a slower second stage, conversions reaching 100% (based upon a 1:1 copolymer composition, irrespective of initial monomer ratio) after a sufficiently long reaction period [5].

In the previous communication [6], evidence for the participation in the copolymerization of a donor-acceptor complex between styrene and aluminum-complexed methyl methacrylate was provided by the nonconventional shape of curves representing the dependence of the reaction rate on the concentration of both monomers at a constant concentration of the aluminum compound and on the concentration of the latter at a constant concentration of the former.

The present communication discusses some kinetic features of the copolymerization reaction.

EXPERIMENTAL

The polymerization reactions were carried out using the same technique and materials as described previously [5, 6].

RESULTS AND DISCUSSION

As previously reported [5], the rate of polymerization in toluene gradually decreases from the beginning of the reaction up to the point where the monomer present in the lower concentration is completely consumed. The yield-time dependence in the early stage of the polymerization, however, indicates that there is an initial period of acceleration, followed by a stage in which the change in the reaction rate is relatively small. Conversion curves for three different temperatures and relatively short reaction times, as compared to the long reaction periods previously reported [5], are shown in Fig. 1. The decay of any monomer, in this case, can be represented by a reasonably good linear plot in the coordinates of a second-order reaction, as shown in Fig. 2.

The energy of activation, obtained from the temperature dependence shown in Fig. 1, is 10.5 kcal/mole for the initial period and 12.4 kcal/mole for the stage in which the increase in yield with time is essentially linear. However, the failure of the lines in Fig. 2 to pass through the origin indicates that the initial rate decreases during the first 15 min faster than would correspond to a bimolecular reaction.

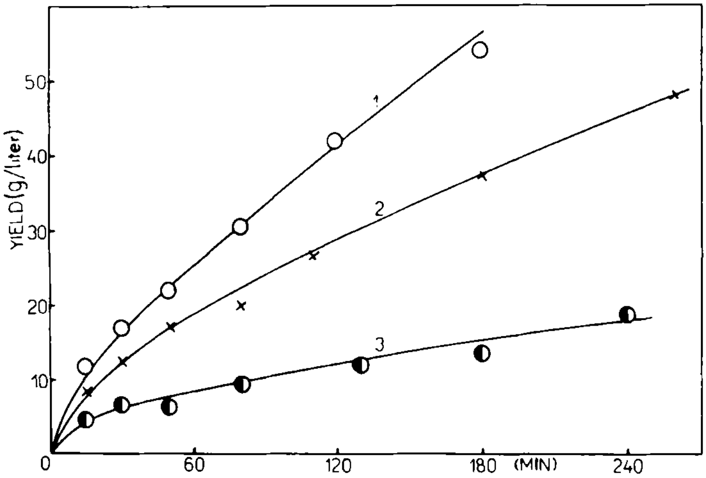

Fig. 1. Dependence of the yield on time in toluene. [MMA] = 0.7 mole/liter; [S] = 2.0 mole/liter; [$AlEt_{1.5}Cl_{1.5}$] = 0.245 mole/liter. Temperature, °C: (1) 60, (2) 30, (3) 1.

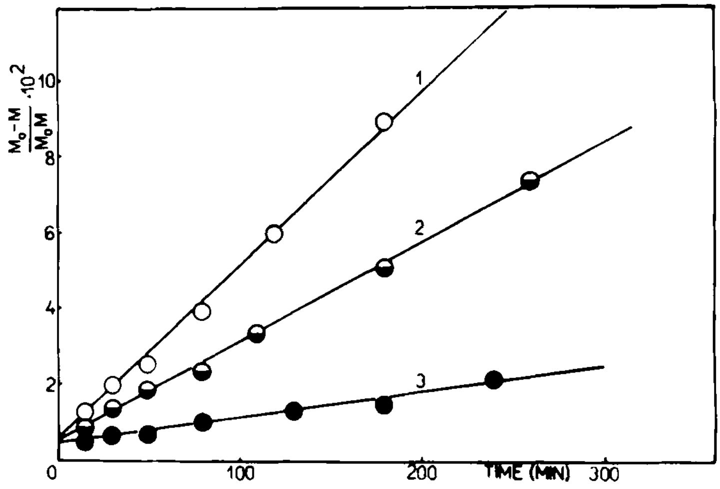

Fig. 2. Second-order plot of the curves from Fig. 1. Conditions given in the legend to Fig. 1.

When a similar plot is made over a wider time interval, the curves deviate from linearity, probably due to viscosity effects. However, the representation of conversion curves for different initial concentrations of the reaction components but for constant molar ratios of components, i.e., for different concentrations of the complex, in the coordinates of a second-order reaction should be independent of the initial concentration of the complex:

$$\frac{1}{[M]} - \frac{1}{[M_0]} = kt \qquad (1)$$

where [M] = concentration of S-MMA-Al complex at time t and $[M_0]$ = initial concentration of complex, assumed to be equal to the concentration of $AlEt_{1.5}Cl_{1.5}$ when both monomers are present in excess.

Figure 3 shows such a plot for the previously reported [5] conversion curves for four different initial concentrations of the complex. It is obvious that the slopes of these lines, which should represent the over-all reaction rate constant, are dependent upon the concentrations of the reaction components. Therefore, it may be concluded that the second-order time dependence is only apparent and not real.

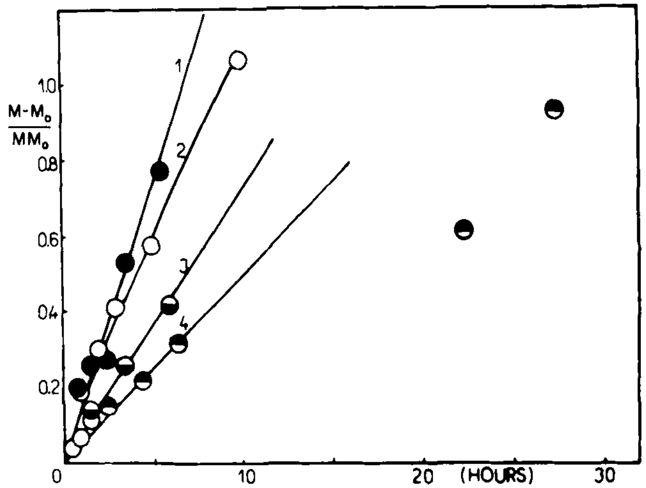

Fig. 3. Dependence of the conversion on time in the coordinates of a second-order reaction for different initial concentrations of the complex in toluene at 30°C. S/MMA/$AlEt_{1.5}Cl_{1.5}$ = 1:1:0.5. [MMA], moles/liter: (1) 0.49, (2) 0.66, (3) 0.86, (4) 1.47. See Ref. 5.

Similarly, a dependence of the reaction rate on the concentration of the complex, of the type

$$R_p = k \cdot M^{\alpha} \tag{2}$$

where α = any positive number and M = concentration of complex, does not describe the experimental data. Figure 4 shows the dependence of log R_p on log $[AlEt_{1.5}Cl_{1.5}]$ where R_p represents the yield after a 2-hr reaction period and $[AlEt_{1.5}Cl_{1.5}]$ represents the concentration at constant S/MMA/Al ratio. The curved shape of the plots provides clear evidence that the change in the concentration of the complex is not determined solely by its consumption in the polymerization. The curves in Fig. 4 are based on equimolar S/MMA ratios but different MMA/Al ratios, i.e., the excess of MMA over $AlEt_{1.5}Cl_{1.5}$ is 2.7 in Curve 1 and 5.5 in Curve 2. Both curves have essentially linear segments at lower concentrations of the complex, with a slope of 1.7 for Curve 1 and 1.3 for Curve 2. Therefore, the apparent reaction order depends upon the concentration of components, probably varying between 1 and 2.

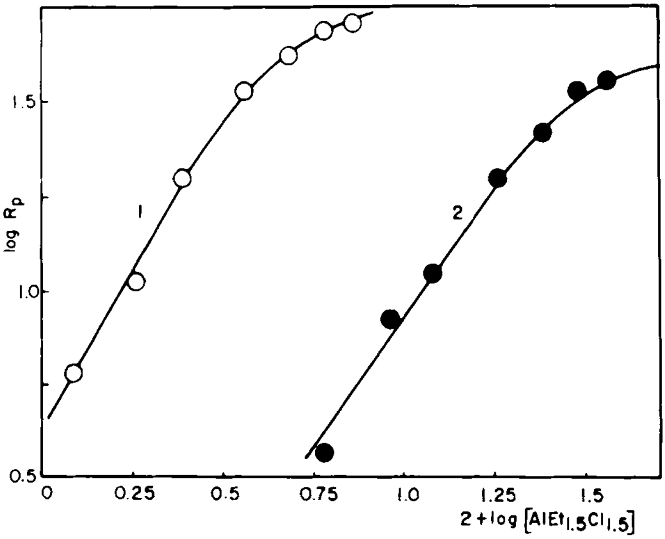

Fig. 4. Dependence of log R_p on log $[AlEt_{1.5}Cl_{1.5}]$. R_p = yield in g/liter after a 2-hr reaction period in toluene at 33°C. S/MMA/Al mole ratio: (1) 1:1:0.37, (2) 1:1:0.18.

The irregularity in the dependence of the reaction rate on the concentration of reactants is even more apparent from the data presented in Fig. 5, where the dependence of the conversion after a fixed reaction period on the concentration of reaction components passes through a maximum.

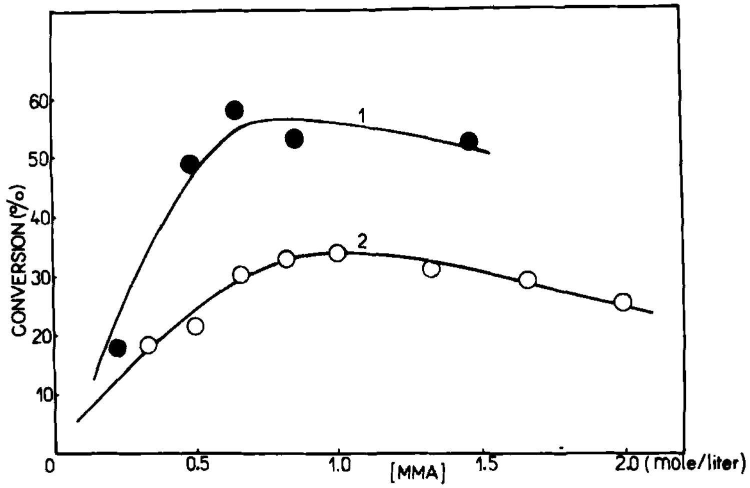

Fig. 5. Dependence of the conversion on MMA concentration in toluene at 33°C. S/MMA/$AlEt_{1.5}Cl_{1.5}$ mole ratio: (1) 1:1:0.5 (20 hr reaction), (2) 1:1:0.37 (3 hr reaction).

All of the data indicate that the course of the reaction is influenced by many factors. One such factor is the dissociation of the polymerizable complex into unreactive monomeric species. This would account for the lower reaction rates at higher conversions than indicated by the kinetic equation applicable to the initial stage of the polymerization.

The dissociation of the polymerizable complex, or at least the decrease in the concentration of the complex as the polymerization proceeds, may be the consequence of the equilibrium nature of the complex-forming reaction. The formation of the complex is the result of the collision of donor and acceptor monomers, i.e., styrene and aluminum sesquichloride-complexed methyl methacrylate.

$$S + MMA\ldots Al\lesseqgtr \rightleftharpoons [S^{+}\,{}^{-}MMA\ldots Al\lesseqgtr] \qquad (3)$$

The reaction is reversible and, therefore, complexes continually form and dissociate.

The presence of a solvent such as toluene reduces the concentration of the complex since donor monomer-solvent and acceptor monomer-solvent collisions are ineffective insofar as complex formation is concerned. The dilution effect has previously been noted in both unactivated, e.g., 2-chloroethyl vinyl ether–maleic anhydride–acrylonitrile [7], and activated, e.g., styrene–methyl methacrylate–$AlEt_{1.5}Cl_{1.5}$ [5], systems.

The initial concentration of the complex is dependent upon the solvent/monomer ratio. As the polymerization proceeds, the complex is consumed by incorporation into the polymer chain. The monomers that make up the equimolar complex consequently disappear at the same rate at which the complex is polymerized. However, since the concentration of the solvent is unaffected by the polymerization, the solvent/monomer ratio increases as the polymerization proceeds. The resultant dilution shifts the equilibrium to the left and reduces the concentration of the complex and increases the concentration of uncomplexed monomers.

Either monomer in excess over the equimolar concentration may act as a diluent. When the reaction is carried out in the presence of a free radical catalyst at a temperature where the catalyst is effective in initiating conventional free radical copolymerization, there is a shift in the product composition as the conversion increases. Thus, the much more rapid homopolymerization of the charge-transfer complex initially results in the formation of an alternating copolymer. In the absence of a radical catalyst and/or at temperatures where thermal polymerization is negligible, the reaction stops when the monomer present in the lower concentration is consumed. However, in the presence of a radical catalyst at suitable temperatures, the increase in the concentration of uncomplexed monomers as the conversion increases results in the formation of conventional free radical copolymer. Since the concentration of uncomplexed monomers is continually changing, the copolymer composition drifts with conversion. This composition drift has been noted in the polymerization of styrene–acrylonitrile in the presence of zinc chloride [8] and ethylaluminum sesquichloride [9] as well as butadiene- (and isoprene-) acrylonitrile in the presence of zinc chloride and ethylaluminum sesquichloride [10, 11].

It is an interesting paradox that the monomer concentration, i.e., free, uncomplexed monomer, may actually increase with conversion and then, under suitable conditions, decrease as conventional copolymerization occurs.

At higher concentrations of the reaction components factors of a purely physical nature become important. These factors include the effect of viscosity on monomer diffusion and a change in the nature of the reaction medium, e.g., a change in the dielectric constant at higher monomer concentrations. The alignment of the complexes in the form of a matrix has already been discussed [5, 6, 12] and may well be the most significant physical phenomenon in the complex homopolymerization.

Another complication in the attempt to determine the kinetic characteristics of the polymerization arises from the fact that the reaction does not attain steady-state conditions. As shown in Fig. 6, molecular weights increase with time, i.e., with conversion, and even pass through a maximum at lower concentrations of the reaction components.

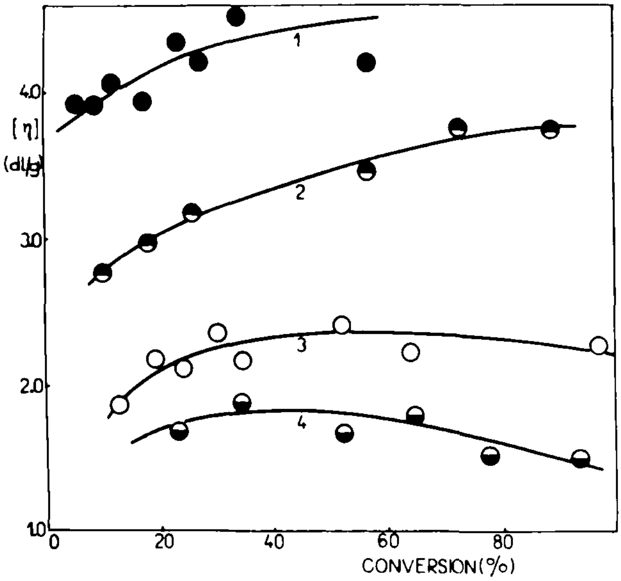

Fig. 6. Dependence of the copolymer molecular weight on conversion in toluene at 33°C. S/MMA/AlEt$_{1.5}$Cl$_{1.5}$ = 1:1:0.5. [MMA], moles/liter: (1) 0.22, (2) 0.66, (3) 0.86, (4) 1.47. [η] measured in toluene at 30°C.

In the presence of a radical precursor, even at temperatures where the latter is normally ineffective as an initiator of conventional radical polymerization, the complex homopolymerization is much faster and the molecular weights are lower than in the spontaneous, uncatalyzed polymerization [4, 5]. When azobisisobutyronitrile is used as the initiator the rate of the polymerization of the complex to alternating copolymer depends approximately linearly on the square root of the initiator concentration, indicating a bimolecular termination. However, this dependence, as shown in Fig. 7 for the polymerization at 10°C, can be considered linear only in the first approximation. The deviations, which are apparent from Fig. 7, are probably due to the interaction of the azobisisobutyronitrile with the $AlEt_{1.5}Cl_{1.5}$, as recently reported in the case of the azo compound and triethylaluminum as well as ethylaluminum halides [13].

The general kinetic features of the copolymerization of styrene and methyl methacrylate in the presence of ethylaluminum sesquichloride clearly indicate the complexity of the reaction. Additional work to clarify the picture and to delineate the contribution and the nature of the physical state of the system as well as the nature of the initiation step in the presence of free radical precursors is in progress.

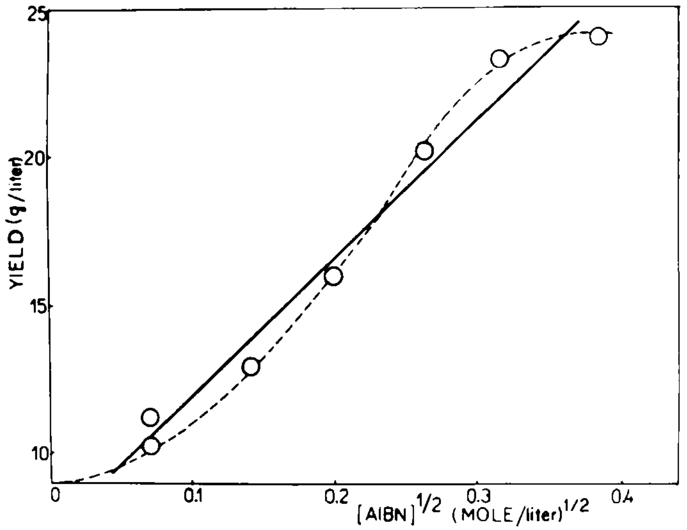

Fig. 7. Dependence of the yield (g/liter after a 2-hr reaction period in toluene at 10°C) on the square root of the concentration of azobisisobutyronitrile. [S] = [MMA] = 1 mole/liter; [$AlEt_{1.5}Cl_{1.5}$] = 0.18 mole/liter.

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