The Dependence of the Rate of Emulsion Polymerization of Methyl Methacrylate on the Soap Concentration

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Synopsis

The dependence of the rate of emulsion polymerization of methyl methacrylate on the concentration of sodium dodecyl sulfate has been studied using the $M^{z+}-N_2H_5OH$ system as initiator (where M^{z+} is Cu^{2+}, Fe^{3+}, and Mn^{3+}). It was found that the rate dependence on soap concentration was different for each initiator. The extent of this variation was:

$$Rp \ \alpha \ [Soap]^{0.18-0.55}$$

The variation is large enough to show that the dependence of the rate of emulsion polymerization on soap concentration is not simply a function of the solubility of the monomer in water, as had been suggested by Gershberg.

INTRODUCTION

The Smith-Ewart theory for emulsion polymerization leads to the conclusion that the rate of polymerization is proportional to the 0.6 power of the concentration of soap. This proportionality has been verified for styrene.[1-3]

Gershberg[4] has studied the behavior of monomers possessing a degree of water solubility. He found that for monomers with a water solubility greater than 0.04% to 0.07%, deviations from the Smith-Ewart theory occur. He proposed that the proportionality constant for the rate dependence of polymerization on soap concentration is $(x \pm 0.07)$. He stated that x varies with changing water solubility and for monomers whose water solubility is less than 0.04% to 0.07%, x is 0.6 as predicted by the Smith-Ewart theory. For methyl methacrylate, Gershberg quoted x to be 0.3 to 0.4.

Brodnyan et al.[5] concluded that the water solubility of the monomer is relatively unimportant and from a particle size study, they found x to be 0.5 for both methyl and n-butyl methacrylates. In contrast to this, Gersh-

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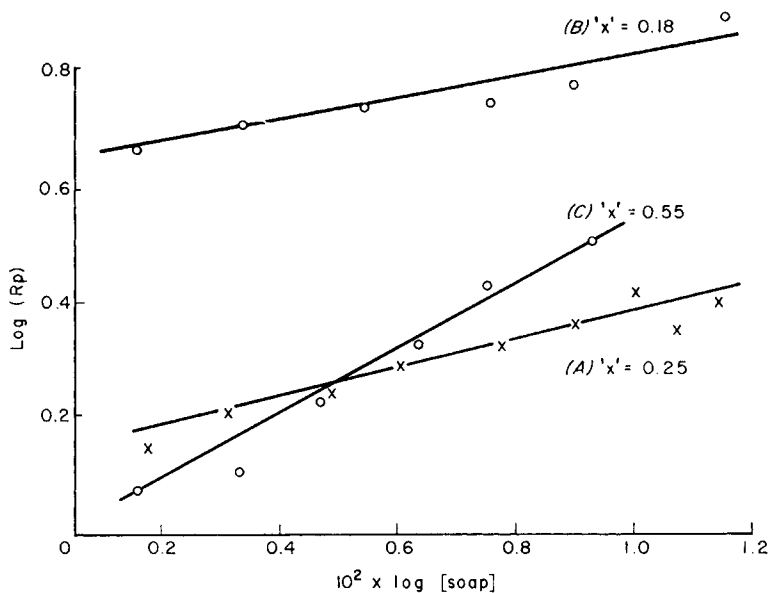
Fig. 1. Dependence of rate of polymerization of methyl methacrylate on concentration of sodium dodecyl sulfate: (A) $Fe^{3+}-N_2H_5OH-10\%$ O_2; (B) $Mn^{3+}-N_2H_5OH-10\%$ O_2 (ordinate is $10 \times \log R_p$); (C) $Mn^{3+}-N_2H_5OH$.

berg[4] concluded that the value of x Brodnyan et al. obtained in the kinetic part of their study was in accordance with his own theory.

Zimmt[6] concluded, from a particle size study, that the emulsion polymerization of methyl methacrylate follows Smith-Ewart kinetics.

It is apparent that some uncertainty exists as to whether the water solubility of the monomer affects the value of x. In an attempt to clarify the situation we have determined the value of x for the emulsion polymerization of methyl methacrylate with sodium dodecyl sulfate as soap and using four similar initiators. These are shown in Table I. The kinetics of the $Cu^{2+}-N_2H_5OH-O_2$ initiating system have been already published in this journal.[7]

EXPERIMENTAL RESULTS

The experimental method was similar to that described by Bond and Lee[7] using their "standard" reaction mixture, except that in the case of $Mn^{3+}-N_2H_5OH$, purified nitrogen was passed over the surface of the reaction mixture.

The results are summarised in Table I and the rate dependencies on the concentration of soap are shown in Figures 1a, 1b, and 1c. Both above and below the maximum and minimum soap concentrations shown in the figures, a high degree of scatter was obtained and at lower soap concentrations, suspension polymerization took place.

TABLE I
Value of x for Methyl Methacrylate Using Different Initiators

Initiator	Reaction temp, °C	Magnitude of R_p, %/min	Value of x
$Cu^{2+}-N_2H_5OH-O_2$	30	10 to 20	0.3 to 0.4 (Bond and Lee[7])
$Fe^{3+}-N_2H_5OH-$ 10% O_2	35	1 to 4	0.25
$Mn^{3+}-N_2H_5OH-$ 10% O_2	35	1 to 3	0.18
$Mn^{3+}-N_2H_5OH$ (Bond and Longbottom[8])	30	0 to 1	0.55

CONCLUSIONS

After examining the results of the three initiators utilizing oxygen (see Table I) we tentatively propose that a trend does suggest itself. It would appear that the greater the magnitude of R_p for a given set of experimental conditions, the greater the value of x. The difference in the value of x observed for the two manganic ion studies shows how necessary it is to define the reaction conditions.

It is immediately apparent from these results that the dependence of the rate of emulsion polymerization on soap concentration is not merely the simple function of monomer water solubility as proposed by Gershberg.

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