

# Solution and Emulsion Polymerization with Partially Neutralized Methacrylic Acid

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## SYNOPSIS

Polymerizations of partially neutralized methacrylic acid (MAA) were performed in both solution and emulsion systems. Polymerizations of MAA in solution were performed at an overall degree of neutralization ranging between 0 and 1. The rate of polymerization of the acid is found to decrease as the degree of neutralization increases due to increased electrostatic repulsion of the dissociated acid species (anions). The degree of neutralization of the unreacted monomer increases as the conversion increases. A kinetic model based on a copolymerization mechanism is used to describe the reaction behavior. Partially neutralized methacrylic acid was also polymerized with styrene in a seeded emulsion system. The reaction rates of both the acid and styrene decrease as the overall degree of neutralization increases. A previously developed emulsion copolymerization kinetic model is extended to account for reaction of the anions and used to investigate the overall "terpolymerization" of the acid, anions, and styrene.

## INTRODUCTION

Carboxylic acid monomers such as methacrylic acid (MAA), acrylic acid (AA), and itaconic acid (IA) are used in a large number of commercial latex products including paper coatings, textile coatings, and adhesives. These monomers are completely soluble in water. Therefore, even in an emulsion polymerization, they react to a significant extent in the aqueous phase. A kinetic model to describe emulsion copolymerization of carboxylated styrene systems was developed by Shoaf and Poehlein.<sup>1</sup> Formation of many of the commercial products using these monomer systems requires strict control of the pH of the reacting system to attain the desired properties in the final product. Often small amounts of base, such as sodium hydroxide, are added that partially neutralize the acid, thus forming anionic species. Partial neutralization of a carboxylic acid monomer such as AA or MAA reduces the overall reactivity of the monomer due to electrostatic effects of the anions. The reduced reactivity of the partially dissociated monomer has been clearly shown by

Katchalsky and Blauer,<sup>2</sup> Pinner,<sup>3</sup> and Kabanov et al.<sup>4</sup>

Mechanisms for polymerization of methacrylic acid in solution for both the unneutralized and partially neutralized cases are examined in this work. Kinetic models are used to describe the reaction behavior of both the undissociated acid and the anion. Effects of the degree of neutralization on the partition behavior and reaction rates are also examined for the MAA-styrene emulsion system. A kinetic model describing the emulsion polymerization behavior of the acid, anion, and styrene in both the particle and aqueous phases is developed and used to investigate the reaction mechanism for this complicated "terpolymerization" system.

## THEORY

### Polymerization of Carboxylic Acids

Free-radical solution polymerization of AA and MAA has been studied by several workers including Katchalsky and Blauer,<sup>2</sup> Pinner,<sup>3</sup> Blauer,<sup>5</sup> Galperina et al.,<sup>6</sup> Gromov et al.,<sup>7</sup> and Mishra and Bhadani.<sup>8</sup> Kinetic information such as reaction rates, propagation and termination constants, activation ener-

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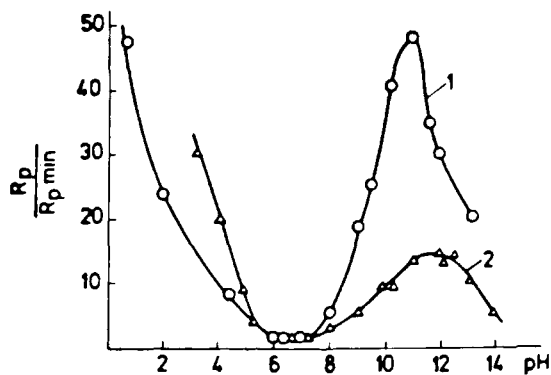
gies plus various effects of solvents and acid dissociation on these parameters have been determined through these studies. A variety of initiator systems as well as solvent species were used.

Galperina et al.<sup>6</sup> and Gromov et al.<sup>7</sup> studied the effect of solvent on radical polymerization of AA, MAA, and fluoracrylic acid. The solvents were water, formamide, and dimethylsulphoxide (DMSO). The initial rates of polymerization were proportional to the first power of the monomer concentration and the one-half power of the initiator concentration. The rate, therefore, could be described by the basic kinetic equation for free-radical polymerization.

$$R_p = k_p \left( \frac{2fk_d[I]}{2k_t} \right)^{1/2} [M] \quad (1)$$

$k_p$  is the propagation constant,  $k_t$  is the termination constant,  $k_d$  is the initiator decomposition constant,  $f$  is the initiator efficiency factor, and  $[M]$  and  $[I]$  are the monomer and initiator concentrations, respectively. Values for  $k_p$ ,  $k_t$ , and activation energies were reported for a range of temperatures. The reactions in water were carried out at low pH (2.2 and below) so that very little of the acid was dissociated. The monomer concentrations ranged from about 2 to 8 wt %.

The dependence of rate on pH, as reported by Plochocka,<sup>9</sup> is illustrated in Figure 1. The rate of polymerization decreases sharply up to pH 6 to 7. This decrease in rate is not surprising since the degree of neutralization (and thus the concentration of anions) increases sharply between pH 4 and 5.



**Figure 1** Relative rates of polymerization vs. pH adjusted by an addition of NaOH for MAA (1) and AA (2) at 60°C. Curve 1:  $R_{pmin} \times 10^5 = 0.115$  mol/L/s,  $[MAA] = 0.92$  mol/L,  $[AIBN] = 5 \times 10^{-4}$  mol/L; curve 2:  $R_{pmin} \times 10^5 = 0.43$  mol/L/s  $[AA] = 1.2$  mol/L,  $[AIBN] = 5 \times 10^{-3}$  mol/L. (Replotted from Plochocka<sup>9</sup>).

The rate then slowly increases to a maximum at a pH of 11 to 12. The increase in rate between a pH of 7 and 12 may be a result of cation binding by the carboxylate radical, which may decrease the electrostatic repulsion with an anionic monomer.<sup>9</sup>

Katchalsky and Blauer<sup>2</sup> developed general rate expressions for the homopolymerization of carboxylic acids. They noticed that at pH > 5.5 the polymerization rate approached zero, so they assumed that the dissociated species did not react. They proposed that the rate of reaction for a partially neutralized carboxylic acid system was proportional to the concentration of undissociated species as given by

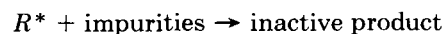
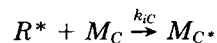
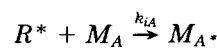
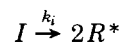
$$\frac{-d[M_{tot}]}{dt} = k_{p11} \left( \frac{fk_d}{k_{t11}} \right)^{1/2} [I]^{1/2} [M_{tot}] (1 - \alpha) \quad (2)$$

where  $[M_{tot}]$  (mol/L) is the total concentration of monomer,  $k_{p11}$  is the propagation constant (L/mol s),  $k_{t11}$  is the termination constant (L/mol s),  $f$  is the initiator efficiency factor,  $k_d$  is the initiator decomposition constant,  $[I]$  is the concentration of initiator, and  $\alpha$  is the fraction of dissociation of the acid monomer.

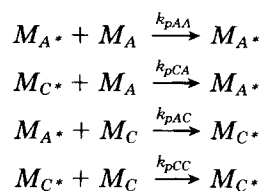
Pinner<sup>3</sup> reported that the absence of polymerization at a pH of 5.5 was probably due to inactivation of  $H_2O_2$ , the initiator used by Katchalsky and Blauer in their studies. Pinner showed that reaction occurs at pH as high as 13 is persulfate is used despite the ionization of the monomer. Blauer,<sup>5</sup> in a later article, stated that his original assertion that ionized monomer is unable to propagate polymerization was in error. He performed runs using AIBN as initiator and obtained polymerization at a pH as high as 12. Blauer<sup>5</sup> then asserted that the dependence of rate of MAA polymerization on the pH suggests that both un-ionized and ionized monomers and radicals do copolymerize.

Thus the acid ( $M_A$ ) and anion ( $M_C$ ) species do polymerize, but they exhibit very different reactivities. Therefore, Pinner<sup>3</sup> proposed that the reaction mechanism is best described by the following set of copolymerization reactions:

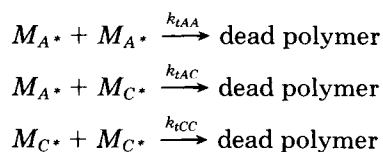
Initiation



## Propagation



## Termination



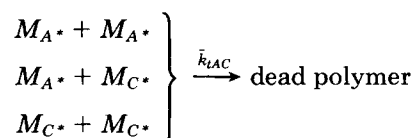
He used the rate equation based on chemical controlled termination to predict the reaction rate.

$$\begin{aligned}
 &\frac{-d([M]_A + [M]_C)}{dt} \\
 &= \frac{(r_A[M]_A^2 + 2[M]_A[M]_C + r_C[M]_C^2)R_i^{1/2}}{r_A^2\delta_A^2[M]_A^2 + 2\phi r_A r_M \delta_A \delta_C [M]_A [M]_C + r_C^2\delta_C^2[M]_C^2} \quad (3)
 \end{aligned}$$

where  $\delta_A^2 = k_{tAA}/k_{pAA}^2$ ,  $\delta_C^2 = k_{tCC}/k_{pCC}^2$ ,  $\phi = k_{tAC}/(k_{tAA}k_{tCC})^{1/2}$  = cross termination coefficient, and  $R_i = 2fk_d[I]$ .

The basic assumption for chemical controlled termination is that the termination reactions are dependent only on the nature of the end unit of the active radical chain. However, there is a great deal of uncertainty concerning the appropriate value for  $\phi$ , which represents the relative tendency for two different types of radical chain ends to terminate.

Atherton and North<sup>10</sup> later showed that many free-radical polymerization termination reactions are diffusion controlled, and the termination rate is independent of the nature of the active radical chain end. This approach utilizes a diffusion-controlled termination constant,  $\bar{k}_{tAC}$ , which depends on the monomer feed composition instead of using a constant  $\phi$  factor.



$\bar{k}_{tAC}$  is a function of the copolymer composition and for the ideal case, eq. (4) may be used.

$$\bar{k}_{tAC} = F_A k_{tAA} + F_C k_{tCC} \quad (4)$$

where  $F_i$  is the fraction of monomer  $i$  in the copolymer being formed.

The reaction rate equation developed by Atherton and North<sup>10</sup> is given by

$$R_p = \frac{(r_A[M]_A^2 + 2[M]_A[M]_C + r_C[M]_C^2)R_i^{1/2}}{\bar{k}_{tAC}^{1/2}[(r_A[M]_A/k_{pAA}) + (r_C[M]_C/k_{pCC})]} \quad (5)$$

where  $r_A$  and  $r_C$  are the reactivity ratios of the undissociated species, and dissociated species as determined from  $Q$  and  $e$  values reported in the literature;<sup>11</sup>  $[M_A]$  and  $[M_C]$  are the concentrations of undissociated and dissociated species; and  $\bar{k}_{tAC}$  is an average termination constant.

The partially neutralized solution polymerization of MAA with the copolymerization reaction mechanism based on diffusion-controlled termination is the subject of the present study. The copolymerization of partially neutralized MAA, however, is unique because the undissociated and dissociated species are in dynamic equilibrium.

Any monomer unit along the polymer backbone may change from  $M_A$  to  $M_B$  and vice versa after polymerization. Such changes result from the equilibrium that exists between the undissociated and dissociated carboxyl groups of the monomer and polymer. When the monomer is combined into a polymer chain, the carboxyl group becomes less likely to release the  $H^+$  ion and thus becomes a somewhat weaker acid relative to the single monomer molecule. Thus, the monomer and polymer exhibit different dissociation constants, and the "average" dissociation constant for the system changes as the relative amounts of monomer and polymer change. The net result is that after an  $M_A$  monomer unit reacts it may be converted to an  $M_B$  and then back to an  $M_A$  again due to the dynamic equilibrium process between the substituent carboxyl groups in the system. Therefore, the copolymer composition cannot be predicted in the conventional sense.

This equilibrium process is further complicated since the actual degree of neutralization of the unreacted monomer changes throughout the polymerization. This phenomenon occurs because the dissociation constant given by eq. (6) for the polymer differs from that of the acid:

$$K_{a_i} = \frac{[H^+][A_i^-]}{[HA_i]} \quad (6)$$

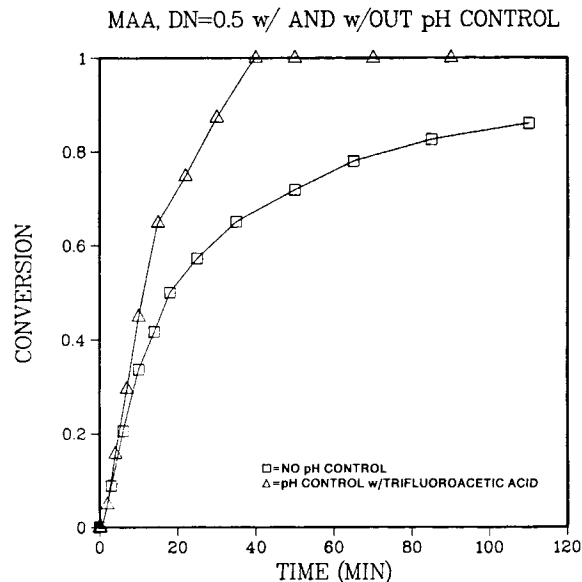
where  $[H^+]$  is the concentration of hydronium ions,  $[A_i^-]$  is the concentration of dissociated monomer  $i$

molecules, and  $[HA_i]$  is the concentration of undissociated monomer  $i$  molecules. The  $pK_a$  value for MAA and polyMAA are 4.36 and 7.0, respectively.<sup>12</sup> Because the  $pK_a$  values of the monomer and polymer differ by 2 to 3 units, the monomer may be considered to be a strong acid relative to the polymer. Hence, any dissociated monomer that reacts and becomes part of a polymer chain will develop a more basic character relative to the unreacted monomer molecules, so it may lose the  $Na^+$  ion (assuming sodium hydroxide is the base used to neutralize a portion of the acid) and become reassociated with an  $H^+$  ion. This equilibrium process will result in the dissociation of an additional monomer molecule. The net effect is that adding a base such as sodium hydroxide ( $NaOH$ ) to a mixture of acid monomer and acid polymer tends to neutralize the acid monomer first. Since the amount of monomer decreases in a reacting system, but the amount of base is constant the effective degree of neutralization of the unreacted monomer will increase as the conversion increases. [Example: Add 1.0 mol of acid, 0.25 mol base ( $DN_{overall} = 0.25$ ). After 0.75 mol of acid has reacted, the 0.25 mol of remaining acid will be completely neutralized (extreme case) resulting in  $DN_{actual} = 1.0$ .]

This changing DN of the unreacted monomer can greatly affect the reaction rates and copolymer compositions over the reaction period in a manner much different from the case where the DN of the unreacted monomer is assumed to remain the same. This assertion was confirmed experimentally by running a MAA reaction with an initial DN of about 0.59. The pH was allowed to change naturally (from 4.5 to 5.4) over the reaction period. The same reaction was then repeated, but trifluoroacetic acid was added throughout the reaction so as to maintain a constant pH (and thus constant DN of unreacted monomer) at the initial value of 4.5. Results from these runs shown in Figure 2 confirm that the reaction rate depends strongly on the DN of the system throughout the reaction period. The reaction with constant pH is much faster because the fraction of unreacted acid molecules that ionize does not increase during the reaction.

The following section describes a method for predicting the actual DN of the unreacted monomer over the entire conversion period. Equilibrium expressions for both the monomer (1) and polymer (2) are given by

$$K_{a1} = \frac{[H^+][A_1^-]}{[HA_1]} \quad (7)$$



**Figure 2** Comparison of reaction rates of 7.0 wt % MAA at initial DN of 0.59 with constant pH (pH control) and with naturally changing pH (no pH control).

$$K_{a2} = \frac{[H^+][A_2^-]}{[HA_2]} \quad (8)$$

(This analysis assumes that an average  $K_a$  value may be used for the polymer. Actually, this value depends on the chain length and chain conformation of the polymer such that a distribution of  $K_a$  values corresponding to the distribution of polymer chain lengths and chain conformations better describes the actual system.) The ratio of the  $K_{a_i}$  values gives

$$\frac{K_{a1}}{K_{a2}} = \frac{x(y-z)}{(M_A - x - y)z} \quad (9)$$

Here,  $x$  is the moles of dissociated monomer,  $y$  is the moles of reacted monomer,  $z$  is the moles of dissociated polymer, and  $M_A$  is the initial moles of monomer charged.

The total moles of dissociated species is

$$[A_1^-] + [A_2^-] = x + z = (DN_0)M_A \quad (10)$$

where,  $DN_0$  is the overall degree of neutralization, not the DN of the unreacted monomer.

Solving for  $z$  and substituting in eq. (9) gives

$$\frac{K_{a1}}{K_{a2}} = \frac{x[y - (DN_0)M_A + x]}{(M_A - x - y)[(DN_0)M_A - x]} \quad (11)$$

The value of  $x$  for any given value of  $y$  (obtained from the conversion) may be obtained by taking the positive root of this quadratic equation. The actual degree of neutralization of the unreacted monomer may then be obtained as a function of the moles of reacted monomer by

$$\text{DN}(y) = \frac{x}{M_A - y} \quad (12)$$

### Emulsion Copolymerization Model with Aqueous-Phase Polymerization

An emulsion copolymerization model that accounts for polymerization in both the particle and aqueous phases was developed by Shoaf and Poehlein.<sup>1</sup> The particle-phase reaction rates were modeled using a development presented by Nomura et al.<sup>14</sup> These equations are reproduced below:

$$R_{pA} = \frac{[1/(1+A)](k_{pAA}[M_A]_p + k_{pAB}[M_B]_p)\bar{n}_t N_p}{N_A} \quad (13)$$

$$R_{pB} = \frac{[A/(1+A)](k_{pBA}[M_A]_p + k_{pBB}[M_B]_p)\bar{n}_t N_p}{N_A} \quad (14)$$

where

$$A = \frac{\bar{n}_B}{\bar{n}_A} = \frac{k_{pAA} r_B [M_B]_p}{k_{pBB} r_A [M_A]_p} \quad (15)$$

An expression for predicting the aqueous-phase free-radical concentration was also developed.

$$[R_{tot}^*] = \frac{\sqrt{(\bar{k}_c N_p)^2 + 8\bar{k}_{tw}(\bar{k}_{des} N_p \bar{n}/N_a + 2fk_d[I_2])} - \bar{k}_c N_p}{4\bar{k}_{tw}} \quad (16)$$

This expression could then be used to predict the rates of reaction of both A and B monomers in the aqueous phases using

$$R_{pAaq} = \left( \frac{k_{pAA} + Ak_{pBA}}{1+A} \right) [R_{tot}^*]_{aq} [A]_{aq} \quad (17)$$

$$R_{pBaq} = \left( \frac{k_{pAB} + Ak_{pBB}}{1+A} \right) [R_{tot}^*]_{aq} [B]_{aq} \quad (18)$$

The overall emulsion copolymerization model then takes the form:

$$R_{ptot} = R_{pAp} + R_{pBp} + R_{pAaq} + R_{pBaq} \quad (19)$$

Details of the overall model development and methods of determining the various parameters in the rate equations are discussed by Shoaf and Poehlein.<sup>1</sup>

### Possible Approach for Modeling Emulsion Copolymerization with Carboxylic Acid Monomers at $\text{DN} > 0$

An extension of the preceding emulsion copolymerization model to account for the dissociated acid species obtained when the acid has been partially neutralized is now presented.

DN is defined as moles NaOH/moles acid fed.  $\alpha_p$  is the fraction of acid in the particle phase that is dissociated, and  $\alpha_{aq}$  as the fraction of acid in the aqueous phase that is dissociated. As long as the value of DN is greater than zero, then the overall system actually consists of three species: undissociated acid (A), styrene (B), and dissociated acid (C). (The  $\alpha$  values are not equal to zero if no base is added. However, they are very small ( $\approx 10^{-4.4}$ ) and may be approximated to be zero.) The following equations may be used to express the reaction rates in the particles.

$$R_{pA} = k_{pAA}[M_A]_p \bar{n}_A \frac{N_p}{N_A} + k_{pBA}[M_A]_p \bar{n}_B \frac{N_p}{N_A} + k_{pCA}[M_A]_p \bar{n}_C \frac{N_p}{N_A} \quad (20)$$

$$R_{pB} = k_{pBB}[M_B]_p \bar{n}_B \frac{N_p}{N_A} + k_{pAB}[M_B]_p \bar{n}_A \frac{N_p}{N_A} + k_{pCB}[M_B]_p \bar{n}_C \frac{N_p}{N_A} \quad (21)$$

$$R_{pC} = k_{pCC}[M_C]_p \bar{n}_C \frac{N_p}{N_A} + k_{pAC}[M_C]_p \bar{n}_A \frac{N_p}{N_A} + k_{pBC}[M_C]_p \bar{n}_B \frac{N_p}{N_A} \quad (22)$$

where  $[M_A]_p$  is the concentration of undissociated acid in the particle,  $[M_B]_p$  is the concentration of styrene in the particle,  $[M_C]_p$  is the concentration of dissociated acid in the particle,  $N_p$  is the number of particles/ $L_{aq}$ ,  $k_{pij}$  is the propagation constant for radical  $i$  with monomer  $j$ ,  $\bar{n}_j$  is the average number of  $j$  radicals/particle, and  $N_A$  is Avogadro's number.

The dissociated species, C, is treated like a third monomer in the above rate expressions. Nomura et al.<sup>14</sup> give expressions for the change in  $n_j$  with time

for a copolymer system. Their analysis may be extended to include the dissociated species, C:

$$\begin{aligned} \frac{d\bar{n}_A}{dt} = & \frac{\rho_e w_A}{N_p} - 2k_{tpAA} \frac{\bar{n}_A^2}{\nu_p} - k_{tpAB} \frac{\bar{n}_A \bar{n}_B}{\nu_p} - k_{tpAC} \frac{\bar{n}_A \bar{n}_C}{\nu_p} \\ & - k_{desA} \bar{n}_A - (k_{pAB} + k_{mAB}) [M_B]_p \bar{n}_A \\ & + (k_{pBA} + k_{mBA}) [M_A]_p \bar{n}_B \\ & - (k_{pAC} + k_{mAC}) [M_C]_p \bar{n}_A \\ & + (k_{pCA} + k_{mCA}) [M_A]_p \bar{n}_C = 0 \quad (23) \end{aligned}$$

where  $\rho_e$  is the rate of adsorption of radicals by the particles,  $w_A$  is the probability of adsorbed radicals becoming an A radical,  $k_{mij}$  and  $k_{tij}$  are chain transfer and termination constants, respectively, and  $k_{des}$  is a desorption constant.

Similar equations may be written for  $d\bar{n}_B/dt$  and  $d\bar{n}_C/dt$ . Summation of these equations gives

$$\begin{aligned} \frac{d\bar{n}}{dt} = & \frac{d(\bar{n}_A + \bar{n}_B + \bar{n}_C)}{dt} \\ = & \frac{\rho_e}{N_p} - 2k_{tpAA} \frac{\bar{n}_A^2}{\nu_p} - 2k_{tpAB} \frac{\bar{n}_A \bar{n}_B}{\nu_p} - 2k_{tpBB} \frac{\bar{n}_B^2}{\nu_p} \\ & - 2k_{tpAC} \frac{\bar{n}_A \bar{n}_C}{\nu_p} - 2k_{tpBC} \frac{\bar{n}_B \bar{n}_C}{\nu_p} - 2k_{tpCC} \frac{\bar{n}_C^2}{\nu_p} \\ & - (k_{desA} \bar{n}_A + k_{desB} \bar{n}_B + k_{desC} \bar{n}_C) \quad (24) \end{aligned}$$

Nomura et al. note that the termination and desorption terms in eq. (24) are at most equal to  $\rho_e/N_p$ . If the rate of desorption is relatively small,  $\rho_e \sim R_i$ , and  $w_A$  is less than unity. Therefore, Nomura et al. state that the last terms (four in this case) in eq. (23) are dominating. ( $\rho_e/N_p \approx 0.01$  to 1 and  $k_p[M_i]_p \bar{n} \approx 100$  based on typical emulsion reaction systems.) The propagation constants are usually much greater in magnitude than the chain transfer rate constants ( $k_p \gg k_m$ ) so eq. (23) can be simplified to

$$\begin{aligned} -k_{pAB} [M_B]_p \bar{n}_A + k_{pBA} [M_A]_p \bar{n}_B \\ - k_{pAC} [M_C]_p \bar{n}_A + k_{pCA} [M_A]_p \bar{n}_C = 0 \quad (25) \end{aligned}$$

Equilibrium between species A and C is described by

$$[M_A]_p = (1 - \alpha_p) [M_A]_{ptot} \quad (26)$$

$$[M_C]_p = \alpha_p [M_A]_{ptot} \quad (27)$$

where  $\alpha_p$  is the degree of neutralization or fraction of dissociation of acid in the particles, and  $[M_A]_{ptot} = [M_A]_p + [M_C]_p$  is the total amount of acid species in the particles.

If this same relationship of dissociated and undissociated acid species applies to the radicals (i.e., the presence or absence of a radical is assumed not to affect whether the carboxyl group is dissociated or undissociated), then

$$\bar{n}_A = (1 - \alpha_p) \bar{n}_{A_{tot}} \quad (28)$$

$$\bar{n}_C = \alpha_p \bar{n}_{A_{tot}} \quad (29)$$

where  $\bar{n}_{A_{tot}} = \bar{n}_A + \bar{n}_C$  is the total number of acid radicals.

Equation (25) may then be rewritten using the expressions given by eqs. (26) through (29). Rearrangement leads to the following expression:

$$\begin{aligned} A = & \frac{\bar{n}_B}{\bar{n}_{A_{tot}}} \\ = & \frac{k_{pAB} [M_B]_p + (k_{pAC} - k_{pCA}) \alpha_p [M_A]_{ptot}}{k_{pBA} [M_A]_{ptot}} \quad (30) \end{aligned}$$

Then,

$$\bar{n}_{A_{tot}} = \frac{1}{1 + A} \bar{n} \quad (31)$$

$$\bar{n}_A = (1 - \alpha_p) \frac{1}{1 + A} \bar{n} \quad (32)$$

$$\bar{n}_B = \frac{A}{1 + A} \bar{n} \quad (33)$$

$$\bar{n}_C = \alpha_p \frac{1}{1 + A} \bar{n} \quad (34)$$

Finally,

$$\begin{aligned} R_{pA} = & \left( k_{pAA} \frac{1 - \alpha_p}{1 + A} + k_{pBA} \frac{A}{1 + A} + k_{pCA} \frac{\alpha_p}{1 + A} \right) \\ & \times (1 - \alpha_p) [M_A]_{ptot} \bar{n} \frac{N_p}{N_A} \quad (35) \end{aligned}$$

$$\begin{aligned} R_{pB} = & \left( k_{pBB} \frac{A}{1 + A} + k_{pAB} \frac{1 - \alpha_p}{1 + A} + k_{pBC} \frac{\alpha_p}{1 + A} \right) \\ & \times [M_B]_p \bar{n} \frac{N_p}{N_A} \quad (36) \end{aligned}$$

$$\begin{aligned} R_{pC} = & \left( k_{pCC} \frac{\alpha_p}{1 + A} + k_{pAC} \frac{1 - \alpha_p}{1 + A} + k_{pBC} \frac{A}{1 + A} \right) \\ & \times \alpha_p [M_A]_{ptot} \bar{n} \frac{N_p}{N_A} \quad (37) \end{aligned}$$

**Reaction Rate in the Aqueous Phase with  $DN > 0$** 

The reaction rate in the aqueous phase is given by

$$\begin{aligned}
 R_{p_{aq}} &= -\left(\frac{d[M_A]_{aq} + d[M_B]_{aq} + d[M_C]_{aq}}{dt}\right) \\
 &= -\left(\frac{d[M_{A_{tot}}]_{aq} + d[M_B]_{aq}}{dt}\right) \\
 &= k_{p_{AA}}[M_{A^{\cdot}}]_{aq}[M_A]_{aq} + k_{p_{AB}}[M_{A^{\cdot}}]_{aq}[M_B]_{aq} \\
 &\quad + k_{p_{AC}}[M_{A^{\cdot}}]_{aq}[M_C]_{aq} + k_{p_{BB}}[M_{B^{\cdot}}]_{aq}[M_B]_{aq} \\
 &\quad + k_{p_{BA}}[M_{B^{\cdot}}]_{aq}[M_A]_{aq} + k_{p_{BC}}[M_{B^{\cdot}}]_{aq}[M_C]_{aq} \\
 &\quad + k_{p_{CC}}[M_{C^{\cdot}}]_{aq}[M_C]_{aq} + k_{p_{CA}}[M_{C^{\cdot}}]_{aq}[M_A]_{aq} \\
 &\quad + k_{p_{CB}}[M_{C^{\cdot}}]_{aq}[M_B]_{aq} \quad (38)
 \end{aligned}$$

where  $[M_j^{\cdot}]_{aq}$  is the concentration of  $j$  radicals in the aqueous phase.

A steady-state concentration is assumed for each type of radical.

$$\begin{aligned}
 k_{p_{AB}}[M_{A^{\cdot}}]_{aq}[M_B]_{aq} + k_{p_{AC}}[M_{A^{\cdot}}]_{aq}[M_C]_{aq} \\
 = k_{p_{BA}}[M_{B^{\cdot}}]_{aq}[M_A]_{aq} + k_{p_{CA}}[M_{C^{\cdot}}]_{aq}[M_A]_{aq} \quad (39)
 \end{aligned}$$

$$\begin{aligned}
 k_{p_{BA}}[M_{B^{\cdot}}]_{aq}[M_B]_{aq} + k_{p_{BC}}[M_{B^{\cdot}}]_{aq}[M_C]_{aq} \\
 = k_{p_{AB}}[M_{A^{\cdot}}]_{aq}[M_B]_{aq} + k_{p_{CB}}[M_{C^{\cdot}}]_{aq}[M_B]_{aq} \quad (40)
 \end{aligned}$$

$$\begin{aligned}
 k_{p_{CA}}[M_{C^{\cdot}}]_{aq}[M_A]_{aq} + k_{p_{CB}}[M_{C^{\cdot}}]_{aq}[M_B]_{aq} \\
 = k_{p_{AC}}[M_{A^{\cdot}}]_{aq}[M_C]_{aq} + k_{p_{BC}}[M_{B^{\cdot}}]_{aq}[M_C]_{aq} \quad (41)
 \end{aligned}$$

In bulk or solution polymerizations the next step is to set the rate of initiation equal to the rate of termination.

$$R_i = R_{term}$$

However, in emulsion polymerization, capture and desorption of radicals must be taken into account.

$$R_i = R_{term} + R_{capture} - R_{des}$$

Substitution of the appropriate expression leads to

$$\begin{aligned}
 R_i = 2\bar{k}_{t_{ABC}}([M_{A^{\cdot}}]_{aq} + [M_{B^{\cdot}}]_{aq} + [M_{C^{\cdot}}]_{aq})^2 \\
 + \bar{k}_c([M_{A^{\cdot}}]_{aq} + [M_{B^{\cdot}}]_{aq} + [M_{C^{\cdot}}]_{aq})N_p \\
 - \frac{\bar{k}_{des}N_p\bar{n}}{N_A} \quad (42)
 \end{aligned}$$

where  $\bar{k}_{t_{ABC}}$  is an average termination constant dependent on  $DN$ , and  $\bar{k}_c$  is an average capture constant. Since  $[M_{A^{\cdot}}]_{aq_{tot}} = [M_{A^{\cdot}}]_{aq} + [M_{C^{\cdot}}]_{aq}$ , rearrangement gives

$$\begin{aligned}
 [R_{tot}]_{aq} &= ([M_{A^{\cdot}}]_{aq_{tot}} + [M_{B^{\cdot}}]_{aq}) \\
 &\quad \frac{[-\bar{k}_c N_p \\
 &\quad + \sqrt{(\bar{k}_c N_p)^2 + 8\bar{k}_{t_{ABC}}(R_i + \bar{k}_{des}N_p\bar{n}/N_A)}]}{4\bar{k}_{t_{ABC}}} \quad (43)
 \end{aligned}$$

Initial experiments suggest that the partition of undissociated and dissociated species between the aqueous and particle phases is not the same. Therefore, a separate value for the fraction of acid in the aqueous phase, which is dissociated, denoted by  $\alpha_{aq}$ , may have to be employed. Expressions for  $[M_{A^{\cdot}}]_{aq}$  and  $[M_{C^{\cdot}}]_{aq}$  are then obtained as follows:

$$[M_{A^{\cdot}}]_{aq} = (1 - \alpha_{aq})[M_{A^{\cdot}}]_{aq_{tot}} \quad (44)$$

$$[M_{C^{\cdot}}]_{aq} = \alpha_{aq}[M_{A^{\cdot}}]_{aq_{tot}} \quad (45)$$

Substitution of eqs. (44) and (45) into eq. (39) and then rearrangement leads to expressions for  $[M_{A^{\cdot}}]_{aq_{tot}}$  and  $[M_{B^{\cdot}}]_{aq}$ .

$$[M_{A^{\cdot}}]_{aq_{tot}} = \frac{[R_{tot}]_{aq}}{1 + G} \quad (46)$$

$$[M_{B^{\cdot}}]_{aq} = \frac{[R_{tot}]_{aq}G}{1 + G} \quad (47)$$

where

$$G = \frac{k_{p_{AB}}[M_B]_{aq} + \alpha_{aq}[M_A]_{aq_{tot}}(k_{p_{AC}} - k_{p_{CA}})}{k_{p_{BA}}\alpha_{aq}[M_A]_{aq_{tot}}} \quad (48)$$

Substitution of these expressions for the total acid and styrene radical concentrations into eq. (49) gives a final expression for the rate of reaction in the aqueous phase, which involves only two measurable parameters ( $[M_A]_{aq_{tot}}$  and  $[M_B]_{aq}$ ), but which accounts for the reaction of three different species (providing that the value for  $\alpha$  in each phase is known).

$$\begin{aligned}
 R_{p_{aq}} &= \left[ k_{p_{AA}}(1 - \alpha_{aq})^2 + \left( \frac{k_{p_{AA}}}{r_{AC}} + \frac{k_{p_{CC}}}{r_{CA}} \right) \alpha_{aq}(1 - \alpha_{aq}) \right. \\
 &\quad \left. + k_{p_{CC}}\alpha_{aq}^2 \right] [M_{A^{\cdot}}]_{aq_{tot}} [M_A]_{aq_{tot}} \\
 &\quad + \left[ \frac{k_{p_{AA}}}{r_{AB}}(1 - \alpha_{aq}) + \frac{k_{p_{CC}}}{r_{CB}}\alpha_{aq} \right] [M_{A^{\cdot}}]_{aq_{tot}} [M_B]_{aq}
 \end{aligned}$$

$$+ \left[ \frac{k_{PBB}}{r_{BA}} (1 - \alpha_{aq}) + \frac{k_{PBB}}{r_{BC}} \alpha_{aq} \right] [M_{B^*}]_{aq} [M_A]_{aq, tot} + k_{PBB} [M_{B^*}]_{aq} [M_B]_{aq} \quad (49)$$

## EXPERIMENTAL

Methacrylic acid and styrene monomers (all > 99% pure) were used as received. Potassium persulfate, sodium hydroxide, and sodium dodecyl sulfate were also used as received. Carboxylated styrene seed particles (28 nm diameter) were supplied by Dow Chemical, Midland, Michigan. High-purity nitrogen (> 99%) was employed.

The following procedure was used for all solution homopolymerizations of the acids. Deionized water was added to a 1.0-L glass reactor, and it was purged with nitrogen. The stirrer consisted of a paddle agitator with a 1.5 in. Teflon blade operated at about 600 rpm. Two separate stainless-steel coils were inserted into the reactor. Heating and cooling of the reactor contents was achieved by circulating hot and cold water through the respective coils. The coils and probes inserted into the reactor for temperature measurement and sampling also served as baffles, which improved mixing in the reactor. The reaction temperature was measured with a 316 stainless-steel type-T thermocouple (temperature range  $-210$ – $160^\circ\text{C}$ ) connected to a time-proportioning digital temperature controller (OMEGA, Model 149) accurate to within  $0.5^\circ\text{C}$ . After the water and seed were brought to reaction temperature, the acid monomer was added, and then the initiator solution was injected. Samples were removed at selected times and injected into a chilled hydroquinone solution to short-stop the reaction. About 5 g of each sample were dried for gravimetric conversion analysis. Partially neutralized runs were conducted by adding enough sodium hydroxide solution to the reactor to obtain the desired initial degree of neutralization. Hydrochloric acid was then added to each

sample vial before drying to reassociate all acid in the sample. All of the acid would not volatilize unless it was completely undissociated due to the heavy cations that associated with the anionic acid species.

The standard recipe for each of the seeded emulsion copolymerization reactions is given in Table I.

All emulsion polymerization reactions were run at  $85^\circ\text{C}$  in a nitrogen purged, agitated, 1.0-L glass vessel similar to the reactor used for the solution polymerizations. The following procedure was used for each run. Carboxylated, styrene seed latex was mixed for 24–48 h with an anionic–cationic ion exchange resin (Bio-Rex MSZ 501) to remove excess surfactant. The amount of surfactant removed from the seed was determined gravimetrically. Deionized water, “cleaned” seed, and SDS (an amount that combined with the SDS remaining in the seed latex to give a concentration of  $4.0 \text{ mmol/L}_{aq}$ ) was added to the reactor. Nitrogen was bubbled into the reactor and heating was begun by pumping hot water through an internal stainless-steel coil. When the reactor temperature reached approximately  $85^\circ\text{C}$ , styrene was slowly added through a dropping funnel. The acid monomer was mixed with an appropriated amount of  $2M$  sodium hydroxide solution, then slowly added in the same manner. (Since diffusion of sodium hydroxide into the hydrophobic polymer particles is negligible, the monomer was partially neutralized before addition to the reactor.) Fast addition of either monomer would tend to “shock” the seed resulting in coagulation. The nitrogen purge line was pulled to the top level of the emulsion after the monomer addition to prevent polymer from coagulating at the interface of the nitrogen bubbles. The initiator solution was then injected.

The system was allowed to equilibrate for 1–2 min, and a sample was taken to make sure that thermal polymerization had not occurred. The relatively short equilibration time was utilized to minimize the risk of thermal polymerization occurring before addition of the initiator. Samples of 20–25 mL were extracted with a syringe at predetermined intervals

**Table I Standard Recipe for Carboxylated Emulsion Batch Copolymerizations**

$\text{K}_2\text{S}_2\text{O}_8$	5.0 mmol/ $\text{L}_{aq}$
Sodium dodecyl sulfate (SDS)	4.0 mmol/ $\text{L}_{aq}$ (CMC = 9.0 mmol/ $\text{L}_{aq}$ )
Seed (particle diameter $\sim 28 \text{ nm}$ )	$\sim 30 \text{ g}$ of solid polymer ( $\sim 4.0 \times 10^{18}$ particles/ $\text{L}_{aq}$ )
Monomer (Acid/styrene ratios)	200 g total (0/200, 20/180, 40/160, 70/130)
DI water	Balance to give 1000 g total reaction mass



throughout the reaction period. The samples were immediately injected into a chilled hydroquinone solution and immersed in an ice bath to quench the reaction. The overall conversion was measured gravimetrically by adding either HCl or trifluoroacetic acid to each sample to reassociate the acid so that it would completely evaporate, then drying about 5 g of each sample overnight in an oven, and performing a mass balance on the dried solids.

Individual monomer conversions were obtained by gas chromatography (GC) using a Varian 3300 gas chromatograph with a 12-ft stainless-steel column packed with Gas Chrom 254, 80–100 mesh packing. (The packed column was supplied by Alltech Associates, Inc. in Deerfield, Illinois.) The column was operated at 220°C. The 5.0-mL reaction sample was diluted in a mixture of SDS solution, “uncleaned” seed, an internal standard solution, and a small amount of trifluoroacetic acid to reassociate all of the unreacted monomer so that it would completely volatilize in the column. The SDS solution and seed were added to help disperse the styrene homogeneously throughout the GC samples. Styrene is essentially insoluble (0.5 g/L) in water.

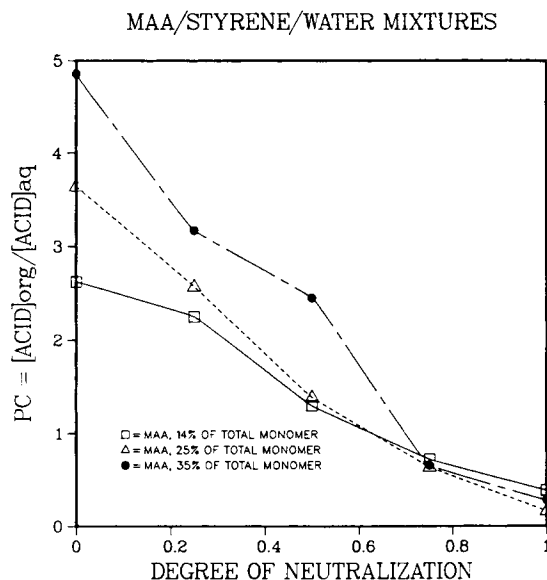
pH measurements were made using a Fisher digital pH meter with a combination electrode. A temperature probe was also immersed into the sample to account for temperature effects on the pH.

## RESULTS AND DISCUSSION

### Monomer Partitioning in Acid–Styrene–Water Mixtures—No Particles

Reaction in the aqueous phase can be significant in emulsion polymerization systems that contain one or more water-soluble monomers. Accurate prediction of the partition of monomers between the aqueous, particle, and droplet phases is necessary for determining reaction rates, copolymer compositions, and surface properties of the latex particles. A model for predicting the partition of monomers between the various phases has been developed for an emulsion copolymer system.<sup>15</sup> The model was limited to unneutralized systems where only two species, undissociated acid and styrene are present. Therefore, further study was needed to understand the effects of partially neutralizing the acid on its partition behavior.

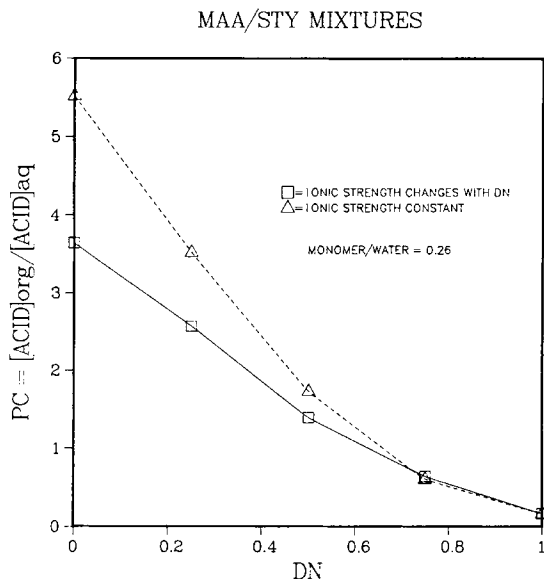
The effect of degree of neutralization (DN) on the acid partition was investigated by adding different levels of sodium hydroxide solution to acid–styrene–water mixtures. Figure 3 reveals that the



**Figure 3** Effect of degree of neutralization on the partition coefficient for MAA in an MAA–styrene–water mixture at various acid levels (25°C).

partition coefficient of MAA decreases significantly with increasing DN. The dissociated (anionic) form of the acid monomer exhibits a negative charge making it more polar than the undissociated form. The increased polarity of the dissociated monomer causes it to be more attracted to the polar water molecules in the aqueous phase as opposed to the relatively nonpolar styrene molecules in the organic phase. Thus as the fraction of dissociated monomer increases, the overall fraction of monomer, which partitions into the organic phase, decreases. The partition coefficient for MAA is also dependent on acid level at low DN, but it becomes relatively independent of acid level as DN approaches 1.0.

Addition of sodium hydroxide to increase DN changes the overall ionic strength of the solution. A simple experiment was performed to examine the effects of increasing DN without changing the overall ionic strength. Mixtures of acid, styrene, water, and sodium hydroxide were made as previously described over a range of DN from 0 to 1. The aqueous phase was separated, and titrations were performed to determine the concentration of acid in each phase. However, sodium chloride was also added in an amount that would yield an ionic strength in solution equivalent to that obtained at a DN of 1. [Example: If 1.0 mole of acid is used, then to obtain a DN of 0.25 while maintaining a constant ionic strength equivalent to that obtained at a DN of 1, 0.25 mol of sodium hydroxide (NaOH) and 0.75 mol of sodium chloride (NaCl) are added to the mixture.]



**Figure 4** Comparison of the partition coefficient of MAA between water and styrene for increasing ionic strength and constant ionic strength at DN between 0 and 1. The monomer/water ratio is 0.26, and MAA represents 25% of the total monomer. ( $T = 25^{\circ}\text{C}$ ).

Results for MAA at constant ionic strength (Fig. 4) revealed that the partition coefficient is higher for the case where the ionic strength is maintained constant than the case when the ionic strength decreases with decreasing DN. The difference in the partition coefficients measured for the two curves reflects the relative difference in the ionic strengths of the solutions over the full range of DN. The difference is large at a DN of 0, while there is no difference at a DN of 1. MAA monomer forms aggregates in solution due to hydrogen bonding between the monomer molecules.<sup>16</sup> Increasing the ionic strength may tend to disrupt these hydrogen-bonded aggregates thus forming a greater number of single molecules that more easily partition into the organic phase.

These preliminary studies show that the DN, the acid level, and the ionic strength of the solution all significantly affect the partition of MAA between styrene and water at various DN. Therefore, the addition of bases and/or buffers to regulate pH or other desired product properties in a multiphase reaction system such as an emulsion can significantly change the partitioning of carboxylic acids between the organic and aqueous phases.

### Solution Polymerization Studies

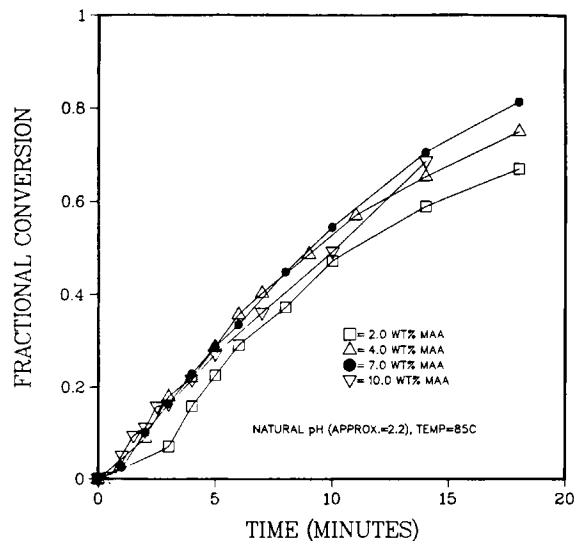
Solution polymerizations of MAA were carried out under each of the conditions listed in Table II.

**Table II** Conditions Used for Solution Polymerizations of Both MAA and AA ( $[I]_0 = 0.001M$ ).

Concentration Acid (wt %)	DN	Temperature ( $^{\circ}\text{C}$ )
2.0	0.0	85
4.0	0.0	85
7.0	0.0	85
10.0	0.0	85
7.0	0.25	85
7.0	0.50	85
7.0	0.75	85
7.0	1.00	85
7.0	0.0	70
7.0	0.0	80
7.0	0.0	90
7.0	0.0	96–98

Conversion-time curves for the natural pH (DN = 0) reactions of MAA at  $85^{\circ}\text{C}$  over a range of concentrations from 2.0 to 10.0 wt % are shown in Figure 5. The basic free-radical solution polymerization equation, which has been shown to apply to many simple solution systems, was used to examine the experimental data.

$$R_p = -\frac{dM}{dt} = k_p \frac{(2fk_d[I])^{1/2}}{(2k_t)^{1/2}} [M] \quad (50)$$



**Figure 5** Conversion-time curves for the MAA solution polymerization at various initial monomer concentrations ( $85^{\circ}\text{C}$ ).

Integration of eq. (50), assuming that only  $[M]$  varies, results in

$$\ln \frac{[M]_0}{[M]} = k_p \frac{(2fk_d[I])^{1/2}}{(2k_t)^{1/2}} t = Kt \quad (51)$$

Reaction samples were obtained over time, and monomer conversions were measured gravimetrically.  $[I]$  can be calculated as a function of time through

$$[I] = [I]_0 \exp(-k_d t) \quad (52)$$

It remained essentially constant over the short reaction period ( $< 20$  min) required for nearly completely conversion of MAA and AA. (i.e.  $[I] = 0.92[I]_0$  after 20 min). A value of  $k_d$  of  $6.89 \times 10^{-5}$  was obtained from the literature.<sup>17</sup> A value of 1.0 was used for the initiator efficiency factor  $f$ .

Gromov et al.<sup>7</sup> assumed that the reaction rate given by eq. (50) applied to both AA and MAA solution polymerizations. (Chapiro and Dulieu<sup>16</sup> and Shoaf,<sup>13</sup> however, showed that the mechanism for reaction of AA is more complicated than the simple solution polymerization scheme.) The value of  $k_p$  should then be independent of monomer concentration. Gromov does not specifically state the actual monomer concentrations utilized in their experiments. However, similar work performed with Galperina et al.<sup>6</sup> involved reactions of AA at concentrations of 3.0–4.0 wt %. The values for  $k_p$  based on the Gromov et al. data were obtained by fitting an Arrhenius expression to the data (which were given for temperature ranges of 0–60°C) and extrapolating to 85°C, the temperature of the reactions performed in this work. These experiments as well as the Gromov et al. were performed at natural pH (approximately 2.2–2.4).

Plots of  $\ln[M]_0/[M]$  versus time should be linear with a slope  $K$  based on the relationship given by eq. (51). Values of  $k_p/k_t^{1/2}$  can be obtained from this slope. Gromov et al.<sup>7</sup> reported values of  $k_t$  for MAA ( $0.12 \times 10^8$  L/mol s) from experiments utilizing the method of alternating illumination. The

values were relatively constant over a range of temperatures from 0 to 60°C, and these values were assumed to apply also at 85°C so that propagation constants could be calculated directly from  $k_p/k_t^{1/2}$  ratios. Values of  $k_p/k_t^{1/2}$  and  $k_p$  (L/mol s) obtained from the experimental data as well as those predicted from the Gromov's et al. data are listed in Table III for the range of monomer concentrations investigated.

The  $\ln[M]_0/[M]$  versus time plots for MAA are shown in Figure 6. Plots of the MAA data results in relatively straight lines as predicted by the assumed first-order kinetic model given by eq. (51). Figure 7 plots  $k_p$  values as a function of initial monomer weight percent for MAA. The data for MAA agree fairly well (within experimental error) with the  $k_p$  values predicted from the Gromov's et al. data.

### Solution Polymerizations: Experimental and Model Results with $DN > 0$

The initial rates of MAA polymerizations in solution were measured over a range of DN from 0 to 1 to check the reproducibility of the results reported by Kabanov et al.<sup>4</sup> The results are shown in Figure 8 for MAA. The rates of reaction decreased with increasing DN as expected.

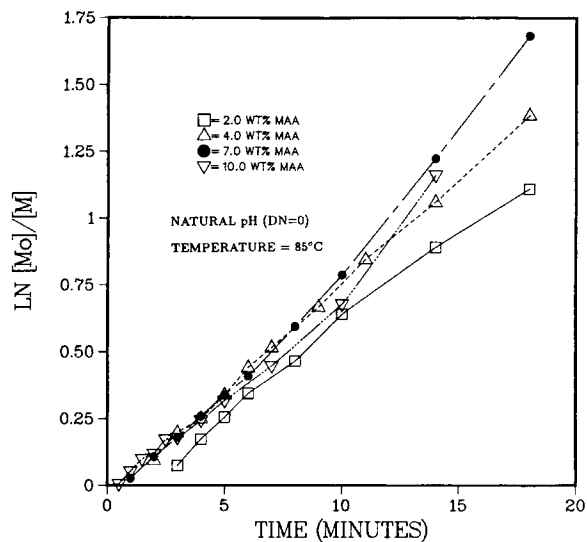
Additional unseeded solution polymerizations of MAA at DN between 0 and 1 were conducted to determine to what extent the DN of the unreacted monomer changed over the conversion period. The pH of these reactions was measured throughout the reaction period by inserting a pH probe and temperature probe into the reactor. The DN of the unreacted monomer could then be calculated with eq. (53) and the concentration of hydrogen ions as determined from the pH measurements.

$$DN = \frac{K_a/[H^+]}{1 + K_a/[H^+]} = \frac{10^{-pK_a}/10^{-pH}}{1 + 10^{-pK_a}/10^{-pH}} \quad (53)$$

Equation (12) is based on the assumption that a single value of  $K_{a2}$  may be used. The value of  $K_{a2}$

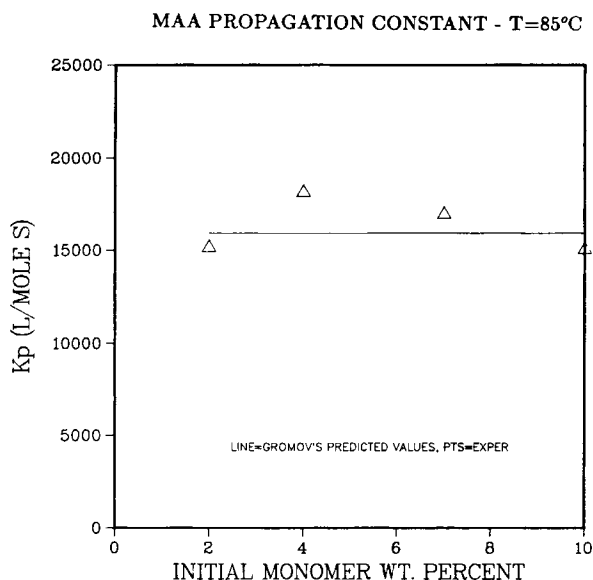
**Table III**  $k_p/k_t^{1/2}$  and  $k_p$  Values for MAA and AA at 85°C

wt %	$k_p/k_t^{1/2}$ (L/mol s) <sup>1/2</sup>	$k_{p_{\text{exper}}}$ (L/mol s)	$k_{p_{\text{Gromov}}}$ (L/mol s)
2.0	4.37	15,200	15,900
4.0	5.24	18,200	15,900
7.0	4.89	16,900	15,900
10.0	4.34	15,000	15,900

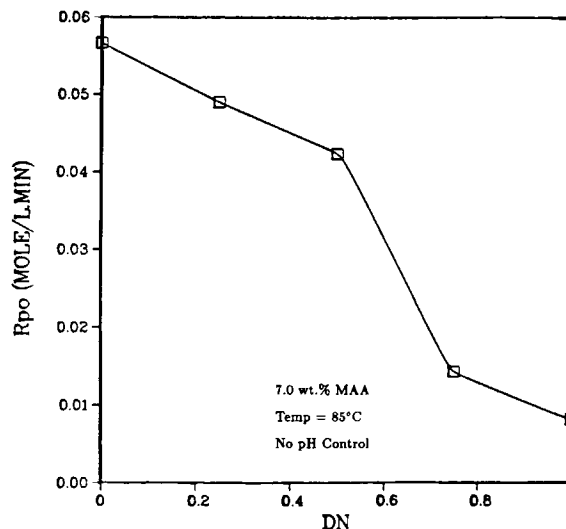


**Figure 6**  $\ln[M_0]/[M]$ -time relationship for 2.0, 4.0, 7.0, and 10.0 wt % MAA solution polymerizations at 85°C and natural pH.

has a large effect on the value of DN predicted from eq. (11) as revealed by Figure 9. The actual DN of the unreacted monomer does increase with conversion as expected (Fig. 10), but the best fit of the experimental DN-conversion data required some modification of  $K_{a2}$  from the average value of  $1.0 \times 10^{-7}$  as reported by Molyneux.<sup>12</sup> The correct value of  $K_{a2}$  for the polymer is uncertain since there are actually many values depending on the lengths and



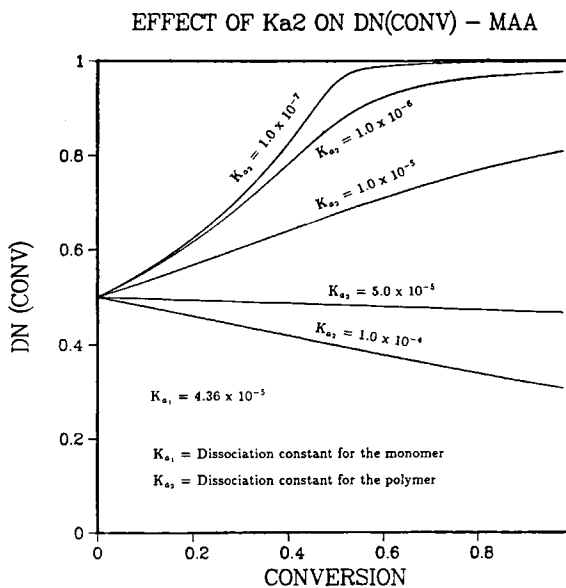
**Figure 7** Dependence of  $k_p$  on initial monomer weight percent for MAA solution polymerization at 85°C.



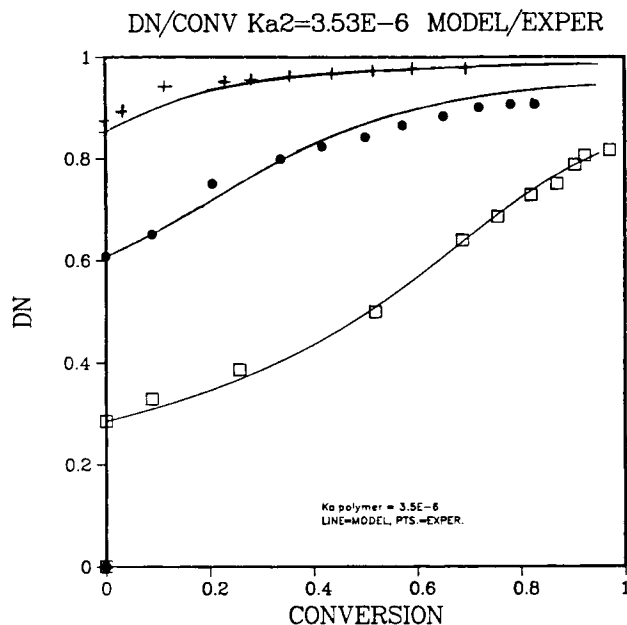
**Figure 8** Initial rates of reaction as a function of DN for 7.0 wt % MAA in solution at 85°C.

conformations of the polymer chains. Therefore,  $K_{a2}$  was adjusted in the model to give the best fit of the data. A single value of  $3.5 \times 10^{-6}$  resulted in consistent fits of the DN versus conversion plots for the full range of initial DN values examined.

The next step was to predict the reaction rate of MAA at various DN accounting for the fact that the DN of the unreacted monomer does change with conversion. Kabanov et al.<sup>4</sup> report a value of 670 L/mol s for the propagation constant ( $k_{pCC}$ ) of the MAA anion and  $2.1E8$  L/mol s for the termination

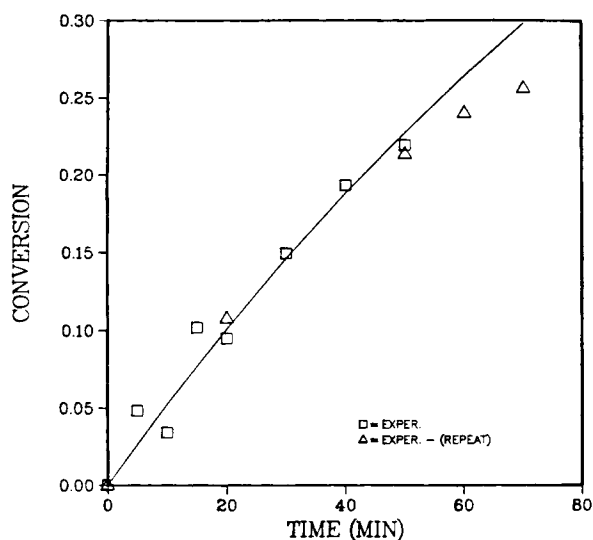


**Figure 9** Effect of  $K_{a2}$  on the predicted DN as a function of conversion with an overall DN of 0.5.



**Figure 10** Comparison of predicted DN as a function of conversion with experimental values ( $K_{a2}$  of  $3.5 \times 10^{-6}$ ).

constant at 23°C. A value for  $k_{pCC}$  at 85°C was obtained by fitting experimental conversion data of MAA obtained at a DN of 1.0 using the basic solution polymerization equation since at a DN of 1.0, only one reaction species, the anions, will be present in the system. The best fit was obtained with a  $k_{pCC}$  of 5000 L/mol s (Fig. 11). (The  $k_t$  value was assumed not to change significantly with temperature. Values



**Figure 11** Fit of conversion-time data for the MAA anion at 85°C using the solution polymerization equation, a value of  $k_t$  of  $2.1 \times 10^8$  (L/mol s) as reported by Plochocka<sup>9</sup> and an adjustable propagation constant,  $k_{pCC}$ . The best fit was obtained with a  $k_{pCC}$  of 5000 (L/mol s).

of  $k_t$  reported by Kabanov et al.<sup>4</sup> for the unneutralized MAA polymerization were constant over a temperature range of 20–60°C.)

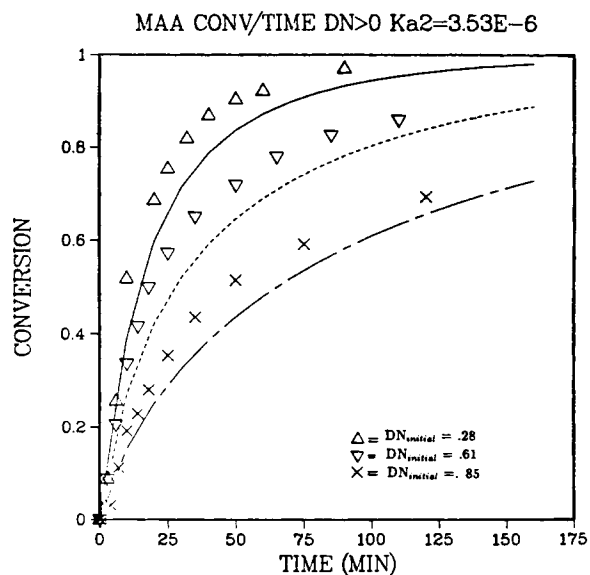
The copolymer model was modified to account for the changing DN with conversion by using eq. (12). The results of the model using a  $K_{a2}$  value of  $3.5 \times 10^{-6}$  are shown in Figure 12. The predicted conversion-time results slightly underestimate the experimental data for all initial DN values.

A further adjustment of  $K_{a2}$  was then made in order to obtain a better fit to the conversion-time data. Figure 13 shows that a good fit of the reaction data is obtained for all initial DN values if a value of  $K_{a2}$  of  $8.0 \times 10^{-6}$  is used. The predicted DN was recalculated using the adjusted  $K_{a2}$  value and compared to the measured values as exhibited in Figure 14. The predicted values are close to the observed values, but in each case the observed values are slightly underestimated.

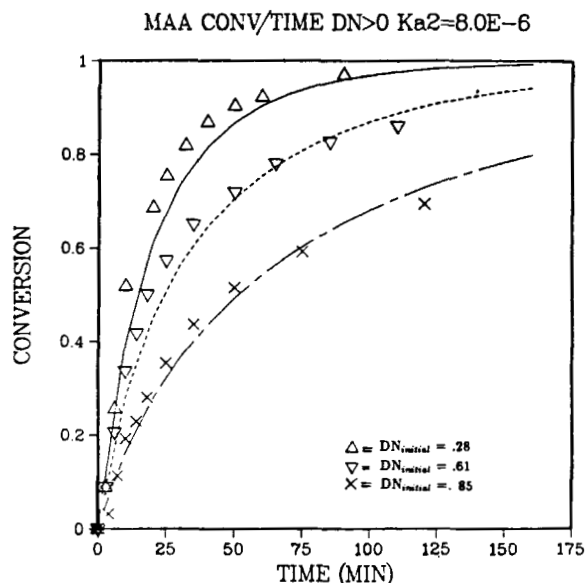
Therefore, good fits of both DN-conversion data and conversion-time data can be obtained using a solution copolymerization model that accounts for the change in DN of the unreacted monomer with conversion for a wide range of initial DN values. However, some discrepancy between the values of  $K_{a2}$  that give consistent fits of both types of data, simultaneously, still remains.

#### Acid-Styrene Emulsion Copolymerization: Experimental and Model Results with $DN > 0$

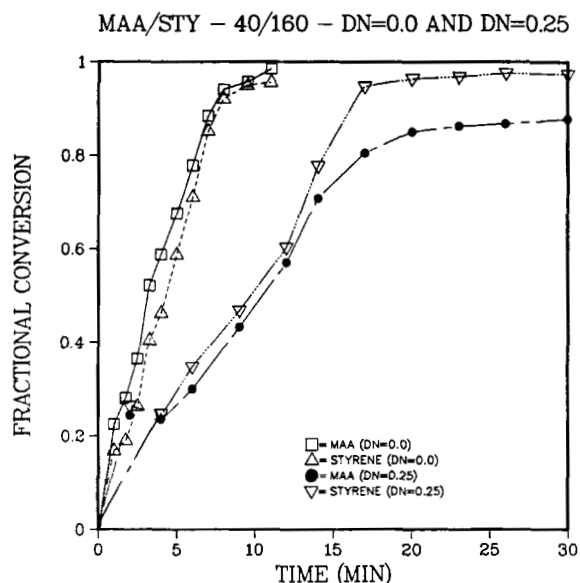
One objective of this study was to determine if partially neutralizing the acid exhibited the same effects



**Figure 12** Comparison of solution copolymerization reaction model results to experimental data for MAA at various DN ( $K_{a2} = 3.5 \times 10^{-6}$ ).



**Figure 13** Comparison of solution copolymerization reaction model results to experimental data for MAA at various DN ( $K_{a2} = 8.0 \times 10^{-6}$ ).

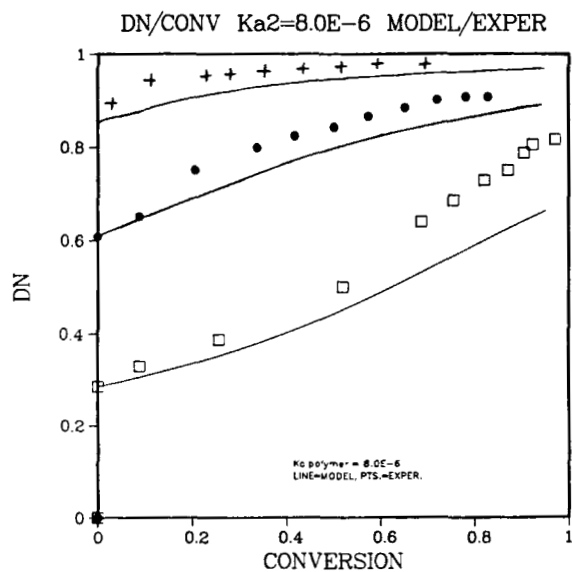


**Figure 15** Experimental conversion profiles for MAA-styrene at overall DN values of 0.0 and 0.25 ( $T = 85^\circ\text{C}$ ).

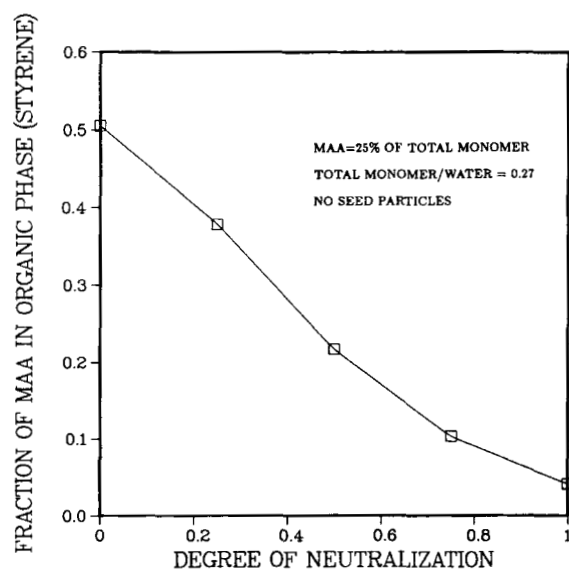
on the reaction rate in an emulsion “terpolymerization” between the acid, anion, and styrene as observed with the solution polymerizations. Experimental methods were developed to address this issue. Initial MAA-styrene emulsion polymerizations were performed at a DN of 0.25. The experimental conversion profiles for both acid (including the undissociated and dissociated species) and styrene at a DN of 0.25 are contrasted to conversion profiles at

a DN of 0.0 in Figure 15. The rate of reaction of MAA was slower at a DN of 0.25 as expected due to the slower rate of reaction of the anions as a result of their increased electrostatic repulsion. However, the rate of reaction of styrene was also slower in both cases for the run at elevated DN.

Figure 16 shows that as the DN increases, the fraction of monomer that partitions into the organic phase decreases. Since the aqueous-phase oligomeric



**Figure 14** Comparison of predicted DN as a function of conversion with experimental values ( $K_{a2}$  of  $8.0 \times 10^{-6}$ ).



**Figure 16** Partition of MAA into the aqueous and styrene phase as a function of DN.

radicals are comprised to a large extent of acid and anion molecules, the rate of entry of these radicals may be slower than when the acid is partially neutralized. The increased polarity due to the negative charge of the anion increases the attraction of the neutralized acid to the polar water molecules in the aqueous phase. The anionic species, therefore, are less likely to partition into the organic phase than the undissociated species. This result suggests that the concentration of free radicals inside the polymer particles ( $\bar{n}$ ) is lower at a DN of 0.25 than at a DN of 0.0 perhaps due to a slower entry rate into the particles of oligomers that contain anionic species. Consequently, a lower concentration of free radicals in the particles (lower  $\bar{n}$ ) will result in a slower rate of reaction of styrene in the particles as observed.

Another factor contributing to the decrease in reaction rate of styrene is that the cross-propagation constant for reaction of styrene with the acid anion is lower than the cross-propagation constant for reaction with the undissociated acid for the MAA-styrene system. The values of the cross-propagation constants for reaction with the anion were calculated from reactivity ratios for styrene and the anion based on  $Q-e$  values reported for the MAA-styrene system.<sup>11</sup> The concentration of anions in the organic phase, however, is relatively small based on the partition data obtained at high DN values.

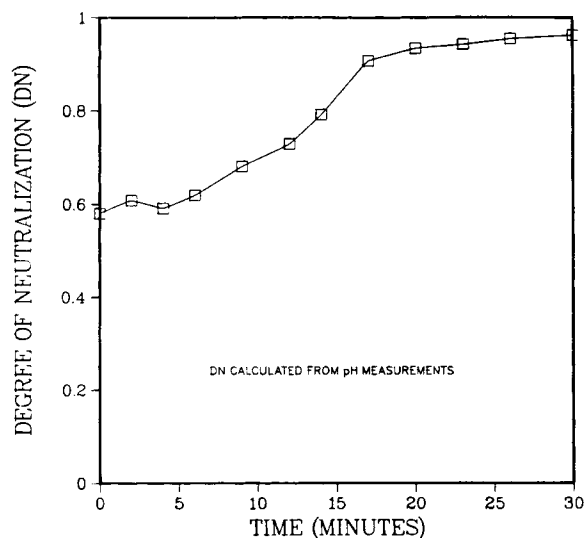
The emulsion copolymerization model was modified to account for the formation and reaction of the dissociated acid, a third reacting monomeric species, due to partial neutralization of the acid with sodium hydroxide. The formation of a third reacting species complicates the reaction mechanism. Modifications of the equations in the kinetic model to account for reaction of all three species, styrene, acid, and the anion, were developed earlier.

Application of the model depends on several parameters that are directly affected by the presence of the dissociated acid. These parameters include the partition coefficients, radical capture and desorption coefficients, termination and propagation constants, and the DN of each phase. Accurate prediction of the values for these parameters cannot be made without a long series of experimental studies to determine the effects of overall DN over a range of monomer/water ratios for each monomer system. Nevertheless, initial estimates can be made for each of these parameters based on previous work performed in this study.

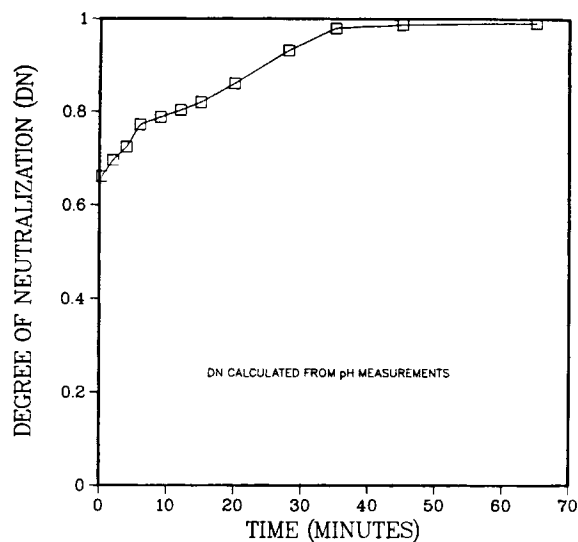
The degree of neutralization changes with conversion due to the changing equilibrium between the monomer and polymer, and also due to the varying partition of monomer into the particles depending

on the relative concentrations of styrene, acid, and anions. Some progress on predicting the changing DN with conversion was discussed earlier for the solution polymerization of MAA. However, the addition of polymer particles and partition of monomers between the various phases greatly complicates the equilibrium between undissociated and dissociated species. Fortunately, this complication can be circumvented by measuring the pH of the reaction mixture over the conversion period and calculating the DN of the unreacted aqueous-phase monomer directly from the pH measurement using the equilibrium expression given by eq. (53).

This approach limits the predictive capabilities of the model because the DN-conversion profile must be known a priori. However, it allows the other aspects of the model to be investigated without having to quantitatively predict the DN of the unreacted monomer in a complex system containing particles with monomer and polymer present in both aqueous and particle phases. Results of calculated DN as determined from pH measurements over the conversion period are presented in Figures 17 and 18 for runs with an overall DN of 0.25 and 0.50 based on the ratio of sodium hydroxide and acid monomer initially added to the system. The initial DN values at zero conversion exceed the overall DN values of 0.25 and 0.50 in part due to disproportional partition of the monomer and sodium hydroxide into the organic phase. As much as 30–40% of the MAA par-



**Figure 17** Change in DN over the conversion period as determined from pH measurements for the reaction of MAA-styrene at an acid (including neutralized acid)/styrene ratio of 40/160 with an initial DN of 0.25 based on total moles base/total moles acid ( $T = 85^{\circ}\text{C}$ ).



**Figure 18** Change in DN over the conversion period as determined from pH measurements for the reaction of MAA-styrene at an acid (including neutralized acid)/styrene ratio of 40/160 with an initial DN of 0.50 based on total moles base/total moles acid ( $T = 85^{\circ}\text{C}$ ).

titions into the particles and droplets. But when styrene, water, and sodium hydroxide were mixed and allowed to separate in a separatory funnel for about 2 h, only about 2.0% of the sodium hydroxide was found to distribute into the styrene phase. Therefore, a significant amount of MAA partitions into the organic phase whereas almost all of the sodium hydroxide remains in the aqueous phase. Thus

the initial measured DN values are higher than if all the acid and base were in the same phase.

A thermodynamic partition model<sup>15</sup> was utilized in making initial estimates of the concentrations of the acid and styrene in each phase. The fraction of acid in the organic phase was then determined as a function of DN from experimental data reported in Figure 16. This organic fraction was distributed evenly between the particles and droplets in the model. Then adjustments in the amount of styrene in the particles were made to compensate for the difference in the original amount of acid estimated to be in the organic phase based on the partition model calculations and the amount based on the experimental partition data in Figure 16 at various DN. This approach provided a method for accounting for the dependence of acid partition on DN.

An estimate for the average desorption coefficient,  $\bar{k}_{des}$ , was made based on the typical range of values calculated for the unneutralized MAA-styrene system. Though the actual value changed as the relative amounts of each monomer changed, typical values were about 2.0 (1/s) for this system. The addition of the anion as a third reacting species made calculation of  $\bar{k}_{des}$  difficult, especially since values for chain transfer and cross-transfer constants are unknown for the anion or any similar dissociated monomeric acid. Therefore, a constant value of 2.0 (1/s) was utilized in the model of the partially neutralized MAA-styrene system.

An estimate of the average capture coefficient,  $\bar{k}_c$ , was also made based on the typical range of val-

**Table IV** Values for Parameters Used in Seeded Emulsion Copolymerization Simulation of MAA and Styrene with  $\text{DN} > 0$  ( $T = 85^{\circ}\text{C}$ )

Parameter	Monomer	Value	Source
$k_p$ (L/mol s)	MAA	15900	Experiment, 5
$k_p$ (L/mol s)	Anion	670	9
$k_p$ (L/mol s)	Styrene	900	17
$k_t$ (L/mol s)	MAA	$0.1 \times 10^8$	7, 18
$k_t$ (L/mol s)	Anion	$2.1 \times 10^8$	9
$k_t$ (L/mol s)	Styrene	$2.5 \times 10^8$	17
$r_{AB}$	MAA-Styrene	0.55	19, 20
$r_{BA}$	Styrene-MAA	0.25	19, 20
$r_{AC}$	MAA-Anion	0.68	11 (Q-e scheme)
$r_{CA}$	Anion-MAA	0.08	11 (Q-e scheme)
$r_{BC}$	Styrene-Anion	1.30	11 (Q-e scheme)
$r_{CB}$	Anion-Styrene	1.10	11 (Q-e scheme)
$\bar{k}_{des}$ (1/s)	Assumed constant	2.0	
$\bar{k}_c$ ( $\text{cm}^3/\text{s}$ )	Assumed constant	$2.0 \times 10^{-14}$	DN = 0.25
$\bar{k}_c$ ( $\text{cm}^3/\text{s}$ )	Assumed constant	$5.0 \times 10^{-15}$	DN = 0.50
$N_p$ (part/L <sub>reactor</sub> )	Assumed constant	$3.0 \times 10^{18}$	$\approx 4.0 \times 10^{18}$ (part/L <sub>aq</sub> )

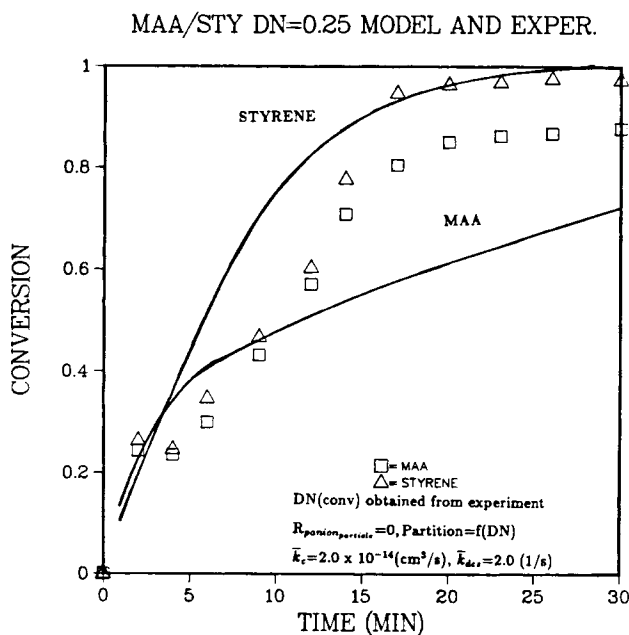


ues calculated for the unneutralized MAA–styrene system. A value of  $2.0 \times 10^{-14}$  ( $\text{cm}^3/\text{s}$ ) was used for the simulation with DN of 0.25. However, a value of  $5.0 \times 10^{-15}$  ( $\text{cm}^3/\text{s}$ ) produced a better fit of the data for the run with a DN of 0.50. This lower value of  $\bar{k}_c$  for the run at DN of 0.50 is consistent with the expected decrease in rate of radical entry into the particles with increased concentration of anions.

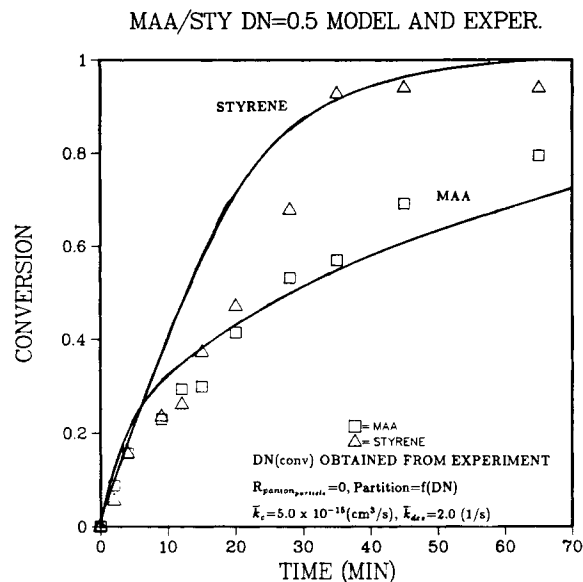
Reactivity ratios were estimated using  $Q$  and  $e$  values reported by Alfrey et al.<sup>11</sup> for the acid and anion and by Brandrup and Immergut<sup>17</sup> for styrene. The reactivity ratios for MAA and styrene were adjusted to correspond to the same values used in the model at a DN of 0.0.

An average termination constant for both the particle and aqueous phases was calculated based on the fraction of each monomer in each phase. Propagation constants were based on values reported in the literature. An overall listing of the kinetic parameters used in the model with DN greater than zero is displayed in Table IV.

Simulations with the initial version of the model, which assumed the DN to be the same in all three phases, resulted in predicted reaction rates of MAA that were too high relative to styrene. The model predicted that at a 40/160 acid (including neutralized acid)/styrene ratio the MAA reached high conversions before the styrene for both the DN of 0.25 and 0.50 cases. However, the data in Figures 19 and



**Figure 19** Comparison of experimental data and model predictions for the conversion profiles of MAA and styrene at an acid (including neutralized acid)/styrene ratio of 40/160 and an initial DN of 0.25 ( $T = 85^\circ\text{C}$ ).



**Figure 20** Comparison of experimental data and model predictions for the conversion profiles of MAA and styrene at an acid (including neutralized acid)/styrene ratio of 40/160 and an initial DN of 0.50 ( $T = 85^\circ\text{C}$ ).

20 reveal that for overall DN values of 0.25 and 0.50, styrene reaches high conversions before MAA. The model was then modified so that only copolymerizations of the undissociated acid and styrene occurred inside the particles, and terpolymerization of all three species occurred only in the aqueous phase (i.e., it was assumed that the concentration of anions inside the particles was negligible). Results from these simulations also shown in Figures 19 and 20 reveal that the model predicts not only the proper trends for the acid and styrene conversion profiles, but the fits of the data are also reasonably good, especially for the case with a DN of 0.50.

The accuracy of the reaction model for partially neutralized systems is limited by the assumptions that must be made in accounting for the many effects of the dissociated species on a large number of important parameters. Much additional work is needed in order to quantitatively determine the effects of these anions on the kinetics of the reaction system. Nevertheless, this portion of the study establishes some important directions for further work related to kinetic modeling of partially neutralized acid–styrene emulsion polymer systems.

## CONCLUSIONS

Simple first-order solution polymerization kinetics may be used to describe the reaction of MAA in

water. Partially neutralizing the acid slows the reaction rate in both solution and emulsion systems. The slower rates are attributed to the increased electrostatic repulsion of the dissociated acid (anions). The degree of neutralization of unreacted monomer increases in a solution polymerization throughout the course of a batch reaction due to the different acid strengths of acid monomer and acid polymer.

Partial neutralization of these acids also results in a decreased partitioning of acid into the organic phase. This decreased tendency of partially neutralized acid species to enter the organic phase probably leads to a lower rate of capture of oligomeric radicals and thus a lower average number of radicals per particle resulting in the decreased rate of reaction of styrene, which was observed experimentally.

A model has been developed to predict both the change in degree of neutralization and polymerization rates throughout the course of a partially neutralized MAA solution polymerization. An emulsion copolymerization model developed for acid-styrene systems was extended to the case where the acid is partially neutralized. Comparison of model and experimental results suggests that very little of the dissociated acid reacts inside the particles.

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## NOMENCLATURE

$A$	parameter relating the relative reactivities of monomer $i$ and monomer $j$
CMC	critical micelle concentration (mol/L <sub>aq</sub> )
DN	degree of neutralization (moles base/moles acid)
$f$	initiator efficiency factor
$F_i$	instantaneous fraction monomer $i$ in copolymer
$[I]$	initiator concentration (mol/L)
$\bar{k}_c$	average radical capture coefficient (cm <sup>3</sup> /s)
$k_d$	initiator decomposition rate coefficient (1/s)
$\bar{k}_{des}$	average radical desorption coefficient (1/s)
$k'_{des}$	volume independent desorption coefficient (cm <sup>2</sup> /s)
$k_{mij}$	chain transfer to monomer (L/mol s)
$k_p$	propagation constant (L/mol s)

$k_{pji}$	propagation constant of monomer $i$ with monomer $j$ (L/mol s)
$k_t$	termination constant (L/mol s)
$\bar{k}_{tji}$	average termination constant of radical $i$ with radical $j$ (L/mol s)
$k_{tw}$	termination constant in the aqueous phase (L/mol s)
$K_{a1}$	acid dissociation constant (monomer)
$K_{a2}$	acid dissociation constant (polymer)
$[M]$	concentration of monomer (mol/L)
$\bar{n}$	average number of free radicals per particle
$N_A$	Avogadro's number ( $6.02 \times 10^{23}$ /mol)
$N_p$	concentration of polymer particles (no./L <sub>aq</sub> )
$r_i$	reactivity ratio = $k_{pji}/k_{pij}$
$R_i$	rate of initiation (mol/L <sub>aq</sub> s)
$R_p$	rate of polymerization (mol/L <sub>aq</sub> s)
SDS	sodium dodecyl sulfate (anionic surfactant)
$T$	temperature (°C)
$t$	time (s)
$x$	moles of dissociated acid monomer
$y$	moles of reacted acid monomer
$z$	moles of dissociated acid polymer

## Greek Symbols

$\alpha$	fraction of dissociated acid monomer
$\beta$	fraction of dissociated radicals
$\phi$	cross-termination coefficient = $k_{tij}/(k_{tii}k_{tjj})$

## Subscripts

aq	aqueous phase
$A$	monomer A (acid)
$B$	monomer B (styrene)
$C$	monomer C (anion)
$d$	droplet phase
$I$	initiator
$m$	monomer
$o$	initial condition
$p$	polymer or particle phase
$P$	polymer or copolymer
$T$ or $tot$	total
$w$	water or aqueous phase
1	monomeric species
2	polymeric species

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