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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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To cite this Article Liaw, Der-Jang and Lee, Kueir-Rarn(1990) 'Polymerization of Vinyl Monomers Initiated By Poly[3-Dimethyl(Acryloyloxyethyl)-Ammonium Propane Sulfonate In Aqueous Solution', *Journal of Macromolecular Science, Part A*, 27: 7, 875 – 895

To link to this Article: DOI: 10.1080/10601329008544811

URL: <http://dx.doi.org/10.1080/10601329008544811>

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POLYMERIZATION OF VINYL MONOMERS INITIATED BY POLY[3-DIMETHYL(ACRYLOYLOXYETHYL)- AMMONIUM PROPANE SULFONATE] IN AQUEOUS SOLUTION

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ABSTRACT

The polymerization of vinyl monomers initiated by poly[3-dimethyl-(acryloyloxyethyl)ammonium propane sulfonate], poly(DAAPS), in aqueous solution was studied under vacuum at 85°C. The polymerization proceeds via a radical mechanism without any further initiator. The polymerization is thought to start with the formation of hydrophobic areas with poly(DAAPS) in the aqueous phase. The initiation mechanism involving hydrogen atom transfer is proposed. The effects of the efficiency of grafting, pH, overall activation energy, and the amount of water content and betaine polymer on the polymerization were investigated. A good linear relationship was obtained between the mass of vinyl monomers and the rate of polymerization (R_p) by applying the Michaelis-Menten equation.

INTRODUCTION

Macromolecular substances, such as starch, cellulose, collagen, enzymes, and polystyrene sulfonate, initiating the radical polymerization of

methyl methacrylate in water without any ordinary radical initiator were studied in series by Imoto et al. [1-12]. The characteristics of such uncatalyzed polymerizations are proposed to be related to the concept of hard and soft hydrophobic areas and monomers [9]. Ouchi et al. also reported that betaine polymers such as carboxybetaine and phosphatebetaine are capable of polymerizing vinyl monomers in aqueous solution without any additional initiator. However, they published only a few experimental results for systems containing a sulfobetaine polymer [11].

Recently, the properties of ampholytic polymers such as poly[3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate] [poly(DMAPS)] and poly[3-dimethyl(acryloyloxyethyl)ammonium propane sulfonate] [poly(DAAPS)] were studied in our laboratory. Of particular interest were solution and thermal degradation properties [13-16]. The present paper is concerned with the polymerization of vinyl monomers initiated by inert betaine-polymer. The effects of the efficiency of grafting, pH value, and the amounts of water content and betaine-polymer on the polymerization are also discussed. Finally, the Michaelis-Menten equation was applied for the relationship between the mass of vinyl monomers and the rate of polymerization (R_p) [2, 8].

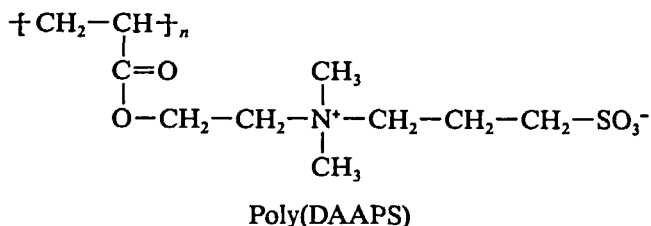
EXPERIMENTAL

Monomer Preparation

The monomer 3-dimethyl(acryloyloxyethyl)ammonium propane sulfonate, (DAAPS), was prepared as described previously [15]. The monomer was characterized by elemental analysis, IR, and NMR, and was found to be quite hygroscopic [mp 145°C (decomposition)] [15].

Polymer Preparation

Poly(DAAPS) was prepared by the polymerization of 3-dimethyl(acryloyloxyethyl)ammonium propane sulfonate with 4,4'-azobis-4-cyanovaleic acid (ACVA) in water as described previously [15]. The intrinsic viscosity was calculated to be 0.50 dL/g in 0.15 M KClO₄ solution at 30°C. The heterogeneous polymer solutions were placed in Spectrapor membrane tubing (molecular weight cut off: 6000-8000) for 72 h to eliminate the unreacted monomer and sodium chloride. The existence of peroxide formation in poly(DAAPS) could not be observed by the KI method.



The vinyl monomers, methyl methacrylate (MMA) and styrene (St), were purified by the usual methods. Vinyl acetate (VAc) monomer was carefully purified as described previously [17]. Water was deionized and distilled.

Procedure

An ampule containing vinyl monomer and a 0.5 M NaCl aqueous solution of poly(DAAPS) was degassed by three freeze-pump-thaw cycles and sealed off under high vacuum ($< 10^{-5}$ mmHg).

The sealed tube was then placed in a constant temperature bath at 85°C for 3 h while agitating. The reaction mixture was poured into a large amount of isopropanol and then allowed to stand at room temperature for 1 day. The precipitate of polymerized product was dried at 80°C *in vacuo*. Conversion of monomer was calculated by means of the following relationship:

conversion of monomer (%) =

$$\frac{(\text{weight of product}) - (\text{weight of fed betaine polymer})}{(\text{weight of fed monomer})} \times 100$$

The efficiencies of grafting of MMA, St, and VAc onto betaine polymer, poly(DAAPS), were calculated according to the following equation, after the extraction of homopolymers for 50 h using a Soxhlet with benzene and *N,N*-dimethylformamide (DMF) [11].

grafting efficiency (%) =

$$\frac{(\text{weight of produced polymer}) - (\text{weight of homopolymer})}{(\text{weight of produced polymer})} \times 100$$

RESULTS AND DISCUSSION

Polymerization of Vinyl Monomers

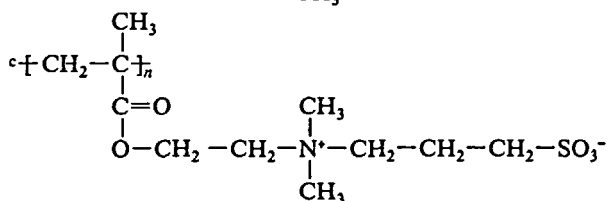
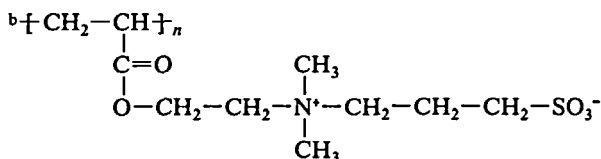
The results of the polymerization of VAc, MMA, and St initiated by ampholytic poly(DAAPS) in an aqueous solution of NaCl are shown in Table 1.

It is clear that monomer conversions in the presence of a betaine-type polymer are substantially increased. However, only low conversions are observed in the absence of an ampholytic polymer. In particular, the conversion is zero for the relatively hydrophilic vinyl acetate monomer. Such a selectivity of vinyl monomer can be explained by "the concept of hard and soft hydrophobic areas (HA) and monomers" as proposed by

TABLE 1. Polymerizations of Vinyl Monomers Initiated by Betaine Polymers^a

Betaine polymer	Conversion, %		
	MMA	St	VAc
None	0.79	1.86	0
Poly(DAAPS) ^b	6.08	4.68	3.47
Poly(DMAPS) ^c	4.20	3.41	1.09

^aVinyl monomer, 3 mL; betaine polymer, 0.1 g; NaCl_{aq} (0.5 M), 10 mL; with shaking; polymerization temperature, 85°C; polymerization time, 3 h.



Imoto et al. [9] as shown in Fig. 1. That is, monomers can be classified as hard and soft according to their solubility in water. In fact, the solubility of vinyl monomers in water is in the order $St < MMA < VAc$. Furthermore, the data in Table 1 for monomer conversions in poly(DAAPS) and poly(DMAPS) parallel this order. This suggests that the same mechanism of initiation is operative for both betaine polymers. The conversion of vinyl monomers in poly(DAAPS) is higher than in poly(DMAPS) which may be due to steric hindrance of the methyl group in the α -carbon of the latter [16].

Proof of Radical Mechanism

The ampule containing vinyl monomer (3 mL), 0.06 g hydroquinone (HQ) or 2,2'-diphenyl-1-picrylhydrazyl (DPPH), 0.1 g betaine-type polymer, and 10 mL NaCl aqueous solution was sealed under vacuum. The ampule was then placed in a constant temperature bath at 85°C for 3 h

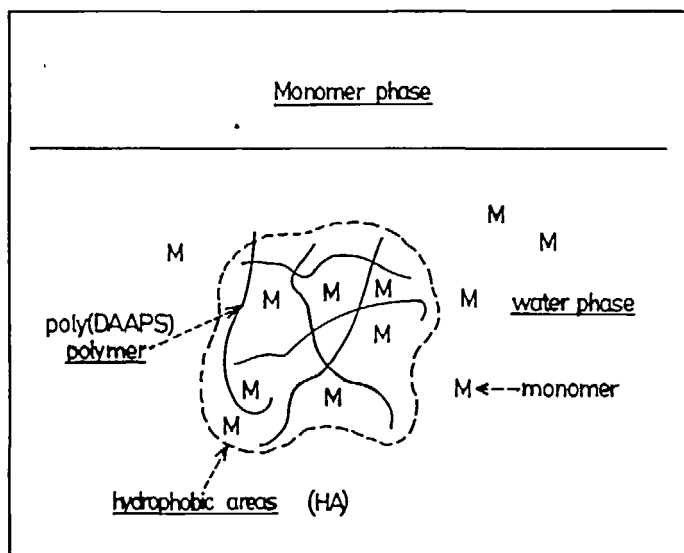


FIG. 1. A schematic of the hydrophobic area and monomer in the uncatalyzed polymerization system.

while agitating (Table 2). From Table 2 it is clear that these radical scavengers completely inhibit the polymerization. Thus, it may be concluded that polymerization proceeds through a radical mechanism.

Initiation Mechanism

From the proof of radical mechanism mentioned above, it is very interesting to realize how the free radical occurs. The initiation mechanism can be expressed in terms of hydrogen transfer in Fig. 2 as proposed by Imoto and coworkers [2, 10].

The vinyl group of monomer is considered to be adsorbed first on the SO_3^- group of the poly(DAAPS) as shown in Fig. 2 [2]. A following partial electron transfer may proceed as presented in

TABLE 2. Effect of Radical Scavenger on the Polymerization of Vinyl Monomers^a

Radical scavenger	Monomer	Conversion, %
None	MMA	6.08
	St	4.68
	VAc	3.47
HQ	MMA	0
	St	0
	VAc	0
DPPH	MMA	0
	St	0
	VAc	0

^aPoly(DAAPS), 0.1 g; monomer, 3 mL; polymerization temperature, 85°C; polymerization time, 3 h; with shaking; NaCl_{aq} (0.5 M), 10 mL; radical scavenger, 0.06 g.

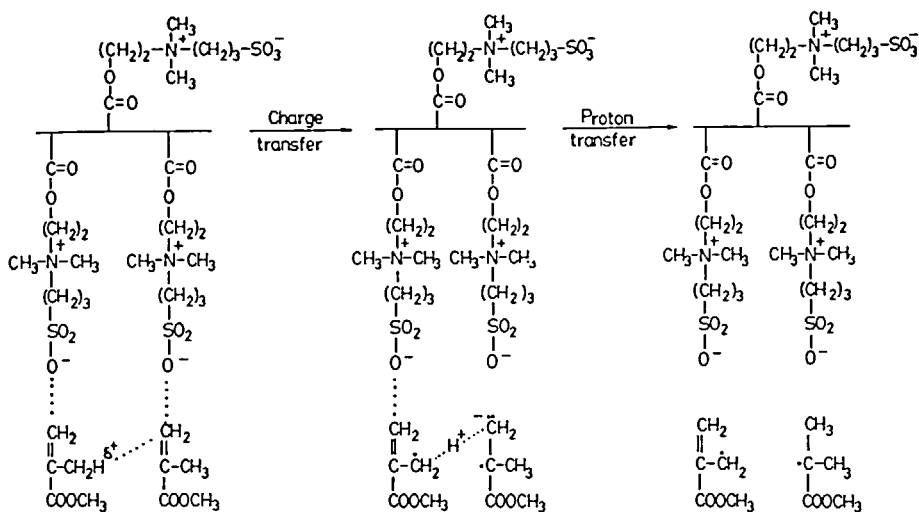
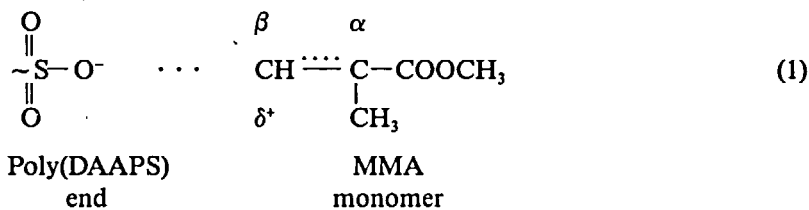
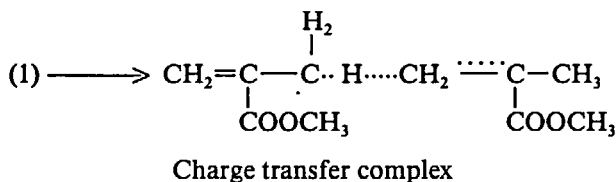
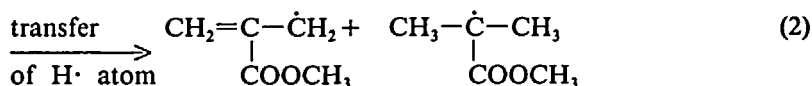


FIG. 2. Initiation mechanism of MMA by poly(DAAPS).



Thus, the electron density around the carbon atom in the α -CH₃ group increases and it becomes easier to form the charge transfer complex between two adsorbed monomers, and then the monomer donates its electron as shown by





This could explain the radical polymerization of MMA with poly(DAAPS). One of the generated radicals is an allyl radical which may facilitate hydrogen transfer [2]. Similar mechanisms can also be proposed in radical polymerizations using other monomers such as St and VAc. Otsu and Sato succeeded in proving this H· transfer mechanism by using the spin-trapping method [18–20].

Estimation of the Efficiency of Grafting

The efficiency of grafting in the polymerization of vinyl monomers initiated by betaine-type polymer poly(DAAPS) was estimated. The results are listed in Table 3. The data show that higher monomer conversions result in higher grafting efficiency. This may be due to the fact that the hard monomers such as MMA and St are easier to incorporate into hydrophobic areas. Graft polymerization may proceed more readily in these areas than homopolymerization.

Phase Where Polymerization Takes Place

The location in which polymerization took place could be investigated by the following method. Since poly(DAAPS) did not dissolve in water, polymerization was carried out in 0.5 M NaCl aqueous solution. The

TABLE 3. Polymerizations of Vinyl Monomers Initiated by Betaine Polymer^a

Monomer	Conversion, %	EG, %
MMA	6.08	45.23
St	4.68	41.90
VAc	3.47	25.38

^aPoly(DAAPS), 0.1 g; monomer, 3 mL; with shaking; NaCl_{aq} (0.5 M), 10 mL; polymerization temperature, 85°C; polymerization time, 3 h.

reaction tubes containing monomer, poly(DAAPS), and 0.5 M NaCl aqueous solution were allowed to stand at 85°C for 3 h without shaking. After polymerization, the upper layers (monomer layer) were pipetted out and poured into isopropanol. The muddy aqueous layers were also poured into isopropanol. The results are shown in Table 4 [11]. As shown in Table 4, monomer layer conversion of VAc is zero. This may be due to the difficulty of VAc thermal polymerization. The conversions of 0.52% in the MMA layer and 0.87% in the St layer could only be by thermal polymerization. These phenomena might be due to the fact that soft monomers such as VAc are difficult to incorporate into the hydrophobic areas. Accordingly, it is concluded that polymerization by a betaine-type polymer is initiated, propagated, and terminated in the water layer.

Structure of Polymerized System by Scanning Electron Microscopy

In order to investigate the polymerization system, the structure of the grafted polymer was studied with a Hitachi S-550 scanning electron microscope (SEM). One drop of the reaction system was mounted on cylindrical brass, freeze-dried under vacuum, and rendered electrically conductive with a coating of gold. Then it was viewed in a scanning electron microscope operating at an accelerating voltage of 20 kV. Figure 3 shows the surface view of poly(DAAPS) before and after polymerization of various monomers. From Fig. 3(A), we can see that the surface is flat. After polymerization with monomers, rough surfaces were obtained, as shown in Fig. 3(B)–(D). This structure suggests that polymerization proceeds mainly in the interior of the hydrophobic areas. This observation

TABLE 4. Phase Where Polymerization Takes Place^a

Monomer	Conversion, %	
	Water layer	Monomer layer
MMA	5.30	0.52
St	3.71	0.87
VAc	3.28	0

^aMonomer, 6 mL; poly(DAAPS), 0.2 g; polymerization temperature, 85°C; polymerization time, 3 h; without shaking; NaCl_{aq} (0.5 M), 20 mL.

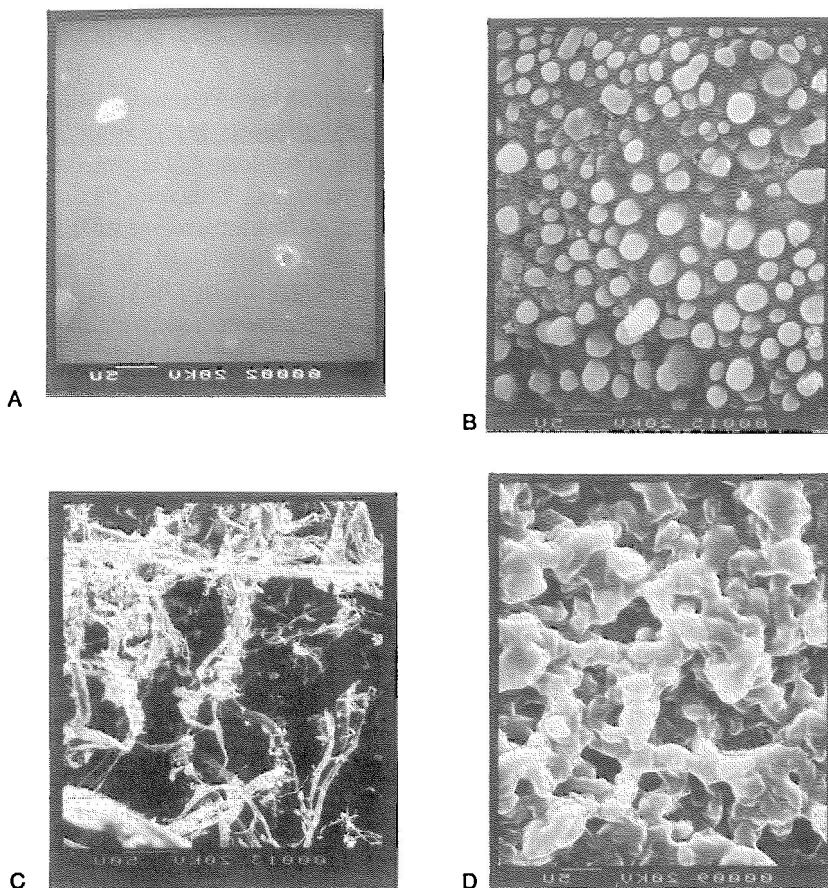


FIG. 3. Surface view of polymerization system. (A) Before polymerization of poly(DAAPS). (B) After polymerization of MMA. (C) After polymerization of St. (D) After polymerization of VAc.

agrees with the result shown in Fig. 7. Poly(DAAPS) in a higher concentration (>0.1 g) became entangled and could not form hydrophobic areas sufficient and suitable to incorporate MMA [7].

Effect of pH of the Aqueous Solution on the Conversion of Vinyl Monomers

In order to observe the effect of pH of the aqueous solution on the conversion of various vinyl monomers, the polymerization of vinyl

monomer by betaine-type polymer, poly(DAAPS), was carried out at various pH values. The results obtained are shown in Fig. 4.

From Figure 4 it is observed that polymerization is maximum at pH 6–7 for MMA, VAc, and St. The interaction of the polymer chain is smallest in the pH range of 6 to 7. In fact, the isoelectronic point of poly(DAAPS) occurs at pH 6–7 (electrophoresis apparatus, Sartorius SM 16531 model with IEF standards). It seems that a betaine-type polymer, poly(DAAPS), in acidic or basic media is a less efficient initiator of vinyl monomers than it is at neutral pH. These phenomena might be due to the fact that the cationic and anionic parts of the betaine polymer can be neutralized by acidic or basic solution.

Relationships between Monomer Conversions and Polymerization Time

Conversions of various monomers initiated by poly(DAAPS) were obtained at 85°C in the order of VAc < St < MMA, as shown in Fig. 5. There are good linear relationships among all of the monomers. Figure 5 also shows that the hydrophobic monomer can easily reach high conversion in the polymerization system.

Effect of the Amount of Water on the Polymerization of MMA

The effect of the amount of water on the conversion of MMA with constant amounts of MMA and poly(DAAPS) was studied. The results obtained are shown in Fig. 6. The conversion of MMA increased with the amount of water up to the volume of NaCl aqueous solution in 12 mL. When the amount of water exceeded 12 mL, the conversion reached a maximum and then leveled off. These phenomena might be due to the inability of the betaine polymer to form a hydrophobic domain with the lower amount of water, thus preventing vinyl monomer incorporation.

Effect of the Amount of Poly(DAAPS) on the Rate of Polymerization of MMA

The conversion of MMA was investigated as a function of added poly(DAAPS) (Fig. 7). The initial amounts of MMA and NaCl aqueous solution were kept constant. When the concentration of poly(DAAPS) exceeded a certain limit (>0.1 g), conversion began to decrease. This phenomenon is probably due to the increase in entanglement of the poly(DAAPS) chains and to the decrease of the hydrophobic domains [8].

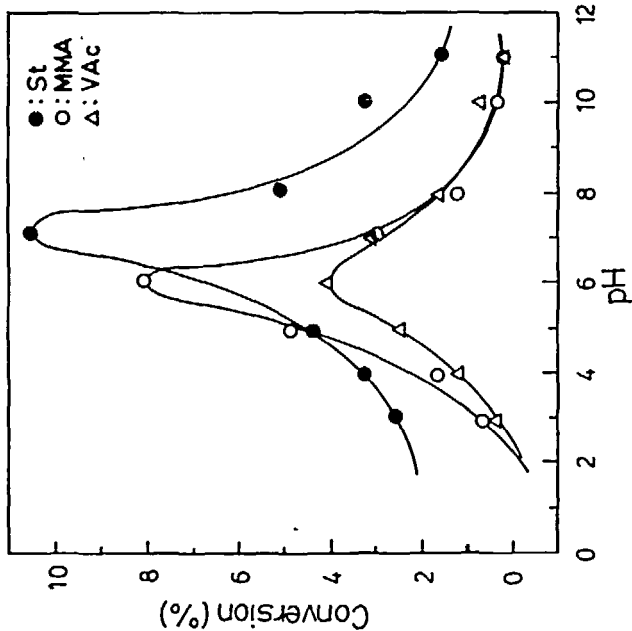


FIG. 4. Conversions of vinyl monomers vs pH of the aqueous solution. Vinyl monomers, 3 mL; poly(DAAPS), 0.1 g; buffer solution, 10 mL; 85°C; 3 h with shaking. Buffer solutions were prepared with following systems: pH 3-5, 0.1 M sodium citrate-0.1 M HCl; pH 6, 0.1 M sodium citrate-0.1 M NaOH; pH 7-8, 0.1 M KH_2PO_4 -0.05 M $\text{Na}_2\text{B}_4\text{O}_7$; pH 10-12, 0.2 M $\text{Na}_2\text{B}_4\text{O}_7$ -0.1 M NaOH.

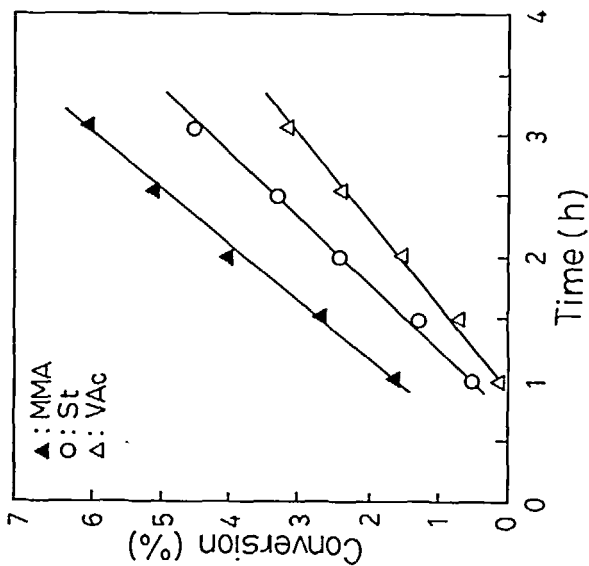


FIG. 5. Monomer conversions vs polymerization time. 85°C, 3 h with shaking. Poly(DAAPS), 0.1g; NaCl_{aq} (0.5 M), 10 mL; vinyl monomer, 3 mL.

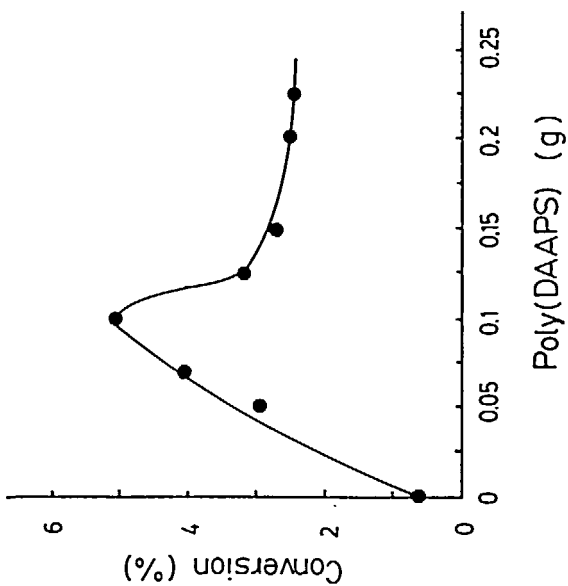


FIG. 7. Effect of the amount of poly(DAAPS) on the polymerization of MMA. MMA, 3 mL; NaCl_{aq} (0.5 M), 10 mL; 85°C; 3 h with shaking.

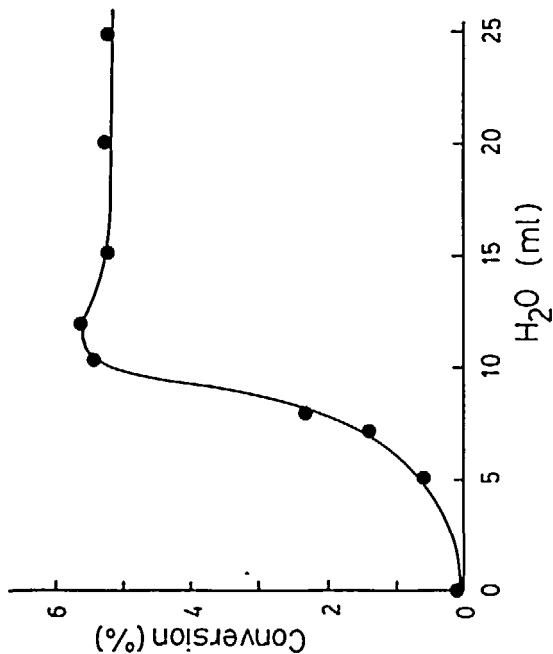


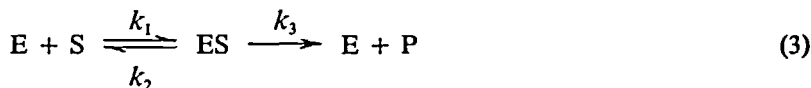
FIG. 6. Effect of the amount of water on the polymerization of MMA in 0.5 M NaCl aqueous solution. Poly(DAAPS), 0.1 g; MMA, 3 mL; 85°C; 3 h.

Effect of the Amount of Vinyl Monomers on the Polymer Yield

An ampule containing various amounts of vinyl monomers, 0.1 g poly(DAAPS) and 10 mL aqueous solution NaCl was heated to 85°C for 3 h with shaking. The polymer yields for the MMA and St polymerizations are shown in Figs. 8 and 9, respectively. The corrected yield was calculated by subtracting the yield of the thermally generated polymer from the overall yield calculated. When the mass of vinyl monomers exceeds a certain limit, the corrected yield becomes constant. This result can be explained by the fact that the incorporable quantity of vinyl monomer in the hydrophobic area is limited. That is, when a sufficient amount of monomer (MMA or St) is charged, the hydrophobic area may be saturated with monomer. Thus, the excess of monomer becomes useless for the corrected yield.

Application of Michaelis-Menten Equation to the Polymerizations of MMA and St

The results from Figs. 8 and 9 were found to fit the Michaelis-Menten equation [2]:



where E is poly(DAAPS), S is MMA or St, ES is the charge transfer complex of vinyl monomers on poly(DAAPS), and P is the radical initiator ($\text{CH}_2=\overset{\cdot}{\text{C}}-\text{COOCH}_3$ or $\text{CH}_3-\overset{\cdot}{\text{C}}-\text{CH}_3$) for MMA as indicated in



Fig. 1. From Eq. (3), Lineweaver-Burk's Eq. (4) [2] is obtained:

$$\frac{1}{R_p} = \frac{K_a}{k_3[E]} \times \frac{1}{[S]} + \frac{1}{k_3[E]} \quad (4)$$

$$K_a = (k_2 + k_3)/k_1$$

Here, R_p is the conversion for the corrected yield. [E] and [S] indicate the concentration and mass for the poly(DAAPS) and monomer, respectively. By application of Eq. (4), R_p was coordinated with the amounts of MMA and St fed as shown in Fig. 10. Straight lines were obtained for

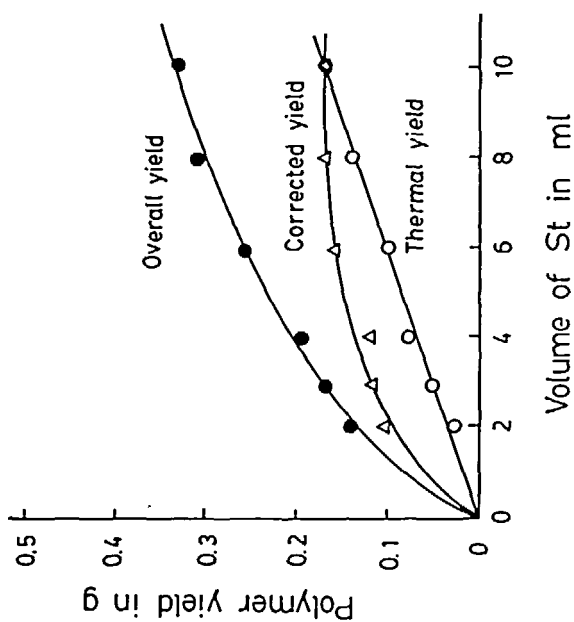


FIG. 9. Polymer yield versus amount of St. NaCl_{aq} (0.5 M), 10 mL; 85°C; 3 h with shaking. (●) Overall yield; poly(DAAPS), 0.1 g. (Δ) Corrected yield; poly(DAAPS), 0.1 g. (○) Thermal yield; poly(DAAPS), 0.0 g.

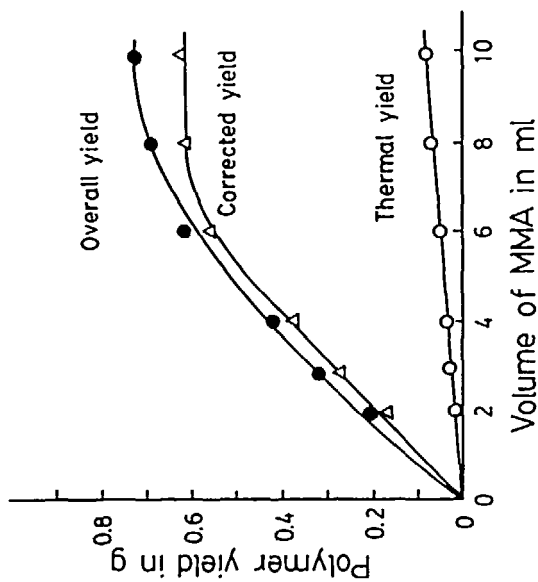


FIG. 8. Polymer yield versus amount of MMA. NaCl_{aq} (0.5 M), 10 mL; 85°C; 3 h with shaking. (●) Overall yield; poly(DAAPS), 0.1 g. (Δ) Corrected yield; poly(DAAPS), 0.1 g. (○) Thermal yield; poly(DAAPS), 0.0 g.

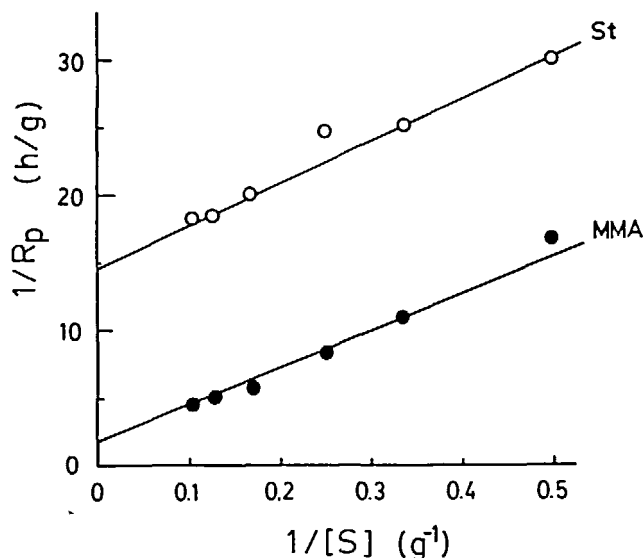


FIG. 10. Application of Eq. (4) to the results obtained from Figs. 7 and 8.

both the MMA and St polymerization systems. From the intercept and the slope of Fig. 10, $k_3[E]$ and K_a could be calculated. The result was shown in Table 5.

Both K_a and $k_3[E]$ values of MMA are larger than those of styrene. This result may be related to the fact that MMA polymerization proceeds via proton transfer ($3H$ in $\alpha\text{-CH}_3$) in the hydrophobic areas.

Estimation of the Overall Activation Energy

In order to obtain the overall activation energy of MMA and St polymerization initiated by poly(DAAPS), the time-conversion curves were

TABLE 5. Values of K_a and $k_3[E]$

Monomer	Poly(DAAPS), g	NaCl, mL	K_a , g	$k_3[E]$, g/h
St	0.1	10	2.06	0.069
MMA	0.1	10	11.35	0.454

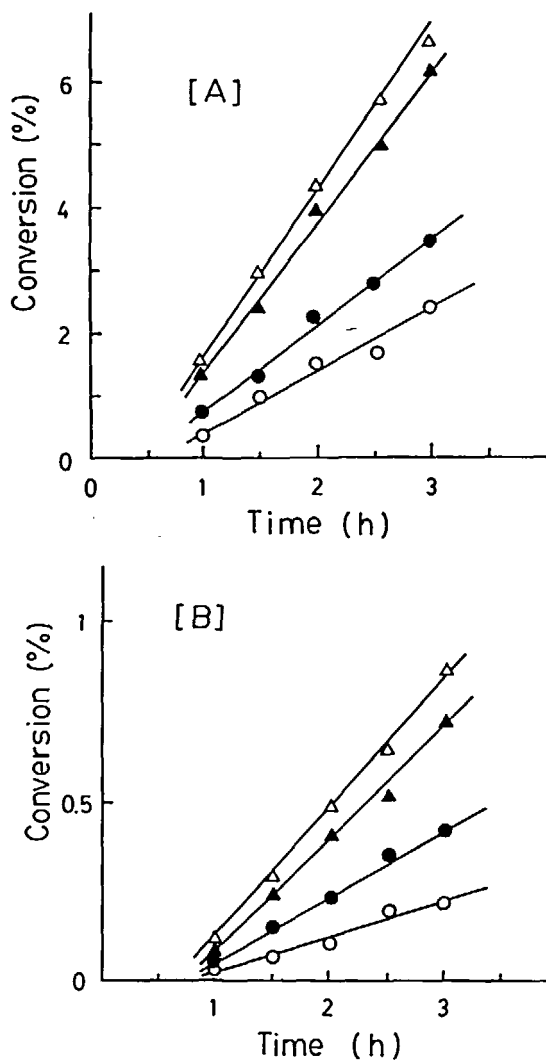


FIG. 11. Time-conversion curves. MMA, 3 mL; NaCl_{aq} (0.5 M), 10 mL; with shaking. (○) 75°C, (●) 80°C, (▲) 85°C, (△) 90°C. [A] Polymerization in the presence of 0.1 g poly(DAAPS). [B] Polymerization in the absence of poly(DAAPS).

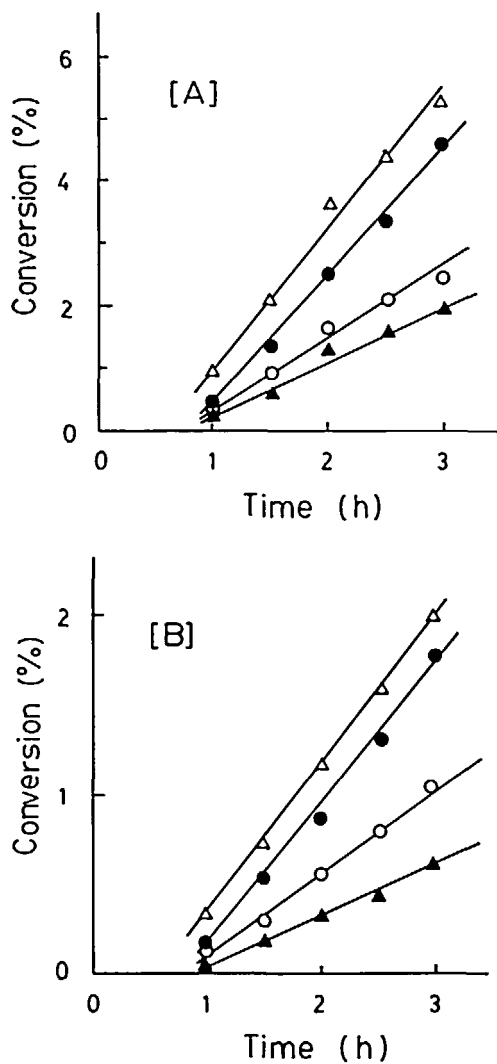


FIG. 12. Time-conversion curves. St, 3 mL; NaCl_{aq} (0.5 M), 10 mL; with shaking. (▲) 75°C, (○) 80°C, (●) 85°C, (△) 90°C. [A] Polymerization in the presence of 0.1 g poly(DAAPS). [B] Polymerization in the absence of poly(DAAPS).

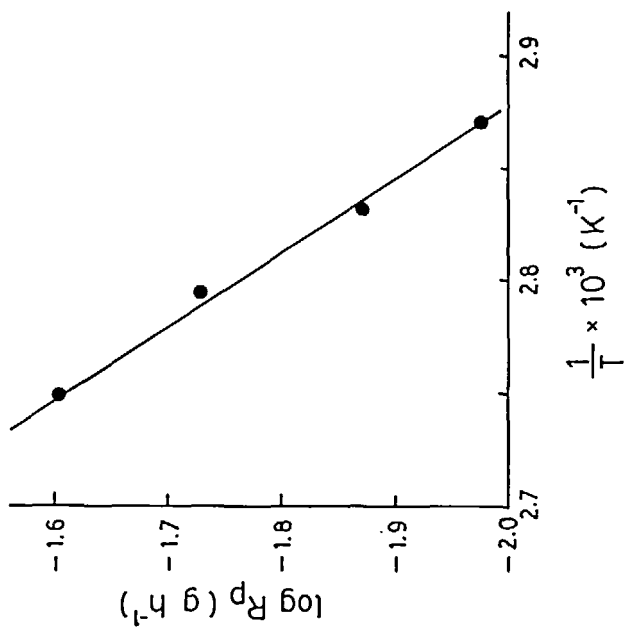


FIG. 14. Arrhenius plots for the polymerization of St with poly(DAAPS).

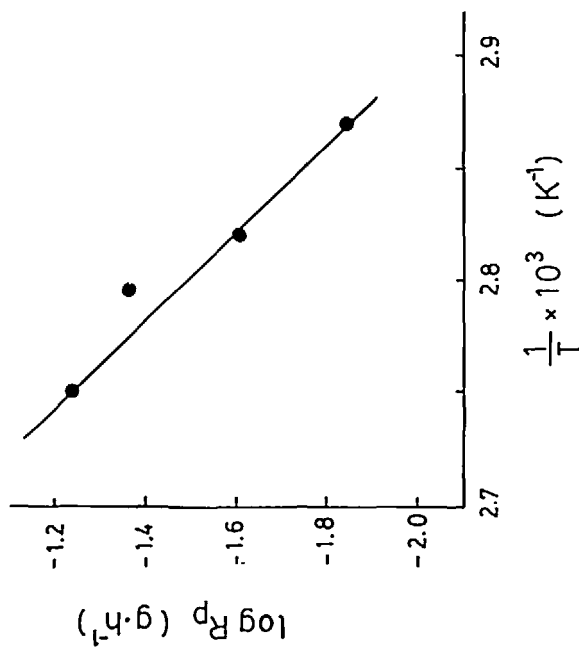


FIG. 13. Arrhenius plots for the polymerization of MMA with poly(DAAPS).

carried out at 75–90°C. The results are shown in Figs. 11 and 12 for MMA and St, respectively. However, no corrected yield was obtained when the polymerization temperature was below 60°C.

By applying the Arrhenius equation, the overall activation energy was estimated to be 95.04 and 62.58 kJ/mol for MMA and St, respectively, as shown in Figs. 13 and 14.

ACKNOWLEDGMENTS

The authors thank the National Science Council of the Republic of China for its financial support. We also thank Miss Mei-Chi Lin for the measurement of the isoelectronic point.

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Received August 14, 1989

Revision received November 29, 1989