

Preparation and Characterization of Polyacrylamide in Cationic Microemulsion

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Received 31 December 1996; accepted 2 June 1997

ABSTRACT: The polymerization of acrylamide in a water/oil cationic microemulsion initiated with a water-soluble radical initiator, potassium persulfate (KPS), was investigated. The kinetics of microemulsion polymerization clearly shows a two-stage process; when the initiator is dissolved in a monomer solution before the emulsification, the reaction rate is higher than it would be if added after the emulsification. The activation energy of the polymerization is affected by the cosurfactant. Information about the microstructures of polyacrylamides is derived from X-ray diffraction, DSC, FTIR, and laser-Raman studies. The results of the studies suggest that the orientation behavior of microemulsion polymerization increases the crystallinity of polyacrylamide and the polar group ($-\text{NH}_2$) is coiled in the inner part of the polymer particles compared to solution and water/oil emulsion polymerizations. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 747–754, 1998

Key words: microemulsion; polymerization; acrylamide; microstructure; potassium persulfate

INTRODUCTION

In 1943, Hoar and Schulman¹ first reported a transparent system which was formed of oil, water, and surfactants, and in 1959, they² named the system "microemulsion." In contrast to conventional emulsions, microemulsions are not white but transparent; they are thermodynamically stable mixtures and do not separate into two phases on standing. Once the conditions are right, formation of the microemulsion occurred spontaneously and little mechanical work (such as ultrasonic or vigorous agitation) is required. Microemulsions have been known for a long time, but the polymerization in microemulsions was not studied until 1980. Stoffer and Bone^{3,4} first reported the microemulsion polymerizations of

methyl methyl-acrylate (MMA) and methylacrylate (MA), but the inverse (water/oil [W/O]) microemulsion systems resulted in phase separation. Leong et al.^{5,6} studied the polymerization of acrylamide in inverse microemulsion; the systems led to the formation of clear and stable microlatexes, and they successfully obtained dispersions with a low intrinsic viscosity. The polymerizations yielded very small latex particles with high molecular weight, but the concentration of surfactant in the systems was high; the weight ratio of surfactant-to-monomer amounted to 5. From then on, a series of studies on polymerizations of acrylamide and its copolymerizations in W/O microemulsions were made by Candau and coworkers.^{7–10} The anionic surfactants aerosol OT (AOT) and AOT [sodium bis(2-ethylhexyl) sulfosuccinat] were used. When nonionic surfactants were added to the systems, the ratio of surfactant-to-monomer was reduced. Cationic surfactants also can be used to prepare microemulsions. Atik and Thomas¹¹ polymerized styrene in an O/W micro-

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Journal of Applied Polymer Science, Vol. 67, 747–754 (1998)
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emulsion–cationic surfactant cetyltrimethyltetrammonium bromide (CTAB) was used, and as a cosurfactant, hexanol was also added into the system and they obtained narrowly distributed latex particles with the order of 20–30 nm in diameter. It was also found that the stability of the microemulsion system was based on the solubility of the polymer in the cosurfactants.¹² Several other researchers have also reported the polymerizations of an oil-soluble monomer in cationic microemulsions with or without a cosurfactant. Cationic surfactants such as dodecyltrimethyltetrammonium bromide (DTAB)¹³ and CTAB were commonly used in microemulsions system. The cosurfactants can be either fatty alcohol (such as hexanol) or long-chain alkane (such as hexadecane).

Water-soluble polyacrylamides are widely used as flocculating and paper-strengthening agents and they also can be applied to enhance the recovery of oil. But up to now, very few studies have been carried out on polymerizations of a water-soluble monomer in cationic microemulsions. In present work, we polymerized acrylamide in an *W/O* microemulsion with CTAB and hexanol as the surfactant and cosurfactant, respectively. The kinetics of microemulsion polymerization was examined and information about the polyacrylamide was obtained.

EXPERIMENTAL

Materials

Acrylamide monomers used for the polymerization are recrystallized from acetone three times. CTAB is recrystallized from an ethanol and acetone mixture (1 : 4 by volume). The initiator KPS is recrystallized from doubly distilled water. Butanol, hexanol, and octanol are all AR grade and vacuum-distilled. Kerosene is commercially available and is purified three times with activated carbon power. Deionized and triply distilled water used throughout the work is deprived of oxygen under a stream of nitrogen.

Polymerization Procedure

The kinetics of polymerization is studied by a dilatometer, and the liquid level of the capillary of the dilatometer is monitored by a cathemeter. When polymerization is achieved, polyacrylamide is precipitated with an excess of acetone and then

washed with methanol until the surfactant is removed; then, the polymer is vacuum-dried at room temperature for 10 h.

Molecular Weight Determination

Polyacrylamide molecular weights are determined in solution at 25°C using the Mark–Houwink relation¹⁴ $[\eta] = 6.31 \times 10^{-5} M^{0.8}$.

Polymer Characterization

The glass transition temperature (T_g) of the polymers are measured with a Perkin-Elmer Model DSC-2 differential scanning calorimeter with a heating rate of 20°C/min. The X-ray diffractogram is run on Rigaku D/MAX-RC 12 kW X-ray diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation at a scan speed of 4°/min. Infrared spectra are recorded on Bruker IFS66V spectrometer; all the spectra are taken with a 4 cm^{-1} resolution. Laser-Raman spectra are obtained using a Bruker RFS100; the scans are collected from 3500 to 50 cm^{-1} with a 4 cm^{-1} resolution.

RESULTS AND DISCUSSION

Rate of Polymerization

Variation in the rate of polymerization of acrylamide in the microemulsion and emulsion systems vs. conversion curves are expressed in Figure 1. As can be seen, the cures of the rate of microemulsion polymerizations in Figure 1(A) and (B) all show two distinct regions, and the reaction rates increase up to ca. 30% conversion, while the cure of conventional emulsion polymerization [Fig. 1(C)] shows three regions. The rate increases below 10% conversion, then decreases, and the apparent plateau region is observed. These significant differences are probably due to the different particle nucleation processes in the two polymerization systems. In emulsion polymerization, the principal loci are monomer-swollen micelles, and the particle nucleation process lasts only up to 10% conversion. In microemulsion polymerization, the nucleation occurs in emulsified monomer droplets, and the nucleation process is continuous throughout the polymerization.^{7,15,16} When the water-soluble initiator KPS is dissolved in an acrylamide solution prior to the emulsification or after the microemulsion is prepared, the different reaction rates are as illustrated in Fig-

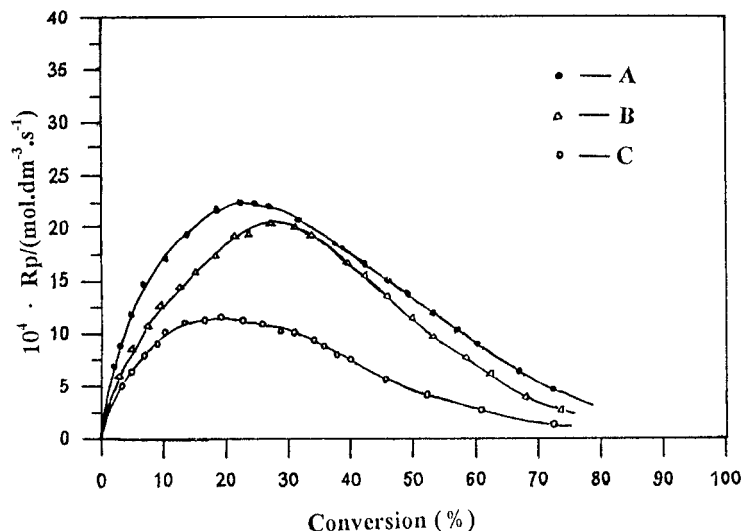


Figure 1 Variation of the rate of polymerization initiated by KPS: (A) the microemulsion in which KPS is dissolved in the monomer solution prior to emulsification, (B) the microemulsion in which KPS is dissolved in system after the emulsification, and (C) the conventional emulsion also to be initiated with KPS.

ure 1(A) and (B). As can be seen, of the two systems, the reaction rate of the former is higher than that of the latter. Since KPS is water-soluble, in the former system, KPS radicals initiate the monomer directly. But the fraction of KPS also can be dissolved in oil, and as compared with the continuous phase oil, the amount of KPS is infinitely little, so we consider that KPS also can be fully dissolved in oil in the microemulsion system. Consequently, the concentrations of KPS radicals in the two systems are the same. The KPS radicals in oil would initiate the acrylamide which dissolved in the oil phase to form the oligomeric radicals first; then, these radicals diffuse into microemulsion droplets to continue the poly-

merization, and at the same time, KPS free radicals entering into the droplet directly is also possible. So, the relatively low reaction rate can be interpreted in this way in that it is highly probable that the microemulsion droplet is covered by a firm interface layer, which prevents the radicals from diffusing into the microemulsion droplet core.

As a cosurfactant, hexanol has been successfully used in microemulsion polymerization, and it has been reported that in the microemulsion system the short-chain alcohols are mainly dispersed at the interface of the water and oil phases; they often act as destabilizers for the latex by desorbing the surfactant from the surface of poly-

Table I Molecular Weights (M), T_g of Polyacrylamide, and Overall Activation Energy (E_a) of Polymerization in Different Systems (Polymerization at 50°C)^a

Polymerization System	Cosurfactant	E_a (kJmol ⁻¹)	$M\eta$	T_g (K)
Solution		57.3	8.8×10^4	457
Emulsion ^b		67.4	5.3×10^5	456
Microemulsion ^c	Butanol	142.9	1.02×10^6	465
	Hexanol	187.3	1.31×10^6	464
	Octanol	235.1	1.17×10^6	465

^a All polymerizations are initiated with KPS 0.4 mM (based on water content).

^b Same basic compositions with microemulsion except for cosurfactant.

^c Basic compositions: water 36 wt %, kerosene 36 wt %, CTAB 14 wt %, and 14 wt % of the various cosurfactants.

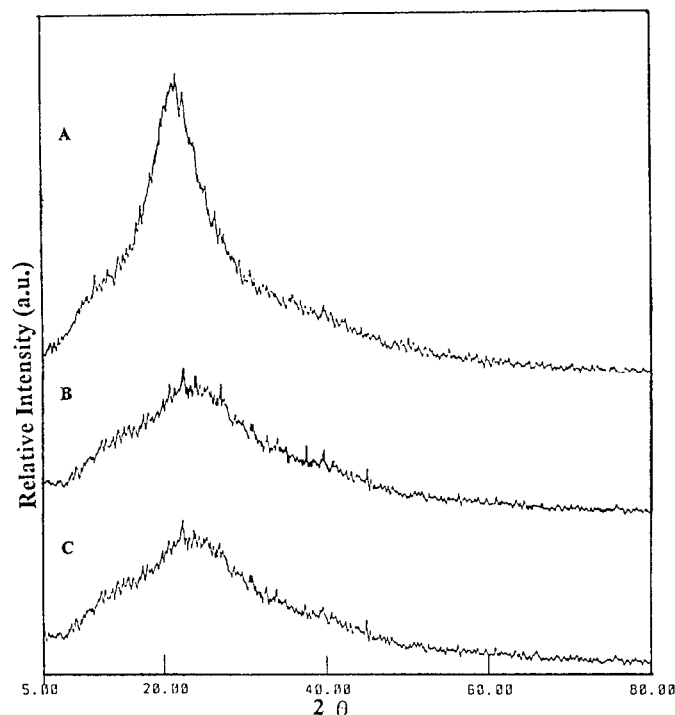


Figure 2 Changes of X-ray diffraction pattern of polyacrylamide prepared from (A) microemulsion, (B) solution, and (C) emulsion.

mer monomer particles.¹⁷ In this work, butanol, hexanol, and octanol are used as cosurfactants. The basic compositions of the microemulsions studied are water 36 wt %, kerosene 36 wt %, CTAB 14 wt %, and 14 wt % of the various cosurfactants. These compositions are used for the kinetics study in which the concentration of acrylamide is about 30 wt % and KPS is 0.4 mM (based on the water content). Following the Arrhenius equation, the overall activation energies E_a of polymerizations are obtained, which are from 142.9 and 187.3 to 235.3 kJ mol⁻¹ according to the sequence of butanol and hexanol to octanol as shown in Table I. In this work, alcohol cosurfactants are all oil-soluble, although the exact data of the interface of the microemulsions are not available. It also can be assumed that there is a sharp boundary layer between the water phase and the alcohol cosurfactant which hinders the diffusion of the radicals. Further evidence supporting this assumption is from the E_a of the solution and the emulsion polymerizations listed in Table I. Compared with butanol, hexanol and octanol are less water-soluble and the E_a values of the polymerization imply that the longer the carbon chain length of alcohol the firmer the interface layer of microemulsion droplets. In addition,

the viscosity of alcohol increases steadily from butanol to octanol.^{18,19} This is attributed to the decreasing of the fluidity of the interface layer, and it has been reported the more fluid the interface layer the easier the radicals can diffuse into the microemulsion droplets.²⁰

Molecular Weights of Polyacrylamides

The various molecular weights of polyacrylamides prepared from different reaction systems are listed in Table I. As can be seen, the highest molecular weights are obtained from the microemulsion and the lowest are obtained from the solution. It has been a concern that alcohol cosurfactants in microemulsion polymerization may also act as a potential chain-transfer agent.¹⁷ Except for the cosurfactants, three polymerization systems have the same compositions, so the difference of the molecular weights of the polymers may be due mainly to the chain-transfer reactions of the cosurfactants. There are no chain-transfer constants of these cosurfactants available for direct comparison, and from the data of molecular weights, we cannot find any relationship between the cosurfactant chain-transfer reaction and the molecular weights of the acrylamide microemul-

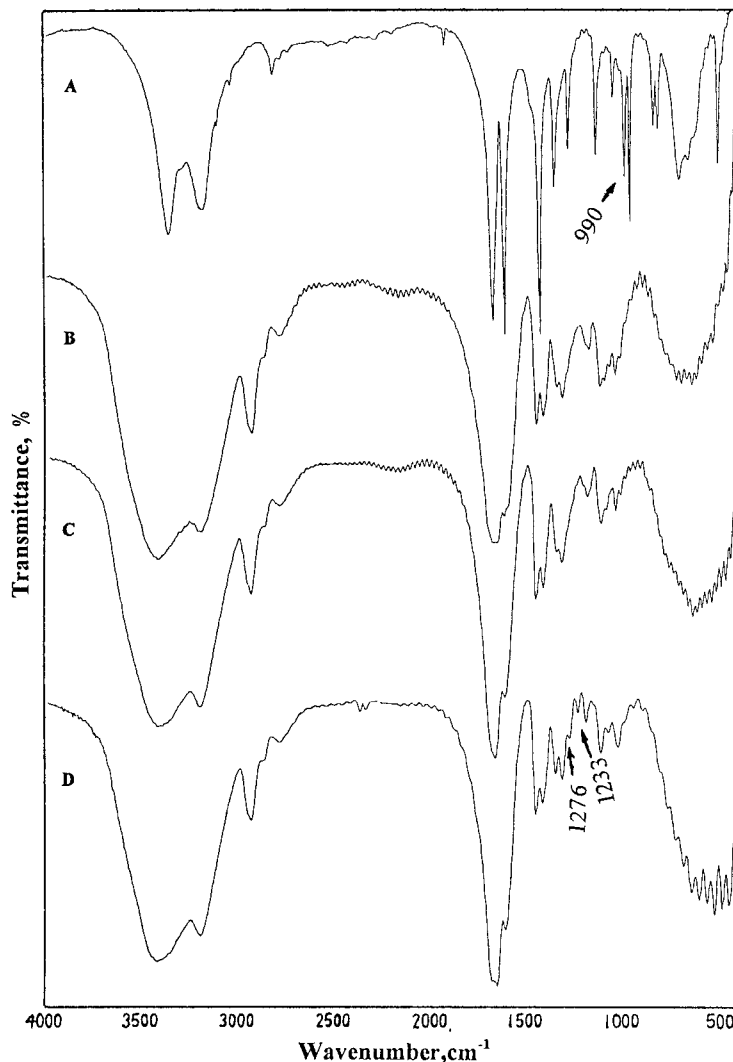


Figure 3 FTIR spectra of (A) acrylamide and polyacrylamide prepared from (B) solution, (C) emulsion, and (D) microemulsion.

sion polymerization. At our present state of knowledge, some mechanisms for microemulsion are not yet clear and it is impossible to draw any general features of microemulsion polymerization.

Characterization of Polyacrylamide

Important information on the structure of polyacrylamide which was prepared in the microemulsion, the conventional emulsion, and the solution are discussed. We begin our discussion by checking the crystallinity of the polymers. X-ray diffraction analysis was carried out. As shown in Figure 2, all the peaks have broad shapes, indicating that the three samples are all amorphous. If we compare cure A with cures B and C, it can be found

that although the polyacrylamide prepared from the microemulsion is still amorphous the degree of crystallinity of the polymer is gradually increased. This implies that the molecular chains of the polyacrylamide in the microemulsion become more ordered, while in solution and emulsion systems, they are much more randomly aligned.

It is well known that the polymer chain architecture determines the physical properties of the polymer such as the glass transition. The glass transition temperature (T_g) of the polymers depends on both the molecular constitution and crystallinity conditions, and it has been the object of experimental and theoretical studies for many years. The various T_g values of polyacrylamide have been given as 438, 461, and 468 K.²¹⁻²³ In

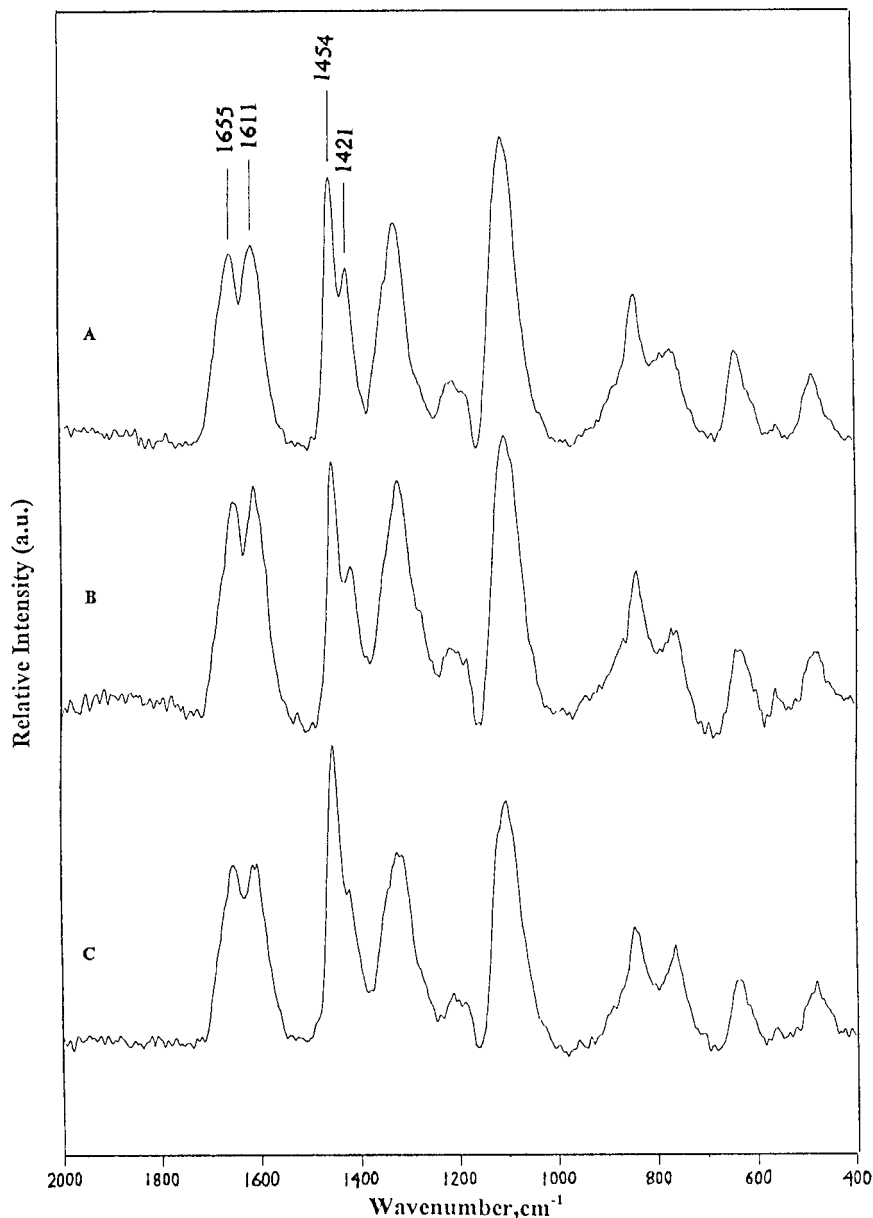


Figure 4 Laser-Raman spectra of polyacrylamide prepared from (A) solution, (B) emulsion, and (C) microemulsion.

this work, Table I shows the variations of the T_g values for the polyacrylamide prepared from three different reaction environments: A: solution; B: emulsion; and C: microemulsion. As can be seen, $T_{g,a} = 457$ K, $T_{g,b} = 456$ K, and $T_{g,c} = 465, 464$, and 465 K (with different alcohol cosurfactants in the polymerization systems). According to the results of the molecular weights of the polyacrylamides given in Table I, the effect of molecular weight on the T_g can be neglected, and the DSC data are in agreement with the crystallinity of the

polymers presented above, namely, the increasing crystallinity increases the T_g of the polymers.

Additional information about the structure of polyacrylamide was obtained from FTIR spectra. The spectra were performed by making KBr pellets from a small amount of the samples, and the resulting spectra were plotted in the transmittance mode as shown in Figure 3. It can be seen that the stretching vibration of the double bond —C=C— in the monomer does not appear [Fig. 3(A)] and only γ (=C—H) at 990 cm^{-1} with a

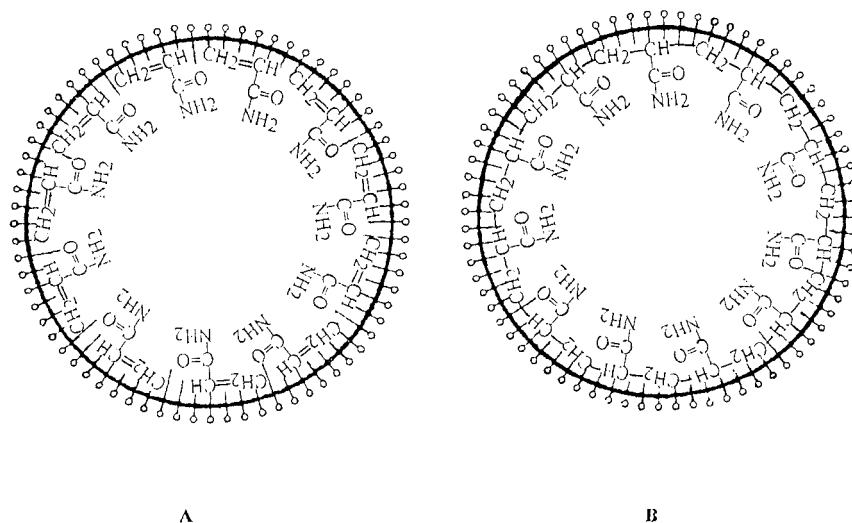


Figure 5 A schematic model for the structure of an acrylamide microemulsion droplet. The hydrophilic tails of the surfactants are partially immersed in the microdroplet core: (A) before the polymerization; (B) after the polymerization.

middle intensity is observed. When the monomer is polymerized, this band almost disappears and only a very small fraction of the unreacted double bond is observed in the polymer, probably due to the end group. The spectrum of polyacrylamide is simple,²⁴ and it is dominated by the absorption of the primary amide group at 3410 and 3195 cm^{-1} , which are assigned to the stretching vibration of N—H, and at 1665 cm^{-1} γ (C=O). The broad absorption in the long wavelength region is associated with deformational vibrations of the hydrogen-bonded NH_2 groups. The long wavelength weak satellite band at 1615 cm^{-1} can possibly be assigned to δ (NH_2). If one compares the three spectra, no pronounced differences are observed; only in the finger region do some new bands at 1276 and 1233 cm^{-1} occur [Fig. 3(D)], but the low-frequency part of the spectrum is rather ambiguous and no conclusions can be drawn from the FTIR spectra.

Figure 4 shows the changes of the laser-Raman spectra (400–2000 cm^{-1}) of the polyacrylamide polymerized in three polymerization environments. The Raman band positions and assignments are as follows: 1655 cm^{-1} γ (C=O), 1611 cm^{-1} δ (NH_2), 1454 cm^{-1} δ (CH_2), and 1421 cm^{-1} δ (C—N + N—H). If we compare three spectra, it will be found that in Figure 4(C), the appearance of the weak absorption band at 1421 cm^{-1} with a decrease of the intensity and together with the increase of the intensity of the band at 1454 cm^{-1} , the intensity of band δ (NH_2) at 1611 cm^{-1} also be decreased; that is, the intensity of the

polar group ($-\text{NH}_2$) of polyacrylamide decreases compared with that in solution and emulsion polymerizations. A similar study on the changing of the conformations of protein with Raman resonance has been reported, and according to the literature,²⁵ these results can be interpreted in this way in that part of the polar group ($-\text{NH}_2$) of the molecular chains of the polyacrylamide polymerized in the microemulsion are tightly coiled in the inner part of the molecular particles.

Based on the above results, we present a simplified picture of the structure of the microemulsion droplet. The water droplets in which monomers dissolved are suspended in the oil phase, and surfactant molecules are located at the interface between the oil and water phases and the hydrophilic groups partially immerse into the microdroplet core as illustrated in Figure 5. Corresponding to the effect of the surfactant, the hydrophobic groups of monomer molecules ($\text{CH}_2=\text{CH}-$) are aligned at the surface of the microdroplets and the hydrophilic groups ($-\text{NH}_2$) are oriented in the center of the microdroplets' core. The concentration of surfactants in conventional emulsion polymerization is relatively low in comparison to the microemulsion polymerization system, and the droplet size (1–10 μm) is larger than that of the microemulsion droplets (10–100 nm); therefore, the orienting effect of the groups by the surfactant in emulsion polymerization is not significant and even can be neglected. In conclusion, the orient effect of the group in microemulsion polymeriza-

tion increases the structural regularity of the polyacrylamide molecular chains which result in increasing of the crystallinity and T_g of the polymers.

CONCLUSION

In this article, the reaction rate of microemulsion polymerization shows only two intervals and the interface is a principal factor which affects the rate of polymerization. From the results of X-ray diffraction, DSC, FTIR, and laser-Raman studies, it was found that the polyacrylamide obtained from microemulsion polymerization has a higher crystallinity and a higher structural regularity of the polymer molecular chains, and the polar group ($-\text{NH}_2$) is confined in the inner part of the polymer particles when compared with conventional emulsion and solution polymerizations.

REFERENCES

1. J. P. Hoar and J. H. Schulman, *Nature*, **152**, 102 (1943).
2. J. E. Schulman, W. Stoeckenius, and L. Prince, *J. Phys. Chem.*, **63**, 1677 (1959).
3. J. O. Stoffer and T. Bone, *J. Disp. Sci. Technol.*, **1**, 37 (1980).
4. J. O. Stoffer and T. Bone, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 2641 (1980).
5. Y. S. Leong and F. Candau, *J. Phys. Chem.*, **86**, 2269 (1982).
6. F. Candau, Y. S. Leong, G. Pouyet, and S. Candan, *J. Colloid Interf. Sci.*, **101**, 167 (1984).
7. F. Candau and Y. S. Leong, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 193 (1985).
8. F. Candau and Z. Zekhnini, *Macromolecules*, **19**, 1895 (1986).
9. F. Candau, Z. Zekhnini, F. Heatley, and E. Franta, *Colloid Polym. Sci.*, **264**, 676 (1986).
10. F. Candau, Z. Zekhnini, and J. P. Durand, *J. Colloid Interf. Sci.*, **114**, 398 (1986).
11. S. S. Atik and J. K. Thomas, *J. Am. Chem. Soc.*, **104**, 5868 (1982).
12. L. M. Gan, C. H. Shew, and S. E. Friberg, *J. Macromol. Sci. Chem., A*, **19**, 739 (1983).
13. M. Antonietti, S. Lohmman, and C. Vanniel, *Macromolecules*, **25**, 1515 (1989).
14. W. Sholtan, *Makromol. Chem.*, **14**, 169 (1954).
15. J. S. Guo, E. D. Sudol, J. W. Vanderhoff, and M. S. El-Aasser, *J. Polym. Sci. Polym. Chem. Ed.*, **30**, 691 (1992).
16. M. T. Carver, E. Hirsch, J. C. Wittmann, R. M. Fitch, and F. Candau, *J. Phys. Chem.*, **93**, 4867 (1989).
17. A. Jayakrishnan and D. O. Shah, *J. Polym. Sci. Polym. Lett. Ed.*, **22**, 31 (1984).
18. A. K. Doblittle, *The Technology of Solvents and Plasticizers*, Wiley, New York, 1954, p. 640.
19. J. A. Monik, *Alcohols*, Van Nostrand, Reinhold, New York, 1968, pp. 162, 155.
20. L. M. Gan, C. H. Chew, I. Lye, L. Ma, and G. Li, *Polymer*, **34**, 3860 (1993).
21. J. Klein and R. Heitzmann, *Makromol. Chem.*, **179**, 1895 (1978).
22. F. Rodriguez, *Principles of Polymer Systems*, McGraw-Hill, New York, 1970.
23. I. Janigova, K. Csomorova, M. Stillhammerova, and J. Barton, *Macromol. Chem. Phys.*, **195**, 3609 (1994).
24. D. O. Hummel, *Atlas of Polymer and Plastics Analysis*, Carl Hanser Verlag, Munich, 1988, p. 386.
25. Z. J. Du, *Spex Speaker*, **22**(2), 1 (1977).