

Investigation on the Inverse Emulsion Polymerization of Acrylic Acid

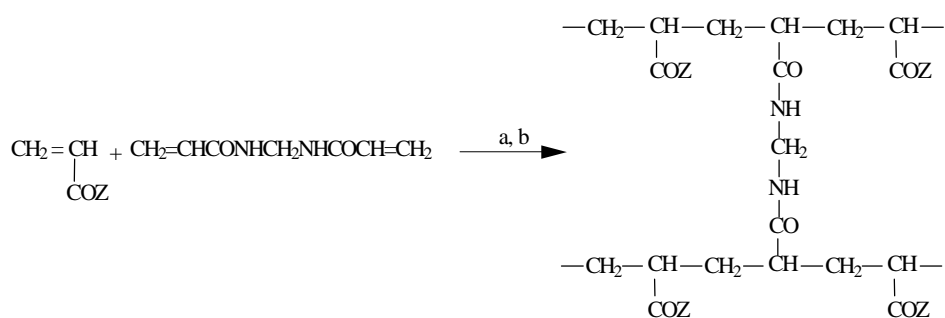
Jian Fang GE*, Feng Ji LU, Wen DING

Department of Polymer Materials, Xi'an Jiaotong University, Xi'an 710049

Abstract: Polyacrylic acid particles in nano-scale were synthesized using an inverse (W/O) emulsion polymerization method. The particle size and size change of inverse micelles which solubilize a part of monomer solution was monitored by PCS (photon correlation spectroscopy) and the particles of polyacrylic acid were viewed in scanning electron microscope for the first time. It was concluded that the inverse micelles were primarily the polymerization reaction sites.

Keywords: Polyacrylic acid, inversion emulsion polymerization, radical reaction.

An aqueous solution of the hydrophilic monomer such as acrylic acid is dispersed in a continuous lipophilic medium using surfactants, which promote the formation of a water-in-oil (W/O) emulsion. The water-in-oil (W/O) emulsion polymerization process has shown superior characteristics¹ such as the low viscosity of the dispersion, easy removal of the reaction heat² and the high molecular weight of the obtained polymer³ *etc.* And it is attractive to investigate the reaction system because the polymerization process is also prospective to prepare particles in nano-scale.



a) AIBN; b) heating

(Z:ONa, OH; lipophilic phase: 120[#] gasoline; co-emulsifier: Span 80 and Tween 80)

Experimental

The continuous lipophilic phase consisted of 120[#] gasoline and co-emulsifiers of Span 80

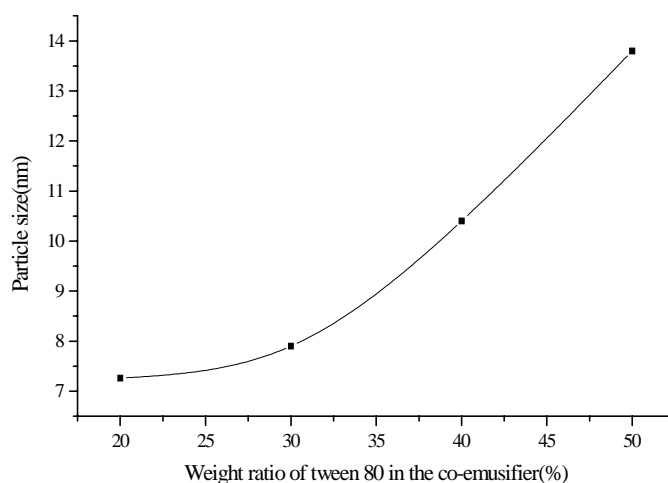
*E-mail: gjf@mmc.edu.cn

(sorbitan monooleate)–Tween 80 (polyethyleneglycolsorbitan monooleate) was used. For the aqueous phase acrylic acid, sodium hydroxide and water were mixed, yielding a W/O emulsion with 70% lipophilic and 30% hydrophilic phase, with 1% crosslinking agent N,N'-methylene-bis acrylamide added. The aqueous phase contained both acrylic acid and sodium acrylate, the degree of neutralization was 90%. The temperature of the lipophilic-hydrophilic mixture was gradually raised and maintained in the vicinity of 65°C for 3 h. The lipophilic AIBN was used as initiator. After cooling to room temperature, the particles were isolated by centrifugation, washed several times with 120[#] gasoline, and then freeze-dried to remove residual gasoline and water. The particles of polyacrylic acid were dried in a vacuum chamber to remove residual water, sputter-coated with a gold layer, and viewed in a scanning electron microscope (S-2700, HITACHI). On the other side, the supernatant was obtained from ultrasonic-made water-in-oil emulsion after its 2 h stationary process, in which the mean sizes of the inverse micelles, in Z-average value, were determined by PCS with Malvern Auto Sizer (England).

Results and Discussion

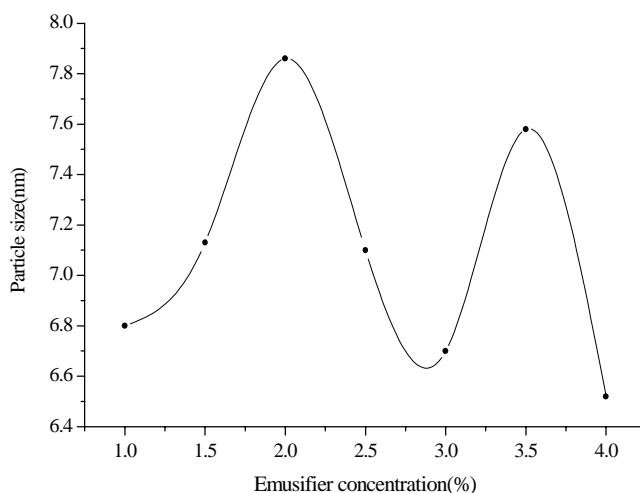
The particle size of the inverse micelles dispersed in 120[#] gasoline medium containing different ratios of Tween 80 to Span 80 is shown in **Figure 1**. The overall emulsifier concentration was kept constant at 2.0%. The size of the micelles increases from 7.8 to 13.8 nm with the increase of the proportion of Tween 80.

Figure 1 Relationship between particle size of W/O micelles and co-emulsifier composition in absence of monomer



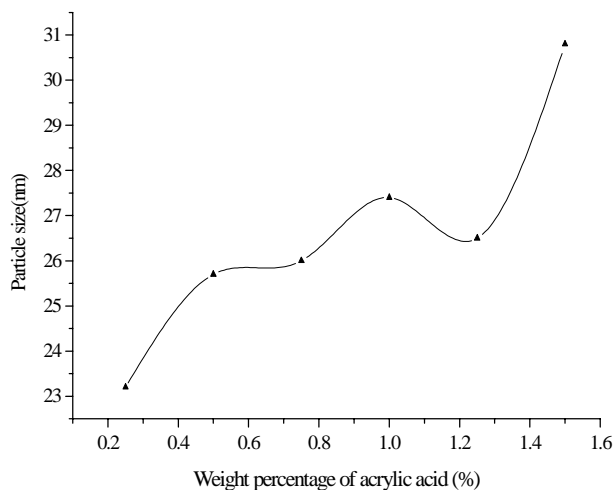
For a given ratio 20/80 of Tween 80/Span 80, the co-emulsifier concentration did not influence significantly the micelle sizes which were in the range of 6.4 ~8.0 nm, *e.g.*, at the range from 1.0 to 4.0%, just as shown in **Figure 2**.

Figure 2 Relationship between particle size of W/O micelles and emusifier percentage in absence of monomer

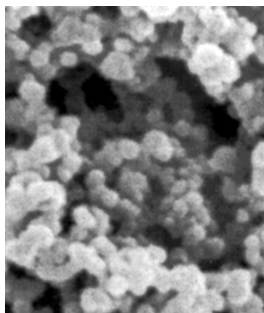


In presence of acrylic monomer, the micelle size increased slightly from 23 to 32 nm with the increase of the inner phase concentration, which implies that only little part of acrylic monomer had been solubilized in the micelles (**Figure 3**).

Figure 3 Relationship between particle size of W/O micelles and monomer weight percentage in presence of monomer



The polymerization has been completed yielding a dispersion of water-swollen polyacrylic acid particles in medium. The surface structure of these particles (with water removed) was analyzed by scanning electron microscopy, showing that the size of the particles is in the range of 50~160 nm (**Figure 4**).

Figure 4 SEM micrograph ($\times 1400$) of the particle surface structure

The results obtained above can be accounted for by the following possible polymerization mechanism. The lipophilic initiator decomposes into radicals, collapses with monomer molecules of acrylic acid and initiates the polymerization in the inverse micelles. Subsequently the inverse micelles, which are more numerous and have a greater contact surface than the emulsion droplets, become the reaction sites. Nanoparticles are formed at the endpoint of the reaction, with larger dimension than that of the primary micelle particles due to the continuous supplement of monomer from the emulsion droplets.

Acknowledgment

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References

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