

PARAMETERS AFFECTING PARTICLE SIZE OF POLYBUTYL – ACRYLATE MICROGELS

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ABSTRACT

The factors affecting particle size of reactive microgels formed during the self-emulsifying copolymerization of unsaturated polyester (UP) with butyl acrylate (BA) have been studied. The parameters discussed are: the proportion of the UP in the monomer mixture, the molecular weight and the carboxyl value of the UP, the phase ratio, the electrolyte concentration and the polar solvent additive. The seeding emulsion polymerization is discussed as well.

It turned out that the particle size of the reactive microgels can be controlled in a definite range by changing the experimental conditions. However the particle size distribution becomes broader as the average diameter increases. It is suggested that the agglomeration of primary particles plays an important role during the growth of microgel particle.

INTRODUCTION

Reactive microgels are internally crosslinked polymers with functional groups on the particle surface. Elastomeric reactive microgels are effective toughener for epoxy resins, which can improve the toughness of epoxy adhesives greatly without significant impairing of the thermal resistance^[1,2]. In order to study the morphology – property relationship of the toughened system, it is important to control particle size of the reactive microgel.

The unique preparation method of reactive microgels is based on the self-emulsifying copolymerization of unsaturated polyesters (UP) with ethylenic monomers^[3,4]. The objective of this research is to work out a way for controlling the particle size of microgels in the range of 40 to 1000 nm. In the present paper the factors affecting the particle size of microgels are studied, and the mechanism of the particle growth during the emulsion polymerization is discussed.

EXPERIMENTAL

1. Preparation of UP

UP used in this study were prepared by melt condensation of 1,6-hexanediol and maleic anhydride. Thus, 1 mol 1,6-hexanediol and 1.15 mol maleic anhydride were heated in a 3-necked flask for 1h at 100 °C, and then 3h at 130 °C. The condensation was continued at 150 – 160 °C under an argon stream. The molecular weight and *cis/trans* ratio of the product depend on the reaction conditions. The product was treated by dissolving in acetone and precipitating with water to cut off the low molecular fraction.

The carboxyl value of UP was determined by titration in acetone with 0.1 N KOH to the thymol blue end point, the molecular weight was determined by VPO, and the *cis/trans* ratio by NMR. The results are given in Table 1.

Table 1 Analysis of unsaturated polyester

No.	Reaction temperature/time (°C) (h)	Carboxyl value (meq/g)	$\overline{M}_n$ (10^3)	<i>cis/trans</i>
UP-1	160/5	0.84	2.08	64/36
UP-2	155/5	0.93	1.72	71/29
UP-3	150/5	1.16	1.39	80/20
UP-4	150/5	1.42	1.46	80/20
UP-5	150/6	0.90	1.75	73/27
UP-6	150/7	1.04	1.65	68/32

2. Preparation of reactive microgels

n-Butyl acrylate (BA) was used in the self-emulsifying copolymerization. The UP was dissolved in degassed distilled water containing NaHCO_3 for neutralizing carboxyl group of the UP. BA was introduced under strict exclusion of oxygen. After vigorous stirring for 15 min, the polymerization was initiated by injection of an aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$. The concentration of the initiator was 10^{-3} mol/dm³. The polymerization was carried on at 70 °C for 6 h.

A Coulter Nanosizer was used for measuring the particle size of the latices, thereby polydispersity index is given. An index 0 or 1 would describe an essentially monosized distribution, whereas 8 or 9 would describe a wide range distribution. TEM pictures of the microgel particles were taken using a Hitachi TEM.

RESULTS AND DISCUSSION

1. Effect of the parameters in emulsion polymerization

In the emulsion copolymerization of UP with BA, the carboxylated unsaturated polyester acts as emulsifier and multifunctional monomer. The carboxylate groups on the microgel particle make the latices stable, therefore enough UP in the monomer mixture is needed for stabilizing the microgel particle. In the experiments, where UP-4 was used, coagulum formed along with microgel when the UP proportion was less than 10%. In Figure 1 the change of particle size with UP proportion is given. The first part of the curve shows the diminution of the particle size with the increase of UP proportion. However, the UP makes the copolymer more water affinitive and the particle size increase with UP proportion when UP proportion exceeds 20%. At still higher UP proportions hydrogel forms.

Properly hydrophilic-lipophilic balanced UP molecule is essential for the self-emulsifying copolymerization. A medium molecular weight of UP is suitable for the preparation of microgels. In case the UP proportion in the monomer mixture was kept at 20wt%, coagulum formed along with microgel if $\overline{M}_n$ of the UP exceeded 2000. The influence of the molecular weight and the carboxyl value of the UP is given in Table 2.

As the molecular weight of the UP increases and the carboxyl value decreases,

there is an increase in the average diameter of the microgel particle, and the polydispersity increases as well.

The phase ratio of water to monomer mixture is also very important. Owing to the small particle size, the system becomes very thick if the water/monomer ratio is too low. The particle size diminishes gradually as the water phase increases. The experimental results are given in Table 3.

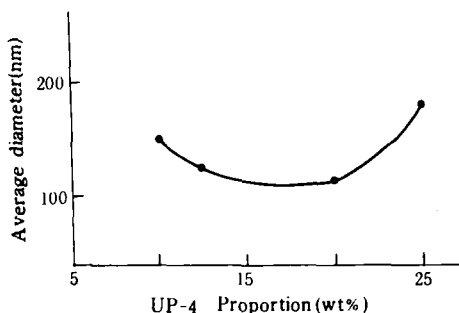


Fig. 1 Influence of the UP-4 proportion on microgel particle size. (water : monomer = 5:1)

Table 2 Influence of the UP structure on microgel particle size

No.	UP Carboxyl value	$\overline{M}_n$ (10^3)	Particle size	
			Average diameter (nm)	Polydispersity
UP-4	1.42	1.46	76	3
UP-3	1.16	1.39	75	3
UP-6	1.04	1.65	95	4
UP-2	0.93	1.72	121	5
UP-5	0.90	1.75	152	6
UP-1	0.84	2.08	300	8

Water/monomer = 5/1

Table 3 Influence of phase ratio on microgel particle size

Water/monomer	Average diameter (nm)	Polydispersity	Remarks
2 / 1	—	—	high viscosity
5 / 1	88	3	
10 / 1	71	3	
15 / 1	62	4	
20 / 1	57	4	

20wt% UP-3 in the monomer mixture

2. Effect of the electrolyte concentration and polar solvents

Particle size of the reactive microgels can be controlled in the range of 50 — 200 nm by regulating the parameters in the emulsion polymerization as described above. In order to prepare latices of larger particle size by emulsion polymerization, it is a common practice to increase electrolyte concentration or to introduce a small amount of polar solvent^[5].

In the copolymerization of UP-3 with BA, microgel particle size increased with the concentration of NaHCO_3 (Table 4). However, the microgel latices were not very stable toward electrolytes, the latices lose their stability if the electrolyte concentration exceeds 10^{-3} mol/ml.

The effect of water soluble polar solvents is similar to that of electrolytes. An adequate amount of ethanol or acetone in the water phase can bring about an increase in

particle size and particle size distribution (Table 5). The polar solvents impair stability of latices, latices are unstable in the presence of 10% ethanol in the water phase.

Table 4 Influence of electrolyte concentration on microgel particle size

Electrolyte concentration (mol/ml)	Average diameter (nm)	Polydispersity
4.45×10^{-5}	52	4
1.17×10^{-4}	70	4
2.26×10^{-4}	87	3
2.89×10^{-4}	100	4
3.65×10^{-4}	400	9

20wt% UP-3 in the monomer mixture water/monomer = 5/1

Table 5 Influence of polar solvent on microgel particle size

Level of polar solvent in water phase	Average diameter (nm)	Polydispersity
control	88	3
1% ethanol	187	6
5% ethanol	~ 1000	9
1% acetone	119	5
5% acetone	118	5
10% acetone	136	5
20% acetone	218	6

20wt% UP-3 in the monomer mixture water/monomer = 5/1

3. Seeding emulsion polymerization

Seeding emulsion polymerization was carried out with the hope of preparing large microgel particles with narrow size distribution. An example is given in Table 6. In the first stage a seed latex - 1 of average diameter 74 nm was prepared. In the second stage an alkaline aqueous UP-3 solution was added to the seed latex - 1. A prolonged stirring (24 — 72 h) was allowed before the introduction of the second part of BA and $K_2S_2O_8$. The idea was let all UP-3 molecules be adsorbed by the seed latex particles, so that in the second stage of the seeding polymerization no new particle should be formed. The result was not as expected. Although a substantial increase in average particle size was achieved in the second stage, the particle size distribution became very broad. The TEM micrograph showed that very small particles were present in the latex along with large one (Figure 2). The experimental result indicates that the diffusion of the polymeric emulsifier molecules through aqueous phase is not easy.

4. Mechanism of the particle growth

According to the classical model of emulsion polymerization proposed by Smith and Ewart^[6], the latex particles grow up through absorption of monomer from water phase. The smaller particles grow up faster, because they have larger specific surface, as a result the particle size distribution becomes narrower with the particle diameter increasing.

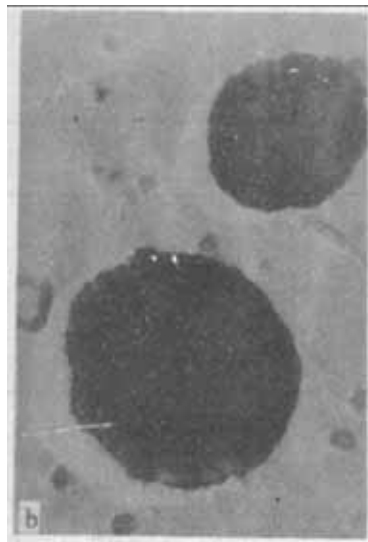
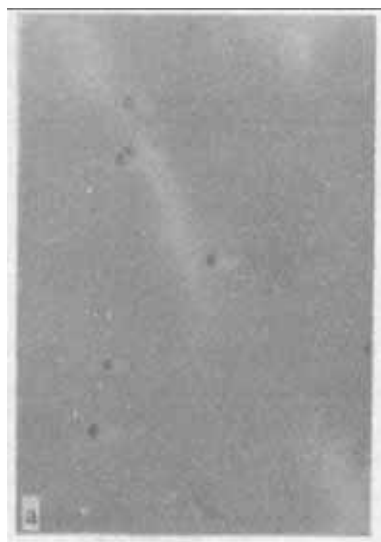


Fig. 2 (a) Transmission electron photomicrograph of seed latex - 1 at 50,000 $\times$ magnification Fig. 2(b) Transmission electron photomicrograph of the 2nd stage at 20,000 $\times$ magnification

Table 6 Seeding polymerization

Composition		Average particle size
1st stage	UP - 3 1 g	74 nm polydispersity 3
	NaHCO ₃ 0.6	
	BA 4	
	Water 40	
	K ₂ S ₂ O ₈ 0.12	
	latex - 1 45	
2nd stage	UP - 1 1	280 nm polydispersity 7
	NaHCO ₃ 0.6	
	PA 3	
	Water 80	
	K ₂ S ₂ O ₈ 0.24	

The growth of the microgel particles during the self-emulsifying copolymerization of UP with BA is obviously different from the particles in classical emulsion polymerization. As shown by the data in Table 2 — 6, increase of the average particle size of microgels is always accompanied by an increase in the polydispersity. All these experimental results support the mechanism of particle growth through agglomeration of primary particles.

In Figure 3 the path of particle growth is given schematically.

The peculiarity of the self-emulsifying polymerization may be traced back to the polymeric emulsifier. The carboxylated unsaturated polyester forms micelles in alkaline aqueous solution. The critical micellar concentration (CMC) should be very low. The CMC of an UP of $\bar{M}_n$ 1470 was 1.6×10^{-6} g/ml^[7]. That is to say, very few free UP molecules are present in the water phase. At the beginning of the polymerization there are UP micelles swollen by BA. When a free radical gets into a micelle or a latex

particle, the polymerization is initiated. As the polymerization goes on, the primary particles absorb more monomer from the water phase, the volume of the particles increases, so that the originally stable particles lose their stability. The polymerizing unstable primary particles can not absorb enough emulsifier from water phase to recover the stability. The unstable particles collide with other latex particle or micelle, and the agglomeration takes place. If the particle agglomeration dominates in the growth of microgel particles, the "most probable distribution" will be resulted.

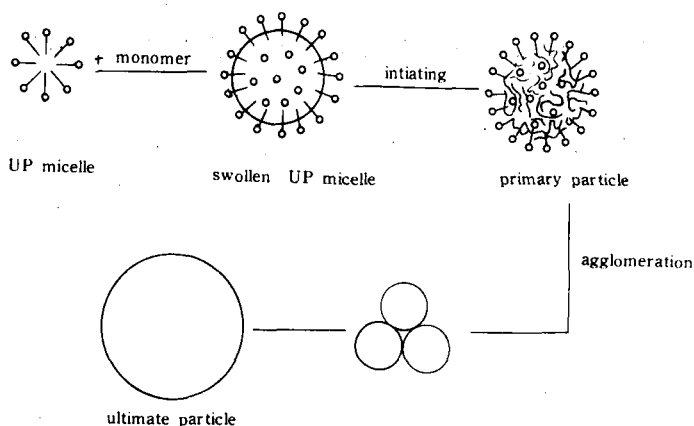


Fig. 3 The path of the particle growth in self-emulsifying copolymerization of UP with BA

Keywords:

Emulsion polymerization; Microgel; Unsaturated polyester.

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