Polymer Microgels Prepared by Emulsifier-Free Emulsion Polymerization of Unsaturated Polyesters and Styrene

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ABSTRACT: In the present work polymer microgels were prepared by emulsifier-free emulsion copolymerization of unsaturated polyesters (UPs) with end carboxyl groups and styrene (St). The nucleation mechanism of UP-St emulsifier-free emulsion polymerization was proposed. The effects of the ratio of the monomers to water, pH, and the ratio of UP to St on the stability of polymerization and the yield of microgels were studied. It was found that the polymer microgels can be used to markedly improve the impact strength of UP. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 3049–3053, 2000

Key words: polymer microgels; emulsifier-free emulsion polymerization; unsaturated polyesters; styrene

INTRODUCTION

Polymer microgels are classified on the basis of microscopic structure and are intermediate between branched and macroscopically crosslinked systems but with the internal structure of a typical network. Microgels have been extensively used in the coatings industry because of their utility for improving the rheological properties of paints, as well as the performance of films. As is well known, the paints based on the conventional alkyd resin tend to become brittle and thus extensibility is gradually reduced because of increased crosslinking in the presence of air. If they are modified by polymer microgels, they appear to be quite resistant to weathering.[1] Moreover, polymer microgels have been used in biochemistry, pharmaceuticals, and other areas.[2–5]

Microgels may be prepared by free-radical polymerization either in dilute solution[6] or more commonly by emulsion polymerization,[7–9] dispersion polymerization,[1,7] and even by precipitation polymerization.[10,11] Emulsion polymerization is more practical and more effective in avoiding macroscopic network formation. However, the emulsifier will remain in the system and play an opposite role in applications. So emulsifier-free emulsion polymerization should be an attractive technique for preparing microgels.

In the current work polymer microgels were prepared by emulsifier-free emulsion copolymerization of unsaturated polyesters (UPs) and styrene (St). We studied the effects of the ratio of the monomers to water, pH, and the ratio of UP to St on the stability of polymerization and the yield of the microgels. The polymer microgels show good compatibility with UP and can markedly improve its impact strength.

EXPERIMENTAL

In these experiments the monomers were all industrial grade. Diethylene glycol (DEG), maleic anhydride, and phthalic anhydride were used without further purification. The St monomer was first washed with 10% NaOH followed by

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Table I Recipe for Preparing UP with Carboxyl End Groups

	DEG	Maleic Anhydride	Phthalic Anhydride
Parts by weight	205	100	150
Parts by moles	1.9340	1.0204	1.0135
—COOH/—OH (molar)		≈1.05 : 1	

distilled water to remove inhibitors. The potassium persulfate (KPS) initiator and the sodium bisulfite (NHS) reducer of analytically pure grade were used without further purification.

The condensation polymerization to prepare low molecular weight UP with carboxyl end groups was carried out in an N_2 atmosphere in a four-necked, 250-mL flask equipped with a stirrer, thermometer, thermostat, and condenser. The reaction temperature was about 170°C. The recipe for preparing UP as mentioned above is listed in Table I. The reaction is terminated when the acid value of the reactant is about 7.5×10^{-4} mol g^{-1} (molecular weight = ~1900).

The emulsifier-free emulsion copolymerization of UP and St was carried out in a four-necked, 250-mL flask equipped with a stirrer, thermometer, thermostat, and feed funnel. The reaction temperature was 70°C. The recipe for preparing microgels by emulsifier-free emulsion copolymerization of UP and St is listed in Table II.

Under the reaction temperature (70°C), UP was dissolved in water. We added an appropriate quantity of ammonium hydroxide to adjust the pH of the dispersion. Then we added the comonomer St into the reaction system to be preemulsified. Finally, we added the initiator and reducer solution into the reactor to initiate the reaction.

RESULTS AND DISCUSSION

Characterization of Polymer Microgels

Degree of Crosslinking

The polymer microgels were extracted in acetone reflux for 48 h to determine the degree of crosslinking. The degree of crosslinking is calculated as follows:

$$D = \frac{M_1}{M_0} \times 100\%$$

where D is the degree of crosslinking, M_1 is the weight of the extracted sample, and M_0 is the weight of the sample before extracting. Parameter D shows the percentage of crosslinked component in the microgel particles. The results are listed in Table III.

It is evident from the table that the degree of crosslinking of the microgels increases with increasing UP content in the monomers, and we can draw a conclusion that UP and polystyrene (PS) are crosslinked in the microgel particles. There is a very small content of the noncrosslinked component.

Morphology of Microgel Particles

The morphology of the polymer microgels was examined by TEM, and Figure 1 is the microscope photograph. It can be seen from the photograph that the microgels have a core–shell structure. Although the outline between the core and shell is not very clear, the shell layer is very sticky and leads to the connection of the microgels. As is well known, PS is very "hard," so it can be concluded that the "sticky" layer on the microgels is UP and the core of the microgels is mostly PS.

Mechanism of Emulsifier-Free Emulsion Copolymerization of UP and St

The end carboxyl groups of UP play an important role in emulsifier-free emulsion polymerization. If UP with or without a few end carboxyl groups were used, the dispersion will arbitrarily coagulate. According to the experiments, the mecha-

Table II Recipe for Preparing Polymer Microgels

	St	UP	APS	NHS	Distilled Water
Parts by weight	x	$100 - x$	0.6–0.8	0.45–0.6	500–1200

Table III Degree of Crosslinking of Microgels Prepared under Different UP/St Ratios

Ratio of UP/St	UP (%) in (UP + St)	Degree of Crosslinking (%)
2.00	66.7	94.3
1.67	62.5	92.2
1.43	58.8	90.8
1.25	55.6	88.7

nism of the polymerization was proposed as shown in Figure 2.

The end carboxyl groups of the UP would turn into a carboxyl anion under alkali conditions (ammonium hydroxide). If the molecular weight of the UP is low enough, the UP is completely dissolved in the medium (distilled water) and the polymerization system looks uniform and transparent [see Fig. 2(a)]. After St is added, a part of the UP is still dissolved in water, a part may be dissolved in St to form a so-called solubilized micelle, and the rest may be absorbed to the surface of the monomer (St) droplets. The solubilized micelle and monomer droplets are steadily dispersed in water because of the repulsion of carboxyl anions attached on the surface. The polymerization system is no longer homogeneous and transparent but is ivory white [see Fig. 2(b)]. After the initiators are added, they are decomposed and radicals generate. Radicals are caught by UP and St molecules and thus polymerization is initiated. More hydrophilic UP chains are linked to hydrophobic PS chains to form amphipathic macromolecules. The hydrophobic ends (PS chains) of several macromolecules are attracted to each other and the hydrophilic ends (UP chains) are pulled out to the aqueous phase. These attracted macromolecules are crosslinked to form particles [microgels; see Fig. 2(c)]. The formed particles absorb monomer from the droplets to propagate.

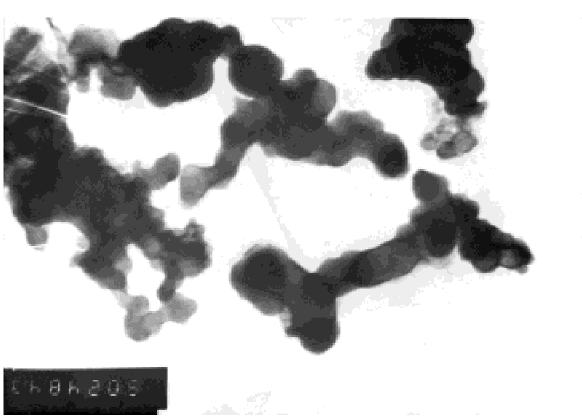

Figure 1 A TEM photograph of the microgels.

The UP and St are both necessary ingredients for the emulsifier-free emulsion polymerization. The emulsion is stabilized by the repulsion of

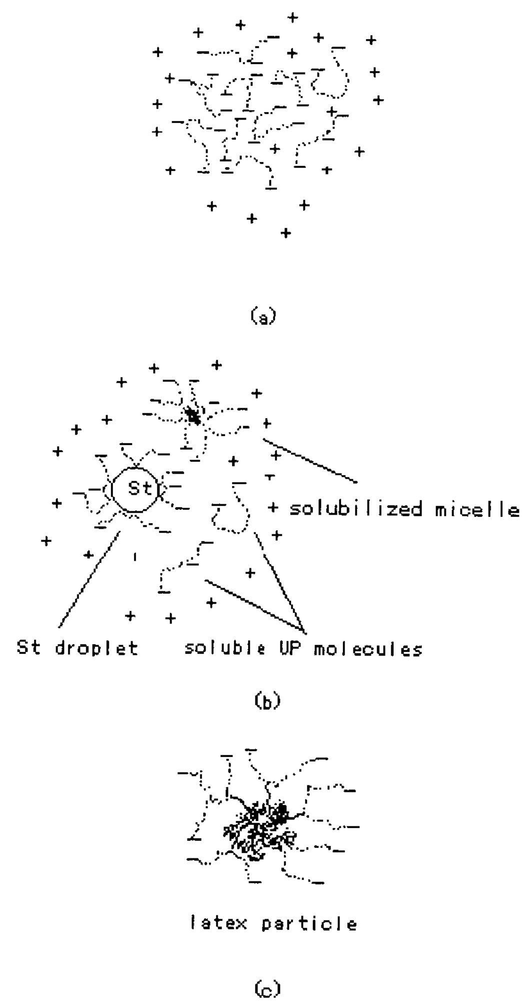

Figure 2 The mechanism of emulsifier-free emulsion polymerization of UP and St. (a) A low molecular weight UP with end carboxyl groups is soluble in distilled water under ammonium hydroxide. (b) After adding St, the UP molecules might be absorbed on the St droplets, might form a solubilized micelle, and might be soluble in the medium. (c) In the latex particles the PS chains swollen by St monomer are absorbed with each other; the UP chains are pulled out to the water.

Table IV Stability of Prepared Emulsions and Yield of Microgels under Different pH Values

pH Value	Yields of Microgels (%)	Stability of Emulsions Prepared
< 6	—	No microgels generate
7	95	Emulsion is ivory white and coagulates after 5 days
8	98	Emulsion is ivory white and still does not coagulate after 15 days
9	60	Lots of macrogels generate
> 9	Very little	Most products are macrogels

UP/St = 1/0.7 (w/w), monomer/distilled water = 1/10 (w/w).

carboxylic anions, which are provided by the UP and located on the surfaces of the particles. But UP cannot be initiated and propagate individually in the absence of St because of steric hindrance. Only when St is added and PS chains formed are grafted onto the UP chains, will the polymerization be carried out and the emulsion be stabilized.

Effects of Various Factors on Stability of Emulsion and Yield of Microgels

pH Value

By adjusting the pH of the reaction dispersion with ammonium hydroxide, almost all the carboxyl groups in the UP molecules are dissociated into carboxylic anions, which can stabilize the particles and droplets during the polymerization. In other words, the pH value substantially determines the ammoniation extent of UP molecules and the quantity of carboxylic anions resulting from carboxyl groups. The stability of the prepared emulsion and the yields of the microgels under different pH values are summarized in Table IV.

When the pH is very low or very high, microgels hardly generate but macrogels do and the prepared emulsions coagulate. When the pH is about 8, the stability of the emulsion is the best and the yield of microgels is the highest. According to the nucleation mechanism mentioned above, it is evident that in acidic conditions few carboxyl groups on the UP chains are dissociated into anions. Only in an alkaline system will the carboxylic anions be turned out enough to stabilize the latex particles. Nevertheless, if the pH is too high (pH > 9), the excessive ammonium hydroxide will act as an electrolyte to reduce the ξ potentials of the latex particles, so the stability of the polymerization system will worsen.

UP/St Ratio

As mentioned above, for the emulsifier-free emulsion polymerization of UP and St, the ratio of UP to St is especially important to the reaction. The ratios of UP/St and the corresponding results obtained are listed in Table V.

If the ratio is too high (UP/St > 2), there is not enough St to graft onto the UP chains so very few latex particles generate. It is known that the polymerization can take place just in the latex particles. As a result, St is consumed quickly but most of the UP molecules cannot continue to self-polymerize because of the steric hindrance. On the other hand, if the ratio is too low (UP/St

Table V Effect of UP/St Ratio on Stability of Emulsion and Yields of Microgels

Ratios of UP/St	Yields of Microgels (%)	Stability of Emulsion
2.50	No microgels	Sticky and yellowish
2.00	88	Ivory white and coagulates after 2 days
1.67	94	Light blue and still stable after 15 days
1.43	98	Ivory white and still stable after 15 days
1.25	92	Ivory white and coagulates in few days
1.00	60	Coagulates in few hours
0.50	Macrogels	Coagulates immediately

Table VI Impact Strength of UP196s Modified by Microgels Prepared under Different Conditions

UP/St in Polymerization	Monomer/ Water in Polymerization	Impact Strength (10^4 N m^{-2})
1.43	0.10	2.22
1.67	0.10	2.74
1.43	0.083	2.89
1.67	0.083	4.14
UP196s (not modified)		1.79

< 1.25), St is helpful in the nucleation of latex particles, but too little UP is not enough for the carboxyl groups which play a critical role in stabilization. Therefore, whether the ratio is too high (>2) or too low (<1.25), the reaction cannot be carried out steadily and few microgels will generate.

Monomer/Water Ratio

In practical production a high solid content is always expected. In other words, the ratio of the monomer to water should be as high as possible. In the present work emulsifier-free emulsion polymerization was carried out under different monomer/water ratios. It was found that the lower the ratio is, the steadier the reaction and when the ratio is higher than 0.125 (total solid content in theory is about 11%), macrogels will generate.

Applications of Polymer Microgels

The powder of the polymer microgels was obtained by dealing the prepared emulsion with 5% HCl, freezing it at under −10°C, and then desiccating it at room temperature. The unsaturated polyester UP196s (Tianjin Synthetic Materials Plant) was modified by adding 3% (weight) of the microgel powder prepared. The impact strengths of the modified UP196s are listed in Table VI. Because many carboxyl groups are distributed on the surface of the microgel particles, the UP196s that carries the hydroxyl group is more crosslinked by the microgels. The impact strength is obviously elevated.

Because the molecular structure of the microgels is very similar to that of UPs, microgels prepared by UP and St are very compatible with UPs. The application of microgels prepared on UPs will be very prosperous.

CONCLUSION

Polymer microgels were prepared by the emulsifier-free emulsion polymerization of St and UP with end carboxyl groups. The nucleation mechanism was proposed. UP and St are both indispensable ingredients for emulsifier-free emulsion polymerization. The pH value, ratio of UP to St, and ratio of monomer to water seriously affects the stability of the reaction system and prepared emulsion and the yield of the microgels. We found that when the pH was about 8, the UP/St ratio was in the range of 1.25–2.00 and the ratio of monomer to water was lower than 0.125, the reaction and emulsion was stable, and the yield of the polymer microgels achieved over 90%. The polymer microgels can be successfully used to modify UPs.

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