Preparation of Acrylic Microgels by Modified Microemulsion Polymerization and Phase Inversion

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Semi-transparent reactive microgel in nanosize has been prepared by modified micro-emulsion polymerization using a common emulsifier, crosslinking agent and functional monomer. The microgels are translucent reactive nanoparticles, with the size of 40–100 nm, consisting of inner-crosslinked polymer up to 40%. FT-IR proved the functional groups, such as epoxy and hydroxy, are on the surface of the microgel nano-particles. Rheological detection demonstrated the apparent pseudoplasticity of the non-aqueous microgel dispersion prepared by the phase transfering from the O/W microlatexes.

Keywords modified microemulsion polymerization, microgels, methyl methacrylate

Introduction

Polymer microgel particles have attracted much attention from both scientific (1–3) and technical (4) viewpoints. Such microgels have been widely used in coating technology as building blocks for the formation of high performance organic coatings due to their rheological and reinforcing properties (5). Microgel particles also have numerous applications in fields such as, drug delivery (6), template for synthesis of metal nanoclusters (7), to name a few.

Two traditional routes for synthesis of microgels are solution polymerization and emulsion/microemulsion polymerization (8). In addition, some newer techniques also have been reported that involve dispersion polymerization (9), precipitation polymerization (10), anionic polymerization, end-linking of polymer chains, and step-growth cross-linking reactions (11). Each has its advantage and disadvantage, and can be chosen for a different goal. Reactive microgels can be synthesized by introducing a comonomer of high functionality, such as diacrylates or divinyl benzene.

The objective of this article is to report the preparation of poly(methyl methacrylate)-based microgels using ethylene glycol dimethacrylate (EGDMA) as a cross-linker, glycidyl methacrylate (GMA) or hydroxyl ethyl methacrylate (HEMA) as functional

monomer, butyl acrylate (BA) as comonomer in modified microemulsion polymerization (12) initiated by ammonium persulfate (APS). Most common surfactants are used such as sodium dodecyl sulfate (SDS) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT). Special attention is paid to the influence of HEMA and EGDMA content in the feed composition on the particles size, and swelling index. The microgels can easily be transferred to an organic solvent for further use.

Experimental

Materials

MMA, BA, HEMA, EGDMA and GMA (Shanghai Chemical Reagent Co.) were vacuum distilled and stored below $0°C$ before polymerization. Sodium dodecyl sulfate (SDS) (B.G. Amresco Inc.) with 99% purity, 1-pentanol (n-Pt) and nonyl phenol Poly (ethenoxy ether) NP-9 (ED:9) (Shanghai Chemical Reagent Co.) were used as received. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) from Professional Chemical Product Co. was purified by petroleum ether extraction after dissolving and filtrating in methanol. Ammonium persulfate (APS) from the Shanghai Aijian Reagent Factory were purified by recrystallization in water. Methanol, chloroform, and butyl acetate (BuAc) of A.R. grade from Shanghai Chemical Reagent Co. were used as received. Deionized water was used throughout this work.

Polymerization and Phase Inversion

The procedure of modified microemulsion polymerization can be found in somewhere (12). In a typical example, the premicroemulsion, composed of the entire amount of surfactant, the auxiliary surfactant, water, comonomer, functional monomer, crosslinker (e.g. 1.0 g AOT, 0.5 g NP-9, 25 g water, 0.08 g BA, 0.08 g HEMA, 0.8 g EGDMA), and 1.0 g MMA, that was slightly higher than its solubility in water, was added into a 100 mL, four-necked flask equipped with a reflux condenser, an addition funnel, a thermometer, a nitrogen gas inlet, nitrogen gas outlet, and a magnetic stirring bar. The premicroemulsion was heated to $75°C$ and stirred under a nitrogen atmosphere to remove oxygen and reach equilibrium. Then, the requisite amount of the initiator, which was dissolved in a minimum quantity of water, was added. When the polymerization started, the rest of the monomers (6.0 g MMA) in the addition funnel were added into the reaction flask in a starving addition manner and polymerized for an additional 2 h. The microlatexes were obtained.

BuAc with the proper proportion was added to microlatexes of the final product in a rotary vacuum evaporator, and water and BuAc were removed by azeotropic vacuum distillation and microgels redispersed in oil phase to form non-aqueous dispersions.

The PMMA microlatexes were precipitated in an excess of methanol from aqueous latexes. The precipitated particles were vacuum-filtered, washed successively with methanol and deionized water, and dried in a vacuum desiccator for 24 h below $50°C$.

Characterization

Particle size and size distribution were determined by dynamic light scattering (DLS) on a Malvern 4700 from Malvern Instruments, Ltd. FTIR spectra were recorded on a

Magna-IR^{TM} spectrometer 550. Rheological curves were measured by Brookfield Digital Rheometer Model DV-III using CPE-40 cone spindle.

The *swelling index* (13) of the microgel, which is mainly a function of its crosslink density, is defined as the ratio of particle volume in the organic phase to particle volume in the aqueous phase, e.g.,

$$SI = [D_W \text{ (organic)}/D_W \text{ (aqueous)}]^3$$

The yield of microgels (microgel %) or the efficiency in microgel formation was determined by the weight fraction of insoluble polymer particles. The latexes were dried to form a film. The soluble part or non-crosslinked polymer, including the surfactant molecules, were extracted by soxhlet extraction apparatus equipped with nylon filter-film in acetone through reflux three times at 75°C from the weighted dry film. The solid content was determined by drying and weight.

Results and Discussion

Effect of the Surfactants and Initiators

Table 1 shows the composition of the microemulsion polymerization samples, and Table 2 shows the properties of the final latexes under different conditions. Both thermal and redox system can initiate the microemulsion polymerization. The appearance of the final latexes is bluish, from transparent to translucent according to their particle size. We can easily obtain nanoparticles with diameters in the range of 30–80 nm using a modified microemulsion polymerization technique. From sampls S1 and S2 or S3 and S4, as expected, it shows that the diameter decreased with increasing the content of surfactant. With the same solid content, the number of particles increased and the specific surface also increased. The swelling index also increases with increasing surfactant concentration.

Table 1
The composition of the prepared sample

Sample[d]	Functional monomer[a] (G)	Monomer MMA[b] (g)	Surfactant[c] (g)	Water (g)	Initiator (g)
P1	HEMA	1 + 6	AOT 1	30	APS 0.05
P2	GMA	1 + 6	AOT 1	30	APS 0.05
S1	HEMA	1 + 5	SDS 0.6	28	APS 0.08
S2	HEMA	1 + 5	SDS 2.2	28	APS 0.08
S3	GMA	1 + 6.5	AOT 1	25	APS 0.05
S4	GMA	1 + 6.5	AOT 1.5	25	H$_2$O$_2$/V$_C$ 0.06/0.09
W1	HEMA	1 + 6	NP/AOT 0.5/0.5	14	APS 0.08
W2	HEMA	1 + 6	NP/AOT 0.5/0.5	30	APS 0.08
W3	HEMA	1 + 6	NP/AOT 0.5/0.5	55	APS 0.08

[a]The functional monomer was 0.08 g whatever the type used.

[b]The first part monomer 1g was in the initial microemulsion and the second part was post-added.

[c]1-pentanol was used as cosurfactant when using SDS as surfactant, and NP-9 as cosurfactant when using AOT as surfactant, the content of cosurfactant was low.

[d]The crossinglinker monomer EGDMA was 0.8 g, BA was 0.08 g.

Table 2

Characteristics of the microgels and the inverse microgels of Table 1

Sample	Dz^a (water) (nm)	Cv %	Dz (BuAc) (nm)	Cv %	SI^b	Solids content (BuAc) %	Microgel %
P1	51	40	95	56	6.5		86
P2	43	67	100	73	12.6		85
S1	45	44	78	65	5.2	22	81
S2	32	62	67	52	9.2	23	83
S3	43	53	100	58	12.6	28	79
S4	34	65	98	61	22.0	28	81
W1	144	74	187	68	2.2		87
W2	60	54	95	66	4.0		86
W3	67	34	73	57	1.3		90

[a]D_z is z-average diameter determined by dynamic light scattering, Cv is standard deviation.
[b]$SI = [Dz(BuAc)/Dz(water)]^3$.

The smaller the particles, the easier the swell. The yield of microgels did not change much with the surfactants.

Influence of the Solid Content on Particle Size and Distribution

From the samples W1-W3 in Tables 1 and 2, it can be noticed that increasing water results in a narrowing of the particle size distribution and smaller particles (4). When the water content was too low, like sample W1, viscosity of the system increased as the polymerization proceeding, and paste was formed in the final product. The formation of macrogels, in the case of low water/monomer ratios, indicates that collision and chemical reactions between polymer particles may occur simultaneously during microemulsion polymerization.

Effect of the Content of Functional Monomer HEMA

The effect of the content of functional monomer HEMA is shown in Tables 3 and 4. When the content of HEMA was in the intermediate range of 0.08–0.16 g, the diameter of the latexes was somewhat small. When the content of HEMA used was 0.32 g, as sample

Table 3

Composition of microgels as a function of the content of HEMA

Sample	Constants (g)		Variables (g)
F1	MMA $1 + 6^a$ g		0.025
F2	EGDMA 0.8 g		0.04
F3	BA 0.08 g	HEMA	0.08
F4	NP/AOT 0.5/0.5 g		0.16
F5	APS 0.08 g		0.32
F6	water 28 g		0.8

[a]The first part monomer 1 g was in the initial microemulsion and the second part 6 g was post-added.

Table 4
Characteristics of the microlatexes and the inverse microgels as a function of
HEMA content

Sample	HEMA (g)	Dz (water) (nm)	Cv %	Dz (BuAc) (nm)	Cv %	SI	Solids content (BuAc) %	Microgel %
F1	0.025	86	44	155	53	5.9	19	80
F2	0.04	156	64	197	43	2.0	14	81
F3	0.08	85	32	128	35	3.4	15	86
F4	0.16	79	34	224	38	22.8	16	88
F5	0.32	306	74	209	48	0.3	17	—
F6	0.8	—	—	—	—	—	—	—

F5, the formation of aggregates of primary microgels was difficult to avoid. The existence of aggregation was indicated by the rise of the particle diameter up to three fold. However, the SI of the sample of F5 was less than 1, it implied that the size of the latex particles measured was the size of aggregates of particles, which loosely aggregated and may redisperse in organic solvent through transfer to oil phase. While further increasing the content of HEMA, macrogelation occurs, like sample F6. As a result, the more the content of HEMA used, the more hydroxyl groups on the surface of the microlatexes, and the higher probability of formation of hydrogen bonds between particles. Therefore, when the content of HEMA was low, it was not adequate to form macrogelation through inter-particle hydrogen bonds, while it was high enough, macroscopic network formed. The swelling index of sample F4 was higher than other samples. It may due to its smaller size and higher content of HEMA without aggregates. The yield of microgels increased slightly with increasing content of HEMA.

Influence of the Content of Multifunctional Monomer of EGDMA

With increasing the content of crosslinking monomer of EGDMA, the diameter of the latex particles decreased as shown in Tables 5 and 6. We suppose that the higher

Table 5
Composition of microgels as a function of EGDMA content

Sample	Constants (g)		Variables (g)
C1	MMA 1 + 6[a] g		0.2
C2	HEMA 0.08 g		0.4
C3	BA 0.08 g	EGDMA	0.6
C4	NP/AOT 0.5/0.5 g		0.8
C5	APS 0.08 g		1
C6	water 28 g		1.6

[a]The first part monomer 1 g was in the initial microemulsion, and the second part 6 g was post-added.

Table 6

Characteristics of the microlatexes and the inverse microgels as a function of EGDMA content

Experiment	EGDMA (g)	D_z (water) (nm)	Cv %	D_z (BuAc) (nm)	Cv %	SI	Solids content % (BuAc)	Microgel %
C1	0.2	126	43	174	76	2.6	17.7	74
C2	0.4	84	57	137	51	4.3	8.7	78
C3	0.6	82	54	121	68	3.2	12.7	82
C4	0.8	70	62	110	55	3.9	15.1	86
C5	1	124	64	187	62	3.4	24.3	90
C6	1.6	—	—	—	—	—	—	—

proportions of crosslinking monomers were used for their synthesis, the more compact structures of reactive microgels were formed by a higher density of crosslinking, but the swelling indexes of this series of samples were of similar value. It may due to the fact that the more surface area with smaller particles were obtained, the more crosslinker located in the surface and did not participate in crosslinking. Therefore, the resulting crosslinking density was similar with an increasing content of crosslinker. Meanwhile, the yield of microgels increased with increasing content of EGDMA. That is, the more the content of crosslinker, the lower content of soluble polymers were formed, which also reduced the crosslinking density. However, when the content of EGDMA was too high, similar to sample C6, with the residual unreacted double-bonds on the surface, chemical reactions between polymer particles may occur simultaneously during polymerization, and macroscopic network formed and macrogelation occurred.

FT-IR Spectra of the Samples with a Different Type of Functional Monomer

The FT-IR spectra of sample P1 (Table1) with hydroxy groups and sample P2 (Table1) with epoxide groups are shown in Figure 1. The absorption bands around $970 \, \text{cm}^{-1}$ and $3500 \, \text{cm}^{-1}$ can be seen obviously for samples P2 and P1, respectively. The frequency of the vibration of epoxide groups is $970 \, \text{cm}^{-1}$, the frequency of the stretch vibration of O–H group of hydroxy compound is usually at $3704–3125 \, \text{cm}^{-1}$. While forming a dry film of the latex sample with hydroxyl groups, the hydroxyl groups interact with each other through hydrogen bonds, the formation of which induces a frequency shift of the bands of O–H group to $3500 \, \text{cm}^{-1}$. The absorption bands of O–H for sample P1 and C–O of epoxide groups for sample P2 show their existence in the surface of microgels prepared by modified microemulsion polymerization.

The Rheological Properties of the Microgels

From the results of samples P1 and P2, we can see the microgels particles with epoxide groups were smaller than those with hydroxyl groups, while the SI of the former was larger than that of the latter. We presume that in the aqueous phase, the particles with hydroxyl groups tend to hydrate or aggregate through hydrogen bonds and so are larger.
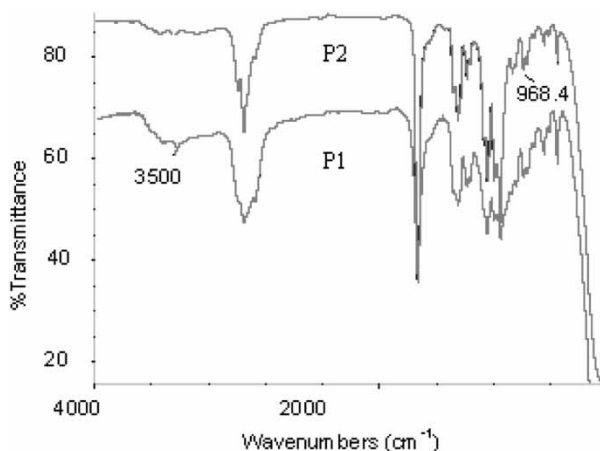
Figure 1. FT-IR spectrum for the sample P1 and P2.

On the other hand, in the oil phase, the polarity of hydroxyl groups will prevent excess, while the epoxide groups stretch more and swell more easily.

The rheology properties of microgel are shown in Figures 2 and 3. Figure 2 shows the rheology curve of samples P1 and P2 with hydroxyl groups and epoxide groups with a solid content of 10%, both demonstrated pseudoplasticity that viscosity decreased with increasing shear rates. Figure 3 shows the rheology curve with a different solid content of sample P1. The pseudoplasticity increased dramatically with increasing solid content and viscosity also increased. Adding shear with an even low rate may cause the viscosity to drop down dramatically as also shown in Figure 3. This phenomenon can be due to the contact and hydrogen bond among microgel particles and formation of a physical network while increasing their content. The properties shown here proved that such microgels can be introduced to coatings to improve the rheological properties and to control 'sagging' on spray application, etc.
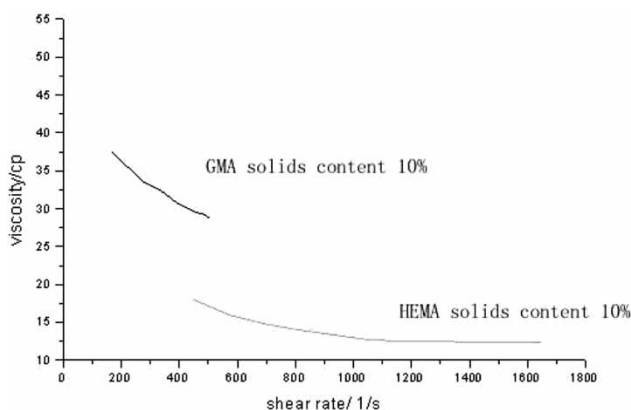

Figure 2. The rheology curve for the comparison between the sample P1 and P2 (P1: sample with HEMA, P2: sample with GMA).
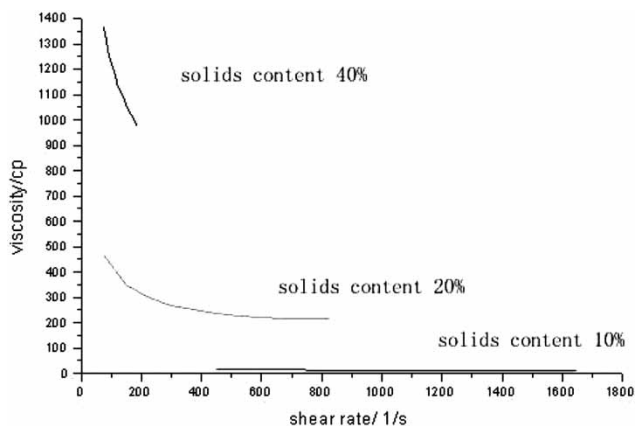
Figure 3. The rheology curve for the sample P1 with different solids content.

Conclusions

Reactive microgels have been prepared with a functional group on the surface as confirmed by FT-IR spectra. The influence of the content of various components has been discussed. Their non-aqueous dispersions exhibit obvious pseudoplasticity and have potential use in coating industry to improving the rheological properties of paints to control 'sagging' on spray application.

Acknowledgments

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