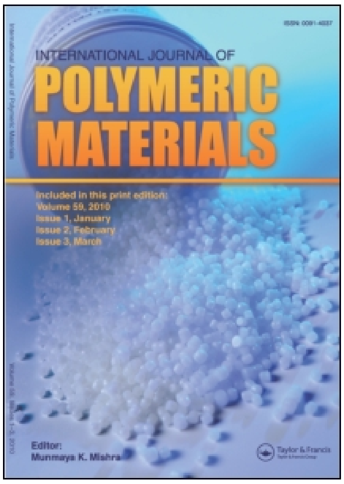

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NOVEL NANOSIZE POLYMER LATEXES PREPARED BY A CORE-SHELL MICROEMULSION COPOLYMERIZATION: PREPARATION AND CHARACTERIZATION

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Polymer nanoparticles were prepared in the methyl methacrylate (MMA)/butyl methacrylate (BA)/HEMA/ metyl acrylate (MAA) microemulsion copolymerization process. A modified core-shell microemulsion copolymerization method was used. With this process high polymer: surfactant weight ratios (15:1 or greater), relatively concentrated (~30 wt%) latexes and small (~60 nm) particle diameters were attained. Properties of the latexes were characterized in detail by TEM, DSC, dynamic light scattering, spectrophotometer, and rotation viscometer.

Keywords: microemulsion, nanosize polymer latexes, acrylate

INTRODUCTION

During the last decade, a great deal of research has been devoted to nanostructured materials. Many publications have appeared dealing with metal, ceramic, semiconductor nanoparticles, and polymer-related nanostuctured materials, for example, polymer/metal (or semiconductor) nanocomposites [1].

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Recently, the study of the preparation of polymer nanoparticles has caught more and more attention. Microemulsion polymerization is the most common method to prepare polymer nanoparticles. It has been widely studied since the first studies by Stoffer [2–3], Atik [4], and others in the early 1980s. A microemulsion may be defined as thermodynamically stable and optically transparent dispersion composed of water, oil, and surfactant; in many cases a cosurfactant is required. Microemulsion polymerization process can yield stable polymer latexes with particle size of about 10 to 100 nm. Since 1980, a number of papers have described microemulsion polymerization [5–21]. However, two major drawbacks have limited the applications of microemulsion polymerization: (1) high surfactant concentration (up to 20 wt% of the total reactor charge) is required to get small particles. Thus, monomer/surfactant weight ratios are usually smaller than 1; (2) the microlatexes can only be made at low concentrations; the polymer content is usually less than 10 wt%. High surfactant levels and low polymer contents limit the application of microemulsion latexes in industry.

In this article MAA and HEMA were used as reactive cosurfactant, and a modified microemulsion copolymerization method to prepare polymer nanolatexes composed of polymer nanoparticles with average diameters ~60 nm, polymer content ~30 wt% and monomer/surfactant weight ratios of 15:1. The resulting polymer latexes had high polymer contents as well as nanosize particles with narrow size polydispersity.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (ICI. Co. UK.), butyl methacrylate (BA) (ICI. Co. UK.).

Methyl acrylate (MAA, analytical grade), Dietheylene Glycol Diacrylate (DEGDA, analytical grade) and 2-hydroxyethyl methacrylate (HEMA, analytical grade) were distilled under reduced pressure before polymerization. Ammonium persulfate ($(NH_4)_2S_2O_8$, APS), purchased from the Institute of Chemical Reagents, Tianjin, China, was recrystallized before use.

AEROSOL 501 surfactant (mixture, main component: disodium isodecyl sulfosuccinate, 35% aqueous solution) was purchased from Professional Chemical Product Co. (USA.).

AEROSOL A-102 surfactant (mixture, main component: polyethyleneglycol alkyl (C10-C12) ethersulfosuccinate, disodium salt, 35% aqueous solution) was purchased from Professional Chemical Product Co. (USA.).

Modified Microemulsion Copolymerization Process

A typical core-shell microemulsion copolymerization procedure is as follows: A 250 ml 4-neck flask equipped with a reflux condenser, a thermometer, addition funnels, Teflon stirrer, nitrogen inlet, and feed inlet, was loaded with emulsion composed of 2.0 g of emulsifier, 70.0 g of water, 0.2 g of APS 0.15 g of $NaHCO_3$ and 1.0 g of component A (0.15 g of DEGDA, 4.5 g of MMA, 7 g of BA, 0.4 g of MAA, 0.8 g of HEMA). The flask was heated to 75°C and kept for 15 min. Then the component A in the addition funnel was continuously and slowly added to the polymerizing emulsion during 3 h with mild stirring (ca. 200 rpm). One hour later, the component B (13.4 g of MMA) was added to the emulsion during 3 h. After the addition was complete, the flask was kept at 75°C for 1 h. After the polymerization, the pH of the microemulsion was adjusted to 8.5.

CHARACTERIZATION

Transmission Electron Microscopy (TEM) (HITACHI-600, Japan)

The high solid content latex was diluted to 1%, then one drop of it was dropped onto a copper sieve that was coated with PVB (poly(vinyl butyrate)), dyed by phospho tungstic acid and dried at room temperature for 3 min.

Dynamic Light Scattering (DLS)

The particle sizes and size distribution were determined using a photon correlation spectroscope (Brookhaven instruments Corp., USA.), equipped with a Argon ionic laser ($\lambda = 515.5$ nm), a BT-9000 AT correlator, and a BI 200 SM photometer (Coherent Corp., USA). The measurements were performed at appropriate dilution at angle $\theta = 90°C$, $\lambda = 515.5$ and $T = 25°C$.

IR Spectroscopy (Nicolet 5DX FTIR, USA)

The samples were prepared as follows: the copolymer was precipitated from latexes with methanol and dried for 48 h. The spectra were averaged from the accumulation of 32 scans with a resoluton of 4 cm^{-1}, in the 4000-5000 cm^{-1} region, all samples were run as KBr discs.

Differential Scanning Calorimeter (DSC) (NETZSCH DSC 204, Germany)

Nitrogen was used as the sweeping gas. Samples (about 15 mg) were heated at a scan rate of 5K/min from $-100°C$ to 150°C.

Spectrophotometer (UV-9100)

The high solid content latex was diluted to 0.6%. The transmittance was measured at $\lambda = 600\,\text{nm}$.

Rotation Viscometer (RHEOTEST-2, Germany)

$25 \times 10^{-6}\ \text{m}^3$ of the latexes was used and tested at 25°C.

Water resistance of the polymers was characterized by soaking in distilled water 23°C and weighing the amount of water absorbed in a preset time. The dimension of the sample is $20 \times 10 \times 0.8\,\text{mm}$; Water absorpotion is defined as $\text{wt}\% = (W - W_o)/W_o$, W_o: weight prior to presoaking, W: weight after soaking for the preset time.

RESULTS AND DISCUSSION

The modified microemulsion copolymerization procedure in the authors' lab includes three steps: (a) a small amount of the core monomer used as seed was added in the initiation of the polymerization; (b) the remainder core and shell monomer were continuously and slowly added into the polymerizing microemulsion; (c) post ammoniated procedure.

The microlatex requires high surfactant concentration to form stable polymer latexes with polymer content of less than 10 wt%. High surfactant levels and low polymer content limit the application of microemulsion latexes in industry. Thus, it is desirable to minimize the surfactant amount and maximize polymer content. Searching and synthesizing new highly efficient surfactants is one of the best methods. The properties of the latex can be effectively improved using reactive surfactant (polymerizable surfactant) instead of the usual surfactant. When the reactive cosurfactant is added to the latex, it can copolymerize with the polymer monomer. The hydrophilic monomer is apt to congregate on the surface of the latex particles, which form a hydrophilic layer attached on the latex particles, thus the stabilization of the particles is improved. Therefore the cosurfactant can partly replace the surfactant. The surfactant amount is minimized, the properties of the latex can be notably improved, and the solids content can be increased.

In this article MAA amd HEMA were used as reactive cosurfactant; recipes used in the polymerization and the properties of the microemulsion are given in Tables 1 and 2. As shown, the particle size of the modified microemulsion obviously decreased when reactive consurfactant (MAA and HEMA) was added to the latex. With the appropriate molar ratio of MAA/HEMA, the microlatexes had high polymer contents as well as nanosize particles with narrow size polydispersity.

When the surfactant (A-501) content varied from 5 to 6.7%, the apparent viscosity of the latex increased, the particle size obviously decreased, and the transmittance of the latex increased. When the surfactant (A-102) was used, latexes with smaller particle size were produced.

The increase of the surfactant content resulted in the creation of a large amount of micelles at the beginning of the polymerization. Thus the number of latex particles increased, and the particle size decreased. The increase of the transmittance also proved that. At the same time, the large number of particles resulted in the increase in the collision of the particles, and the apparent viscosity of the latex increased accordingly.

As shown in Table 2, the particle size of the microlatexes increased from 63.2 nm to 78 nm as the [APS] changed from 0.67% to 0.33%. With the increase of the [APS], the free radical flux increased, and as a result the fraction of micelles that capture free radicals to become

TABLE 1 Recipes Used in the Modified Microemulsion Polymerization

No.	Consurfactant (wt%) MAA	Consurfactant (wt%) HEMA	Surfactant (wt%) A-501	Surfactant (wt%) A-102	Crosslinking agent DEGDA	Core MMA	Core BA	Shell MMA
H	1.5	2.5	3.0	—	0.5	15	23.0	58
H0	—	—	5.0	—	0.5	16.7	25.0	58.3
H0-2	—	—	5.0	—	0.5	16.7	25.0	58.3
H1	1.33	2.67	5.0	—	0.5	15	23.3	58
H3	1.33	2.67	6.7	—	0.5	15	23.3	58
H4	1.33	2.67	—	6.7	0.5	15	23.3	58
H8	1.33	2.67	—	6.7	0.5	15	23.3	58
H5	1.33	2.67	—	6.7	0.5	15	23.3	58
H6	1.25	2.75	—	7.0	0.5	15	23.5	57.3
H7	1.33	2.67	—	6.7	0.5	15	23.3	58

TABLE 2 Influence of Temperature and Initiator of the Microemulsion

	H0	H0-2	H4	H7	H8
APS (wt%)	0.67	0.67	0.67	0.33	0.67
Temperature (°C)	70	75	75	70	70
Particle size (nm)	114.7	102.1	63.2	78	77.9

active particles increased, leading to increased Rp (the rate of polymerization) and decreased particle size [22].

The dependence of particle size on reaction temperature is illustrated in Table 2. The particle size decreased as the temperature increased from 70°C to 75°C. With increase in the reaction temperature, the rate of decomposition of initiator and propagation rate constant increased [23]. Thus the rate of polymerization increases that can successfully account for the increase in the total number of polymer particles and thus decrease in the particle size.

Figure 1a and b show the particle size distribution of the latex from recipes H3 and H4. The distributions, which were obtained from dynamic light scattering measurements, are very narrow. The mean diameter of the latex H3 is 74.3 nm, with 3.5% of the particles below 70 nm and 3.1% over 79 nm. For the latex H4, the mean diameter is 63.2 nm, with 13% of the particles below 55 nm and 9% over 74 nm.

This study used seeded microemulsion. At the beginning of the reaction, a few seed drops of monomer were added to the solution (consisting of all the emulsifier and initiator), and a transparent microemulsion was formed. The dimension of the dispersed phase was less than 100 nm, far less than the dimension of the monomer

TABLE 3 Properties of the Latexes

No.	η_{app} (kPa.s)	$\gamma(s^{-1})$	Degree of water adsorption (%)	Tg (°C)	Transmittance (%)	D(nm)	Solids content (%)
H	19.8	1310	16.1	23.4, 98.5	—	95.2	48
H0	—	—	—	45.6, 87.2	17.2	114.7	30
H1	2.96	1310	12.3	20.6, 94.5	37.8	94.0	30
H3	3.52	1310	11.3	19.1, 92.5	51.7	74.3	30
H4	3.39	1310	9.5	16.2, 92.8	53.8	63.2	30
H5	1.22	1310	7.7	22.9, 91.5	47.9	79.2	30
H6	1.31	1310	9.6		—	84.1	20

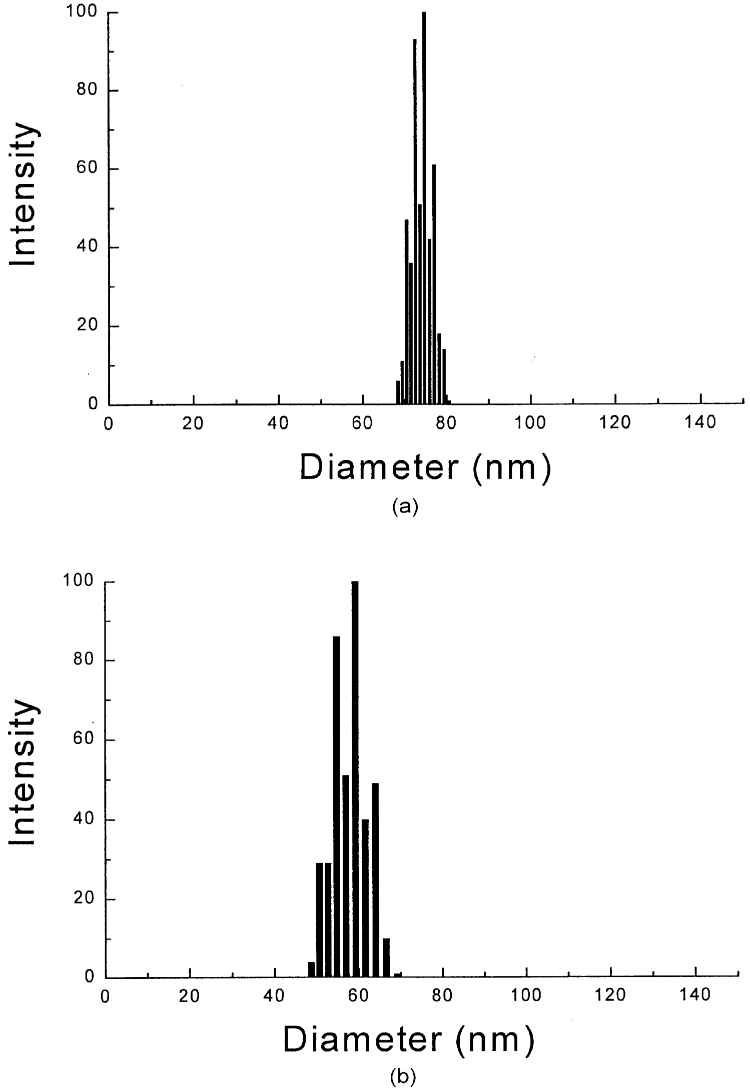


FIGURE 1 Particle size distribution of the latex from recipes H3 and H4.

droplets in traditional emulsion (10–20 μm), while corresponding to the dimension of the monomer-swollen soap micelles (40–50 μm). In microemulsions, the size of the droplets is very small; they have large specific surface, so they can easily catch radicals. Then the remainder monomer is slowly added and caught by microlatex droplets. The microlatex droplets grow up gradually.

Tracking the change of the particle size in polymerization H, it can be seen in Figure 2, at the very beginning, that the particle size of the microlatex was about 36 nm, then it gradually increased with the addition of the monomer, and finally became steady.

IR Spectroscopy

The composite sample was characterized by IR spectroscopy, (see Figure 3 and 4). The figures both exhibited strong bands at 1733 cm^{-1} (υ C=O), at 2993 cm^{-1} (υ CH_3), at 2950 cm^{-1} (υ CH_2), at 1150 cm^{-1}, 1192 cm^{-1}, 1240 cm^{-1}, and 1270 cm^{-1} (υ C-C-O-C), at 1450 cm^{-1} (δ CH_2), at 1380 cm^{-1} (δs CH_3).

Figure 4 shows there were two kinds of hydroxyl stretching bands in the range of 3000 to 3600 cm^{-1} compared with Figure 3. The bands at 3440 cm^{-1} (υ OH), and 3530 cm^{-1} (υ OH) illustrate the participation of HEMA and MAA in the copolymerization.

TEM Results

Illustrated in Figure 5a and b were the transmission electron micrographs of H1 and H4. The latex particle is a small elastomer particle, and its boundary is rather blurry when observed by TEM. Thus the

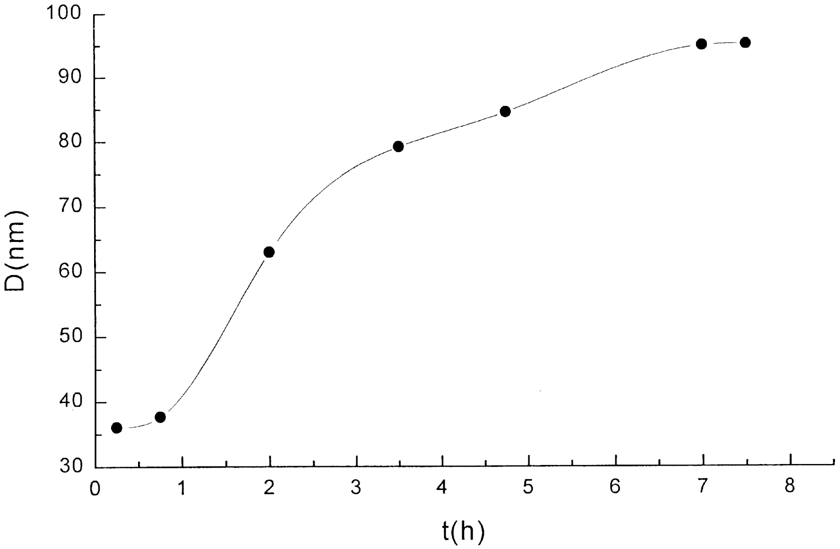


FIGURE 2 Particle diameter changes versus reaction time during the core-shell emulsion polymerization.

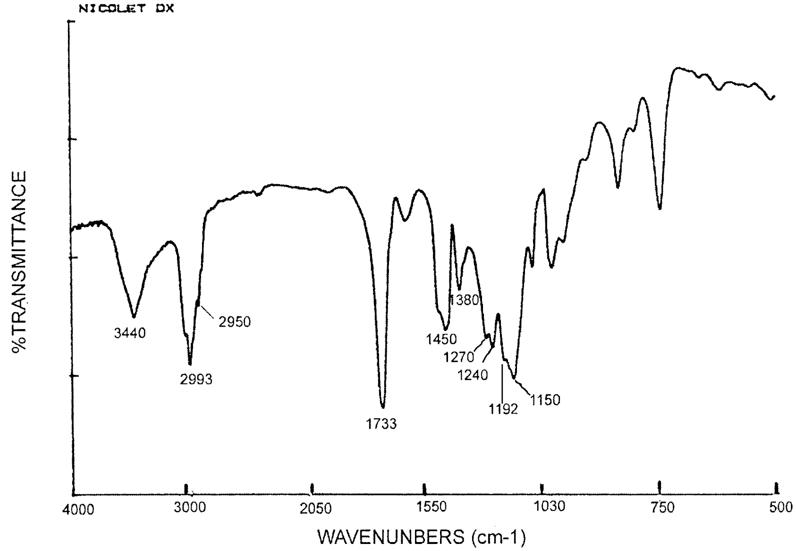


FIGURE 3 IR spectrum of the copolymer (MMA/BA).

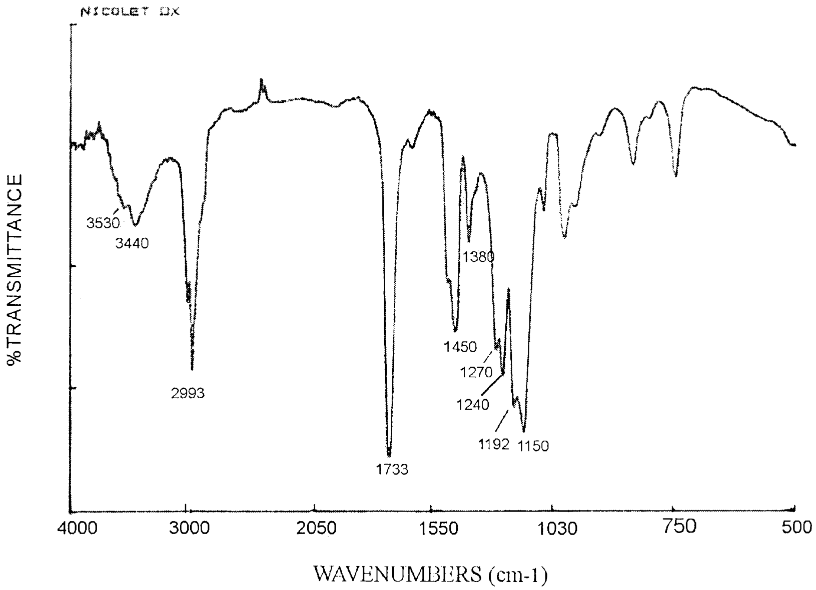
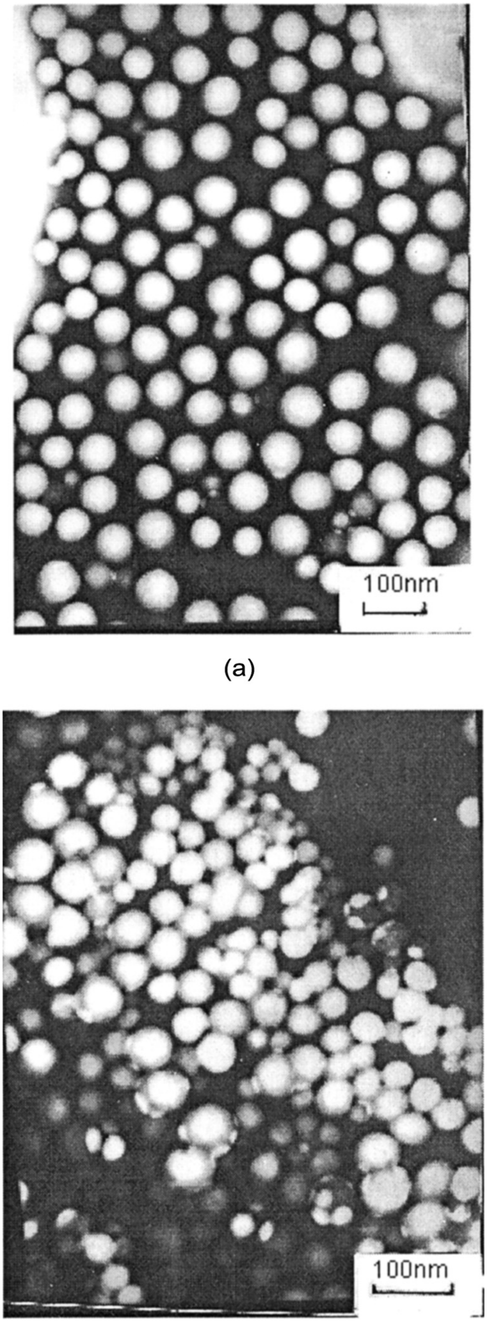


FIGURE 4 IR spectrum of the copolymer (MMA/BA/MAA/HEMA).



(a)

(b)

FIGURE 5 Transmission electron micrographs of H1 and H4.

latex was dyed by phosphotungstic acid. As shown in Figure 5, the particles had uniform size, and were evenly dispersed. From the micrographs, the average diameters were 70 to 80 nm and 40 to 60 nm, respectively. These values are comparable with the 94 nm and 63 nm measured by light scattering.

Viscosity

The apparent viscosity of the latex related greatly to the shear rate and changed a lot under different shear rates. The hydromechanic properties cannot be clarified by a single viscosity. So in the experiment, apparent viscosity under different shear rates was measured by rotation viscometer. It can be seen from Figure 6 that the apparent viscosity increased slightly as the shear rate increased (shear thickenning) and the shear stress increased as the shear rate increased. From that facts, it can be concluded that the flow of the latex obeyed expanded fluid body.

Thermal Analysis

Glass transition temperature, Tg, of the copolymers was measured by DSC. As shown in Table 3, two obvious glass transitions were measured; one is Tg of core, the other is shell.

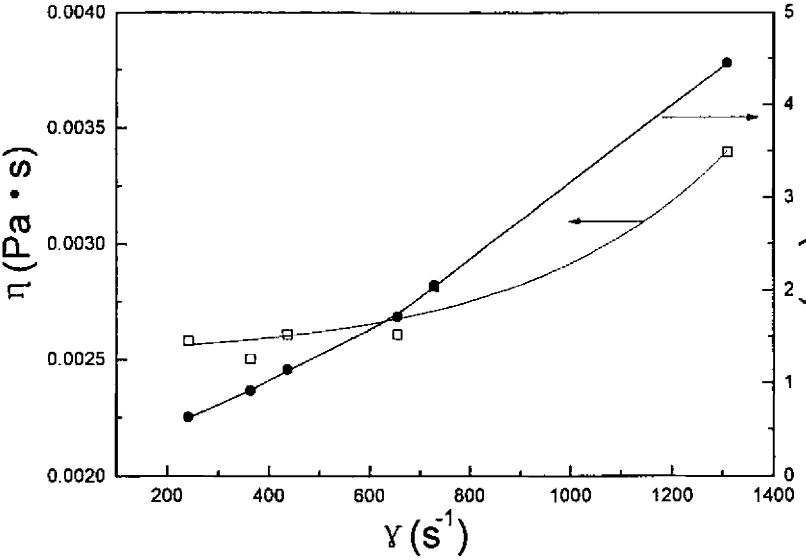


FIGURE 6 Effect of γ on $\eta_{\mathrm{app.}}$ and σ for latex H4.

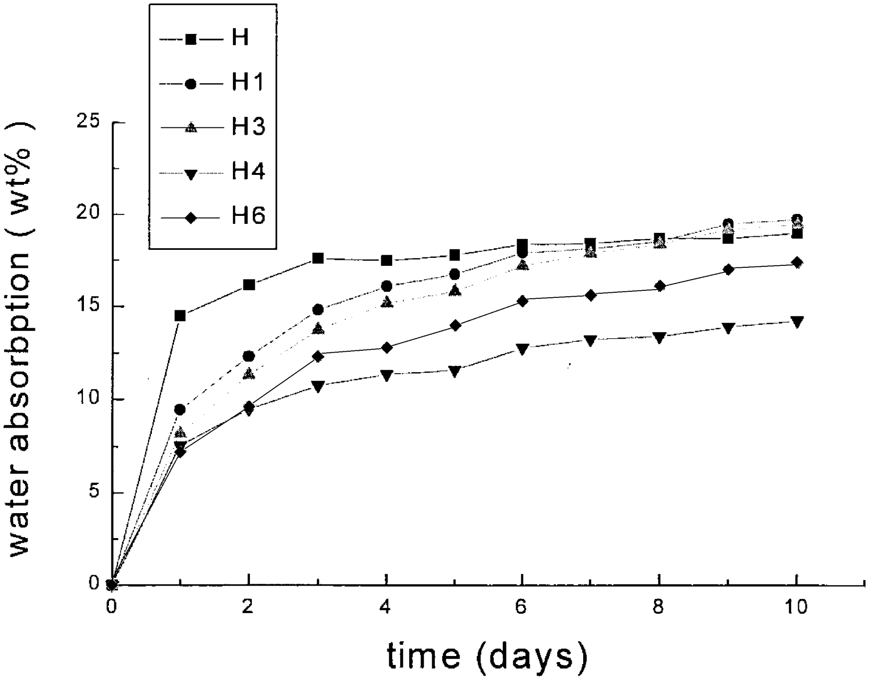


FIGURE 7 Water absorption curves for copolymer.

Water Absorption

Figure 7 is the absorption curves for copolymer series "H". The water absorption of the copolymer decreased when the surfactant A-501 changed to A-102. It can be seen from H1 and H3 that the water absorption changed a little when the amount of A-501 increased from 5% to 6.7%.

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