

Microemulsion Polymerization of Siloxane with Nonionic Surfactants as Emulsifiers

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ABSTRACT: Polysiloxane nanolatexes were prepared by the microemulsion polymerization of octamethylcyclotetrasiloxane (D_4) with nonionic polyoxyethylene alkyl ether and polyoxyethylene aryl ether as surfactants, ethylene glycol or aminoethanol as a cosurfactant, and potassium hydroxide or dipotassium dimethylsilanolate (**I**) as an initiator. The effect of the different initiators and the amount of cosurfactant on the microemulsion polymerization rate of D_4 was investigated. The initiator, potassium hydroxide, had a similar catalytic activity to **I**, and adding the cosurfactant changed a common siloxane emulsion to a microemulsion. At a same reaction conditions, the polymerization rate of D_4 with aminoethanol as a cosurfactant was much faster than that of ethylene glycol. The kinetics of this siloxane micro-

emulsion polymerization was consistent with Morgen–Kaler theory. The transparency value of the resultant polysiloxane nanolatex was more than 95% when the amount of ethylene glycol was more than 25% and the siloxane amount was about 30 wt % of the reaction mixture. A nanolatex of polydimethylsiloxane-*co*-polyvinylmethylsiloxane, which was crosslinked with potassium persulfate, revealed that the mean diameter of the droplets was 32 nm with a narrow distribution. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3587–3593, 2003

Key words: polysiloxanes; silicones; emulsion copolymerization; TEM

INTRODUCTION

A microemulsion is a special heterophase system where stable droplets of one phase with sizes of 10–100 nm are dispersed in a continuous phase.^{1–4} A major difference between macroemulsions and microemulsions comes from the amount of surfactant added to stabilize the systems. This amount is much larger for microemulsion (more than 10% of the total mass), which considerably restricts the potential uses of microemulsion polymerization because high solid contents and low surfactant amounts are desirable for most applications. Since polymerization in microemulsions was proposed in 1980s,^{5,6} the research on microemulsion polymerization has developed rapidly because of its applications in the preparation of nano-sized catalysts, nanoparticles for drug delivery, and polymer nanolatexes.^{7–12}

Among polymerization in microemulsions, the microemulsion polymerization of siloxanes has proven very attractive because polysiloxanes possess special physical and chemical properties, including good electrical isolating properties, good thermal stability, extremely low surface tension, and humidity permeabil-

ity. Recently, there have been many reports on the microemulsion polymerization of siloxanes with cationic or anionic surfactants as emulsifiers^{13–15} and on the preparation of inorganic fractal porous silicas made by the hydrolysis of tetraethoxysilane in a bi-continuous microemulsion.¹⁶ However, there have been only a few studies on the microemulsion polymerization of siloxanes with nonionic surfactants as emulsifiers. Revis reported a nonionic polydimethylsiloxane emulsion with a mean particle size of polysiloxane droplets of about 65 nm by the emulsion polymerization of octamethylcyclotetrasiloxane (D_4), with an ethoxylated alcohol nonionic surfactant as the emulsifier and an organosilanolate as the initiator.¹⁷ Halloran prepared an oil-in-water polysiloxane microemulsion with a particle size of 15.1 nm, with ethoxylated lauryl ether as the surfactant and 1-pentanol as the cosurfactant.¹⁵ The total amount of the surfactant and cosurfactant used in this microemulsion was 24 wt % of the microemulsion mixture, and the content of siloxane was only 7.6 wt % of the microemulsion. It seems that polymerization in microemulsions with high solid contents and low surfactant amounts is difficult. Moreover, the microemulsion polymerization rate (R_p) of siloxane with nonionic surfactants as emulsifiers is slower than that of ionic surfactants.

Here we report the preparation of stable polysiloxane nanolatexes with a relatively low amount of surfactants and a high content of polysiloxane.

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EXPERIMENTAL

Materials

D_4 from GE Toshiba (Tokyo, Japan) with 99% purity, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4^{Vi}) from Yuxing Organosilicon Material Plant (Zhejiang, Nanjing, China) with 98% purity, and ethoxylated (EO = 40) nonylphenol (NP-40), polyoxyethylene (EO = 15) lauryl ether (AEO-15), and polyoxyethylene (EO = 25) stearyl ether (PPJ-O) from Jinling Petrochemical, Ltd., Corp. (China) were used as received. Ethylene glycol (EG; 99%), potassium hydroxide (82%), sodium sulfate (99%), acetic acid (99.5%), ethanol (99.5%), and phosphotungstic acid (98%) were all chemically pure reagents from Nanjing Chemical Reagent Factory (China) and were used as received. Aminoethanol (AE; Beijing Chemical Factory, China; 98%), and potassium persulfate (Shanghai Aijian Reagent Factory, China; 98%) were chemically pure reagents. Dipotassium dimethylsilanolate (I) was prepared with a method described in the literature.¹⁷

Preparation of polysiloxane nanolatices

Polysiloxane nanolatices were prepared by the emulsion polymerization of D_4 , for example, 78.0 g of D_4 , 13.5 g of PPJ-O, 7.5 g of NP-40, 6.0 g of AEO-15, and 150.0 g of distilled water were added into a 500-mL four-necked glass flask equipped with a reflux condenser and a stirrer. The flask was heated to 80°C, and then, 10.0 g of 25.0 wt % potassium hydroxide aqueous solution was added into the flask, and the mixture was stirred at a temperature of $80 \pm 0.5^\circ\text{C}$. At the desired polymerization time, about 1 g of the reaction sample was taken out of the flask with a burette, cooled to room temperature, and weighed with an analytical balance. It was then neutralized with a 25 wt % acetic acid aqueous solution and dried in an oven at 150°C for 2 h.

To crosslink the polydimethylsiloxane in the nanolatex droplets, D_4^{Vi} was introduced into polydimethylsiloxane by emulsion copolymerization with D_4 . The preparation process was similar to that described previously. The resultant emulsion was neutralized with acetic acid at the end of polymerization, the desired amount of $\text{K}_2\text{S}_2\text{O}_8$ (1 wt % of the reaction mixture) aqueous solution was added to the resultant emulsion, and the reaction mixture was stirred at 80°C for 10 h under N_2 .

Measurements

The transparency of the polysiloxane nanolatex was measured with a visible spectrophotometer (722S, Shanghai Analytical Instrument Factory, China) with incident light at wavelength of 580 nm, and distilled

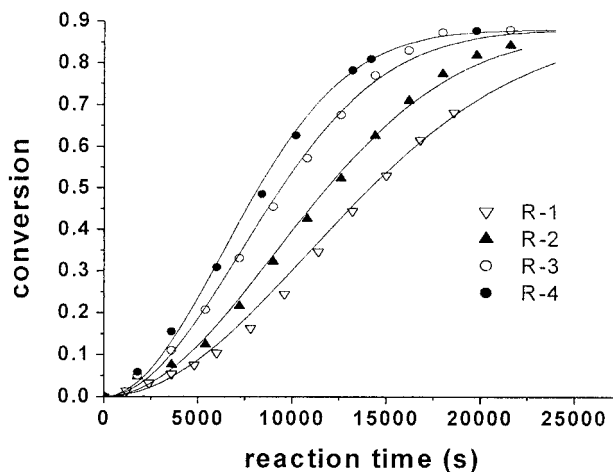


Figure 1 Experimental f of D_4 versus t for the microemulsion polymerization of D_4 . Solid lines are the fit of eq. (4) to data with chosen A values of 8.4×10^{-9} , 1.2×10^{-8} , 1.6×10^{-8} , and 2.5×10^{-8} for reactions R-1 to R-4, respectively. Reaction data for R-1 to R-4: $[D_4] = 1.02\text{M}$, $[\text{NP-40}] = 35.0\text{ g/L}$, $[\text{AEO-15}] = 35.0\text{ g/L}$, and temperature = 80°C. $[\text{I}] = 6.23 \times 10^{-2}\text{ M}$ for R-1, $7.95 \times 10^{-2}\text{ M}$ for R-2, $9.72 \times 10^{-2}\text{ M}$ for R-3, and 0.1146M for R-4.

water was used as a reference with a transparency value of 100%.

To measure the molecular weight of polysiloxane after polymerization, the polysiloxane in the nanolatex was precipitated with ethanol, and the polysiloxane was washed with ethanol three times and then put in an oven at 120°C for 8 h to remove water, ethanol, and low-molecular-weight siloxanes. The intrinsic viscosity ($[\eta]$) of the resultant polysiloxane was measured in a constant-temperature bath at $25 \pm 0.2^\circ\text{C}$ with an Ubbelodhe viscosimeter, and toluene was used as solvent.

The measurement of transmission electron microscopy (TEM) was performed on a Jeol TEM-100 (Japan). Before TEM measurement, the nanolatex sample that contained the crosslinked silicone particles was diluted with distilled water, placed onto a copper grill covered with nitrocellulose, and then negatively stained with a 1.0% (w/v) phosphotungstic acid aqueous solution.

RESULTS AND DISCUSSION

Microemulsion polymerization of D_4 with nonionic surfactants as emulsifiers

First, with nonionic surfactants as emulsifiers, the microemulsion R_p of D_4 with different amounts of I was investigated. The conversion (f) of D_4 versus polymerization time is presented in Figure 1. As shown in the curves of R-1 to R-4 at the same reaction conditions, R_p of D_4 increased with increasing concentration of initi-

ator in the reaction mixture, and also, the final maximal conversion (f_m) of D_4 was about 90%.

The kinetics of microemulsion polymerizations has been reported in a number of studies.^{8,18-22} According to Morgen-Kaler theory, in the aqueous free-radical-initiated microemulsion polymerization of a monomer, when the polymerization temperature is higher than its glass-transition point during the course of the reaction and when (1) there is no bimolecular termination and (2) the capture of aqueous free radicals is fast, the fractional f of the monomer can be expressed as follows:

$$f = 1 - \exp(-At^2/2) \quad (1)$$

where t is reaction time and

$$A = k_p C_0 \rho_0 / M_0 \quad (2)$$

where k_p is the propagation rate constant and C_0 is the initial monomer concentration in the particles at the point at which sufficient polymer has formed to absorb all of the available monomer. ρ_0 is the rate of production of primary free radicals from the initiator decomposition, and M_0 is the initial macroscopic concentration of the monomer. A is fully determined by the experimental data. From eq. (1), one can derive $\partial f / \partial t$ as a function of f :

$$\frac{\partial f}{\partial t} = (1 - f) \sqrt{-2A \ln(1 - f)} \quad (3)$$

and the rate maximum will occur at 39.3% monomer f .²²

In this work, polydimethylsiloxane was a viscous liquid at the reaction conditions, the polymerization catalyst was KOH, $\text{KOSi}(\text{Me})_2\text{OK}$ (**I**) was a water-soluble alkali, and there was no bimolecular termination. These satisfied the conditions of Morgen-Kaler theory. Because the f_m of D_4 to high-molecular-weight polysiloxane was in the range 85–95%^{23,24} and according to the experimental data, f_m was set to be 0.9. Thus, eqs. (1) and (3) were modified as:

$$f = 0.9 - 0.9 \times \exp(-At^2/2) \quad (4)$$

$$\frac{\partial f}{\partial t} = (0.9 - f) \sqrt{-2A \ln(1 - f/0.9)} \quad (5)$$

As a result, the rate maximum occurred at 35.4% [$0.9 \times (1 - e^{-0.5})$] of the monomer f .

In Figure 1, the solid lines are the fit of eq. (4) to the data with chosen A values of 8.4×10^{-9} , 1.2×10^{-8} , 1.6×10^{-8} , and 2.5×10^{-8} for reactions R-1 to R-4, respectively. We found that the experimental data fit these solid lines well. Thus, it seemed that the kinetics

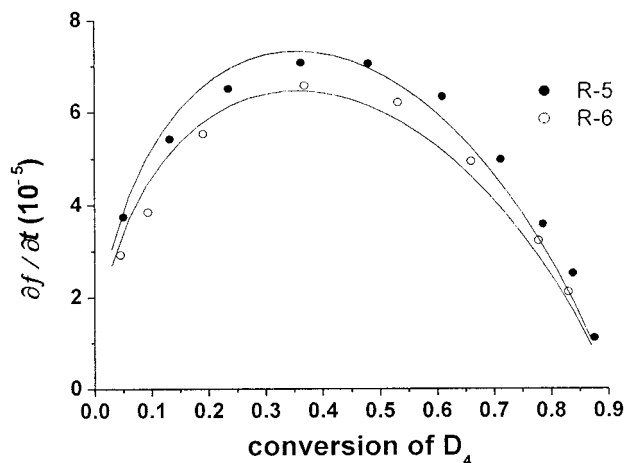


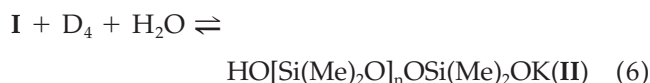
Figure 2 $\partial f / \partial t$ versus f of D_4 with **I** or potassium hydroxide as the initiator. The solid lines are the fit of eq. (5) to the data with chosen A values of 1.8×10^{-8} and 1.4×10^{-8} for reactions R-5 and R-6, respectively. $[D_4] = 1.02M$, $[\text{NP-40}] = 35.0 \text{ g/L}$, $[\text{AEO-15}] = 35.0 \text{ g/L}$, and temperature = 80°C . $[\text{I}] = 0.10M$ for R-5, and $[\text{KOH}] = 0.20M$ for R-6.

of the microemulsion polymerization of D_4 in this study obeyed Morgen-Kaler theory.

Effects of different catalysts on R_p of D_4

As an alternate, KOH was chosen as the polymerization initiator. Its catalytic activity was compared with that of **I** at the same reaction conditions. The concentration of the initiator in the reaction mixture of R-5 (catalyzed by **I**) and R-6 (catalyzed by KOH) was $0.20M$ according to the KOH concentration. As shown in curve R-6 in Figure 2, KOH catalyzed the microemulsion polymerization of D_4 as well as **I**, except $\partial f / \partial t$ of R-6 was a little slower than that of R-5. Thus, it seemed that potassium hydroxide had a similar activity to **I** and could be chosen as an initiator for the nonionic microemulsion polymerization of D_4 due to economic considerations. As also shown in Figure 2, the experimental data of $\partial f / \partial t$ fit the solid lines determined from eq. (5) with the chosen A values, and the $\partial f / \partial t$ maximum of R-5 and R-6 occurred at about 36% of the D_4 f as predicted before.

We thought that there were reversible reactions in the initial stage of the emulsion polymerization of dimethylsiloxane as shown in equilibrium eqs. (6) and (7):



The actual polymerization initiators were not **I** and KOH but the water-insoluble silanolate **II** formed at

TABLE I
 η of the Polysiloxane Nanolatices at Different Na_2SO_4 Concentrations

Concentration of Na_2SO_4 (wt %)	0	0.5	1.0
η at 20°C (cp)	345	64	30

Reaction data of these microemulsion polymerizations of D_4 : $[\text{D}_4] = 0.99\text{M}$, $[\text{PPJ-O}] = 50.9\text{ g/L}$, $[\text{NP-40}] = 28.3\text{ g/L}$, $[\text{AEO-15}] = 22.6\text{ g/L}$, $[\text{KOH}] = 0.253\text{M}$, temperature = 80°C.

the initial stage, which assembled on the interface between water and siloxane, with its hydrophilic group, $\equiv\text{Si-O-K}$, in the water phase and the hydrophobic group, $(\text{SiMe}_2\text{O})_n$, in the siloxane phase. The polymerization of D_4 took place on the interface between water and siloxane, catalyzed by $\equiv\text{Si-O-K}$.

Thus, this explains why the nonionic emulsion R_p of D_4 was slower than that of a cationic or an anionic one. In an ionic emulsion polymerization, the initiator, such as dodecylbenzenesulfonic acid or dodecyl trimethyl ammonium hydroxide, is also an emulsifier, which could form micelles, with all the catalytic active groups assembled on the interface between water and siloxane. However, in the nonionic emulsion polymerization of D_4 and in case of the reversible reactions shown in eqs. (6) and (7), only partial I and KOH reacted with D_4 to form II, which had catalytic activity. The unmicellized I and KOH dissolved in water did not catalyze the D_4 polymerization.

Effects of sodium sulfate on the microemulsion polymerization of D_4

When the other conditions were fixed, the concentration of sodium sulfate in the reaction mixture (from 0 to 1.0 wt % of the emulsion) did not significantly change the emulsion R_p of D_4 , according to the measurement of D_4 R_p at same reaction conditions (detailed experimental data is not shown here). From the results of the centrifugation experiment at a speed of 3000 rpm and the transparency values of the resultant polysiloxane nanolatices, we also found that the effects of sodium sulfate on the stability and particle size of polysiloxane nanolatices could be ignored. However, sodium sulfate could significantly decrease the viscosity (η) of the resultant polysiloxane nanolatices when its amount was increased in the reaction mixture, as shown in Table I.

Effect of the cosurfactant on the microemulsion R_p of D_4

It is well known that to obtain a microemulsion, a cosurfactant always be used in the emulsion mixture. In this work, water-soluble EG or AE was used as a cosurfactant to form microemulsions. R_p ($R_p = M_0 \cdot \partial f / \partial t$) versus the f of D_4 with different amount of EG

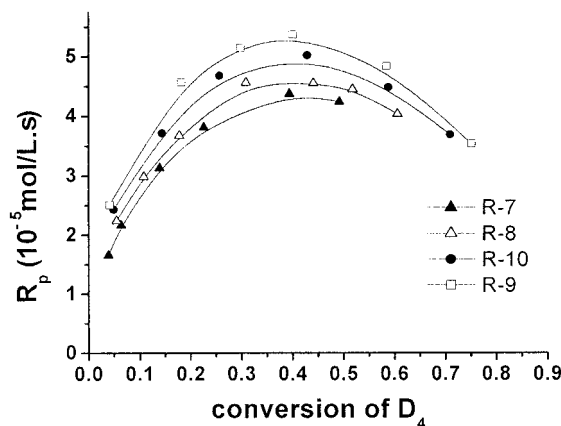


Figure 3 R_p versus f of D_4 with different amounts of EG as a cosurfactant. $[\text{D}_4] = 0.99\text{M}$, $[\text{PPJ-O}] = 50.9\text{ g/L}$, $[\text{NP-40}] = 28.3\text{ g/L}$, $[\text{AEO-15}] = 22.6\text{ g/L}$, $[\text{KOH}] = 0.168\text{M}$, and temperature = 80°C. $[\text{EG}] = 0\text{ g/L}$ for R-7, 113.2 g/L for R-8, 188.7 g/L for R-9, and 283.0 g/L for R-10.

or AE in the reaction mixture is shown in Figures 3 and 4.

As shown in Figure 3, when EG was added to the reaction mixtures R-8 (EG content = 113.2 g/L), R-9 (EG content = 188.7 g/L), and R-10 (EG content = 283.0 g/L), R_p of D_4 increased compared to that of the emulsion polymerization without EG (R-7). As also shown in Figure 3, R_p of R-9 was faster than that of R-8 and R-10. Also, as shown in the experiment, when amount of EG was increased to 566 g/L at the same reaction conditions, R_p of D_4 was very slow, the D_4 f was only 8%, and the final resultant could not form a stable emulsion after 5 h of polymerization at 80°C. Thus, there was a best amount of EG (R-9, about 20 wt % to the reaction mixture) with a maximum of R_p of D_4 . The increasing EG amount may have made

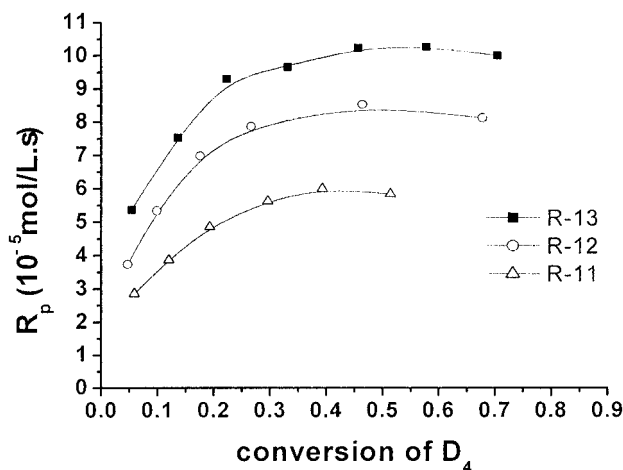


Figure 4 R_p versus f of D_4 with different amounts of EG or AE as a cosurfactant. $[\text{D}_4] = 0.99\text{M}$, $[\text{PPJ-O}] = 50.9\text{ g/L}$, $[\text{NP-40}] = 28.3\text{ g/L}$, $[\text{AEO-15}] = 22.6\text{ g/L}$, $[\text{KOH}] = 0.211\text{M}$, and temperature = 80°C. $[\text{EG}] = 188.7\text{ g/L}$ for R-11, $[\text{AE}] = 55.6\text{ g/L}$ for R-12, and 188.7 g/L for R-13.

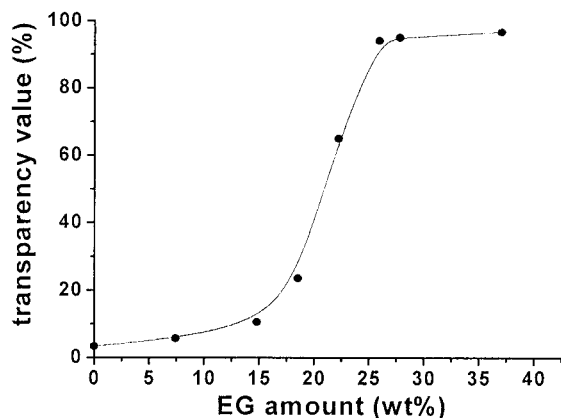


Figure 5 Change of the transparency value of polysiloxane nanolatexes with different amounts of EG in the emulsion. $[D_4] = 0.99M$, $[PPJ-O] = 50.9$ g/L, $[NP-40] = 28.3$ g/L, $[AEO-15] = 22.6$ g/L, $[KOH] = 0.168M$, and temperature = $80^\circ C$.

the droplets smaller, and this increased R_p of D_4 , but the catalyst was less active in EG than in water, and increasing the EG amount decreased R_p . These two opposite effects of the amount of EG on the D_4 R_p resulted in the previously observed phenomenon.

Instead of EG, AE was used as a cosurfactant. A stable emulsion could be formed in this system as well as in the EG system. R_p of D_4 versus its f is shown in Figure 4. R_p of the emulsion polymerization with AE as cosurfactant was much faster than that with EG as a cosurfactant under the same reaction conditions. It seems that the cosurfactant AE enhanced the catalytic activity of the initiator and promoted the polymerization of siloxane. However, to prove this, more work needs to be done.

Effect of EG amount on the transparency of the polysiloxane nanolatexes

The transparency of an emulsion is decisively dependent on the size of the droplets in the emulsion. The smaller the droplet size is, the larger the transparency value will be. The transparency value of the polysiloxane nanolatexes after polymerization with different amounts of EG is displayed in Figure 5. As shown in Figure 5, the transparency value of the resultant polydimethylsiloxane nanolatex was markedly influenced by the amount of EG added to the reaction mixture.

When the amount of EG was between 0 and 15 wt % of the polysiloxane emulsion, the transparency value of the emulsion just changed from 3 to 13.5% at incident light with a wavelength of 580 nm. When the amount of EG was between 20 and 25 wt % of the microemulsion, the transparency value was changed from 35 to 90%, this indicated that increasing EG amount in the reaction mixture could dramatically improve the transparency of the polysiloxane nanola-

tex, and that the polysiloxane emulsion changed from a common emulsion to a microemulsion. When EG amount was between 25 and 45 wt % of the reaction mixture, the transparency value of the resultant nanolatex was maintained at about 95%.

This result indicates that EG was an efficient cosurfactant at these reaction conditions for siloxane to form a stable microemulsion.

Molecular weight of the polysiloxane in the nanolatexes

It is well known that the molecular weight of polydimethylsiloxane is low in an emulsion prepared by nonionic emulsion polymerization. As described in a patent,¹⁷ the η of the polysiloxane prepared by nonionic emulsion polymerization was only 411 mm²/s, corresponding to a molecular weight of 18,000, as calculated from Barry's η -number-average molecular weight (M_n) relationship of high-molecular-weight polydimethylsiloxane.²⁵ If a higher molecular weight polymer is required, the resultant emulsion should be stood at room temperature for a long time before the polymerization catalyst is neutralized.²⁴

M_n of the polysiloxane in the resultant nanolatexes of this study was calculated from its $[\eta]$ according to Barry's $[\eta]$ - M_n relationship.²⁵ As shown in Figure 6 and Table II, the M_n of polysiloxane obtained from nonionic emulsion polymerization with an EG amount of 283.0 g/L was larger than that without EG. However, when the reaction mixture stood at room temperature for a further 40 h before the polymerization catalyst was arrested, the M_n of polysiloxane increased

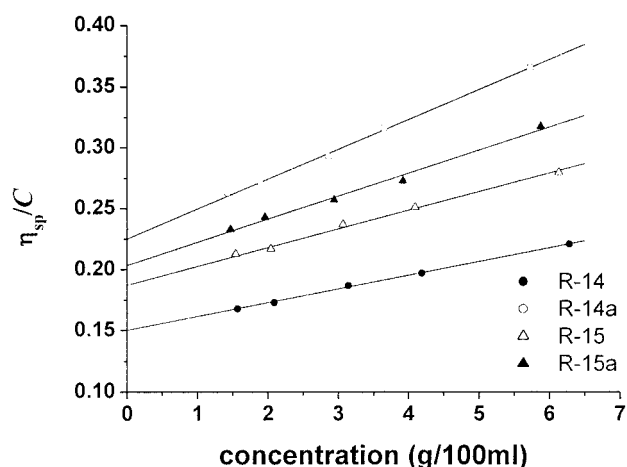


Figure 6 η_{sp}/C versus C for polysiloxane of R-14, R-14a, R-15, and R-15a. $[D_4] = 0.99M$, $[PPJ-O] = 50.9$ g/L, $[NP-40] = 28.3$ g/L, $[AEO-15] = 22.6$ g/L, and $[KOH] = 0.256M$. $[EG] = 0$ g/L for R-14 and 283.0 g/L for R-15. The emulsions of R-14 and R-15 were neutralized after polymerization at $80^\circ C$ for 8 h, and R-14a and R-15a stood at room temperature for additional 40 h after polymerization at $80^\circ C$ for 8 h and were then neutralized.

TABLE II
[η] and M_n values of Polysiloxanes

	Reaction			
	R-14	R-14a	R-15	R-15a
EG amount (g/L)	0	0	283	283
[η] (25°C in toluene)	0.150	0.225	0.187	0.206
M_n^a	23000	42000	32000	37000

^a M_n was calculated with Barry's [η]- M_n relationship: [η] = $2 \times 10^{-4} M_n^{0.66}$.

from 23,000 (R-14) to 42,000 (R-14a) and from 32,000 (R-15) to 37,000 (R-15a) for the emulsion without EG and with an EG amount of 283.0 g/L, respectively. Obviously, the increase in the molecular weight of polysiloxane for the emulsion without the addition of EG was larger than that with the addition of EG.

TEM photography of crosslinked nanolatex droplets

To investigate the droplet size in the polysiloxane nanolatexes, TEM measurement was used. The polysiloxane in the emulsion droplets was a viscous liquid and coalesced on removal of the water. Thus, it was difficult to observe the shape and size of the droplets by TEM measurement. To address this issue, the polysiloxane in the emulsion droplets was crosslinked before measurement by TEM. A copolymer nanolatex of 40 wt % vinylmethyl siloxane and 60 wt % dimethyl siloxane was prepared with 20 wt % EG and 30 wt % total polysiloxane content. $K_2S_2O_8$ was then used to crosslink the vinyl-substituted polydimethylsiloxane in the emulsion droplets. The transparency values of such a nanolatex were 22 and 20% before and after crosslinking, respectively. Figure 7 shows the TEM photograph of the crosslinked polydimethyl-methylvinylsiloxane nanolatex after it was stained with phos-

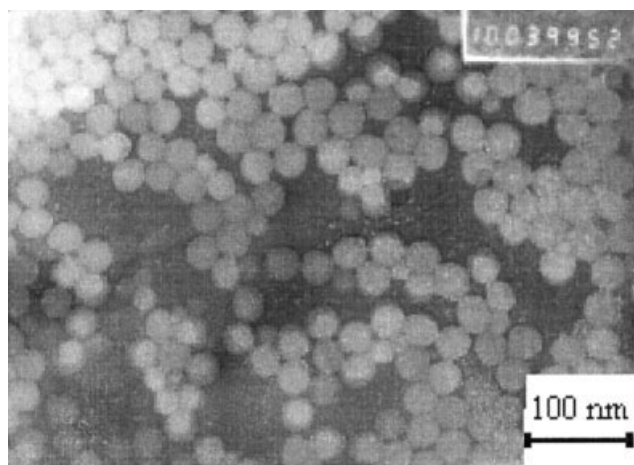


Figure 7 TEM photograph of the droplets in the polysiloxane nanolatex.

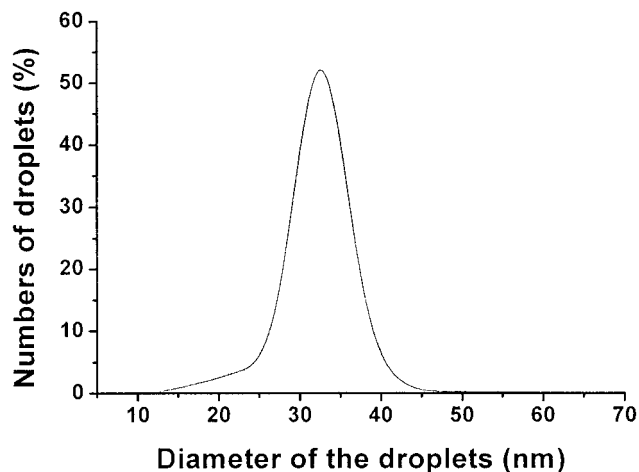


Figure 8 Particle size distribution of the droplets in the polysiloxane nanolatex.

photungstic acid. The diameter of the global droplets of silicone in the nanolatex mostly ranged between 20 and 40 nm, with a mean size of 32 nm, as shown in Figure 8. Moreover, a narrow distribution of droplets was observed, as shown in Figure 8.

This result indicates that the droplets in the silicone copolymer emulsion were nanoparticles with a mean size of 32 nm, and it was also expected that the mean particle size of the droplets in the polydimethylsiloxane nanolatex with a transparency value more than 20% was less than 32 nm.

CONCLUSIONS

Polysiloxane nanolatexes were prepared by the microemulsion polymerization of D_4 with nonionic polyoxyethylene alkyl ether and polyoxyethylene aryl ether surfactants as emulsifiers, EG or AE as a cosurfactant, and potassium hydroxide or I as an initiator.

The effect of the different initiators and the amount of cosurfactant on the microemulsion R_p of D_4 was investigated. The kinetics of the siloxane microemulsion polymerization were consistent with Morgen-Kaler theory. The initiator, potassium hydroxide, had a similar catalytic activity to I, and the addition of the cosurfactant changed a common polysiloxane emulsion to a microemulsion. At same reaction conditions, R_p of D_4 with AE as a cosurfactant was much faster than that of EG.

The transparency value of the resultant polysiloxane nanolatex was more than 95% when the amount of EG was more than 25% and the polysiloxane amount was about 30 wt % of the reaction mixture. A nanolatex of polydimethylsiloxane-*co*-polyvinylmethylsiloxane, which was crosslinked with potassium persulfate, revealed that the mean diameter of the global droplets was 32 nm with a narrow distribution.

References

1. Hoar, T. P.; Schulman, J. H. *Nature (London)* 1943, 152, 102.
2. Schulman, J. H.; Stoeckenius, W.; Prince, L. M. *J Phys Chem* 1959, 63, 1677.
3. Friberg, S. E.; Bothorel, P. *Microemulsions: Structure and Dynamics*; CRC: New York, 1986.
4. Moulik, S. P.; Paul, B. K. *Adv Colloid Interface Sci* 1998, 78, 99.
5. Stoffer, J. O.; Bone, T. *J Dispersion Sci Technol* 1980, 1, 37.
6. Stoffer, J. O.; Bone, T. *J Polym Sci Polym Chem Ed* 1980, 18, 2641.
7. Leong, Y. S.; Candau, F. *J Phys Chem* 1982, 86, 2269.
8. Candau, F.; Leong, Y. S.; Fitch, R. M. *J Polym Sci Polym Chem Ed* 1985, 23, 193.
9. Bleger, F.; Murthy, A. K.; Pla, F.; Kaler, E. W. *Macromolecules* 1994, 27, 2559.
10. Barton, J. *Prog Polym Sci* 1996, 21, 399.
11. Larpent, C.; Tadros, T. F. *Colloid Polym Sci* 1991, 269, 1171.
12. Antonietti, M.; Basten, R.; Lohmann, S. *Macromol Chem Phys* 1995, 196, 466.
13. Ona, I.; Ozaki, M.; Tanaka, O. U.S. Pat. 4,784,665 (1988).
14. Ge, R. P. Eur. Pat. 459,500 (1991).
15. Halloran, D. G. U.S. Pat. 6,071,975 (2000).
16. Aikawa, K.; Kaneko, K.; Tamura, T.; Fujitsu, M.; Ohbu, K. *Colloids Surf A* 1999, 150, 95.
17. Revis, A. U.S. Pat. 5,502,105 (1996).
18. Gao, J. S.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Part A: Polym Chem* 1989, 27, 691.
19. Caver, M. T.; Hirsch, E.; Wittman, J. C.; Fitch, R. M.; Candau, F. *J Phys Chem* 1989, 93, 4867.
20. Antoniette, M.; Bremser, W.; Schmidt, M. *Macromolecules* 1990, 23, 3796.
21. Gao, J. S.; Sudol, E. D.; Vanderhoff, J. W.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1992, 30, 703.
22. Morgan, J. D.; Lusvardi, K. M.; Kaler, E. W. *Macromolecules* 1997, 30, 1897.
23. Eaborn, C. *Organosilicon Compounds*; Butterworths: London, 1960; p 227.
24. Weyenberg, D. R.; Findlay, D. E.; Cekada, J. R. J.; Bey, A. E. *J Polym Sci Part C: Polym Symp* 1969, 27, 27.
25. Barry, A. J. *J Appl Phys* 1946, 17, 1020.