Model System for Surfactant-free Emulsion Copolymerization of Hydrophobic and Hydrophilic Monomers in Aqueous Solution

Guangzhao Zhang,† Xinglin Li,† Ming Jiang,*,† and Chi Wu*,‡,§

Department of Macromolecular Science and The Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China, The Open Laboratory of Bond-Selective Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, China, and Department of Chemistry, The Chinese University of Hong Kong, Hong Kong

Received March 24, 2000. In Final Form: August 4, 2000

Polymeric nanoparticles were formed when a carboxylated polystyrene solution in tetrahydrofuran was added dropwise into water. The hydrophobic association of the chain backbones was balanced by the hydrophilic repulsion of the carboxylic groups. The resultant particles were very stable in water and resembled those formed in surfactant-free emulsion copolymerization. The formation and stabilization of such particles were studied by a combination of static and dynamic laser light scattering. The particle size decreases as the carboxylation extent [COOH] increases in the range 7−26 mol %. Further increase of [COOH] leads to an increase of the particle size. On the other hand, as [COOH] increases, the monotonic decrease of the average particle density $\langle\rho\rangle$ and the increase of the ratio of the average radius of gyration to the average hydrodynamic radius ($\langle R_g\rangle/\langle R_h\rangle$) reveal the swelling of the particles, indicating a gradual change of their structure from spherelike to clusterlike. Using longer polymer chains or more ionizable counterions results in smaller particles. Our results indicate that the formation and stabilization are controlled by a delicate balance between hydrophobic and hydrophilic interactions. More hydrophilic groups stabilizing a larger total interfacial area generally lead to smaller particles.

Introduction

As a fundamental issue, the stabilization of colloidal particles and biological structures in water has attracted scientists for a long time. van der Waals interaction and a repulsive electric double-layer force were first proposed to account for the stabilization.[1] Later, for some uncharged molecules and particles also stable in water, Langmuir[2] and Derjaguin[3] suggested that the hydration force arising from the strongly bound and oriented first layer of water molecules on surfaces drove the stabilization. Recently, Israelachvili et al.[4−6] studied the forces between two surfaces in liquids and found that the hydration force was not monotonically repulsive but attractive or oscillatory. Consequently, they suggested that the stabilization should be attributed to entropic repulsion depending on the surface characteristics.[4]

Previously, we showed that the water-insoluble ionomer chains could form surfactant-free polymeric nanoparticles that are stable in water if a special microphase inversion procedure was adopted.[7] Such particles resemble those formed in surfactant-free emulsion copolymerization of hydrophobic and hydrophilic monomers. To better understand the formation and stabilization of these particles, we prepared surfactant-free polymeric particles by using a series of narrowly distributed carboxylated polystyrene (CPS) chains with different lengths and amounts of hydrophilic groups and systematically studied their formation and stabilization under different conditions by using a combination of static and dynamic laser light scattering.

Experimental Section

Narrowly distributed CPS samples ($M_w = 6.43 \times 10^3$, 2.74×10^4, 6.65×10^4, and 1.58×10^5 with $M_w/M_n < 1.1$) with carboxylic groups randomly distributed along their chains were obtained by partially carboxylating polystyrenes; the preparation and characterization were detailed elsewhere.[8,9] The carboxylation extent ([COOH]) was determined by titrating CPS in tetrahydrofuran (THF) to a phenolphthalein end point with a sodium methylate solution in a mixed solvent of toluene/methanol (90/10, v/v). The lithium salts of CPS (LiCPS) were prepared by neutralizing CPS in THF with lithium methylate in the same mixed solvent. The surfactant-free particles were prepared by adding dropwise a CPS THF solution with an initial concentration of 1.0×10^{-3} g/mL to an excess of water under ultrasonification.[7] The resultant colloidal dispersions were transparent and stable in water. The final THF/H_2O volume ratio was 1:100.

A modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi-τ digital time correlation (ALV5000) and a solid-state laser (ADLAS DPY425II, output power = 400 mW at $\lambda_0 = 532$ nm) as light source was used. The refractive index increment (dn/dC) was determined by a differential refractometer.[10] The details of LLS instrumentation and theory can be

---

* To whom correspondence should be addressed. Telephone: (852) 26096106. Fax: (852) 26035057. E-mail: chiwu@cuhk.edu.hk.

† Fudan University.

‡ University of Science and Technology of China.

§ The Chinese University of Hong Kong.

[1] Hunter, R. J. *Foundations of Colloid Science*; Clarendon: Oxford, 1989; Vol. 1.

[2] Langmuir, I. *J. Chem. Phys.* **1938**, *6*, 873.

[3] Derjaguin, B. V.; Churaev, N. V. In *Fluid Interfacial Phenomena*; Croxton, C. A., Eds.; Wiley: Chichester, 1982; Chapter 15; p 663.

[4] Israelachvili, J. N.; McGuiggan, P. M. *Science* **1988**, *241*, 795.

[5] Israelachvili, J. N.; Pashley, R. M. *Nature* **1983**, *306*, 249.

[6] Israelachvili, J. N.; Wennerstrom, H. *Science* **1996**, *379*, 219.

[7] Li, M.; Jiang, M.; Zhu, L.; Wu, C. *Macromolecules* **1997**, *30*, 220. Li, M.; Jiang, M.; Wu, C. *J. Polym. Sci., Polym. Phys.* **1997**, *35*, 1593. Li, M.; Zhang, Y.; Jiang, M.; Zhu, L.; Wu, C. *Macromolecules* **1998**, *31*, 6841.

[8] Hird, B.; Eisenberg, A. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 1337.

[9] Zhu, L.; Liu, L.; Jiang, M. *Macromol. Rapid Commun.* **1996**, *17*, 37.

[10] Wu, C.; Xia, K. Q. *Rev. Sci. Instrum.* **1994**, *65*, 587.

10.1021/la000453h CCC: $19.00

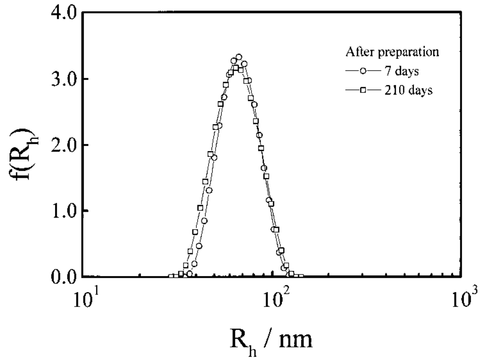

Figure 1. Standing time dependence of hydrodynamic radius distributions $f(R_h)$ of CPS particles, where [COOH] = 14.5 mol % and $M_{w,chain} = 6.43 \times 10^3$ g/mol.

found elsewhere.[11,12] In static LLS, the angular dependence of the excess absolute time-averaged scattering light intensity, known as the excess Rayleigh ratio $R_{vv}(q)$, of dilute polymer solutions with different concentrations (C) can lead to the weight average molar mass (M_w) and the root-mean-square z-average radius of gyration of the polymer chain in solution ($\langle R_g^2\rangle_z^{1/2}$ or written as $\langle R_g\rangle$). In dynamic LLS, the Laplace inversion of a measured intensity–intensity time correlation function $G^{(2)}(q,t)$ in the self-beating mode can result in a line-width distribution $G(\Gamma)$.[12,13] For a pure diffusive relaxation, $G(\Gamma)$ can be transferred into a transitional diffusion coefficient distribution $G(D)$, since $(\Gamma/q^2)_{C\to 0,q\to 0} \to D$, or a hydrodynamic radius distribution $f(R_h)$ via the Stokes–Einstein equation, $R_h = (k_BT/6\pi\eta)D^{-1}$, where k_B, T, and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. All the LLS measurements were done at 25.0 ± 0.1 °C. The CPS dispersions were clarified using a 0.5-μm Millipore filter.

Results and Discussion

Figure 1 shows that the nanoparticles made of the CPS chains were very stable even after ~7 months. It should be stated that removing the 1% THF from the dispersion did not change $f(R_h)$, indicating that the THF has no effect on the stabilization of the particles. In contrast, polystyrene homopolymer chains are not able to form surfactant-free particles stable in water. Therefore, a small amount of hydrophilic moiety (COOH) is essential for the stabilization. Considering that the dissociation constant of benzoic acid is only 6.46×10^{-5} at 25 °C, the ionization of COOH is so limited that the stabilization should not be solely attributed to electrostatic repulsion, which was confirmed by the fact that once the particle formed, its size was independent of the ionic strength. The hydrophilic interactions driving the stabilization should include the hydrogen bonding between COOH and water, the electrostatic repulsion between COO^- groups, and the interaction between COO^- and water. Our preliminary experiments showed that precipitation instead of a stable dispersion occurred if the CPS THF solution was not added dropwise but poured into water. In the particle formation, after each drop of the CPS THF solution is added into water, the insoluble hydrophobic backbones tend to collapse and associate with each other to minimize their interface with water, while the hydrophilic carboxylic groups try to stay on the periphery to reduce the interfacial energy even though not all of them are able to locate on the interface.[14,15] The dropwise addition and initial dilute solution provided more chances for the carboxylic groups to locate on the particle surface instead of being buried inside so that the hydrophilic stabilization was enhanced. Note that the CPS chains are practically "frozen" inside the particle due to the strong hydrophobic interaction, and the interparticle fusion is difficult, if not impossible. In this sense, the hydrophobic interaction is responsible not only for the particle formation but also for the particle stabilization. Accordingly, the formation of the particles is dependent not only on a delicate balance between hydrophilic and hydrophobic interactions but also on the mechanism of particle formation.

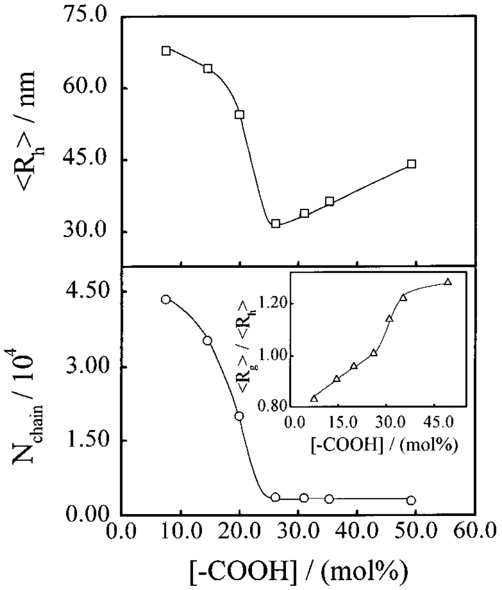

Figure 2. Carboxylation extent dependence of the average hydrodynamic radius ($\langle R_h\rangle$), the average number of CPS chains (N_{chain}) inside each particle, and the ratio of the average radius of gyration to the average hydrodynamic radius ($\langle R_g\rangle/\langle R_h\rangle$) of CPS nanoparticles, where $N_{chain} = M_{w,particle}/M_{w,chain}$ and $M_{w,chain} = 6.43 \times 10^3$ g/mol.

Figure 2 shows that both the particle size and the average number of the CPS chains inside each particle (N_{chain}) decrease as [COOH] increases in the range 7.4–26.1 mol %. A similar trend was also observed for different polymeric colloids.[7,16–18] For a given polymer/water interface, the average surface area stabilized by each hydrophilic moiety should be a constant.[7,17,18] Consequently, more hydrophilic moieties can stabilize a larger total surface area corresponding to smaller particles. However, in the range 26.1–49.2 mol %, the particle size ($\langle R_h\rangle$) increases from 32 to 44 nm, while the average number (N_{chain}) of the CPS chains inside each particle almost remains constant. Figure 3 reveals that, in this higher [COOH] range, $f(R_h)$ splits into two peaks respectively located at in the range ~10–20 and ~25–80 nm, much different from the narrowly distributed $f(R_h)$ values shown in Figure 1. A dilution of the dispersion from 1.0×10^{-5} to 1.0×10^{-6} g/mL shifts the peak position and weighting; namely, the peak corresponding to larger particles becomes smaller, while the peak corresponding to smaller particles becomes larger and shifts to ~10 nm, indicating the dissociation of the particles. When the carboxylation extent is high, the hydrophobic polystyrene segment between two neighboring carboxylic groups, on

---

(11) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.

(12) Chu, B. *Laser Light Scattering*, 2nd ed.; Academic Press: New York, 1991.

(13) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Plenum Press: New York, 1976.

(14) Ceska, G. W. *J. Appl. Polym. Sci.* **1974**, *18*, 427; **1974**, *18*, 2493.

(15) Szajdzinska-Peitek, E.; Wolszczak, M.; Plonka, A.; Schlick, S. *J. Am. Chem. Soc.* **1998**, *120*, 4215.

(16) Qiu, X.; Kwan, C. M. S.; Wu, C. *Macromolecules* **1997**, *30*, 6090.

(17) Qiu, X.; Wu, C. *Macromolecules* **1997**, *30*, 7921.

(18) Wu, C.; Akashi, M.; Chen, M. *Macromolecules* **1997**, *30*, 2187.

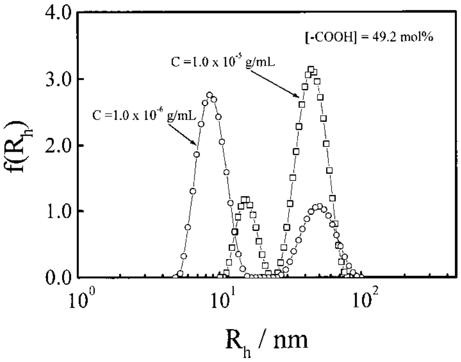

Figure 3. Effect of dilution on the hydrodynamic radius distribution $f(R_h)$ of CPS particles formed with a high carboxylation extent, where $M_{w,chain} = 6.43 \times 10^3$ g/mol.

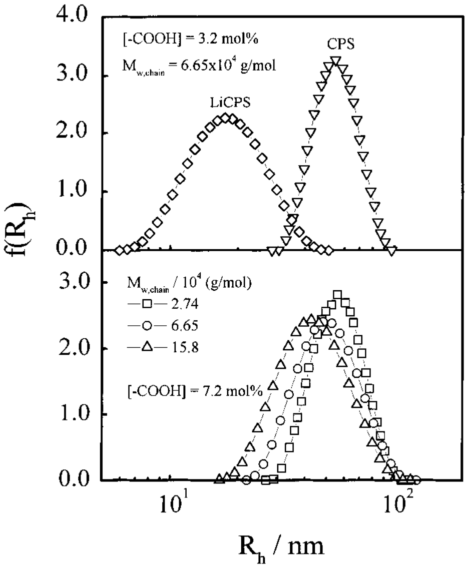

Figure 4. Counterion and chain length dependence of the hydrodynamic radius distribution $f(R_h)$ of CPS particles.

average, becomes short and the association of these segments inevitably traps more carboxylic groups inside, resulting in a less compact structure. The CPS chains inside these particles are more mobile so that the dilution breaks up the particles. On the other hand, it is known that the ratio of the average radius of gyration to the average hydrodynamic radius $\langle R_g \rangle / \langle R_h \rangle$ increases as the structure or conformation extends. For example, for a uniform nondraining sphere, a hyperbranched cluster, and a coil chain, the ratios of $\langle R_g \rangle / \langle R_h \rangle$ are 0.774, ~1.0–1.3, and ~1.5–1.8, respectively.[19–22] The increase of $\langle R_g \rangle / \langle R_h \rangle$ from 0.8 to ~1.3 as [COOH] increases from 7.4 to 49.2 mol % shown in the inset of Figure 2 indicates a gradual transition of the particle structure from a compact spherelike one into a swollen hyperbranched clusterlike one.

Figure 4 shows that the counterion and the chain length also affect the stability and size of the particles. LiCPS with more hydrophilic groups (COOLi) formed much smaller particles compared with those of the corresponding CPS. This is because groups with higher hydrophilicity have more chance to stay at the particle/water interface than inside particles. Our LLS results directly confirm that the increase in both the hydrophilicity and the density of hydrophilic groups on a particle surface would reduce the particle size and promote its stability, as found in surfactant-free emulsion copolymerization.[14,23–27] Figure 4 also shows that the particle size decreases as the CPS chain length increases even though each chain, statistically, has the same carboxylation extent. As we have discussed before,[17] there exists a competition between intrachain contraction and interchain association in the particle formation. The domination of the intrachain contraction leads to smaller particles. For a given weight concentration, a longer chain can be viewed as several connected short chains. Therefore, the intrachain contraction should be easier for a longer chain due to geometric constraints.

The effects of the nature and amount of hydrophilic groups as well as the chain length on the particle size and stability experimentally support Israelachvili's theory;[6] namely, the entropic repulsion arising from the particle surface properties drives the particle stabilization. We also found that when [COOH] > 26 mol %, adding styrene monomer into the dispersion led to the swelling of the clusters, indicating that styrene was preferentially absorbed inside the clusters. The swollen clusters are stable in water, suggesting that, in surfactant-free emulsion copolymerization of hydrophilic and hydrophobic monomers, the initially formed hydrophobically associated copolymer chains could serve as seeds in polymerization.

In conclusion, surfactant-free polymeric nanoparticles stable in water can be formed via a microphase inversion if a delicate balance between hydrophobic and hydrophilic interactions is carefully established. The structure of such formed particles is governed by hydrophilic interactions determined by the hydrophilic groups located on the periphery and the hydrophobic interaction coming from the hydrophobic backbones inside the particles. More hydrophilic groups can stabilize a larger total interface area so that the particle size generally decreases as the number of hydrophilic groups increases. On the basis of the above study, we know that a fast chain propagation and a high polymerization degree in surfactant-free copolymerization can lead to smaller particles stable in water.

Acknowledgment. The financial support of the National Basic Research Project—'Macromolecular Condensed State Program', the National Natural Science Foundation of China (NNSFC No.29992590), the National Distinguished Young Investigator Grant (1996, 29625410), and the Research Grants Council of Hong Kong Government Earmarked Grant 1999/2000 (CUHK4209/99P, 2160122) is gratefully acknowledged. The laser light scattering facility was made available by the Open Laboratory of Bond-Selective Chemistry in USTC.

LA000453H

---

(19) Buchard, W. In *Light Scattering Principles and Development*; Brown, W., Ed.; Clarendon Press: Oxford, 1996; p 439.

(20) Burchard, W.; Schmidt, M.; Stockmayer, W. H. *Macromolecules* **1980**, *13*, 1265.

(21) Douglas, J. P.; Roovers, J.; Freed, K. F. *Macromolecules* **1990**, *23*, 4168.

(22) Vagberg, L. J. M.; Cogan, K. A.; Gast, A. P. *Macromolecules* **1991**, *24*, 1670.

(23) Okubo, M.; Kanaida, K.; Matsumoto, T. *J. Appl. Polym. Sci.* **1987**, *33*, 1511.

(24) Sakota, K.; Okaya, T. *J. Appl. Polym. Sci.* **1976**, *20*, 1745.

(25) Guillaume, J. L.; Pichot, C.; Guillot, J. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1937.

(26) Pan, T. C.; Kuo, J. F.; Chen, C. Y. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 709.

(27) Lee, D. Y.; Kim, J. H. *J. Appl. Polym. Sci.* **1998**, *69*, 543.