

Formation of Novel Polymeric Nanoparticles

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ABSTRACT

We have found that not only block copolymers but also ionomers can self-assemble in a selective solvent to form surfactant-free nanoparticles. The self-assembly can be induced by chemical reaction, polymer–polymer complexation, and microphase inversion in addition to the temperature. A recently developed microwave method for the preparation of uniform surfactant-free polymeric nanoparticles is also reviewed. Our results have revealed that for a given dispersion, the particle surface area occupied per stabilizer (surfactant, polymer chains, and ionic groups) is close to a constant.

Introduction

The formation of polymeric nanoparticles actually contains two parts: (1) the micronization of a material into

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nanoparticles and (2) the stabilization of the resultant nanoparticles. As for the micronization, one can start with either small monomers or a bulk polymer. Emulsion polymerization as a conventional preparation method can make polymeric particles in the size range 10^2 – 10^3 nm which has been gradually broadened. For example, the seeded emulsion polymerization was developed to make latexes larger than 10^3 nm,^{1,2} while the miniemulsion and microemulsion polymerizations were invented to prepare particles in the ranges 50–200 and 20–50 nm, respectively.^{3,4} It is known that in microemulsion polymerization, a large amount of surfactant/cosurfactant has to be added to make small nanoparticles. The addition of surfactant limits not only the polymer solid content in the dispersion but also their applications. The removal of surfactant from a resultant dispersion without affecting its stability is extremely difficult, if not impossible.

Much effort has been spent on studying ways to increase the solid content and reduce the amount of surfactant added. For example, a continuous and slow addition of monomers dropwise into a microemulsion during polymerization and a semicontinuous addition of monomers into dispersion formed via microemulsion polymerization were developed to make full use of surfactant to increase the solid content.^{5,6} In a Winsor I-like polymerization system,^{7,8} a monomer upper layer was saturated with a small amount of water and dodecyltrimethylammonium bromide (DTAB) and a lower oil-in-water microemulsion layer. The upper layer acted as a monomer reservoir for the microemulsion polymerization in the lower layer. In this way, a series of polystyrene (PS) latex dispersions in the size range 46–97 nm were prepared with a solid content as high as 15 wt % and a surfactant content as low as 1%.

Until now, it has remained a challenge or a dream to prepare concentrated uniform surfactant-free polymeric nanoparticles (10–100 nm in size) that are stable in water. There is a growing tendency to use protein and other natural polyelectrolytes, besides low molar mass surfactant, to stabilize nanoparticles, especially in the food and pharmaceutical industries. Polymeric nanoparticles in water can also be stabilized by ionic groups introduced by initiation, copolymerization, or surface modification, and by hydrophilic polymer chains grafted or adsorbed on the particle surface, which is schematically shown in Figure 1.

As for the formation of polymeric nanoparticles, it has recently been found that block copolymers can self-assemble into nanoparticles in a selective solvent in which only one block is soluble.^{9–13} Most of the past studies in this direction dealt with commercially available block copolymers, such as block copolymers made of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO).^{14–16}

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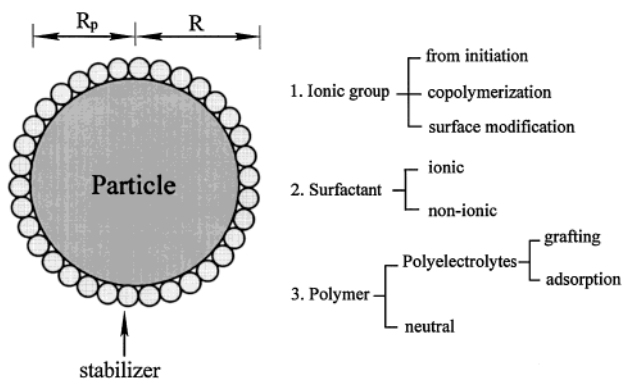


FIGURE 1. Schematic representation of stabilization of polymeric nanoparticles, where the surface area per stabilizer is constant for a given dispersion.

Clearly, our attention should be directed to the design, synthesis, and self-assembly of specially functionalized polymeric nanoparticles for various applications. Another long-standing problem is how to quantitatively, or at least semiquantitatively, tailor the size of resultant nanoparticles.

In this Account, we summarize our recent efforts toward the formation and stabilization of novel polymeric nanoparticles. We wish to show that not only block copolymers, but also ionomers, can self-assemble in a selective solvent to form surfactant-free nanoparticles. The self-assembly can be induced by chemical reaction, polymer–polymer complexation, and microphase inversion, in addition to temperature. We also would like to show a recently developed novel method of using microwave radiation to prepare uniform surfactant-free nanoparticles. Our results have revealed that, for a given dispersion, the particle surface area (s) occupied per stabilizer is constant. Using this principle, we can control the particle size by varying the macroscopic monomer-to-stabilizer weight ratio.

Structural Models for Stabilization of Nanoparticles

After studying a range of polymer dispersions stabilized by surfactant,^{17,18} ionic groups,¹⁹ and polymer chains,²⁰ we have found that for each given stable dispersion, the average surface area (s) occupied per stabilizer is an important parameter. As shown in Figure 1, $s = A_t/N_s$, with A_t and N_s being the total available particle surface area and the total number (N_s) of stabilizers on the surface. $A_t = 4\pi R_p^2(W_m + \gamma W_s)/(4/3 \pi R^3 \rho)$, where W_m and W_s are the initial macroscopic weights of monomer (or polymer) and stabilizer, respectively; γ is the weight fraction of stabilizer on the surface; and ρ is the particle's average density. $N_s = N_A(\gamma W_s)/M_s$, with N_A and M_s being Avogadro's constant and the stabilizer's molar mass. Therefore,

$$s = \frac{A_t}{N_s} = \left[\frac{4\pi R_p^2 (W_m + \gamma W_s)}{4/3 \pi R^3 \rho} \right] / \left(\frac{N_A \gamma W_s}{M_s} \right) \quad (1)$$

Assuming that the stabilizer layer has a thickness $\Delta R = R$

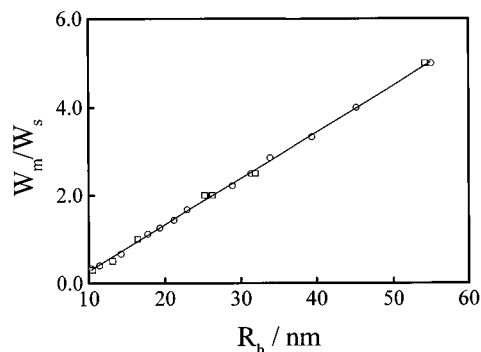


FIGURE 2. Typical plot of W_m/W_s versus R for the emulsion polymerization of styrene in the presence of CTAB as a stabilizer.

– $R_p \ll R$, we can rewrite eq 1 as

$$\begin{aligned} \frac{W_m}{W_s} &= \gamma \left(s \frac{N_A \rho R^3}{3 M_s R_p^2} - 1 \right) \\ &\cong \gamma s \frac{N_A \rho}{3 M_s} R + \gamma \left(s \frac{N_A \rho}{3 M_s} \Delta R - 1 \right) \quad (2) \end{aligned}$$

This clearly shows that W_m/W_s is a linear function of R . The slope and intercept can, respectively, lead to s and ΔR if we know γ since ρ and M_s are constants for a given dispersion.^{17,18} The structural model and eq 2 have been successfully applied for a number of polymeric nanoparticle dispersions and different stabilizers.

Stabilized with Surfactant. It is generally known that, in microemulsion polymerization, the particle size decreases as the surfactant concentration increases. In the middle of 1990s, we have experimentally established a quantitative relationship between the particle size and the fleet ratio, the monomer-to-surfactant weight ratio.^{17,18,20} Figure 2 shows a typical plot of W_m/W_s vs R_h for PS latex prepared by microemulsion polymerization in the presence of cetyltrimethylammonium bromide (CTAB) as a stabilizer,^{17,18} where R_h was measured by dynamic laser light scattering (LLS). On the basis of eq 2 and setting $\gamma = 1$, we estimated that $s \approx 0.2 \text{ nm}^2$ and $\Delta R \approx 1 \text{ nm}$, which are more reasonable than previously reported data.^{21,22}

Stabilized with Grafted Polymer Chains. Using water-soluble PEO chains end-capped with styrene or MMA as stabilizer, it has been shown that surfactant-free PS and poly(methyl methacrylate) (PMMA) nanoparticles can be prepared by emulsion polymerization. In this method, surfactant-free PS or PMMA particles were stabilized by the PEO chains grafted on the surface.²⁰ We found that for both the PS and PMMA particles, W_m/W_s is a linear function of R_h , even when PEO chains with different lengths were used, as shown in Figure 3.

It is interesting to note that the slope for the PMMA particle is much larger: because the acrylate group on MMA is relatively more hydrophilic than the benzene ring on styrene, each PEO chain can stabilize a larger surface area when the core is made of PMMA. Figure 3 shows that the slope is independent of the chain length. Equation 2 shows that the slope is a function of s/M_s . Figure 3 reveals

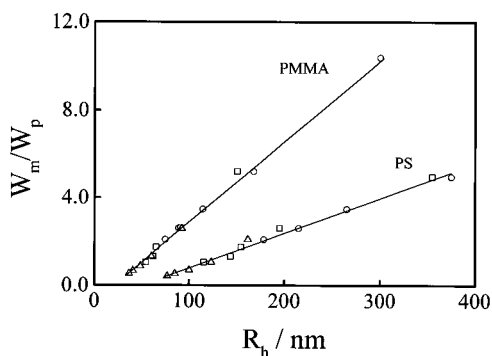


FIGURE 3. Typical plot of W_m/W_p versus R_h for dispersions obtained by emulsion polymerization of styrene in the presence of the short PEO chains as a stabilizer.

that s/M_s is constant. On the other hand, s is proportional to the square of the chain size (R_{chain}), i.e., $s \sim R_{\text{chain}}^2$. Therefore, we have $R_{\text{chain}} \sim M_s^{0.5}$, revealing that the PEO chains on the particle surface behaved like unperturbed chains.

Stabilized with Soluble Block Chains. Equation 2 can also be used for the self-assembly of $A_m B_n$ or $A_m B_n A_m$ type block copolymers in a selective solvent,²³ where m and n are the numbers of the repeating units of the soluble A and insoluble B blocks, respectively. Considering that the surface area stabilized by each A block is a constant for a given polymer/solvent system, we can derive a simple scaling similar to eq 2 for the core-shell nanostructure. Assuming that the core radius is R_c , the shell thickness is δ , the core density is a constant ρ_c , and each nanostructure on average contains N copolymer chains, we have $\rho_c(4/3)\pi R_c^3 \propto Nn$. On the other hand, the surface area of the core ($4\pi R_c^2$) is related to the average surface area (s) occupied per soluble block, i.e., $4\pi R_c^2 \propto sN$. Considering each soluble block as a grafting chain with an unperturbed coil conformation, we have $s \propto m$. Therefore,

$$R_c^{-1} \propto \frac{m}{n} \quad (3)$$

This shows that, for a given insoluble block length, $R_c^{-1} \propto m$, while for a given soluble block length, $R_c^{-1} \propto n^{-1}$. Figure 4 shows a replot of the data presented in ref 16 for PEO-*b*-PPO block copolymers in water. For a given series of block copolymers with a fixed m , R_c^{-1} is, indeed, proportional to n^{-1} . On the other hand, a replot of the results shown in refs 15 and 16 confirmed the prediction of eq 3 for the case of a constant n .²³

Stabilized with Adsorbed Polymer Chains. Using the same structural model, we studied the adsorption of linear polymer chains on particle surfaces.^{24,25} Our results showed that the average hydrodynamic volume per chain adsorbed on the surface can be scaled by the number of the chains adsorbed on each particle, as shown in Figure 5. Considering that on a unit area, the density profile ($\rho(z)$) of the adsorbed chains is a function of the distance (z) away from the surface, we have

$$\int_0^\infty \rho(z) dz = W_{\text{polymer}} \propto n_{\text{chain}} \quad (4)$$

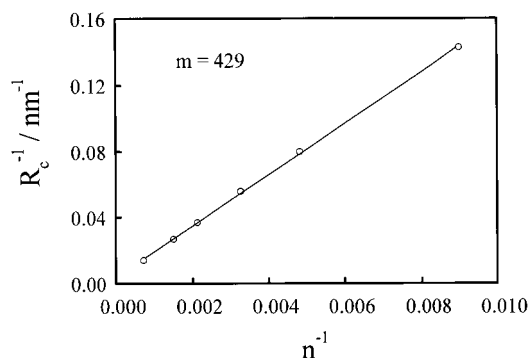


FIGURE 4. Replot of the data presented in Table 3 of ref 14 for the self-assembly of block copolymer, poly(ethylene oxide)-*block*-poly(propylene oxide) ($E_m P_n$) in water at 25 °C, where R_c is the radius of the core and n is the number of the repeating units of the insoluble block.

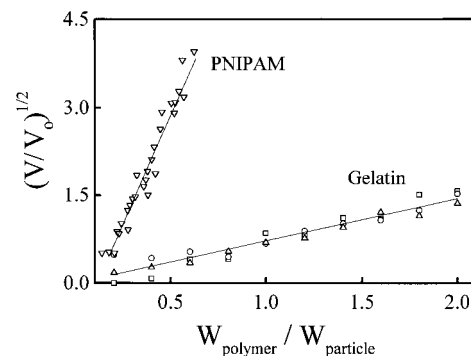


FIGURE 5. Adsorption dependence of the average hydrodynamic volume (V) of the adsorbed polymer layer on the particle, where V_0 is the volume of the bare particle and $W_{0\text{particle}}$ and W_{polymer} , respectively, are the total weights of the particles and the polymer chains adsorbed on the particles. ∇ , The adsorption of PNIPAM on PS latex; \circ , \triangle , \square , the adsorption of gelatin on different β -carotin nanoparticles.

Assuming that $\rho(z)$ can be scaled by a characteristic length (ξ), we can rewrite eq 4 as $\xi \int_0^\infty \rho(z/\xi) d(z/\xi)$. The observed scaling, $v_{\text{chain}} \propto n_{\text{chain}}$, suggests that $\xi \propto n_{\text{chain}}$ and $\rho(z/\xi)$ is invariant.

Stabilized with Ionic Groups. It has recently been found that ionomers, i.e., polymer chains with only a few mole percent ionic groups attached to the chain backbone, can form narrowly distributed nanoparticles that are stable in water if a special microphase inversion method is used.^{19,26,27} The microphase inversion is a redispersion process, namely, dissolving ionomer in a water-miscible solvent, such as acetone or tetrahydrofuran (THF) and then adding the ionomer solution dropwise to an excess of water. As expected, the solvent immediately mixes with water and the insoluble hydrophobic chains undergo an intrachain contraction and interchain association, while the ionic groups are forced to stay on the periphery during the microphase inversion. It is these small amounts of ionic groups that stabilize the resultant nanoparticles. Using this method, we were able to make surfactant-free PS nanoparticles as small as a few nanometers. Figure 6 shows two typical size distributions of such obtained stable colloidal particles, respectively. The particle size can be controlled by controlling the initial

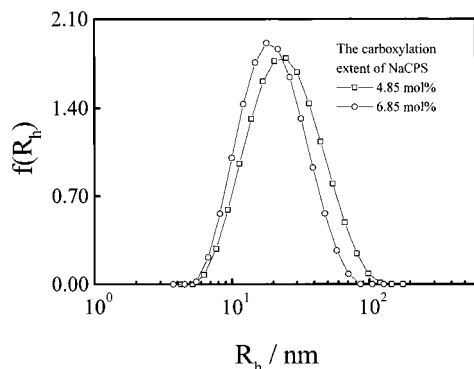


FIGURE 6. Surfactant-free nanoparticles made of randomly carboxylated polystyrene ionomers dispersed in water by microphase inversion.

ionomer concentration, the content of ionic groups, and the counterions. The dispersion was so stable that there was no detectable change in its size distribution over months.

The question is how such nanoparticles can be stabilized and what determines the particle size. During the aggregation, the surface area (S) of the particle is proportional to the square of its radius (R), the number (N_{ionic}) of the ionic groups on the surface is proportional to the associated chain number (N_{chain}) per aggregate, and N_{chain} is further proportional to the mass of the particle (M_{particle}). For a uniform particle, $M \propto R^3$. Therefore, the average surface area occupied per ionic group $s = S/N_{\text{ionic}} \propto R^{-1}$. As the aggregation proceeds, R increases and s decreases. For a given ionomer in water, there should exist a minimum value of s at which the particle surface is fully “covered” by the ionic groups and further coagulation becomes impossible because of electrostatic repulsion. A combination of static and dynamic LLS results showed that s remained constant ($\sim 3 \text{ nm}^2$) for the carboxylated polystyrene even when the particle size varied in the range 8–20 nm.¹⁹

Formation of Novel Nanoparticles via Self-Assembly

As mentioned before, block copolymers in a selective solvent can undergo self-assembly to form nanoparticles with a core–shell structure.^{9–13} Normally, the self-assembly is induced by a temperature variation, as shown in the case of PEO-*b*-PPO block copolymers.^{14–16} Recently, we have found that the self-assembly can also be induced by chemical reaction, polymer–polymer complexation, and microphase inversion.

Temperature-Induced Self-Assembly. Recently, we prepared a new kind of nanoparticles with a liquid crystal core via the self-assembly of poly(styrene-*block*-(2,5-bis-[4-methoxyphenyl]oxycarbonyl)styrene) (PS-*b*-PMPCS).^{28–30} The rod-like PMPCS block is a mesogen-jacked liquid crystalline polymer and is soluble in *p*-xylene at temperatures higher than 100 °C, so that *p*-xylene at a lower temperature is a selective solvent. Instead of neutron scattering, we are able to use a combination of the average radius of gyration ($\langle R_g \rangle$) and the average hydrodynamic

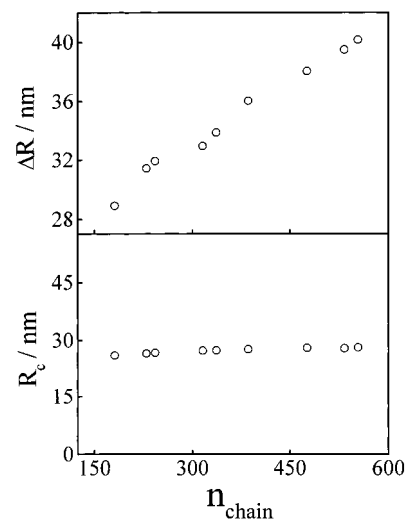


FIGURE 7. Association chain number (n_{chain}) dependence of average radius of the PMPCS core (R_c) and average thickness of the PS shell (ΔR) of self-assembled PS-*b*-PMPCS nanostructure at 25 °C.

radius ($\langle R_h \rangle$) respectively measured in static and dynamic LLS to estimate the core radius (R_c) and the shell thickness (ΔR) because

$$\frac{\langle R_g \rangle}{\langle R_h \rangle} = \left\{ \frac{3[Ax^2 - (1+A)x^5 + 1]}{5(1+A)(1-x^3)} \right\}^{1/2} \quad (5)$$

where we have assumed that the core–shell nanostructure is made of two concentric spheres with two different but uniform densities,^{31–33} A is the core-to-shell mass ratio, a constant for a given diblock copolymer, and $x = R_c/R$ or R_c/R_h . Therefore, for each pair of measured $\langle R_g \rangle$ and $\langle R_h \rangle$, we are able to find a corresponding x from eq 4 and calculate R_c and ΔR since $R_c = \langle R_h \rangle x$ and $\Delta R = \langle R_h \rangle - R_c = \langle R_h \rangle (1 - x)$.

Figure 7 shows that R_c is nearly independent of n_{chain} , but ΔR increases with n_{chain} . It is worth noting that the values of R_c are sufficiently close to the contour length of the PMPCS block ($\sim 31 \text{ nm}$), revealing that when more copolymer chains are self-assembled, the insoluble rod-like blocks are simply inserted into the core while the soluble coil-like PS blocks are forced to stretch in the shell. Further calculation shows that, as n_{chain} increases from 180 to 554, the surface area occupied per PS block decreases from 47 to 18 nm² and the core density increases from 0.19 to 0.47 g/cm³, further indicating the packing of the PMPCS blocks in the core and the elongation of the PS blocks in the shell, as schematically shown in Figure 8. The stretching of a coil-like block in the shell has previously been reported.^{34–36} However, to our knowledge, a core with a constant size is rare. The behavior of the swollen PS blocks is similar to that of the polymer chains grafted on a surface, but very different from the adsorption of polymer chains.²⁴

The temperature-induced self-assembly of poly(*N*-isopropylacrylamide) (PNIPAM) grafted with short PEO chains is another good example.^{37,38} At room temperature, both PNIPAM and PEO are water-soluble, while at tem-

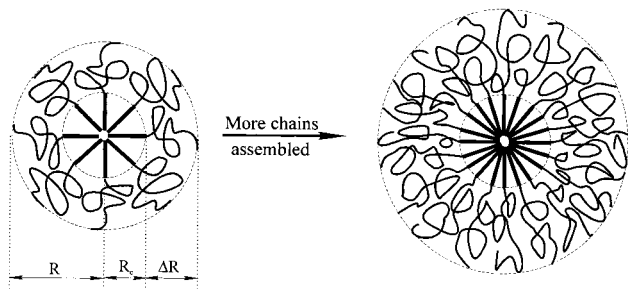


FIGURE 8. Schematic of a core-shell nanostructure formed by a self-assembly of coil-rod diblock copolymer chains in a selective solvent.

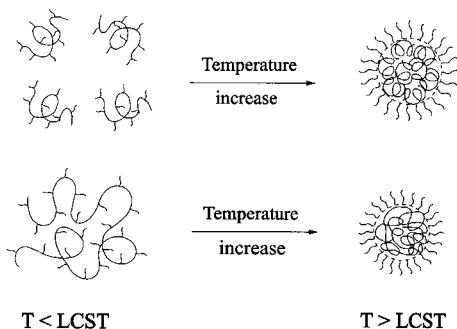


FIGURE 9. Schematic representation of the self-assembly of PNIPAM-*g*-PEO copolymer chains (or a single chain) in water to form a core-shell nanostructure with PNIPAM as the core and PEO as the shell.

peratures higher than ~ 32 °C, PNIPAM becomes hydrophobic and undergoes an intrachain “coil-to-globule” transition and an interchain aggregation to form nanoparticles. Our results showed that the particle size decreased as the number of the PEO chains grafted on the PNIPAM chain backbone increased; a lower copolymer concentration and a fast heating rate could also lead to smaller nanoparticles. With a proper control of the formation conditions, we were able, *for the first time*, to completely suppress the interchain association and construct a single-chain core-shell nanostructure,³⁸ as schematically shown in Figure 9.

Chemical Reaction-Induced Self-Assembly. As schematically shown in Figure 10, upon heating a diblock copolymer, poly(4-methyl styrene-*block*-phenyl vinylsulfonide) (PMS-*b*-PVSO), in THF, the soluble and flexible PVSO block could be converted into an insoluble and rigid polyacetylene (PA) block via a chemical reaction,^{39,40} resulting in a core-shell nanostructure with the PA blocks as the core and the PMS blocks as the shell. The reaction and self-assembly rates could be simply controlled by controlling the reaction temperature in the range of 30–80 °C. The pictures in Figure 10 show that, as the reaction proceeded, the solution gradually changed from colorless to light yellow and finally to dark red. LLS results confirmed the formation of soluble polyacetylene nanoparticles coated with a layer of poly(4-methyl styrene) in the size range 30–60 nm.³⁹

Complexation-Induced Self-Assembly. We have found that the complexation between polyacrylate or polymethacrylate and hydroxyl-containing polystyrene (PS-

(OH)) in toluene could result in insoluble complexes.^{41–43} On the basis of this finding, we synthesized a poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) diblock copolymer and studied its complexation with PS(OH) in toluene. As expected, the complexation between the PMMA block and PS(OH) led to an insoluble core, while the soluble PS blocks prevent a macroscopic precipitation, resulting in stable polymeric nanoparticles.⁴⁴ Figure 11 shows that before the complexation, both PS-*b*-PMMA and PS(OH) are narrowly distributed and have a similar size around ~ 6 –7 nm. After mixing two dilute solutions of PS(OH) (4.0×10^{-5} g/mL) and PS-*b*-PMMA (5.0×10^{-4} g/mL), we observed a bimodal size distribution. The peak located at ~ 300 nm clearly represents the aggregation induced by the complexation. The peak located at ~ 7 nm disappeared if more PS(OH) chains were added, indicating that it represents individual PS-*b*-PMMA chains. The particle size can be regulated by the initial concentrations of PS-*b*-PMMA and PS(OH) and also by the mixing order.⁴⁴

Microphase Inversion-Induced Self-Assembly. Recently, we have successfully micronized poly(ethylene oxide-*block*- ϵ -caprolactone) (PEO-*b*-PCL) diblock copolymer into small, narrowly distributed core-shell nanoparticles that are stable in water via a microphase inversion; namely, the original solvent (THF) was suddenly replaced by a nonsolvent (water) when 1 mL of a THF solution of PEO-*b*-PCL was added dropwise into 99 mL of deionized water under ultrasonication.⁴⁵ The aggregation of the insoluble PCL blocks led to a core, while the soluble PEO blocks formed a protective corona. Such formed PEO-*b*-PCL nanoparticles are biodegradable in the presence of Lipase PS (enzyme). LLS study showed that the biodegradation of the PCL core could result in a dissolution of the nanoparticles, as shown in Figure 12. The initial slope of C_t/C_0 vs t leads to the biodegradation rate (v_0) defined as $[dC_t/dt]_{t=0}$. The inset shows the enzyme concentration dependence of v_0 , and the line represents a least-squares fitting of v_0 (g/mL·min) = $6.327 \times 10^{-5} E_0^{2.0 \pm 0.1}$. Using pyrene as an imitative drug and fluorescence probe, we have shown that hydrophobic drugs could be loaded into the PCL core in the micronization process. The biodegradation could effectively destroy the PCL core and release pyrene in a controllable fashion.

Preparation of Nanoparticles by Microwave Irradiation

Recently, we have shown that surfactant-free stable PS nanoparticles could be prepared by using microwave radiation with potassium persulfate (KPS) as the initiator in water.^{46,47} In comparison with conventional heating, this novel method can shorten the reaction time by a factor of ~ 20 , result in narrowly distributed nanoparticles, and lead to moderately distributed polymer chains inside the nanoparticles. Our results revealed that the particle size could be well controlled by varying the monomer-to-initiator weight ratio. It should be stated that using microwave irradiation to initiate a chemical reaction is not new, but it has several distinct advantages in the

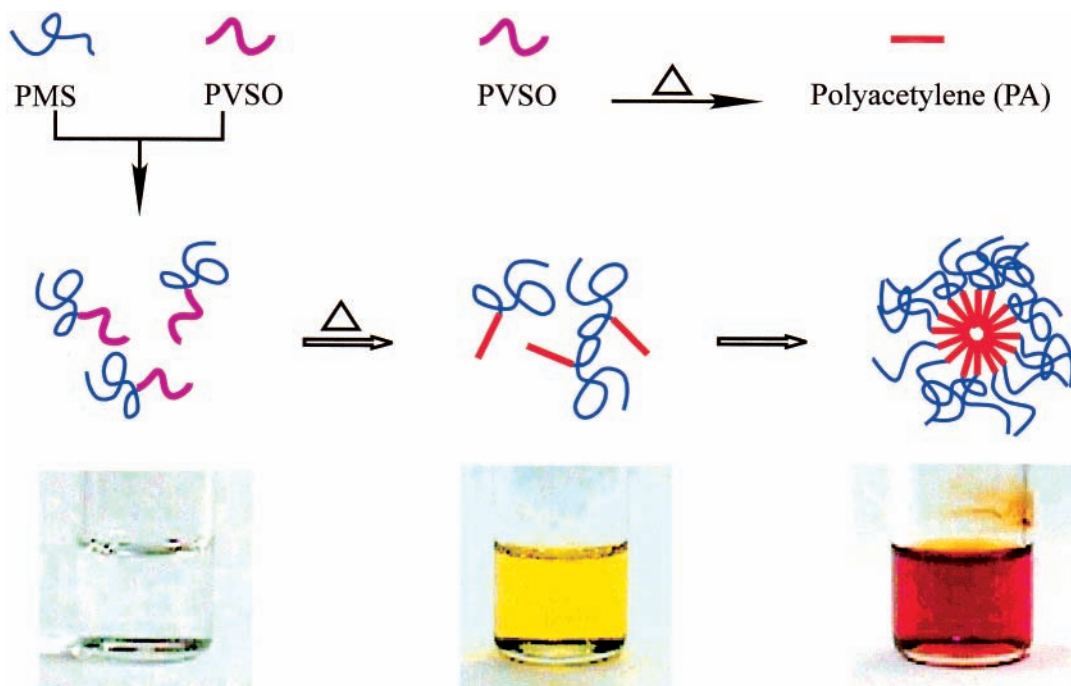


FIGURE 10. Schematic of chemical reaction-induced self-assembly of poly(4-methyl styrene-*block*-phenyl vinylsulfoxide) (PMS-*b*-PVSO) diblock copolymer chains in solution upon heating. The color change reflects the conversion of PVSO to polyacetylene.

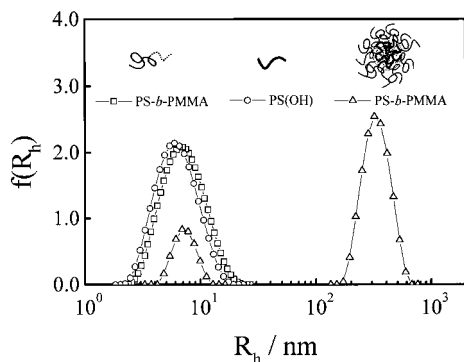


FIGURE 11. Hydrodynamic radius distributions $f(R_h)$ of PS-*b*-PMMA and PS(OH) in toluene before and after mixing the two solutions, where the initial concentrations of PS(OH) and PS-*b*-PMMA are 4.0×10^{-5} and 5.0×10^{-4} g/mL, respectively.

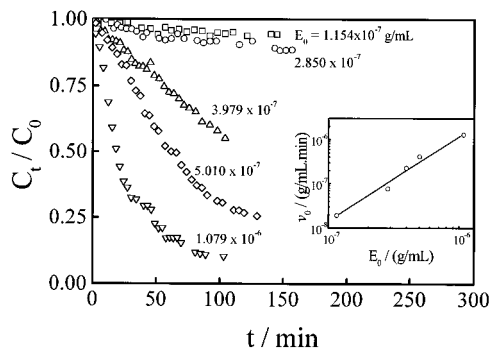


FIGURE 12. Enzyme concentration dependence of the biodegradation kinetics of the PEO-*b*-PCL nanoparticles at 25 °C, where $C_0 = 5.392 \times 10^{-3}$ g/mL. The inset shows the enzyme concentration dependence of the initial biodegradation rate (v_0).

preparation of polymeric nanoparticles in water. For example, it can quickly and uniformly heat the entire reaction mixture to a desired temperature, resulting in a



FIGURE 13. Modified microwave oven for emulsion and micro-emulsion polymerization.

simultaneous initiation. Moreover, the fast variation of electric and magnetic field of microwave irradiation can stir water molecules and increase the dispersion energy. This might explain why the nanoparticles prepared under microwave radiation are smaller and more narrowly distributed.

Figure 13 shows a typical microwave reactor. It is a domestic microwave oven (Whirlpool-VIP20) with a double emission system, operating at 2450 MHz with a maximum output power of 900 W. The oven was slightly modified so that a flask equipped with a glass stirrer, a reflux condenser, a thermometer, and a feeding head could be assembled inside it. Note that a brass tube was connected to the open hole on the top to prevent the leakage of

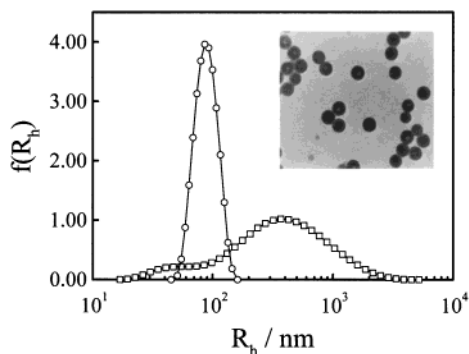


FIGURE 14. Comparison of the hydrodynamic radius distribution $f(R_h)$ of PS nanoparticles prepared with microwave irradiation (O) and a conventional heating (□).

microwaves. Another modification was the addition of a high-frequency electric ON-and-OFF controller (the box on the top) so that the output microwave power could be better regulated. Typically, under the irradiation, the reaction temperature of ~ 70 °C could be reached within 1–2 min. The temperature was maintained by a reduced microwave irradiation of only 80 W. In this way, more than 98% of the styrene monomer could be polymerized within ~ 40 min. Even in the absence of surfactant, the resultant nanoparticles were still narrowly distributed and stable for months.^{46,47}

Figure 14 shows a comparison of hydrodynamic radius distribution $f(R_h)$ of the nanoparticles respectively prepared by microwave irradiation and conventional heating. It is clear that the conventional heating resulted in a broader size distribution and also took a much longer time to reach the same extent of conversion. Our results showed that the average hydrodynamic volume of the nanoparticles is a linear function of the initial monomer concentration if the initiator concentration was kept as a constant, indicating that on average each nanoparticle contained a constant number of individual polymer chains. We also found that the average number of polymer chains inside each nanoparticle is independent of the monomer concentration but increases with the initiator concentration, and the average length of the PS chains formed inside the nanoparticles is independent of the initiator concentration but increases with monomer concentration,^{46,47} indicating that this free radical polymerization has a “living” character. Moreover, it has recently been found that, using microwave irradiation, we could prepare a very concentrated (up to 40 wt %) uniform PS nanoparticles (down to ~ 60 nm) in the presence of only 1.82 wt % of anionic surfactant (sodium dodecyl sulfate).

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