A New Technique for Preparing Monodisperse Polymer Particles. II. Phase Separation Mechanisms

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SYNOPSIS

Nylon 6 polymer particles with a narrow-size distribution are made by phase separation of different concentrations of polymer solutions. At concentrations above 0.15 wt %, the diameter of the precipitated particles increases linearly with the increasing of polymer concentration. The experimental results suggest that coagulation plays an important role in particle growth during the propagation stage. A mechanism is proposed for the formation of monodisperse polymer particles during phase separation. The uniformity of the precipitated nylon 6 particles decreases when the cooling process is slowered. The surface morphologies of the nylon 6 particles are controlled by changing the drying conditions. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric particles with extremely narrow-size distributions and well-characterized surfaces have long been interested in both academic and industrial applications. For example, they have been used in modeling of physical phenomena, calibration of instruments, immunological analysis, medical research, biological separation, and chromatographic and catalytic supports. The first monodisperse polymer particles were prepared at Dow Chemical, apparently by accident, by Backus and Williams in 1947[1] and were reproduced by Bradford and Vanderhoff in 1952.[2] Since then, techniques for preparing monodisperse polymer particles have been extensively investigated, but only few have been successful. In general, the successful techniques are based upon polymerization methods.

Vanderhoff and co-workers[2-5] used a successive seeded emulsion polymerization technique to prepare monodiperse polymer spheres in a wide particle size range, depending on monomer:polymer ratio as well as the number of seeding steps. Ugelstad et al.,[6,7] however, have successfully developed an efficient technique, a two-step activated swelling method, to prepared monodisperse polymer particles. Another emulsion polymerization technique, emulsifier-free polymerization,[8,9] was also used to produce micron size polymer particles with a narrow-size distribution. All of these emulsion polymerization methods require multiple ingredients such as monomer, initiator, and emulsifier. The time required for preparing 10 μm particles may take 1 day to a week, depending upon the method being used. The numerous ingredients and the time involved are two shortcomings of the emulsion methods.

Recently, production of uniform micron size polymer particles was also carried out by dispersion polymerization. Almog and co-workers[10] prepared monodisperse polystyrene and poly(methyl methacrylate) particles in the size range of 1–6 μm by dispersion polymerization in a series of alcohols. Their approach involved the use of a polymeric stabilizer in combination with a quaternary ammonium salt as an electrostatic costabilizer. Ober et al.,[11] however, used nonionic cellulosic derivatives as steric stabilizers in the dispersion polymerization of styrene and showed that uniform particles up to 10

μm can be made. Moreover, El-Aasser et al.[12] have studied the effects of polymerization parameters, such as monomer concentration, type of costabilizer, initiator type and concentration, crosslinking monomer, and diluent on average diameter and uniformity of polystyrene particles.

In addition to the conventional polymerization methods, other alternative techniques such as aerosol techniques and atomization methods have also been developed to produce monodisperse polymer particles. Matijević et al.[13,14] prepared different uniform polymer colloids up to 30 μm by chemical reactions in aerosols. Levendis et al.,[15] however, produced monodisperse spherical polystyrene and poly(methyl methacrylate) particles by atomization of monomers and dissolved polymer precursors in a thermal reactor. More recently, Hou et al.[16] developed a phase separation process to prepare uniform spheres of different polyamide polymers. Hou's phase separation process is a relatively easy and fast technique of making micron size monodisperse polymer particles, which comprises only two steps: (1) dissolve a polymer in its theta solvent, which usually is a mixture of its good solvent and poor solvent, and (2) induce phase separation by lowering the solution temperature past its theta temperature to produce uniform polymer particles. Hou's phase separation method requires very simple ingredients and the whole process can be done in the order of minutes, which is an important alternative technique of producing micron size monodisperse polymer particles. Continuing the previous work,[16] in this article, mechanisms of the formation of uniform polymer spheres during phase separation of a polymer solution will be studied.

EXPERIMENTAL

The polymer used in this study is poly(caprolactam), nylon 6, which was received from Aldrich Chemical Co. The molecular weight and molecular weight distribution of the nylon 6 was characterized by gel permeation chromatography at Jordi Associates, Inc. The nylon 6 was dissolved in hexafluoroisopropanol containing 0.01 M of sodium trifluoroacetate and filtered before injecting to a Jordi Gel Mixed Bed column (25 × 10 cm i.d.) at room temperature. The injection size was 100 μL of a 0.25 wt % solution. The sample was monitored at 8× on a Jordi Waters Model 401 refractive index detector and was calibrated with poly(methyl methacrylate) standards. The average molecular weights of the nylon 6 polymer are shown in Table I.

Table I   The Average Molecular Weight of Nylon 6 Polymer Measured by Gel Permeation Chromatography

M_n	M_w	M_z	Dispersity
16,000	34,000	59,500	2.12

Formic acid (Aldrich Chemical Co.) was used as a good solvent and distilled water, Acetone (Fisher Scientific Co.), and methanol (Aldrich Chemical Co.) were used as nonsolvents for the nylon 6 polymer.

The nylon 6 polymer was dissolved in formic acid by magnetic stirring at room temperature for 2 h to prepare different concentrations of clear solutions. The polymer solutions were titrated at room temperature with distilled water to the point to where the clear solution turned cloudy. The cloudy solutions were heated up to 80°C to form clear solutions again. They remained at 80°C for 2 h to make sure the polymer was completely dissolved before cooling. The polymer solutions were then cooled from 80°C to 0°C by putting them into a temperature-controlled water bath for 30 min to precipitate the nylon polymer out of the solutions. Stirring should be avoided during the phase separation.

The precipitate was diluted with different nonsolvents and dried under a fume hood to form dry powders for further analysis. The sizes and surface morphologies of the precipitated polymer particles were characterized by using an ETEC Autoscan scanning electron microscope. The electron micrograph negatives were enlarged and approximately 300 particles were measured on a Zesis MOP-3 image analyzer. The data was then analyzed by a computer to determine the number average diameter and standard deviation of the particles.

RESULTS AND DISCUSSION

In general, for a given polymer, if the solvent chosen becomes progressively poorer as the temperature is lowered, eventually the solution may reach a temperature below which the solvent and the polymer are no longer miscible in all proportion. The mixtures of the polymer and solvent over a certain composition will separate into two phases. The temperature when the polymer solution begins to phase separate is called theta temperature, θ. From the microscopic viewpoint, when temperatures are above the theta temperature, the interaction between

polymer chains and solvent molecules is so strong so that the polymer chains are extended and slide over one another when they collide. However, when the temperature of the solution is lowered below the theta temperature, the interaction between polymer chains and solvent molecules is decreased. The polymer chains contract or flocculate upon collision to form a second phase. This phenomenon is known as phase separation. It has been reported that, in an extremely dilute solution, polymer chains with the same molecular weight form monodisperse particles when they precipitate individually.[17,18] However, this phenomenon becomes vague when the

concentration of polymer solution is increased or the molecular weight distribution of polymer is broad, because each precipitated particle may contain various numbers of polymer chains or different chain lengths and, therefore, ends up to a broad particle size distribution. This problem has not been investigated until recently when Hou et al.[16] demonstrated that, under certain conditions, uniform nylon polymer particles can be made by phase separation of relatively concentrated polymer solutions, regardless of polymer chain lengths.
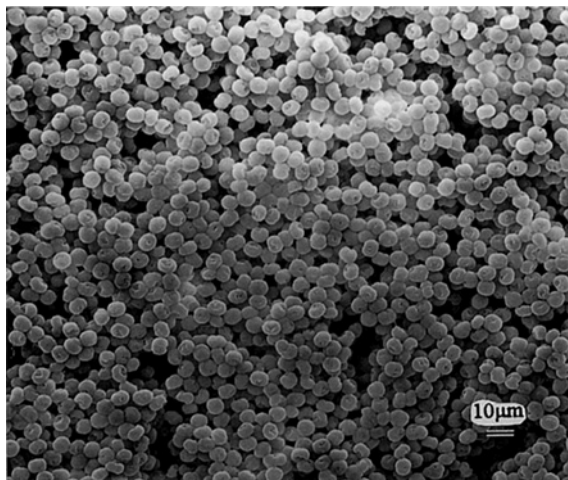
It is known that, in a polymer–solvent system, polymer chains with longer chain lengths are less
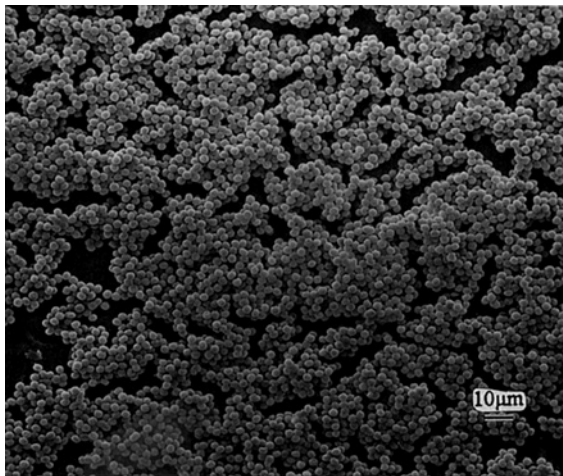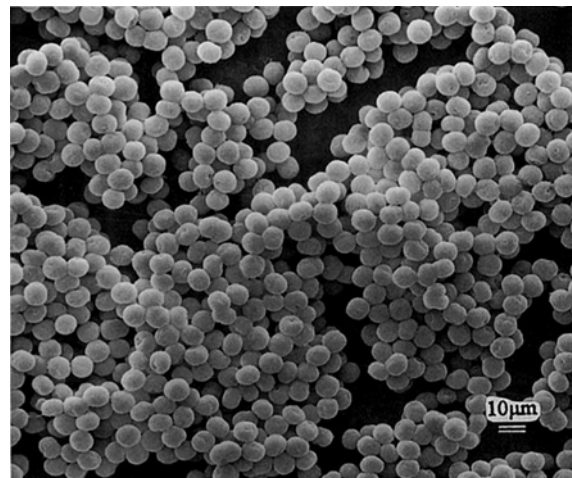

(a)
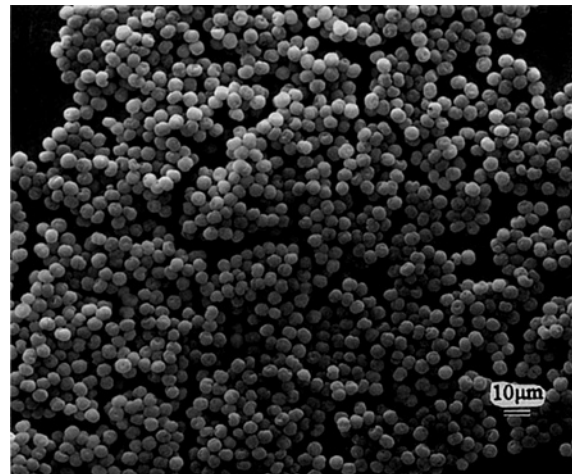
(b)

(c)

(d)

Figure 1 Scanning electron micrographs of nylon 6 particles precipitated from different concentrations of polymer solutions, (a) 0.06 wt %, (b) 0.15 wt %, (c) 0.6 wt %, (d) 1.2 wt %.

soluble than those with shorter ones. Thus, for the nylon 6 polymer having a broad molecular weight distribution (see Table I), at the theta temperature, the polymer chains do not precipitate out of solution simultaneously. Instead, the longer polymer chains come out of solution earlier and form colloidal particles (nuclei) suspended in the solution, where the shorter polymer chains are still dissolved. At this stage, the nucleation stage, nuclei formed homogeneously throughout the solution in the order of seconds.

Following nucleation, the nuclei grow up to a certain size in the second stage, the propagation stage. Three propagation mechanisms are considered: (1) the nuclei grow by capturing the later precipitating shorter polymer chains from the solution during Brownian collisions, (2) the shorter polymer chains form new nuclei and grow individually, and (3) the earlier-formed nuclei coagulate between themselves together with newly precipitated polymer chains to form a final particle.

Although the molecular weight distribution of the nylon polymer is broad, the ratio of the longer polymer chains that form the nuclei at the first stage to the more soluble shorter chains is constant at different concentrations of polymer solutions. That is, there is the same amount of soluble shorter polymer chains surrounding each nuclei regardless of polymer concentration after the nucleation stage. Therefore, if each nucleus grows individually by capturing the surrounding shorter polymer chains without undergoing coagulation between themselves, the final particle size should be independent of the polymer concentrations. Figure 1 shows the SEM photographs of nylon 6 particles precipitated from different concentrations of polymer solutions. The diameter and polydispersity of the particles are summarized in Table II, which shows that the precipitated polymer particles have a narrow size distribution and the diameter increases with the in-
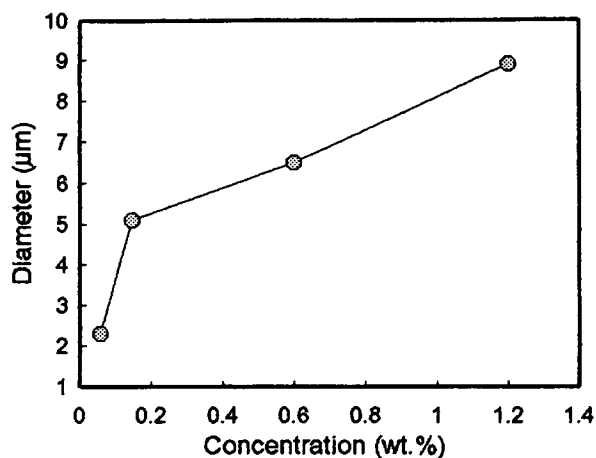

Figure 2 Effect of polymer concentration on the diameter of nylon 6 particles made by the phase separation process.

creasing of polymer concentration. This result suggests that the growth mechanism of the nylon particles at the second stage barely follows the first propagation mechanism proposed.

On the other hand, if some of the soluble shorter polymer chains form new nuclei during the propagation stage and grow individually, the final particles should have a broad distribution. This is due to the fact that each nucleus has a different propagation time. Particle-formed earlier grow for a longer period of time should have a larger size than the nuclei formed at the later stage. Because the SEM photographs show that the precipitated nylon particles have fairly narrow size distribution, the above mechanism obviously does not dominate the propagation process. Further, lowering of the surface energy by growth of existing particles is thermodynamically favored over formation of new nuclei.

In a colloidal dispersion, the dispersed particles are extremely unstable due to strong van der Waals attraction force. Usually, a surfactant is introduced to provide a electrostatic and/or steric repulsion to prevent coagulation. In our case, the earlier-formed nuclei are also very unstable due to the absence of surfactant. Therefore, coagulation may quickly occur between these nuclei at the beginning of the propagation stage. Consequently, as the solution temperature is being lowered, the shorter polymer chains continuously come out of the solution and aggregate with themselves or with the coagulated nuclei until the system reaches a thermodynamic equilibrium at which the Gibbs free energy reaches a minimum. If coagulation is the dominant mechanism at the propagation stage, we expect that the final diameter of the precipitated particles will be proportional to
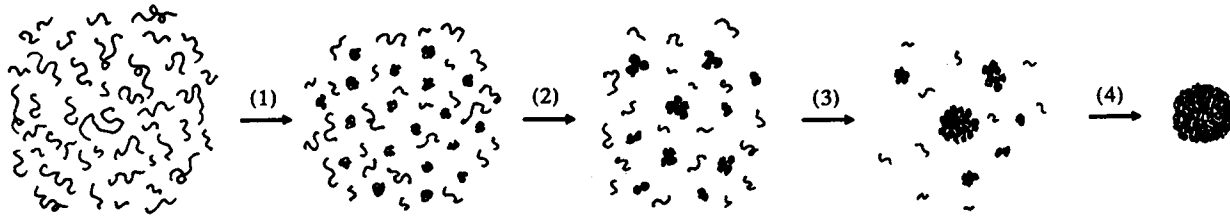
Table II   The Diameter and Polydispersity of the Precipitated Nylon 6 Particles Made by Phase Separation of Different Concentrations of Polymer Solutions

| Polymer Concentration wt %	Particle Diameter μm	Standard Deviation μm	Polydisperse Index
0.06	2.3	0.09	1.04
0.15	5.1	0.55	1.11
0.60	6.5	0.53	1.08
1.20	8.9	0.39	1.04

Figure 3 Schematic representation of the formation of polymer particles during phase separation.

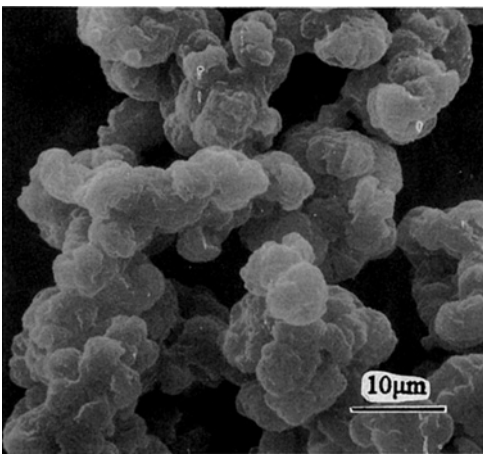the polymer concentrations of the solutions, because coagulation is based on collisions between particles. The higher the polymer concentration, the higher the frequency of collision; thus, the larger the final particle size. Indeed, Figure 2 shows a linear relationship between the particle diameter and polymer
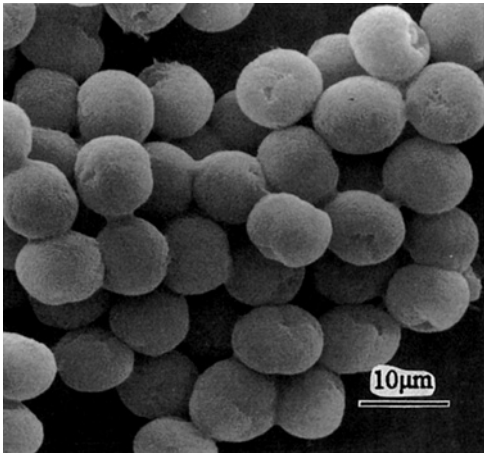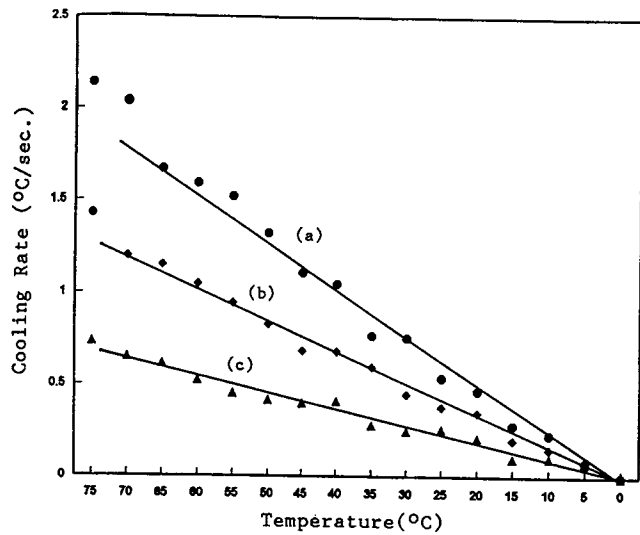

(a)
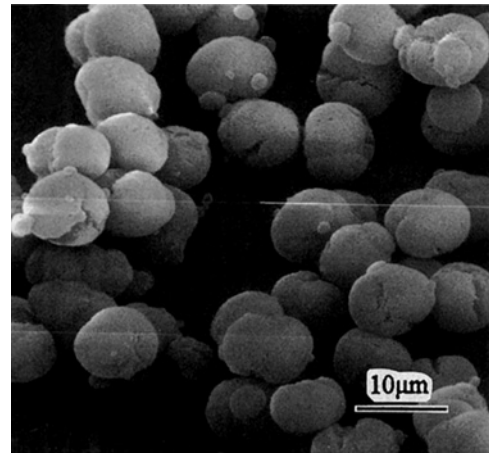
(b)

(c)

(d)

Figure 4 (a,b and c) Scanning electron micrographs of nylon 6 particles precipitated from 1.2 wt % polymer solution at different cooling conditions; (d) shows the cooling rate vs. temperature of the three different cooling conditions.
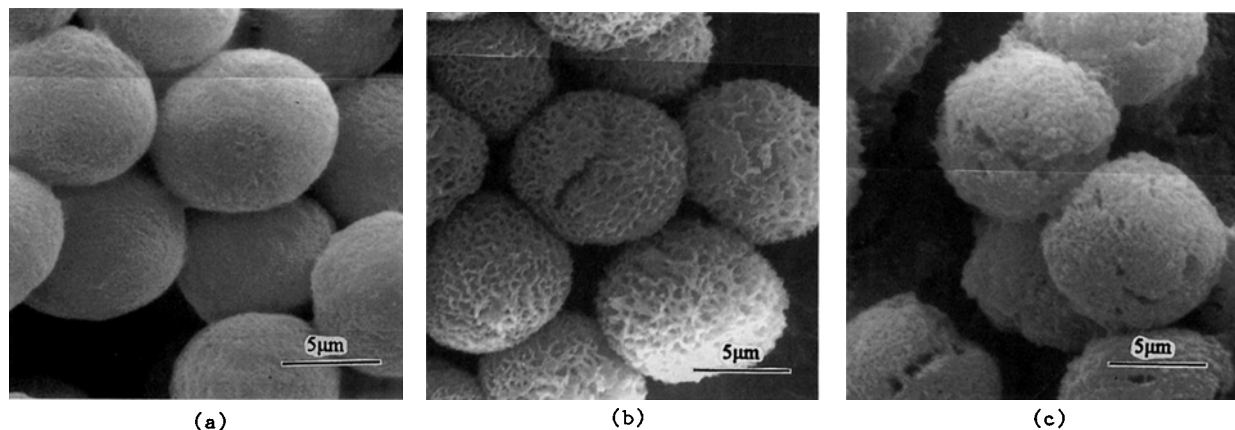
Figure 5   Scanning electron micrographs of nylon 6 particles precipitated from 1.2 wt % polymer solution and dried under different nonsolvent dilutions (a) acetone, (b) methanol, and (c) water.

concentration at the concentrations above 0.15 wt %, which suggests that coagulation mechanism plays an important role during the second stage especially in this concentration range.

According to the weight average molecular weight of the polymer (from Table I) and the density of the solvent mixture, we can calculate the number of polymer chains per μm^3 at different concentrations. Furthermore, if we assume that the gyration radius of the polymer chain in the solution is approximately 80Å based upon its molecular weight[19,20], we can estimate the critical concentration of the polymer solution at which polymer chains begin to overlap. The estimated result shows that the critical concentration is about 1.25 wt %, which indicates that there is no overlap or entanglement between the polymer chains in our working concentrations before phase separation. This further suggests that, when the phase separation begins, the individually coiled polymer chains must undergo coagulation by means of Brownian collision in order to bring the polymer chains together to form a large particle.

A simplistic view of the phase separation mechanism is schematically shown in Figure 3, in which the temperature and polymer chain distribution are completely homogeneous through out the solution. When the solution temperature reaches the theta temperature, the longer polymer chains precipitate out of the solution and form colloidal particles (as shown in the step 1). These particles are thermodynamically unstable and quickly coagulate together due to Brownian collisions (as shown in the step 2). While the solution temperature is further lowered, the shorter polymer chains subsequently precipitate out of solution and aggregate with them-

selves as well as with the earlier formed particles (as shown in the step 3). Eventually, the residual soluble polymer chains completely come out of solution and a final particle is formed (as shown in the step 4). If the homogeneity is kept through out the solution during the whole phase separation process, each final precipitated particle should have the same size, because every polymer chain in the solution has the same opportunity to coagulate with the others. The same type of homogeneous coagulation has also been known in the aggregative nucleation during dispersion polymerization[21] and the formation of monodisperse inorganic particles by precipitation.[22,23]

Figure 4 shows the effect of different cooling conditions on the uniformity of the precipitated particles. Figure 4(d) shows the cooling rate vs. temperature of three different cooling processes. At the fast cooling condition (curve a), the particles with a narrow size distribution are well obtained [see Fig. 4(a)]. However, nonuniform particles are formed [as shown in Fig. 4(b) and (c)] when the cooling processes are slow (curve b and curve c). We think that during the slow cooling, the nucleation as well as the propagation stage is prolonged. Therefore, the first formed nuclei have more time to coagulate before shorter polymer chains precipitate out of the solution, which results in larger but fewer nuclei in solution, and their size distribution may, as well, be broaden at the early propagation stage. During this period, some coagulated nuclei may be too big to remain suspended in the solution and finally settle to the bottom. Consequently, when the shorter polymer chains come out of the solution at the later stage, they are statistically favored to collide and

coagulate with themselves to form new particles that have different sizes from the earlier-formed particles. The decrease in uniformity of the precipitated particles as the cooling process slowered is shown in Figure 4. Figure 5 shows the effect of nonsolvent on the surface morphologies of the precipitated nylon 6 particles after drying. Acenton, a basic solvent, methanol, an acidic solvent, and water are used to dilute the precipitated particles, respectively. We believe that the differences of the surface morphologies of these particles are due to the solubility of the nonsolvents, the interfacial tension between the polymer, and the nonsolvents and the evaporation rate of the nonsolvents. However, the theories and mechanisms of forming the different surface morphologies are out of the scope of our discussion.

It is known that when particles grow over a certain size, they can no longer undergo Brownian motion; instead, the particles start to settle due to the gravity. This may result in a heterogeneous system, especially at the later stage of propagation. In addition, the cooling rate as well as the temperature from the wall of glass vials to the center of the solution may not have been as homogeneous as possible because of inefficiency of heat transfer, which may also cause a heterogeneous system. These factors could affect nucleation as well as propagation during phase separation and, therefore, the final particle sizes. We believe that with better control of the gravity as well as heat transfer of the system, a narrower size distribution may well be obtained.

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