

# A New Technique for Preparing Monodisperse Polymer Particles

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## SYNOPSIS

A procedure is described for preparing fairly uniform spheres of three different nylon polymers by phase separation. The mean diameter and polydisperse index were 5  $\mu\text{m}$  and 1.056 for Griltex nylon, 5.7  $\mu\text{m}$  and 1.046 for nylon 6/6, and 12.9  $\mu\text{m}$  and 1.016 for nylon 6. The phase separation is done by taking a 1 wt % solution in a theta solvent above the theta temperature and cooling it rapidly. The spheres of the three nylons have various degrees of roughness. Formation of highly uniform particles during phase separation is discussed in a preliminary way. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

Polymeric particles with monodisperse size have long been noticed as an important feature for some specific applications, particularly in pharmacy and chromatography. However, monodisperse particles were not successfully prepared until 1955.<sup>1</sup> Since then, techniques for preparing monodisperse particles have been extensively studied but only few have been successful. The successful techniques are usually based upon polymerization and are mostly in aqueous systems. Basically, they can be classified into five major processes: successive seeded emulsion polymerization,<sup>2,3</sup> emulsifier-free polymerization,<sup>4,5</sup> dispersion polymerization,<sup>6,7</sup> two-step swelling technique,<sup>8,9</sup> and chemical reactions in aerosols.<sup>10,11</sup> In general, particle size can be controlled from sub-micron up to a 100 microns depending upon the method being used and the condition of the polymerization.

All those methods require multiple ingredients such as monomer, initiator, inhibitor, and emulsifier. The time required for preparing 10  $\mu\text{m}$  particles may take half a day to several weeks depending upon the method being used. The numerous ingredients and the time involved are two shortcomings of the polymerization methods. In addition, only a few polymers, e.g., polystyrene and poly(methyl methacry-

late), have been prepared as monodisperse particles by those methods. Therefore, a technique that has simple ingredients, has an easy and fast procedure, and can be used with a wide range of polymers is an important alternative to the traditional techniques.

Using a very dilute polymer solution with a monodisperse molecular weight, monodisperse particles can be formed by rapid drying or quenching techniques.<sup>12,13</sup> Unfortunately, there have been no reports concerned with the formation of monodisperse particles from semidilute or concentrated polymer solutions. It is not difficult to realize that in an extremely dilute solution two polymer chains with the same length will form two particles with the same size if they precipitated individually. However, it seems improbable to form monodisperse particles if the polymer has various chain lengths or the concentration is not very dilute, because each particle may contain various numbers of polymer chains or different chain lengths that may end up with a broad size distribution. This is not true if the phase-separation process can be well controlled to assemble the same number of repeat units in each particle. In this paper, experimental results will be offered to illustrate this idea.

## EXPERIMENTAL

### Materials

The polymers used in this study are three different types of polyamide: Griltex nylon (a nylon 6/nylon

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**Table I Conditions of Phase Separation of Different Polymer Solutions**

Figure No.	Polymer	Solvent	Polymer Conc (wt %)	Initial Cooling Rate (°C/s)	Approximate Time to Cloud Point
1	Nylon 6	Formic acid/water	1.0	1.0	10 s
2	Nylon 6,6	Formic acid/water	1.0	1.0	10 s
3	Griltex nylon	Ethanol	1.0	1.0	100 s
4	Griltex nylon	Ethanol	1.0	0.05	50 min

12/nylon 6,12 random copolymer) reported by EMS-American Grilon/Emser Industries to have a molecular weight of 50,000, and nylon 6,6 and nylon 6 from the Aldrich Chemical Co. Ethanol as received from Midwest Grain Products was used as a theta solvent for Griltex nylon. Formic acid (Fisher Scientific Co.) and D.D.I. water mixture was used as a theta solvent for nylon 6,6 and nylon 6. Isopar G (from Exxon) and methanol (from Fisher) were used as nonsolvents for Griltex nylon and nylon 6,6 and nylon 6, respectively.

The polymers we used in this study are all commercial products without further purification or fractionation. Therefore, the molecular weight (as well as the chain length) distributions are probably broad.

### Procedures

The procedure for preparing uniform nylon particles has only two steps: First, dissolve the nylon polymer in a theta solvent in a vial for 2 h at 70°C with magnetic stirring to form a clear polymer solution that has a concentration of 1 wt %. Second, lower the temperature of the solution quickly by putting the vial into an ice bath to precipitate the polymer out of the solution. The initial rate of cooling is 1°C/s. Stirring should be avoided during the phase separation, which is rapid. The precipitate is then washed with a nonsolvent at low temperatures until

the theta solvent is removed and the suspension is stored in the nonsolvent for further studies. Table I summarizes the particle preparation procedures.

## RESULTS AND DISCUSSION

The particle-size distribution is given in Table II for each of the polymers, and we see that they have fairly narrow size distributions. Particularly for the sample of nylon 6, the coefficient of standard deviation is equal to 6.25%, which is considered as monodisperse. Figures 1–3 bear out this uniformity. It should be noted that these phase-separation experiments were carried out in glass vials that were immersed into a cooling bath without stirring. Therefore, the cooling of the solution may not have been as homogeneous as possible. This could affect the nucleation as well as the diffusion during phase separation and thus explain the lack of perfect monodispersity. We believe that with better control of the cooling system, as well as cooling rate, a narrower size distribution may well be obtained.

Conversely, when Griltex nylon is precipitated more slowly, the particles are nonspherical and tend to fuse together as seen in Figure 4. Here, the preparation of the particles differed from the spherical particles of Figure 3 only in the slowing of the initial cooling rate, 0.05°C/s vs. 1.0°C/s for Figure 3.

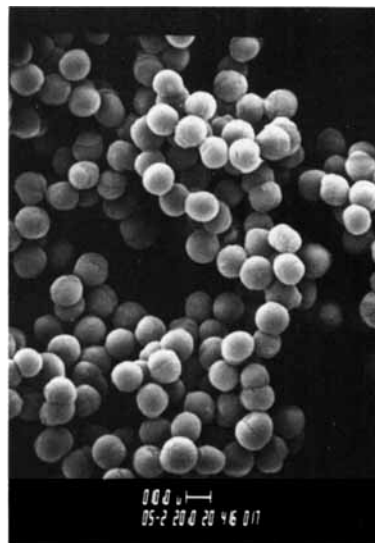
The De Genne's reptation theory states that

**Table II Size Analysis of the Precipitated Polymer Particles from SEM**

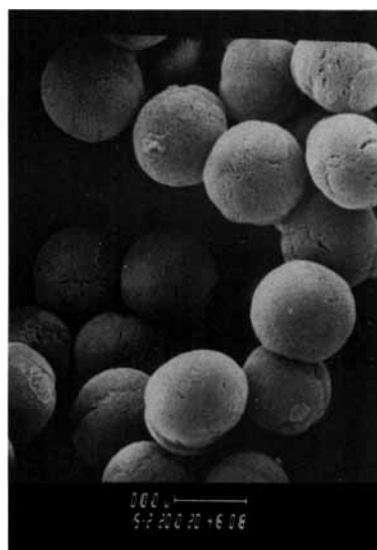
Figure No.	Particle Diameter (nm)	Standard Deviation (nm)	Coefficient of Standard Deviation (%)	Polydisperse Index
1	12,856	743	6.25	1.016
2	5,704	724	12.69	1.046
3	4,957	709	14.28	1.056
4	Could not be determined			



(a)



(b)



(c)

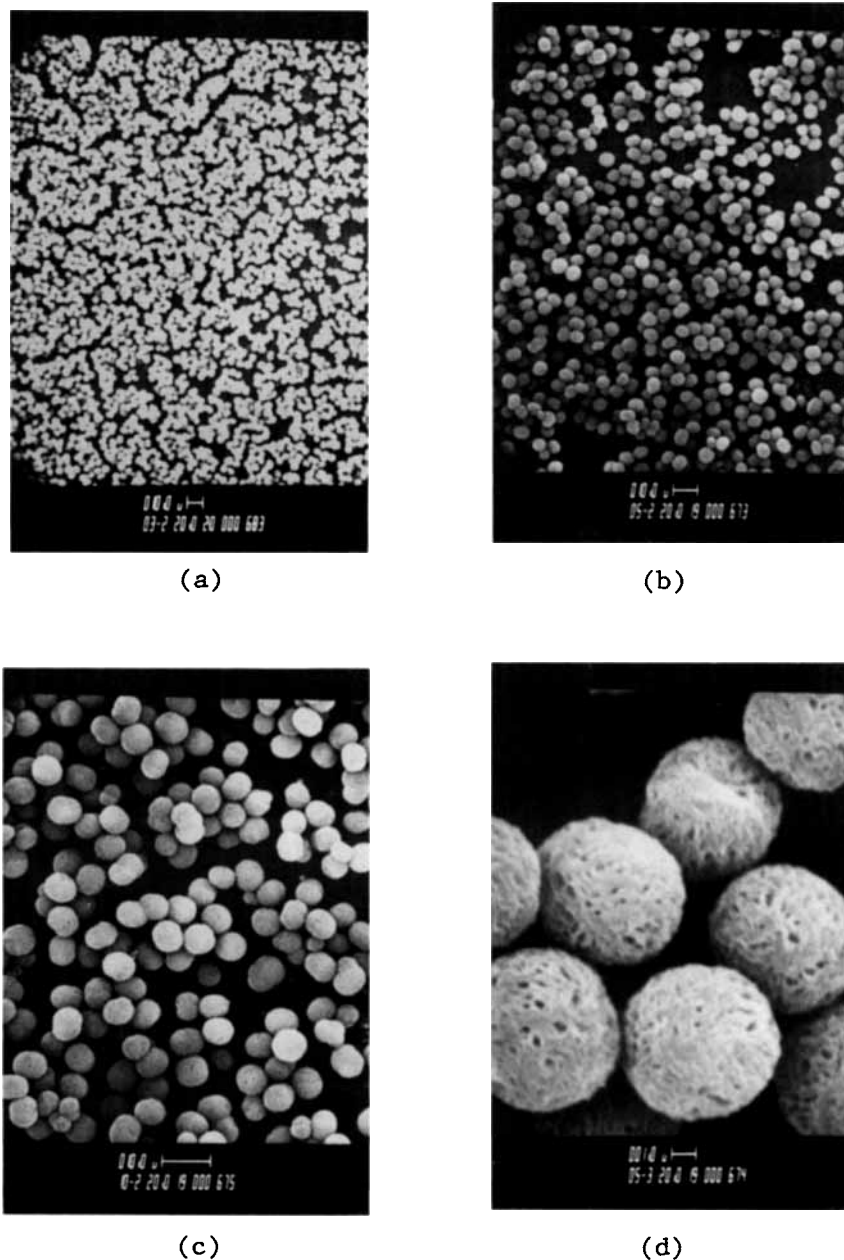


(d)

**Figure 1** SEM photographs, (a) 100 $\times$ , (b) 500 $\times$ , (c) 1500 $\times$ , and (d) 5000 $\times$ , of nylon 6 particles precipitated from formic acid/water mixture at an initial cooling rate, 1 $^{\circ}$ C/s.

polymer chains move in a snakelike fashion in the bulk state.<sup>14</sup> In solution, more space allows the polymer chains to move more easily, therefore it can be imagined that a polymer chain moves in solution like a sea snake swimming in an ocean. At very low concentration, although polymer chains move freely in the solution, the collision frequency is low. But when the polymer concentration is increased, the polymer chains collide with each other more often.

When temperatures are higher than the theta temperature ( $T_{\theta}$ ), the interaction between polymer chains and solvent molecules is strong enough to cause the polymer chains to slide over one another when they collide. However, when the temperature of the solution is lowered and the interaction between polymer chains and solvent molecules is decreased, the polymer chains flocculate upon collision and form a second phase. This phenomena is known



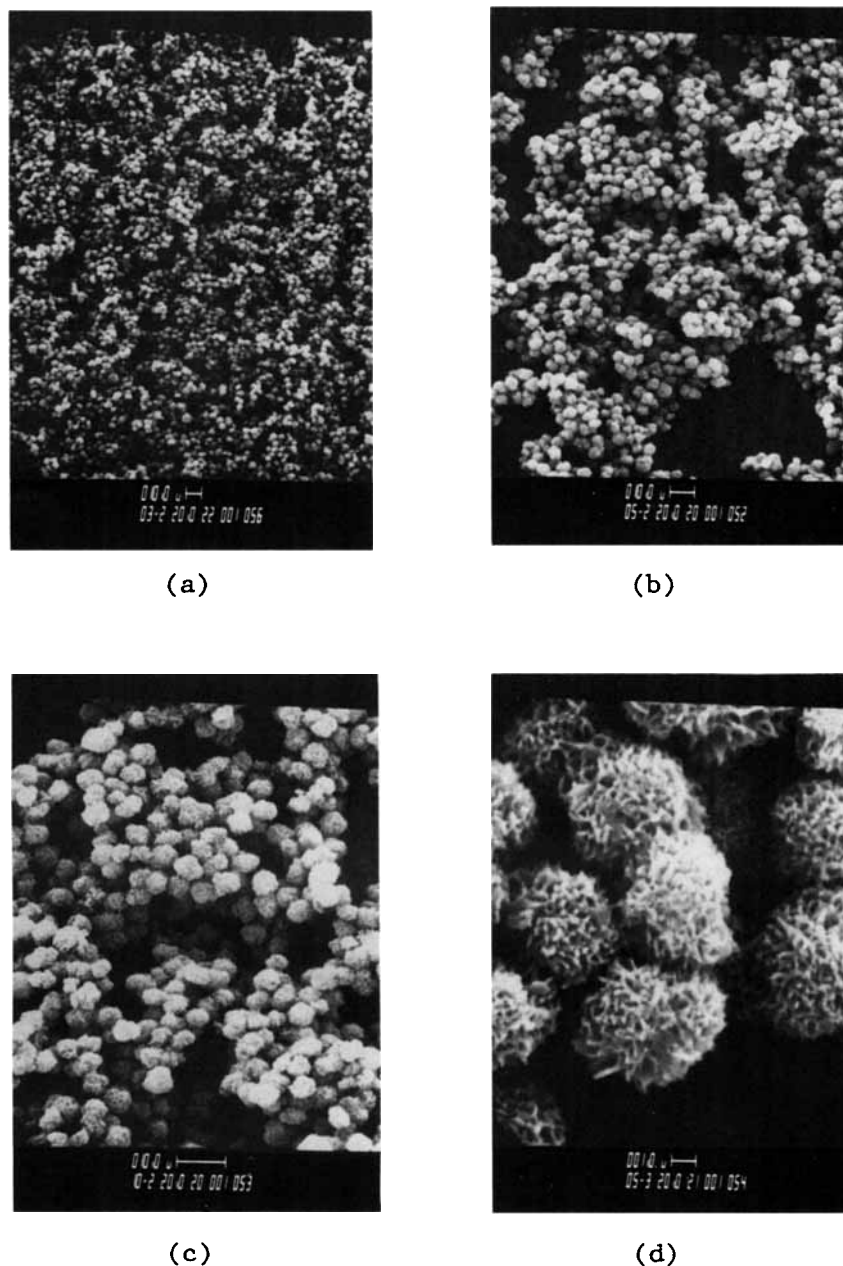
**Figure 2** SEM photographs, (a) 300 $\times$ , (b) 500 $\times$ , (c) 1000 $\times$ , and (d) 5000 $\times$ , of nylon 6/6 particles precipitated from formic acid/water mixture at an initial cooling rate, 1 $^{\circ}$ C/s.

as phase separation and it has been successfully described by thermodynamic theories.<sup>15</sup> One requirement, however, is that time must be long enough for thermodynamic equilibrium.

In our situation where we cool the solution rapidly, we probably do not have a true thermodynamic equilibrium. For instance, the polymer chains are not of equal length and the smaller, more soluble, chains probably precipitate along with the bigger

ones rather than remaining in the bulk solution longer. In other words, kinetics dominate the process. Whereas we have not studied the mechanism of the formation of spherical particles, per se, we offer the following comments upon it based on this work and upon work with pigmented nylon spheres prepared similarly.<sup>16</sup>

We believe that we have homogeneous solutions at 70 $^{\circ}$ C. Even though there is a distribution of chain

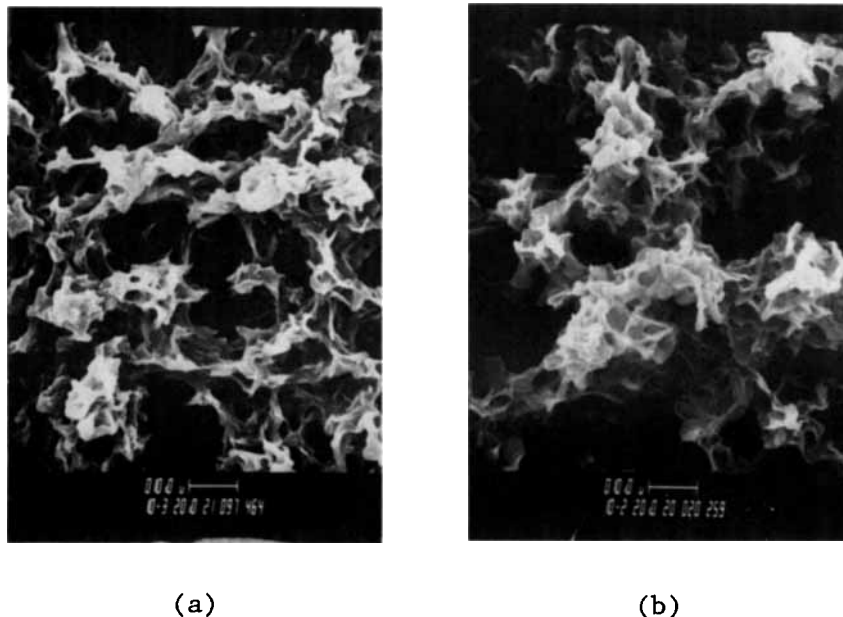


**Figure 3** SEM photographs, (a) 300 $\times$ , (b) 500 $\times$ , (c) 1000 $\times$ , and (d) 5000 $\times$ , of Griltex nylon particles precipitated from ethanol solution at an initial cooling rate, 1 $^{\circ}$ C/s.

lengths, any given volume segment would contain the same distribution as any other segment of equal volume. (We estimate roughly about  $6 \times 10^8$  chains per particle for the Griltex particles in Fig. 3.) When the solution is cooled quickly, a large number of nuclei form; most likely each nucleus is a number of associated molecules. This is indicated by our work with pigmented particles. When pigments are present, they serve as nuclei, and we find that the more pigment particles, the smaller the uniform diameter

of the final polymer/pigment particles. The nucleation period is obviously short and new nuclei do not continue to form as evidenced by the uniform final size. Further, lowering of the surface energy by growth of existing particles is thermodynamically favored over formation of new nuclei.

An alternate mechanism would have a continuation of nucleation and growth with a coalescence of variously sized particles into final particles that are uniform in size. This model is not satisfying in-



**Figure 4** SEM photographs, (a) and (b) 1000 $\times$ , of Griltex nylon precipitate formed after phase separation of ethanol solution at a low initial cooling rate, 0.05 $^{\circ}$ C/s.

tuitively, especially in light of the experience with uniformly sized pigmented nylon particles.

Our simplistic view has a large number of nuclei growing so rapidly by diffusion of chains that they gather up all the chains, regardless of length, in some volume surrounding the nucleus. There is not time for one growing particle to be favored over another and a high degree uniformity in the particle size results.

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