Creation of Functional Materials by Use of a Slow Crystallization Process in the Nonequilibrium State. I. Porous Polyamide Microparticles

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ABSTRACT: Recently a number of investigations have focused on the self-organization process from the nonequilibrium state as a new technique that may be used to develop many functional materials. In many cases, amorphous polymers were used and semicrystalline polymers were seldom used in spite of their importance. In this study, we basically investigated the crystal structure, crystalline process, and inner structures of polyamide by using slow phase separation and crystallization process from the nonequilibrium state of the polymer solution. We were able to observe the crystalline lamella growing twisted from the center of the particle. Between these lamella layers, narrow pores were created. From this investigation, we developed a new method to create functional materials of polyamide, the semicrystalline polymer. Porous spherical particles may be properly applied to functional materials such as adsorption materials, catalyst support materials, and so on. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2428–2432, 2003

Key words: porous particle; polyamides; semi-crystalline polymer; phase separation; self-organization

INTRODUCTION

Polymeric materials are divided into two groups, either bulk plastic material or functional soft material. The chemical structures of many of the functional soft materials are designed to have specific functions such as light, electric, adhesive, diffusion, and surface properties and thus far results of many investigations have been reported.

Recently a number of investigations have focused on the self-organization process from the nonequilibrium state as a new technique that may be used to develop many functional materials. For example, polymer blends,[1,2] block copolymers,[3–8] polymer solutions,[9–11] and condensation polymerization[12,13] have all been applied in the creation of unique structures and used as functional materials. In many cases, for easier control, amorphous polymers were used in the above studies. Also most of the nonequilibrium states are extremely unstable and are obtained at midstage of the process toward achieving a stable structure.

On the other hand, many of the semicrystalline polymers, such as polyethylene, polypropylene, and polyamide, are classified as bulk plastic materials and dealt with as having few valuable properties. There has been scant research that uses semicrystalline polymers in creation of functional materials, and thus there is almost no example that uses the process of crystallization: their crystal structure, crystallization process, and inner structures of such polymers have yet to be the focus of beneficial analysis. It seems possible to create new materials by applying semicrystalline bulk polymers to the process using nonequilibrium, and also using the crystallization process positively. During the research process, we would surely be able to obtain new information about the basic physical properties of semicrystalline bulk polymers.

In this study, we created porous microparticles from polyamide, which is a typical example of a semicrystalline bulk polymer, by using phase separation and a slow crystallization process from the nonequilibrium state.

EXPERIMENTAL

The semicrystalline polymer we mainly used was polyamide [nylon 6 (1013B, Ube Industries, Japan)]. The nylon 6 was dissolved with *m*-cresol and a homogeneous polymer solution was obtained. Polymer concentrations were 1, 5, and 10 wt %, respectively. Water of the same weight was then added to the solution with stirring. In addition a homogeneous polymer solution was obtained. After a certain concentration of methanol was added to this polymer solution, phase separation and turbidity were observed. Figure 1 shows the polymer concentration dependency of the phase separation critical point of methanol. These solutions are stable as homogeneous for several days.
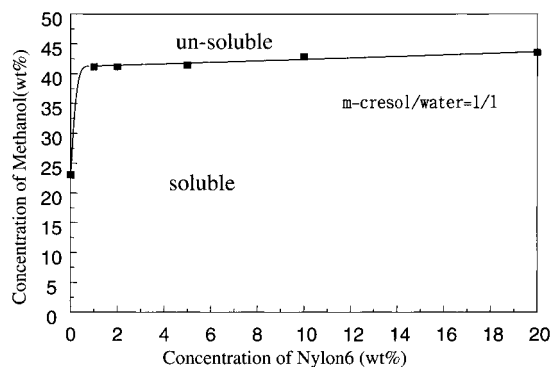
Figure 1. Nylon 6 concentration dependency of phase diagram of nylon 6 *m*-cresol·water solution and methanol. Top region is the nonsoluble region and bottom region is the soluble region.

However, when the concentration of methanol even slightly exceeds the critical concentration, the solution was relatively stable for only several minutes. However, the solution was in the nonequilibrium state because the phase separation and the turbidity began within only a few minutes. For example, when the ratio of 5 wt % *m*-cresol polymer solution, water, and methanol was 1 : 1 : 5, the solution began to be turbid within 1 min and it took about 10 min for the end of phase separation. Porous microparticles were generated in the solution. Figure 2 shows SEM images of the particles. Figure 3 shows the amount of the methanol dependency relative to the shape of the particles. From this figure, when the amount of the methanol was insufficient, the shape of the particle is not spherical but is rather like twin fans connected at each edge in a dumbbell-like shape.[14] When methanol was added
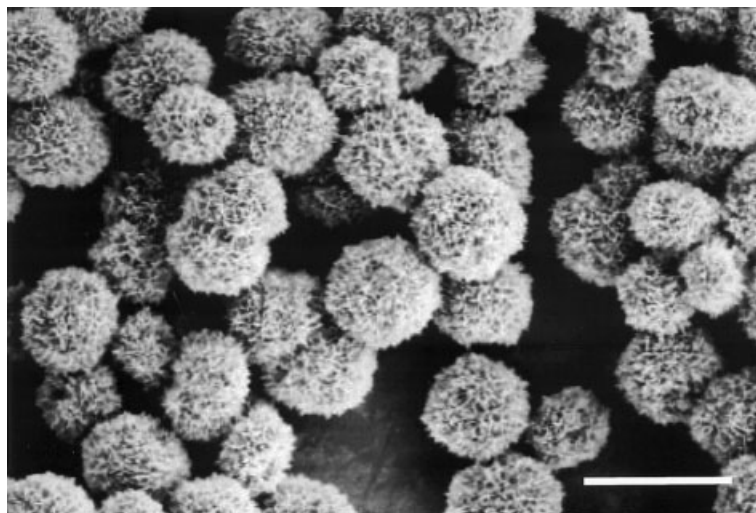

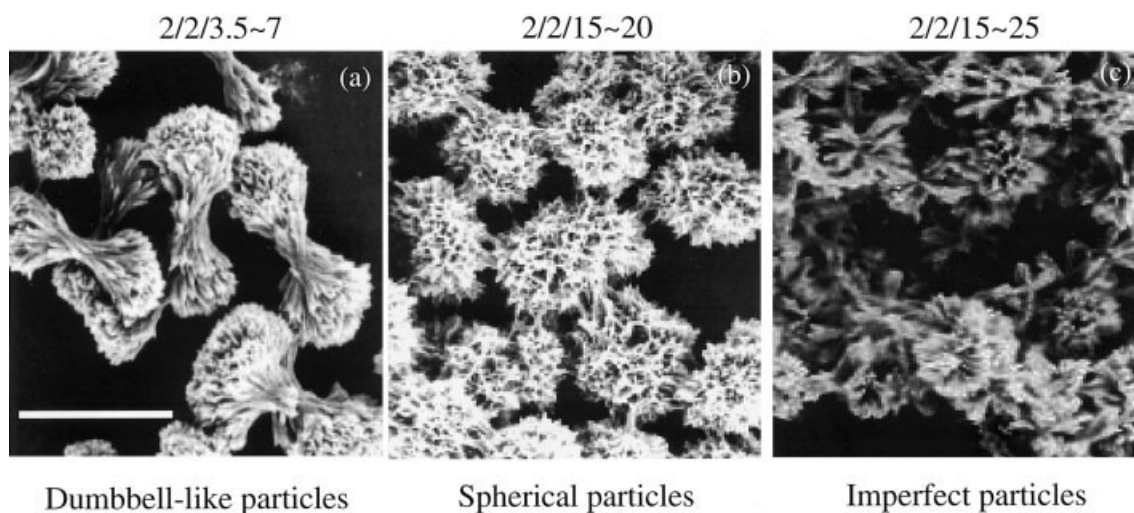**Figure 2.** SEM image of nylon 6 porous particles. White bar = 10 μm.

Figure 3. SEM images of nylon particle structures. The *m*-cresol, water, and methanol ratio of each sample is (a) 2/2/3.5–7, (b) 2/2/15–20, (c) 2/2/15–25. White bar = 10 μm.
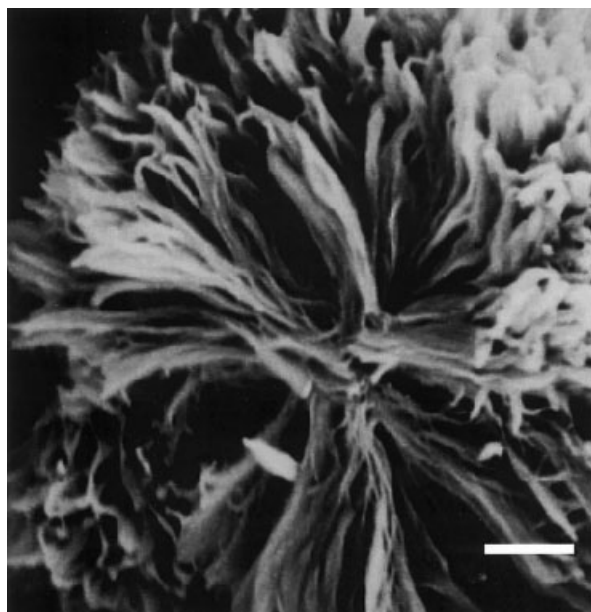
Figure 4. SEM image of cross section of porous nylon particle. White bar = 1 μm.

in excess, the particles began to grow connected to each other, and aggregate particles were obtained.

STRUCTURAL AND CRYSTALLINE CHARACTERIZATION

Number-average and volume-average diameters (D_n and D_v) and the polydispersity (PD) of the porous spherical particle were obtained by using the following equations. X_i (diameter of each particle) was read from over 100 particles of the SEM image.

$$D_n = \sum X_i / n \qquad (1)$$

$$D_v = \sum X_i^4 / \sum X_i^3 \qquad (2)$$

$$\mathrm{PD} = D_v / D_n \qquad (3)$$

Typical values of these parameters are $D_n = 7.8$ μm, $D_v = 8.4$ μm, and PD = 1.08. It is thus almost a monodisperse system.

The average pore size and surface area, measured by the adhesion of N_2 gas, were 0.04 μm and 10,800 m^2/kg each.

From these values, the spherical porous particles are thought to be single spherical crystals of nylon 6. Cross sections of these spherical porous particles are shown in Figure 4. It is clear that the particle is composed by lamellas, extending in a twisted manner from the center of the particle. The microporosity was created by the space between lamellas. Individual spherical porous particles appeared to be single spherulites. In this case, spherical particles grew at the same rate and almost simultaneously, so the particles have almost same size and shape.

Figure 5 shows DSC curves of these spherical porous particles and polyamide film. The peak at about 220°C is the melting point of the ordinal nylon 6 crystal.[15] This spherical porous particle has another lower temperature melting peak. The melting temperature depends on the thickness of the lamellar crystal,[16,17] so the particle has a thin lamellar crystal. The degree of crystallization of this particle is about 60%, determined by fusion heat capacity. By using this measure, the pore size can be controlled by annealing the particle. Figure 6 shows SEM images of the particles annealed at different conditions.

RESULTS AND DISCUSSION

By using the self-organization slow crystallization process from the nonequilibrium state of the semicrystalline polymer, porous spherical particles can be obtained. The phase separation and crystallization process from this solution proceeded slowly enough that we could observe the growth of the polymer spherical crystal. In the case of the nonequilibrium solution, the ratio of 5 wt % m-cresol polymer solution, water, and methanol was 1 : 1 : 5, and the solution was filtered at suitable intervals. Figure 7 shows SEM images of the shape of the particles at each sampling time. From this figure, we are able to recognize how the particles grow. At first the shape of the particle was that of a dumbbell
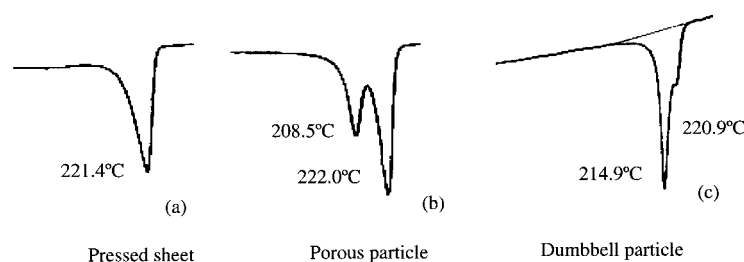

Figure 5. DSC thermal properties of nylon pressed sheet and porous particles: (a) pressed sheet, (b) porous particle, and (c) dumbbell particle. Heating ratio is 5°C/min for first run.

Before heat treatment   After heat treatment   After heat treatment
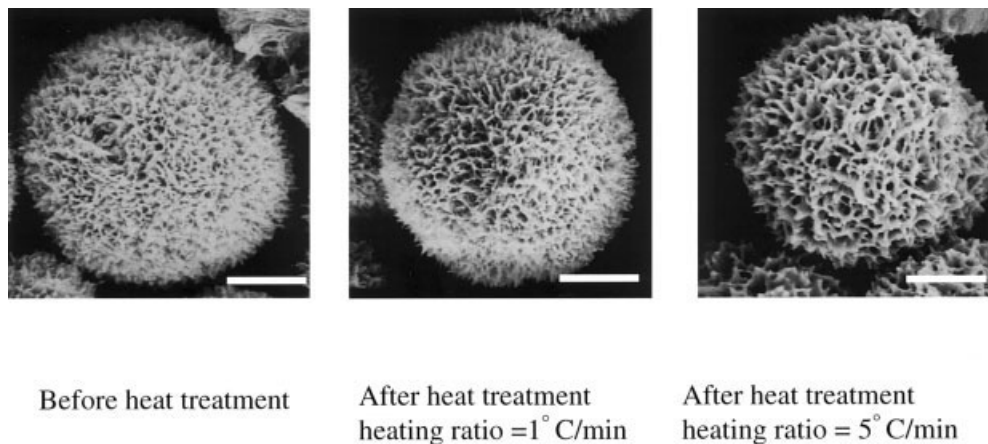heating ratio =1° C/min   heating ratio = 5° C/min

Figure 6. SEM images of porous nylon 6 particles before and after heat treatment: (a) SEM image before heat treatment; (b) and (c) SEM images after heat treatment. Heating ratio of (b): 1°C/min; heating ratio of (c): 5°C/min.
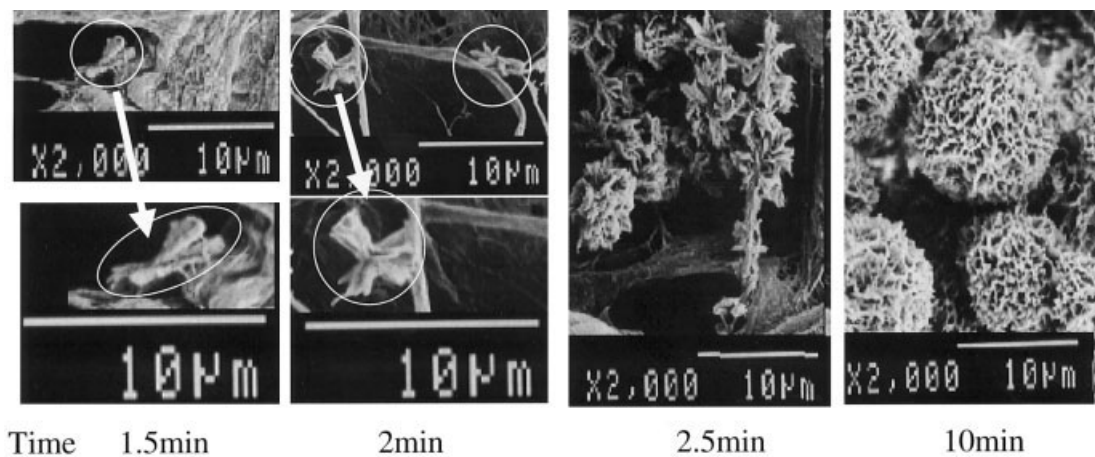

Time   1.5min   2min   2.5min   10min

Figure 7. Forming process of porous nylon particles.
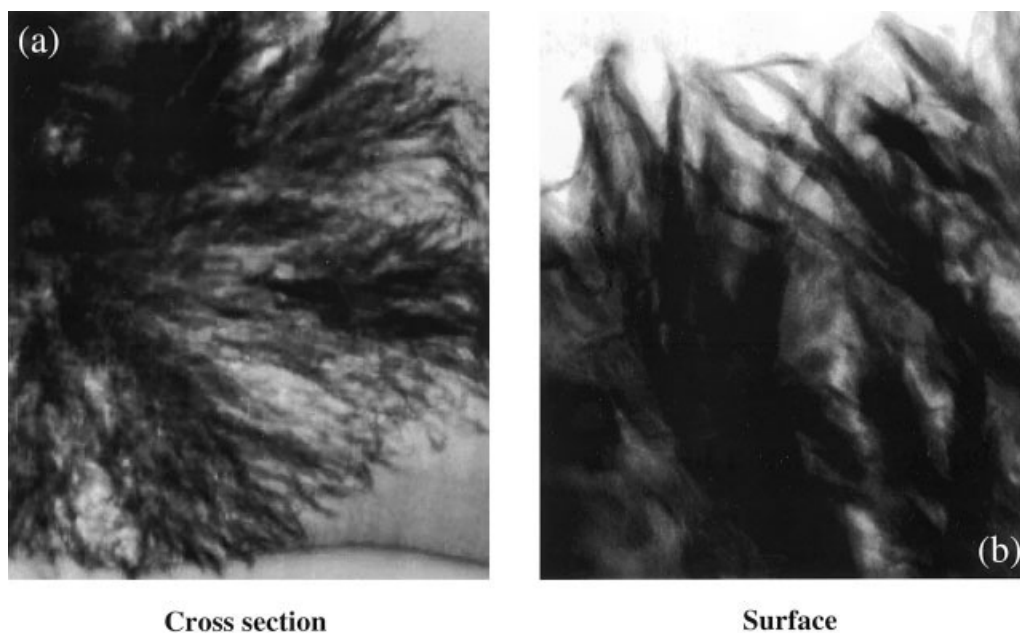

Cross section   Surface

Figure 8. TEM images of (a) cross section and (b) surface of porous nylon particles.

structure. After 10 min, the growth of porous spherical particles was completed. From this figure, we also understand that the porous spherical particles constituted the spherical crystal itself and the process was the slow crystallization process from the nonequilibrium state of the polymer solution.

Figure 8 shows a TEM image of the cross section of the porous spherical particle. We recognize that the lamella grows in a twisted manner. The porosity is attributed to the space between layers of the lamella.

CONCLUSIONS

In this study, we developed a new method to create functional materials of semicrystalline polymers. This method uses slow phase separation and a crystallization process from the nonequilibrium state of the polymer solution. In this case, the crystalline lamella grows by twisting from the center of the particle. Between these lamella layers, narrow pores are created. These porous spherical particles may be properly applied to functional materials such as adsorption materials, catalyst support materials, and so on.

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