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Supercritical Antisolvent Process for a Series of Substituted Para-Linked Aromatic Polyamides

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Introduction

Structural modifications to the backbone of poly(*p*-phenylene terephthalamide) (PPTA), such as bulky lateral substituents and noncoplanar biphenylene moieties, facilitate this polymer's processing, either by increasing its solubility or by lowering the melting temperature.[1] A recent study by Yeo et al.[2] suggests that supercritical antisolvents (SAS) can be a promising route for the processing of para-linked aromatic polyamides. The formation of either polycrystalline spherulites or microfibrils under different processing conditions suggests that the rate of contact between antisolvent and polymer solutions and the presence of an external shearing force during the nucleation step can have a significant influence on the structure and morphology of precipitated polyamide. It was found that in the batch mode of operation the injection rate of antisolvent affects the crystallinity of the spherulites and that continuous operation leads to the formation of a fibrous morphology over the temperature, pressure, and concentration ranges investigated.

In that study, however, only one type of substituted polyamide (combination of noncoplanar 2,2′-dimethylbiphenylene with a phenyl-substituted terephthalic acid moiety; polyamide **3** in Figure 1, same as polyamide **8** in ref 1) was employed. The purpose of this study is to process different types of less-substituted polyamides with a supercritical antisolvent and to investigate the influence of a variety of substitution concepts (e.g., lateral bulky substituents or noncoplanar biphenylene units) on the resulting morphology under conditions similar to those used in the previous study.[2] We selected two different substituted polyamides for this work: one is methyl-substituted PPTA (polyamide **1** in Figure 1) and the other is a combination of the noncoplanar 2,2′-dimethylbiphenylene unit with terephthalic acid (polyamide **2** in Figure 1).

Experimental Section

Polyamides **1** and **2** were synthesized according to previously published procedures.[1] The inherent viscosity of 0.5% (w/v) polyamide **1** in sulfuric acid is 4.86 dL/g, and that of 0.5% (w/v) polyamide **2** in *N,N*-dimethylacetamide/LiCl (4% (w/v)) solution is 6.0 dL/g. We use the symbol % (w/v) to denote grams of solute per 100 cm^3 of solvent.

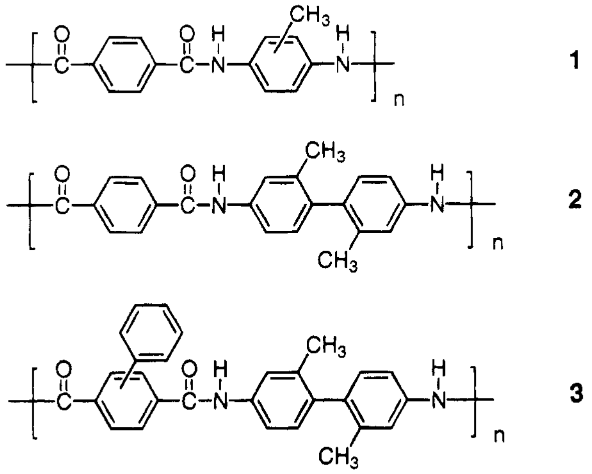

Figure 1. Chemical structures of the polyamide samples.

N,N-Dimethylacetamide (DMAc; Sigma, lot no. 30H2621) with the addition of lithium chloride (LiCl; J. T. Baker, lot no. 29333) is used as a solvent for the two polymers. The salt is needed to dissolve polyamides **1** and **2**: neither solubility nor swelling of the polymers is observed in pure DMAc. In contrast, no salt was needed for the solubilization of polyamide **3** in dimethyl sulfoxide (DMSO) or dimethylformamide (DMF).[2] Liquid carbon dioxide of bone-dry grade (99.8%) is purchased from MG Industries. Polyamide **1** and polyamide **2** are dissolved in 2.3% (w/v) of LiCl in DMAc solution and in 4.0% (w/v) of LiCl in DMAc solution, respectively, in the concentration of 0.1% (w/v).

A detailed description of the SAS experimental apparatus and operating procedure are given elsewhere.[2,3] In the batch mode of operation, a high-pressure window cell (Jerguson gauge, Model 1940) is loaded with 20 mL of the polymer solutions. It should be noted that the solutions contain LiCl in addition to polymers. Carbon dioxide is injected from the bottom of the cell to increase the cell pressure from 1 bar to the desired pressure. The dissolution of the carbon dioxide in the liquid phase causes the expansion of the solution and polymer nucleation.[2,3] Injections are made at two different rates: 20.6 and 0.8 bar/min. After precipitation of a sufficient quantity of polymer, the remaining solution is drained from the cell. Additional carbon dioxide is injected from the top of the cell to compensate for pressure drop due to the draining. In the continuous mode of operation, carbon dioxide flows downward at 103.4 bar. The polymer solution is pumped cocurrently into the cell through a nozzle, causing rapid contact of the two phases and very rapid precipitation of the polymer. All the experiments are conducted at 35°C. The morphology of the precipitated polymer is examined by scanning electron microscopy (SEM; Model JEOL JSM 840A). The specimens are sputter-coated with gold−palladium.

Results and Discussion

In the present study, contrary to previous SAS investigations,[2−4] the mother liquid solvent (DMAc) contains more than one solute (polyamide and LiCl), which leads to coprecipitation. This occurs in both the batch and continuous modes of operation. In the former case, as the cell pressure increases, polyamide precipitation occurs first, at lower pressure, followed at higher pressure by LiCl precipitation. At 35 °C, the precipitation pressures of polyamide **1** and LiCl are 47 and 62 bar, respectively, and those of polyamide **2** and LiCl are 47 and 54 bar, respectively. Therefore, the batch experiment can be performed so as to obtain a purely polymeric precipitate by simply pressurizing the system to 50 bar, followed by drainage of the remaining solution. In continuous operation, the fast exposure of the polymer solution to the supercritical antisolvent

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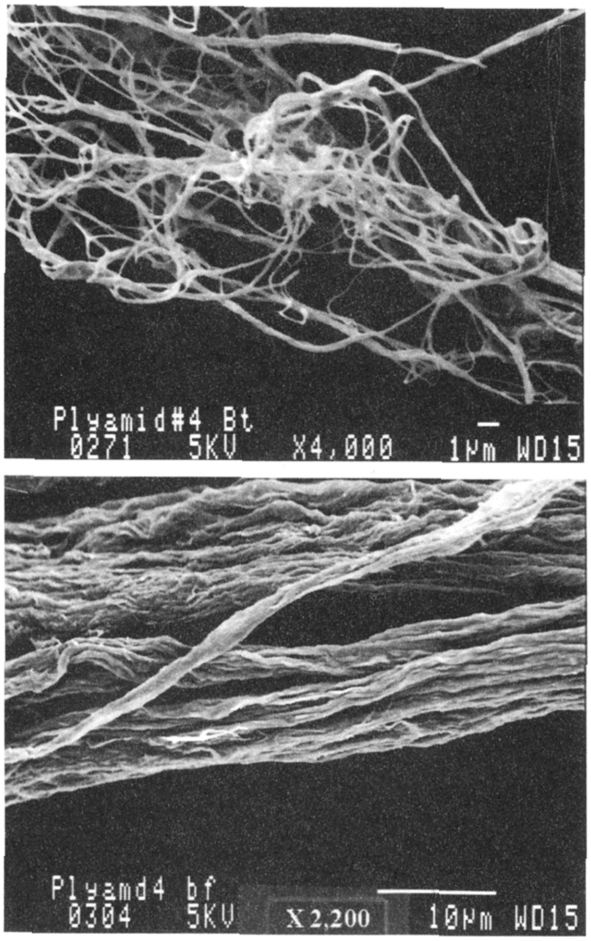

Figure 2. Polyamide **1** fibers produced in the batch mode of operation (0.1% (w/v) polyamide **1** in DMAc/LiCl (2.3% (w/v)) solution, 35 °C, pressurized from 1 to 50 bar): (a, top) CO_2 injection rate, 0.8 bar/min; (b, bottom) CO_2 injection rate, 20.6 bar/min.

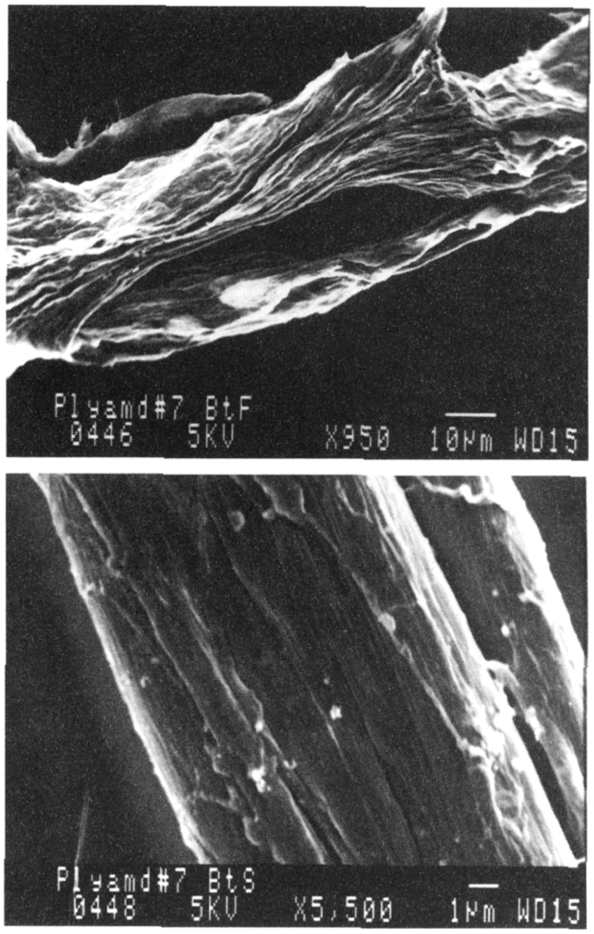

Figure 3. Polyamide **2** fibers produced in the batch mode of operation (0.1% (w/v) polyamide **2** in DMAc/LiCl (4.0% (w/v)) solution, 35 °C, pressurized from 1 to 50 bar): (a, top) CO_2 injection rate, 0.8 bar/min; (b, bottom) CO_2 injection rate, 20.6 bar/min.

gives rise to simultaneous precipitation of LiCl and polyamide. This coprecipitation leads to an undesirable mixture of the two solid compounds inside the cell. The precipitate is a highly viscous, pastelike phase containing both solids, as well as residual solvent. In this study, therefore, only experimental results from the batch studies are presented.

Figures 2 and 3 show SEM photomicrographs of polyamides **1** and **2** processed at two CO_2 injection rates: 0.8 and 20.6 bar/min. Visual observation through the cell window shows that at the injection rate of 0.8 bar/min the cell contents remain quiescent and undisturbed by CO_2 bubbles. At the higher injection rate, however, turbulence is induced by the CO_2 throughout the polymer nucleation and growth steps. It is found that both injection rates lead to a fibrous morphology. This result differs from that of our previous study,[2] in which polyamide **3** formed a spherulitic network of lamellar crystals under similar conditions. These results can be explained by the difference in molecular structures of the three polymers. Molecular structure is one of the most important factors affecting the formation of liquid crystalline phases in polymer solutions. Polyamide **1** exhibits a lyotropic phase behavior in sulfuric acid solution [the critical concentration for the onset of lyotropic behavior in 100% sulfuric acid is between 8 and 9% (w)] and polyamide **2** exhibits lyotropic phase behavior in DMAc/LiCl (4% w/v) solution, while there is no indication of lyotropism for polyamide **3** in any of the solutions investigated, even at high concentrations.[1] Two reasons may be responsible for the absence of lyotropic behavior of polyamide **3**. (1) Any bulky lateral substituent lowers the axial ratio of the polymer backbone, which increases the critical concentration for the formation of a lyotropic solution. (2) The chain stiffness may be substantially reduced by orthosubstituents in the terephthalic acid moiety.[1] Therefore, the higher degree of extended rigid chain character (high axial ratio of polymer chain and high chain stiffness) in polyamides **1** and **2** leads to fibers, while the lower degree of extended rigid chain character in polyamide **3** leads to spherulites (particles) under similar conditions.

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References and Notes

(1) Hatke, W.; Schmidt, H.-W.; Heitz, W. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1387.

(2) Yeo, S.; Debenedetti, P. G.; Radosz, M.; Schmidt, H.-W. *Macromolecules* **1993**, *26*, 6207.

(3) Yeo, S.; Lim, G.; Debenedetti, P. G.; Bernstein, H. *Biotechnol. Bioeng.* **1993**, *41*, 341.

(4) Dixon, D. J.; Johnston, K. P.; Bodmeier, R. A. *AIChE J.* **1993**, *39*, 127.

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