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Radiolytic Synthesis of Polyaniline Nanofibers: A New Templateless Pathway

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Polyaniline is an electrically conductive polymer which is relatively easy to process and has simple, reversible acid/base doping/de-doping chemistry. It is a promising candidate for the development of electronic devices, especially sensors.[1−10] Heightened interest in one-dimensional electrical conductors and the need to produce nanoscale electrical connections has caused recent research to focus on polyaniline nanofibers.[11−17] The high surface areas of these fibers make them more responsive than bulk polyaniline to gases,[18−20] an extremely desirable property for sensing applications.

Polyaniline fibers are frequently fabricated from “hard” templates, such as the channels of microporous membranes[13] and zeolites,[14] by employing “soft” micellar templates, often surfactants, or by seeding.[16,17,20] Although these templates, whether hard or soft, allow the desired high-aspect ratios to be achieved, they complicate the synthesis and the extraction of the final product. Template removal is tedious when hard templates are employed. Soft templates limit the range of chemicals that can be used. For polyaniline, only a few acids such as β-naphthalenesulfonic acid[16] or camphorsulfonic acid,[22,23] have been reported to function both as dopants and soft “internal” templates. More recently, a different method has been reported for the synthesis of polyaniline nanofibers without using any templates. In this method, polymerization is performed at the interface of an immiscible organic/aqueous biphasic system.[18] This synthesis procedure involves volatile organic solvents such as carbon tetrachloride, benzene, and carbon disulfide. Zhang et al. recently reported a seed-mediated approach to synthesize polyaniline nanostructures, which decreases the use of organic solvents.[20] This procedure requires seeds of polyaniline nanofibers or carbon nanotubes. Here, we show that polyaniline nanofibers can be produced in a “templateless” fashion in a single stage by irradiating aqueous solutions of aniline, ammonium peroxydisulfate (APS), and hydrochloric acid (HCl) with gamma rays. The procedure can be carried out completely in an aqueous phase. Ionizing radiation can be used to control the aspect ratio of the polymer formed.

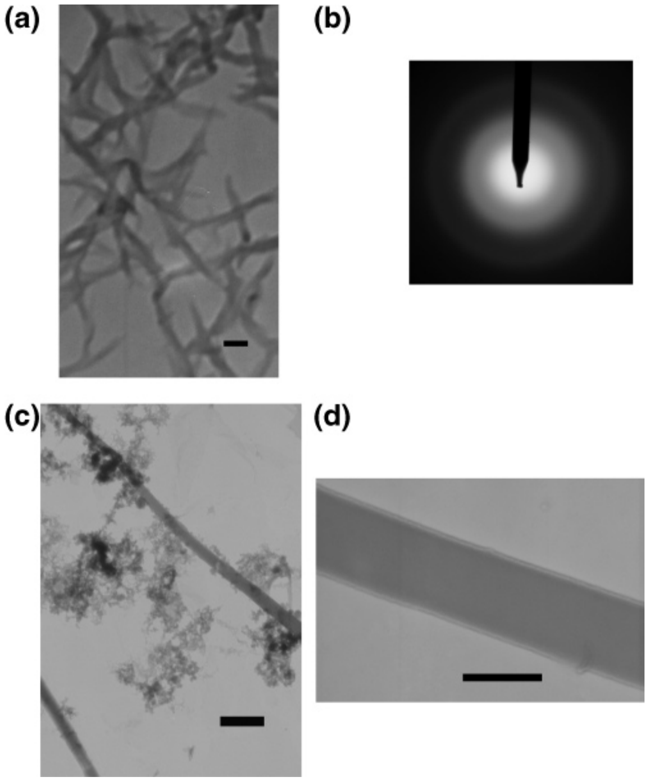

Figure 1. (a) Bright-field TEM micrograph of polyaniline fibers produced by irradiating an aqueous solution containing 0.1 M aniline, 0.002 M APS, and 0.3 M HCl. The scale bar represents 200 nm. (b) SAED of the nanostructures found in (a). (c) Bright-field micrograph of polyaniline fibers produced after irradiation of aqueous solution containing 0.1 M aniline, 0.05 M APS, and 0.3 M HCl. The scale bar represents 2 μm. (d) High magnification micrograph of a rodlike fiber. The scale bar represents 250 nm. All samples were exposed to a total dose of 3.5 kGy, at a dose rate below 1.5 kGy·h^{-1}.

An example of polyaniline nanofibers formed by radiolysis is shown in Figure 1a. The predominant morphology was

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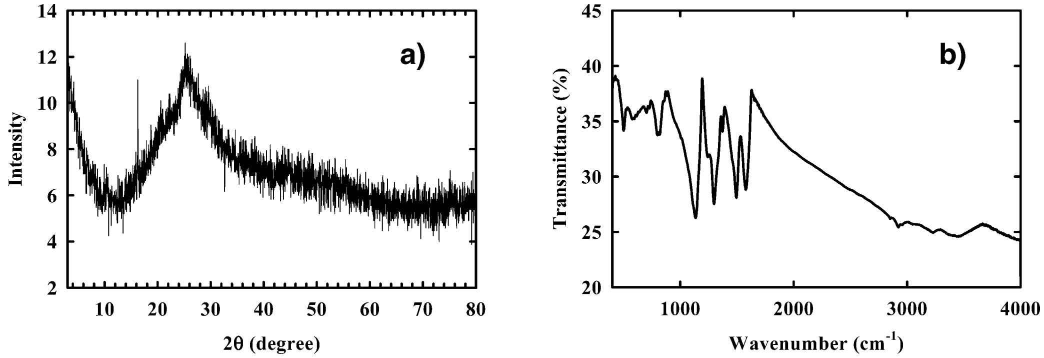

Figure 2. (a) XRD spectra of HCl-doped polyaniline fibers produced by irradiating an aqueous solution containing 0.1 M aniline, 0.02 M APS, and 0.3 M HCl. (b) FTIR of HCl-doped polyaniline fibers produced by irradiating an aqueous solution containing 0.1 M aniline, 0.02 M APS, and 0.3 M HCl. All samples were exposed to a total dose of 3.5 kGy, at a dose rate below 1.5 kGy·h^{-1}.

that of fibers with typical diameters of 50−100 nm and lengths of 1−3 μm. The morphology was comparable to that obtained with other templateless procedures.[18,20] These structures were formed from parent solutions with typical concentrations of 0.1 M aniline, 0.3 M HCl, and APS concentrations between 0.002 and 0.1 M. Virtually all polymerized polyaniline was found in high-aspect-ratio structures; globular structures represented less than 5% v/v of the polymer recovered. A typical selected-area electron-diffraction (SAED) measurement is reported in Figure 1b. The broad Debye−Scherrer rings indicate that the fibers are poorly ordered, if not completely amorphous.

Polyaniline prepared from solutions with APS concentrations between 0.05 and 0.1 M contained not only fibers, but also much larger rodlike structures. A typical TEM micrograph, showing these nanorods along with nanofibers, is shown in Figure 1c. A close-up of a rodlike structure is shown in Figure 1d. These rods had typical lengths between 5 and 10 μm and diameters between 250 and 500 nm. The SAED of the rodlike structures was comparable to that of the nanofibers (Figure 1b). The rods and fibers represented about 5% v/v and 90% v/v, respectively, of the total polyaniline. We note that rodlike polyaniline is typically produced only with hard templates, so our method is a novel way of producing these structures.[16]

Polyaniline nanofibers were also characterized with X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Representative results for both are shown in Figure 2. XRD (Figure 2a) confirms the primarily amorphous character of the fibers. The peak centered at $2\theta = 25°$ may be ascribed to the periodicity parallel to the polymer chain, while the weak peaks at higher angles may be caused by the periodicity perpendicular to the polymer chain.[24] FTIR of polyaniline fibers (Figure 2b) exhibits absorption peaks corresponding to the stretching of quinonoid (1570 cm^{-1}) and benzenoid rings (1490 cm^{-1}), and to N−H stretching (3400 cm^{-1}), in good agreement with previous spectroscopic characterizations of polyaniline.[25] These results indicate that the chemical structure of polyaniline was not substantially altered by irradiation. This is not surprising, since the benzene ring of polyaniline is notoriously resilient to radiation damage, and our doses are comparatively low.[26,27]

The mechanism of nanofiber formation appears to be quite complex, and we cannot currently provide a complete explanation for it. However, we feel that we have clarified some relevant issues. Ionizing radiation affected the morphology of the polymer, but did not strongly affect the polymerization reaction. Polymerization proceeded spontaneously when APS was added to an aniline/HCl solution, but fibers were not produced unless the solutions were irradiated. Polymerization was not induced by irradiation of the monomer alone, since only very small quantities of polymer were formed when solutions without initiator were irradiated. We conclude that polyaniline self-assembles when polymerization is carried out under irradiation, consistent with previous observations of radiation-induced self-assembly in a variety of polymers.[28] Irradiation of aqueous suspensions of preformed, bulk polyaniline alters somewhat the polymer morphology, but does not produce fibers.

Additional insight into the fiber formation mechanism was provided by a series of experiments in which the morphology of the polymer was studied as a function of polymerization time and radiation dose. When aniline was polymerized without irradiation, spherical aggregates with diameters between 20 and 40 nm were formed, as shown in Figure 3a. These aggregates merged, without showing any directional preference, and formed globular structures, some of which are also evident in Figure 3a. When samples were irradiated, spherical aggregates similar to those observed in un-irradiated samples were formed, but their diameters were 4−5 times larger. In addition, nanoparticles resembling hollow spheres were formed, with diameters between 50 and 100 nm (Figure 3b). These diameters were similar to those of the fibers observed with longer irradiation times. The hollow aggregates appeared to play an important role in fiber formation, since they tended to stick to and link spheres, which then coalesced in an anisotropic fashion, as shown in Figure 3c. The characteristics and precise formation conditions of these hollow nanoparticles are currently being investigated.

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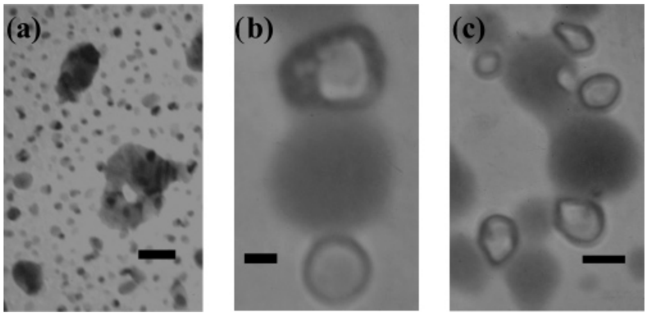

Figure 3. Bright-field TEM micrographs of a sample with a composition of 0.1 M aniline, 0.02 M APS, and 0.3 M HCl. (a) Un-irradiated sample, 8 min after addition of the APS initiator. The scale bar represents 100 nm. (b) Sample exposed for 3 min to γ-radiation at a dose rate of 2.4 kGy·h^{-1}, for a total dose of 0.12 kGy. The APS initiator was added 4 min before the beginning of the irradiation. The scale bar represents 50 nm. (c) Sample treated similar to (b). The scale bar represents 100 nm.

In summary, we have reported a novel procedure for the synthesis of polyaniline nanofibers and nanorods. The synthesis is templateless; fibers can be extracted after a few simple washing cycles, and the polymer can be doped with simple acids, such as HCl. Using our procedure, nanofibers are routinely obtained and, for a narrow range of compositions of the initial solution, rodlike structures as long as 10 μm can be produced. The mechanism of formation of the nanofibers appears to be related to the formation, during irradiation, of hollow spheres, which coalesce in a way reminiscent of diffusion-limited colloidal aggregation.[29,30]

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Supporting Information Available: Experimental information including materials, irradiation, and characterization information (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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