

## Template-Directed Synthesis of Lamellar Polystyrene Nanomaterial

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(Received June 4, 2007; Accepted August 13, 2007; Published October 2, 2007)

KEY WORDS Polystyrene / Template / Synthesis / Nanomaterial /  
[doi:10.1295/polymj.PJ2007066]

Template-directed synthesis is one convenient and versatile method for generating nano-materials. Since Mobil's scientists succeeded in synthesis of a novel mesoporous silicate called MCM-41,<sup>1</sup> increasing attention had been focused on the preparation of nanostructural materials with surfactant liquid crystal template.<sup>2–6</sup> More and more inorganic nanomaterials had been synthesized by surfactant liquid-crystal template mechanism.<sup>7–9</sup> However, to my knowledge, there has been no report on the synthesis of nanostructural polymeric materials with surfactant liquid crystal template.

Here, we report on the preparation of a novel lamellar polystyrene nano-material synthesized by free radical polymerization with sodium dodecyl sulfate (SDS) as surfactant liquid crystal template. In a typical preparation, a suspension consisting of 1.8 g of SDS, 0.96 g of KCl, and 40 mL of deionized water was formed by slowly adding the deionized water to the stirred mixture of the other two components in a three-necked flask. The suspension was stirred for 2 h. A solution of KCl (3.84 g) and deionized water (160 mL) was then introduced, and the mixture was continuously stirred for 0.5 h. Polymerization of polystyrene (PS) was then carried out at 50 °C and taken 20 h to complete by starting with the addition of 0.008 g of initiator ammonium persulfate (APS) and 8 mL of freshly distilled styrene to the mixture. The crude product was separated from the turbid system by a centrifugal process and then purified by washing with 50% ethanol-water. The resulting white powder was finally dried in a vacuum oven. During purification, the temperature was always kept below 50 °C to ensure that the conformation of PS was not changed. In polymeric system, the template structure was confirmed by XRD (appearance of three obvious peaks appearing at  $2\theta = 2.4^\circ$ ,  $4.8^\circ$  and  $7.1^\circ$ ). They were typical characteristic of lamellar liquid-crystal of SDS.<sup>10</sup> XRD results showed that the SDS surfactant had a lamellar liquid crystal structure in polymeric system, and kept the structure well during the whole polymerization.

The composition of product was confirmed by Infrared (IR). IR spectra of obtained products and ordinary atactic PS were compared, from which no obvious difference in position and shape of absorption bands was found. Furthermore, characteristic absorption of SDS (such as  $1220\text{ cm}^{-1}$  and  $985\text{ cm}^{-1}$ ) was hardly detected.<sup>11</sup> Moreover, the result of the atomic absorption spectroscopy (AAS) showed the content of potassium in the purified product was only 3.4 mg/g. The results of IR

and AAS showed that SDS and KCl were almost completely removed during purification. Therefore, after purification, obtained white powder was pure polystyrene. GPC measurements showed the PS had a molecular weight ( $M_n$ ) of  $0.11 \times 10^6$  and a molecular weight distribution ( $M_w/M_n$ ) of 3.6.

The polystyrene was investigated by the transmission electronic microscopy (TEM). TEM observation clearly confirmed that the polystyrene exhibited a layered image as presented in Figure 1. The polystyrene had a structure with large extensions in two dimensions (x and y dimension, *i.e.*, diameter) and a very short extension along the third axis (z-direction, *i.e.*, thickness). Hence, the layered image in Figure 1 is attributed to the lamellar nanostructure of polystyrene, which can be described as lamellar polystyrene (L-PS). As can be seen from Figure 1, the thickness of individual L-PS particles was very small so that they were almost transparent. By AFM experiments, the thickness of the individual L-PS particles was only 2–3 nm. Moreover, the thickness of L-PS particles was uniform and its plane was very smooth. From images of Figure 1, the plane of L-PS particles had irregular shape and size. The plane size of L-PS was nano-scale (several hundred nanometers). Therefore, from the results of TEM and AFM, we confirmed that lamellar polystyrene nanomaterial was prepared successfully.

The tacticity of L-PS was confirmed by <sup>13</sup>C-NMR. From the result of <sup>13</sup>C-NMR, the L-PS had split and broad absorptions at 144.8–146.2 ppm (Figure 2), which suggested that this polystyrene was essentially atactic. Figure 3 showed the DSC curves of L-PS. The L-PS was scanned to 280 °C for the first scan, and the result was shown in Figure 3a. After cooling to ambient temperature, the L-PS was scanned to 280 °C again, and the result was shown in Figure 3b. During the first scan, L-PS displayed two exothermic peaks, one at 105 °C, and the other at 154 °C. The subsequent scan showed glass transition ( $T_g$ ) only, and both exothermic peaks disappeared. Similar DSC curves have been reported in the case of polystyrene microspheres.<sup>11</sup> The first exothermic peak was due to the sintering of polystyrene nano-particles, and the loss of surface area results in the energy release. The second exothermic peak was due to the special molecular chain structure of polystyrene nanomaterials. However, it was surprising, the enthalpy of the second exothermic peak was 21.8 J/g, which was more than that of isotactic PS (19.5 J/g) or syndiotactic PS (9.2 J/g).<sup>12</sup> This was perhaps the first report that atactic polystyrene dis-

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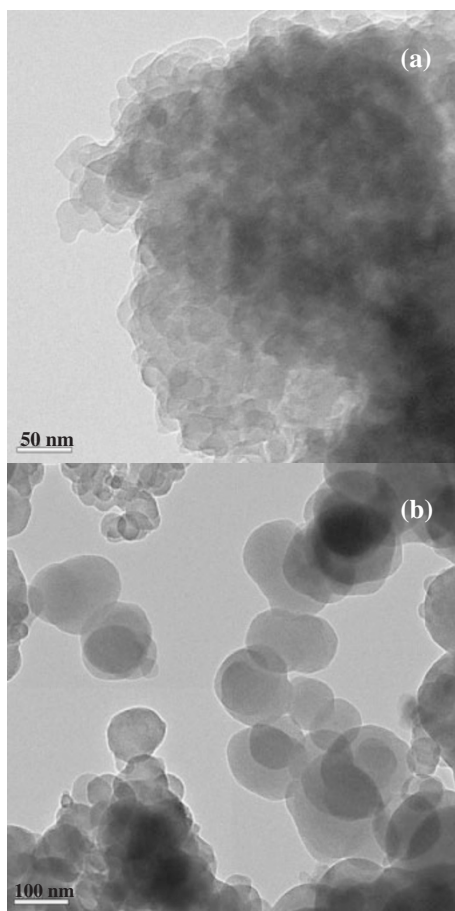


Figure 1. TEM images of L-PS particles.

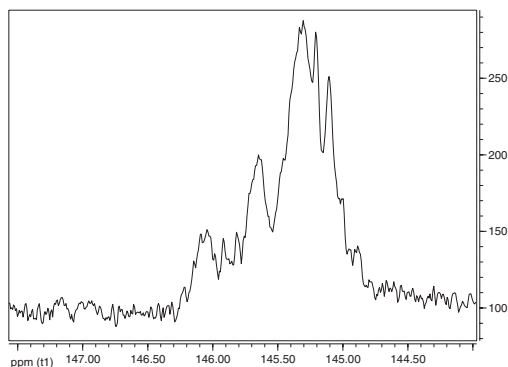


Figure 2. <sup>13</sup>C-NMR spectra of L-PS.

play this result. Therefore, L-PS must have an especial molecular chain structure, which had never been discovered before.

Usually, polymer particles obtained by radical polymerization in aqueous system possess spherical shape.<sup>13</sup> Lamellar nano-morphology of L-PS was due to the especial templates of polymerization. In lamellar liquid-crystal of SDS, there is lamellar and hydrophobic space, which was polymeric position of Styrene (Figure 4). Therefore, as product formed in lamellar template, a novel molecular chain structure of polymer was prepared. Liquid crystal template-directed synthesis led to a novel polystyrene nanomaterial.

Our works concluded that a kind of novel nanostructural PS

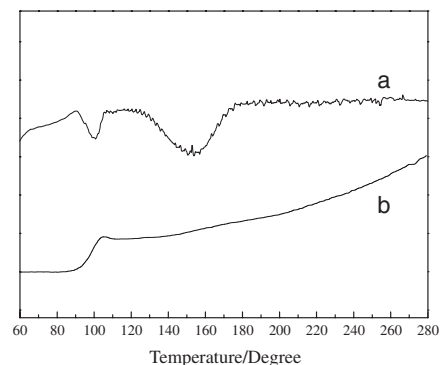


Figure 3. DSC thermograms of L-PS: (a) first scan. (b) second scan.

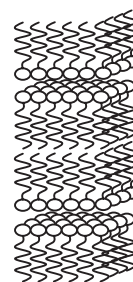


Figure 4. Schematic Representation of the SDS lamellar liquid crystal template.

lamels could be prepared by free radical polymerization in surfactant liquid crystal template. This research provided a general and versatile technique for preparing novel polymer nanomaterial.

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