An Approach towards Nano-size Crystals of Poly(acrylic acid): Polymerization Using Layered Double Hydroxides as Template

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A new approach has been proposed and was shown to be a feasible method to produce nanosized polymer crystals of poly(acrylic acid). The new approach involves in situ polymerization of acrylic acid in the interlayers of a layered double hydroxides (LDHs) followed by exchange of the polymer anion for carbonate. The key is the use of LDHs as a template.

Polymers have a wide variety of applications as molecular devices and commodity materials.[1–3] Generally, the space for the reaction of the monomers is lager than the nanosized atoms or molecules, which results in difficulties in controlling the architecture and the size of the product. Many methods have been developed to prepare polymers. Template synthesis[4–6] has evolved as an effective and simple approach. In template synthesis, the desired material is produced within the template, which is subsequently dissolved to allow the release and collection of the product. To date, most of the work in this area has entailed the use of "track-etch" polymeric filter membrances[4] and porous silica,[5,6] resulting in polymeric nanowires, nanotubules, nanofibers, and ordered mesoporous polymers.

This paper reports a novel method to prepare nanosized crystals of polymer. The key point is the use of layered double hydroxides (LDHs)[7] as the template. LDHs are hydrotalcite-like compounds or anionic clays. They are a family of lamellar solids of the general formula $[\mathrm{M^{II}}_{1-x}\mathrm{M^{III}}_{x}(\mathrm{OH})_2](\mathrm{A}^{n-})_{x/n}\cdot m\mathrm{H_2O}$. Their structures can be described as brucite-like layers in which part of the divalent metal cations have been substituted by trivalent cations resulting in positively charged layers.[8] The intercalated anions may balance the charge of the layers, and host and guest interact through electrostatic forces and other weaker forces such as hydrogen bonds. There have been a few reports of the intercalation of polymeric guests in LDHs to obtain nanocomposite materials.[9,10] To the best of our knowledge, the present paper is the first report regarding the synthesis of poly(acrylic acid) using LDHs materials as template producing nanocrystals.

This approach is depicted in Figure 1. The reaction system is defined as the assembly of two components, a monomer acrylate and a template (Mg–Al–$\mathrm{NO_3}$–LDHs) providing a restricted reaction space. The in situ polymerization occurs in the interlayer region of the LDHs and is initiated by potassium persulphate. The produced polymers are collected by exchange of the polymeric anion for carbonate.

The nitrate LDHs precursor ($\mathrm{NO_3}$–LDHs) was prepared with separate nucleation and aging step method (see SI), and acrylate-inserted compound (**AA–LDHs**) was obtained by the ion exchange method under nitrogen. After the formation of the monomer-intercalated LDHs material, in situ free radical polymerization of the monomers in the interlayer region was carried out using the water-soluble initiator, potassium persulphate, to produce the polymerized product (**PAA–LDHs**). The XRD patterns for the three LDHs materials exhibit a set of (00l) reflections indicating long-range order in the stacking dimension, which are characteristic of a well-crystallized layered phase. Compared with the precursor, the **AA–LDHs** has a phase with an increased basal-plane repeat distance as shown by the shift in the (003) reflection to a lower angle. The **PAA–LDHs** produced a XRD powder pattern similar to that of the **AA–LDHs**,

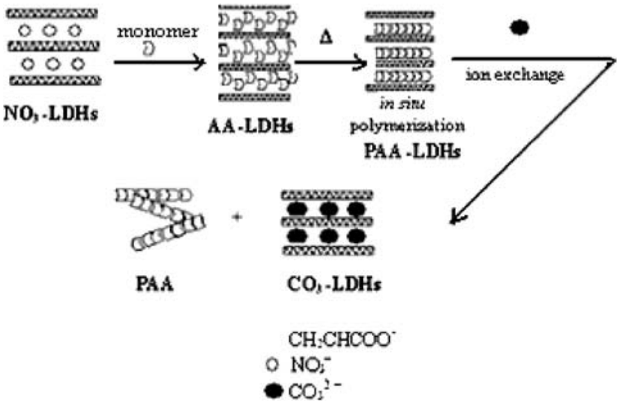

Figure 1. Schematic of the approach for the preparation of nano-size **PAA** crystals.

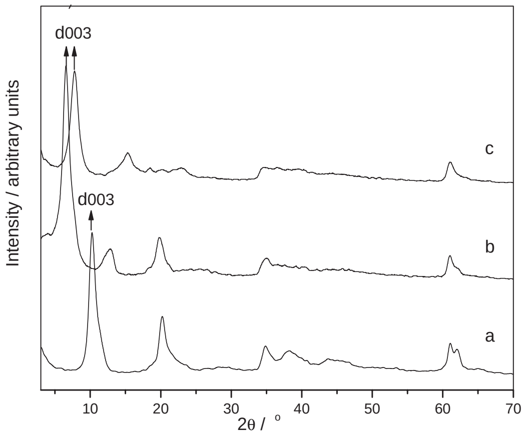

Figure 2. XRD powder patterns for (a) $\mathrm{NO_3}$–LDHs, (b) **AA–LDHs** and (c) **PAA–LDHs**.

indicating the maintenance of the layered structure after the free radical polymerization.

LDHs materials exhibit absorption characteristic of both the intercalated anions and the LDH sheet. The absence of the nitrate-related vibrations and the appearance of an acrylate anion vibration at 1640 cm^{-1} ($\nu_{c=c}$) was observed for **AA–LDHs**, and the symmetric and asymmetric stretches of RCO_2 at 1560 and 1450 cm^{-1}, respectively, were also evident. Absorption bands at 2927 and 2855 cm^{-1} attributed to the symmetric and asymmetric stretches of $–CH_2–$, and the sharp peaks at 1563 and 1452 cm^{-1} characteristic of RCO_2^- were evident for **PAA–LDHs**.

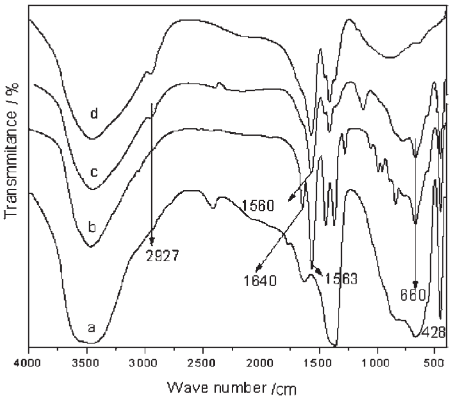

Figure 3. IR spectra of (a) NO_3–LDHs, (b) **AA–LDHs**, (c) **PAA–LDHs**, and (d) **PAA**.

Much effort has been expended to release and then collect the polymers formed in the restricted geometry of the LDH template. This study finally focused on the exchange of the polymer anion for the carbonate anion to the layers of LDHs. After preliminary investigations, it was found that 2 M carbonate solution gave the best results. Acetone was added dropwise to the mixture after the ion exchange reaction to precipitate the **PAA**. The recovery yield of **PAA** was 85.0%.

The IR spectrum of **PAA** [Figure 3c] was similar to that of **PAA–LDHs**, except for the disappearance of the peaks associated with the metal–oxygen vibration in the range of 400–700 cm^{-1}. ^{1}H NMR spectrum of **PAA** (see SI) displayed resonance peaks at 1.359 and 1.948 ppm associated with the β-hydrogen of **PAA**, and the peak at 4.742 ppm was due to α-hydrogen. Owing to the extreme irradiation sensitivity of **PAA** crystals, the sample was coated with a carbon film and special care was taken in TEM examination to avoid serious irradiation damage. Figure 4a shows the typical transmission electron microscope morphology of **PAA**. The electron diffraction pattern (Figure 4b) indicated that the **PAA** was crystalline. High-resolution transmission electron microscopic observation revealed that the crystal size was 50–80 nm. GPC results showed that the molecular weight was 20778 and the polydispersity was 1.58.

Since LDHs was used as a template in the preparation of **PAA**, the formation of the nanosized crystals was attributed to a special property of the template. The polymerization occurred in the restricted geometry of the template. The layers of the LDHs template are positively charged and the monomers are negatively charged. Because of the strong electrostatic repulsion between the monomers and the LDHs, the orientation and arrangement of the monomers in the interlayer space of the template was much more regular than in free space. Therefore, the polymers produced in the interlayer space of the template were able to crystallize.

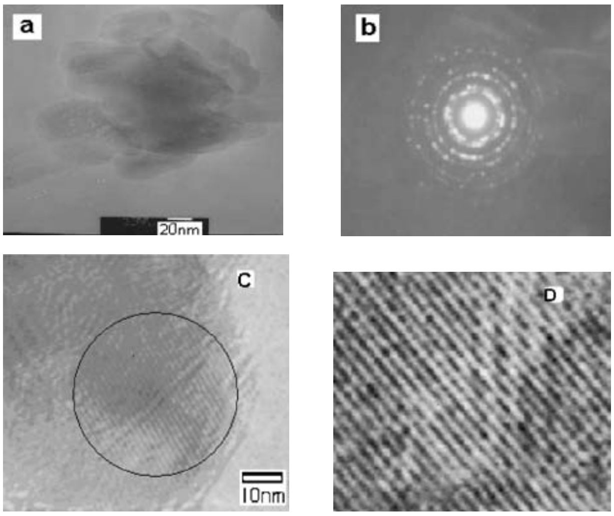

Figure 4. (a) Transmission electron microscope examination of **PAA** (b) electron diffraction pattern (c) HR-transmission electron microscope image of the crystal lattice of **PAA** (d) the enlarged and optically processed image of (c).

Beside the study reported here, poly(styrene sulfate) was also prepared by the same method described above and similar results were obtained. In conclusion, LDHs are effective tools in the preparation of nano polymer crystals. The mechanism of the formation of crystals is currently being studied in our group.

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