Fabrication of Poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] Nanofibers

Qingchun Zhao*[1,2] and Ling Xu[1,2]
[1]*Anhui Key Laboratory of Advanced Building Materials, Anhui Institute of Architecture & Industry, Hefei 230022, Anhui, P. R. China*
[2]*Department of Material Science and Engineering, Anhui Institute of Architecture & Industry, Hefei 230022, Anhui, P. R. China*

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In this paper, we report a facile chemical route to fabricate polymer nanofibers under ambient conditions using aqueous/organic polymerization. The chemical structures of obtained polymers were investigated by infrared spectra and ^{1}H NMR. Scanning electron microscopy (SEM) observation shows poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] nanofibers with average diameter 100–140 nm and several micrometers length. A possible mechanism for the formation of polymer nanofibers was investigated.

One-dimensional (1D) nanostructures, such as nanowires and nanofibers, have been intensively studied in recent years because of their intriguing properties and potential applications. Fabrication of polymer 1-D nanostructures has been carried out both chemically and electrochemically by polymerizing the monomer with the aid of either a "hard" or a "soft" template. Examples of hard templates include zeolite channels,[1] track-etched polycarbonate,[2,3] and anodized alumina.[4] Soft templates, such as surfactants,[5] micelles,[6–8] liquid crystals,[9] thiolated cyclodextrins,[10] and polyacids,[11] are reported to be capable of directing the growth of polyaniline 1-D nanostructures with diameters smaller than 100 nm. Physical methods, including electrospinning[12] and mechanical stretching,[13] have also been used to make polymer nanofibers. The above those nanofibers do not include any metal ions. Here we report a facile chemical route to prepare polymer nanofibers in which Zn^{2+} ions are included under ambient conditions using aqueous/organic polymerization. The nanofibers have nearly uniform diameters between 100 and 140 nm with lengths varying several micrometers.

Acrylic acid and PCl_3 were purchased from GL Biochem shanghai Ltd. Zinc oxide, acetone, and poly(ethylene glycol)(2000) were purchased from Guangdong Ltd. Deionized water was used for preparation of all aqueous solutions.

To synthesize CH_2=CH–COCl, PCl_3 (0.2 mol), and acrylic acid (0.2 mol) were added to a three-necked round bottomed flask with a condenser and stirrer. The flask was heated to 50 °C for 4 h. The above liquid was poured into a bottle and sealed after cooling to room temperature.

To synthesize CH_2=CHCOO(CH_2CH_2O)$_n$OCCH=CH_2, poly(ethylene glycol)(2000) (20 g, 0.01 mol) was added to a three-necked round-bottomed flask and acetone (10 mL) was added. This solution was stirred for 5 min, and then CH_2=CH–COCl (0.02 mol) was added. After the flask was heated to 55 °C for 8 h, the crude product was then washed with deionized water to remove unreacted poly(ethylene glycol) and CH_2=CH–COCl. The product was dried overnight at 40 °C in vacuo.

Poly[acrylic acid-*co*-acrylic poly(ethylene glycol) ester] was synthesized via aqueous free-radical polymerization. A total of 10 g of CH_2=CHCO(OCH_2CH_2O)$_n$OCCH=CH_2 and 0.01 g of $(NH_4)_2S_2O_8$ was dissolved in 25 mL of acetone. Then 10 g of aqueous zinc acrylate (80%) was added dropwise (1 h) to the solution. After the solution was stirred for 10 h at 60 °C under a dry nitrogen atmosphere, the crude product was washed with acetone and ethanol to remove unreacted CH_2=CHCOO(CH_2CH_2O)$_n$OCCH=CH_2. The composition of polymer was determined by 400 MHz ^{1}H NMR (Bruker DPX-400) in D_2O and infrared spectrum (Bruker FT-IR Vector-22).

To prepare poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] nanofibers, 10 g of poly[acrylic acid-*co*-acrylic poly(ethylene glycol) ester] was dissolved in 50 mL of a mixed solution (the volume ratio of water to acetone was about 20:30). After the solution was bubbled with N_2 for 20 min to eliminate oxygen, it was irradiated with γ-rays with 6000 Gy.

A Fourier transform infrared (FTIR) spectrum (Figure 1a) of acrylic poly(ethylene glycol) ester confirmed the characteristic peaks of the C–O stretching modes at 1261 cm^{-1}. The –CH_2 and C–H stretching peaks of acrylic poly(ethylene glycol) ester appeared at around 2900 cm^{-1} and the band at 1733 cm^{-1} was assigned to C=O stretching vibrations. In addition, a peak at 1636 cm^{-1}, which is related to the C=C stretching mode, and a peak at 1100 cm^{-1}, which is related to the C–O–C stretching mode were observed. These results demonstrate the successful reaction of CH_2=CH–COCl monomers with poly(ethylene glycol) and the acrylic poly(ethylene glycol) ester has been synthesized. The reaction is as follows:

$$2CH_2{=}CH{-}COCl + HO(CH_2CH_2O)_nH \rightarrow CH_2{=}CHCOO(CH_2CH_2O)_nOCCH{=}CH_2 + 2HCl \quad (1)$$

Figure 1b is a Fourier transform infrared (FTIR) spectrum of poly[acrylic acid-*co*-acrylic poly(ethylene glycol) ester]. The –CH_2 and C–H stretching peak of poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] appear at around 2896 cm^{-1} and the band at 1741 cm^{-1} was assigned to C=O stretching vibrations. The peak at 1098 cm^{-1}, which is related to the C–O–C stretching mode, in addition, the peak at 1636 cm^{-1}, which is related to the C=C stretching

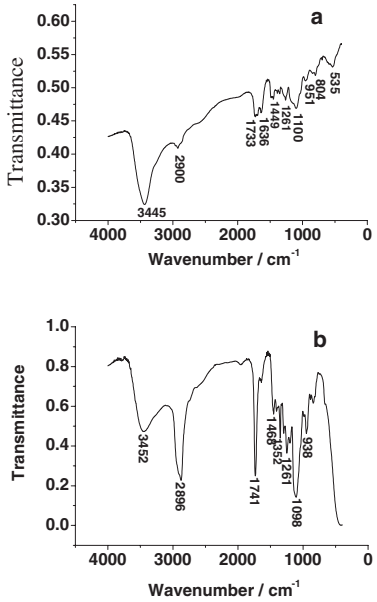
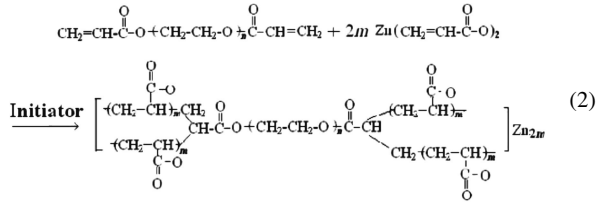


Figure 1. Infrared spectrum; a) acrylic poly(ethylene glycol) ester; b) poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester].

mode, disappeared. These results demonstrate successful polymerization of zinc acrylate monomers with acrylic poly(ethylene glycol) ester and poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] has been synthesized. The polymerization is as follows:



(2)

In ^{1}H NMR spectrum of the acrylic poly(ethylene glycol) ester (Figure 2a), the peaks at 3.6–3.7 ppm were attributed to the hydrogen atoms of the $-CH_2CH_2O-$ groups. The signals at 6.0 ppm were assigned to the hydrogen atoms attached directly to the (carbon–carbon) double bonds and those at 2.2 ppm correspond to the hydrogen atoms of the methyl groups (rudimental acetone). The peaks at 4.0–4.5 ppm correspond to the hydrogen atoms of the ether groups. The 2.8 ppm peaks correspond to the hydrogen atoms of the ethylene groups (rudimental ethanol). 1.2 ppm peaks correspond to the hydrogen atoms of the methylene groups. Conversely, it is found that the peaks in around of 6.0 ppm disappeared in the spectrum of poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] after polymerization (Figure 2b), confirming the successful polymerization of vinyl monomers with acrylic poly(ethylene glycol) ester. It also should be noted this result is in agreement with those above.

The synthesized products were characterized by scanning electron microscopy (SEM) (JEOL JSM-6300). The SEM (Figure 3) micrographs reveal that optimization of the experimental parameters allows macroscopic preparation of poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] nanofibers. In Figure 3a, SEM observation shows that the products consist of a large number of polymer nanofibers with several micrometers length. In Figure 3b, SEM observation shows polymer nanofibers with average diameter about 100–140 nm.

The obtained polymer nanofibers were further characterized by X-ray powder diffraction, using a $D_{\max}\gamma$A X-ray diffractometer

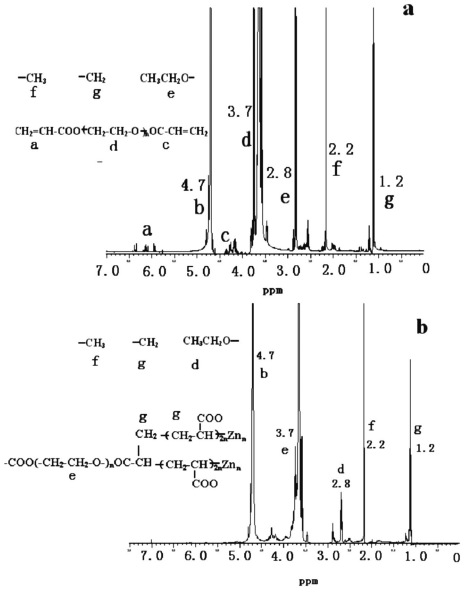


Figure 2. ^{1}H NMR spectrum; a) acrylic poly(ethylene glycol) ester, b) poly-[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester].

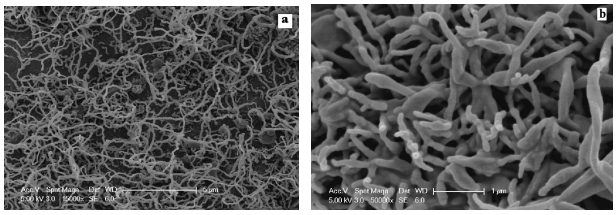


Figure 3. Scanning electron microscopy (SEM) images of obtained zinc acrylate-*co*-acrylic acid poly(ethylene glycol) ester nanofibers.

with Cu Kα radiation ($\lambda = 1.54178$ Å), results show obtained polymer nanofibers are amorphous (The Figure is not shown).

A possible mechanism for the formation of polymer nanofibers may be as follows: At a desired mixed solution that is opaque (the volume ratio of water to acetone is about 20:30), poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] may form colloid bundles. After the colloid bundles are irradiated by γ-rays, cross-linked structures are produced between the poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] (poly(zinc acrylate) will cross-link with γ-rays irradiation) and the polymer nanofibers are obtained.[14]

The solubility parameters for a mixing solvent were found to play a significant role in the formation of colloid bundles. The solubility parameters for a mixing solvent can be calculated using the following equation:[15]

$$\delta_{\text{mix}} = \Phi_1'\delta_1 + \Phi_2'\delta_2 \quad (3)$$

Where Φ_1' and Φ_2' are the volume fraction for the two solvents, and δ_1 and δ_2 are the solubility parameters for the two solvents. The water solubility parameter is 23.2 and the acetone solubility parameter is 10. When the volume fraction for water increases (excess 30: 30), the δ_{mix} will increase. Poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] can be dissolved in the mixing solvent, the obtained solution is transparent, colloid bundles can not be formed. When the volume fraction for acetone increase (excess 20:40), the δ_{mix} will decrease. Poly[zinc acrylate-*co*-acrylic poly(ethylene glycol) ester] can not be dissolved in the mixing solvent and precipitate.

In conclusion, the results presented here demonstrate that radical polymerization of a functional and cross-linking monomer with acrylic groups can be used to prepare polymer nanowires. The solubility parameters for a mixing solvent were found to play a significant role in the formation of colloid bundles. In addition, this synthetic method might be expanded to allow the fabrication of 1D polymer nanocomposites, which include ZnS, ZnSe semiconductor polymer materials. We anticipate that this method will provide a platform for the fabrication of diverse and multifunctional polymer nanocomposite fibers, which may have potential applications in fabricating devices with optical, electrical, and magnetic properties.

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