Synthesis, Morphology, and Luminescence Properties of Poly(urethane-acrylate) Nanowires Bonding with the Eu(III) Complex

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ABSTRACT: Photoluminescent poly(urethane-acrylate) (PUA) nanowires are designed and synthesized through copolymerization of a presynthesized-europium (Eu) complex with active vinyl groups and a vinyl functionalized PUA macromonomer matrix, initiated by azobisisobutyronitrile. This procedure provides a method to prepare PUA-Eu nanowires through in situ polymerization. Based on this, a series of PUA-Eu nanowires with diameters of 80−300 nm are successfully obtained in templates of anodized aluminum oxide by in situ polymerization. The obtained PUA-Eu nanowires display different morphologies such as sharp, round, and flat head by controlling the casting conditions. Furthermore, the PUA-Eu nanowires exhibit unique luminescence properties provided through Eu(III) elements, and the luminescence intensity significantly enhances with the increase in Eu complex concentration. PUA-Eu nanowires have longer fluorescence lifetimes than that of Eu complexes and PUA-Eu plates.

INTRODUCTION

The recently developed nanostructures have caused concern owing to their large exterior surface area compared with bulk.1−2 One-dimensional (1D) nanostructure materials, such as nanorods, nanotubes, nanowires, and nanoarrays, exhibit intriguing applications in sensor devices,3−4 energy storage devices,5−8 and optoelectronics.9,10 Various synthetic and manufacturing methods have been employed to fabricate 1D polymeric nanostructures. The anodized aluminum oxide (AAO) nanotemplate method is considered to be one of the most effective techniques.11−14 AAO nanotemplate possesses extraordinary properties, including desirable diameters (ranging from tens to hundreds of nanometers) and large specific surface areas. Porous AAO membranes are usually used as a template to prepare 1D polymer nanostructures because of the simple preparation method, low-cost, and high uniformity of the nanostructures.15−17 Many methods can be used for preparing polymer nanowires and nanocables through the AAO template, such as electrodeposition,18,19 self-assembled,20 chemical vapor deposition,21 photolithographic approaches,22 layer-by-layer deposition,23,24 and physical wetting.25

The rare earth (RE) complexes have been attractive materials because of their distinct and desired luminescence performances, for instance, low excitation energy, good monochromaticity, and long fluorescence lifetimes.26,27 Nevertheless, the complexes are not easy to process and have poor heat resistance which hinder their application in fabrica-

With the development of synthetic techniques, RE complexes can be designed and incorporated into the polymer matrix, making a series of new materials with improved luminescence properties and process flexibility.28−32 Two approaches are always used to prepare RE polymers: doping and copolymerization.33−35 The former has been proved as a simple, versatile, and facile approach. However, it is difficult to achieve uniform dispersion and good interfacial interaction between RE complexes and the polymer matrix by doping method, which leads to the decrease of fluorescence performances of the composites. The uniform dispersion of complexes in the polymer matrix is the main reason to improve luminescent efficiencies. The composite nanofibers containing the RE complex and polymer were prepared by electrospinning technology. Compared with the pure complex, the thermal stability of photoluminescence was significantly improved in composite fibers.29 The europium (EU) complex/PMMA copolymers with good luminescence properties were synthesized, and the luminescent intensity increased proportionally with the increase of the content of EU complexes in the nanofibers.30−32
introducing other functional units. The in situ polymerization of the RE complex incorporating with molecular chains inside the AAO template, providing the feasibility for introducing RE functional units in optoelectronic applications.

In this paper, we propose a novel technique to fabricate the bonding-type RE polyurethane nanoarrays by in situ polymerization inside the AAO nanotemplates. We initially synthesized a series of PUA-Eu prepolymer terminated with active allyl groups of acrylates, comprising an Eu complex and MPUA. Subsequently, the PUA-Eu prepolymer was transferred into the AAO nanotemplates, and in situ polymerization was carried out inside the AAO nanochannels at a certain temperature. The influences of wetting time on morphologies of the formed nanoarrays and the content of the Eu complex on the template, providing the feasibility for introducing RE functional materials and the content of the Eu complex clearly indicate its possibility of in situ polymerization of the RE complex, indicating that the double bond is not destroyed and has polymerized activity.

RESULTS AND DISCUSSION

Structure and Properties of the Eu(III) Complex. The structures of the Eu(III) complex were solved and refined using the SHELXL-97 programs. The crystallographic data of ours and reporter are summarized in Table 1. The crystal structure of Eu(III) complex is shown in Figure 1.

Table 1 indicates that the Eu(III) complex crystallizes in a monoclinic system, space group $P_c$ (no. 7). In the asymmetric unit, there are three different crystallographic Eu(III) ions, nine crotonic acid ligands, and four coordinated water molecules that is consistent with reported. It indicated that the complexes and the organic molecules that is consistent with reported. It indicated that we successfully synthesized the Eu(III) complex 
\[
[\text{Eu}_3(\text{MeCH/CHCO}_2)_{9}(\text{H}_2\text{O})_{4}]\text{H}_2\text{O/ EtOH}]_n
\]
containing the functional group of the carbon–carbon double bonds (C=C–), which establishes the foundation for the preparation of bonding-type RE-polymer materials.

Figure 2 is the Fourier transform infrared (FTIR) spectra of crotonic acid and the Eu(III) complex. Comparing with the

![Figure 1. Structure of the Eu(III) complex (remove the H atoms).](image)

![Figure 2. FTIR spectra of crotonic acid and the Eu(III) complex.](image)
showed in Figure 4. It can be clearly seen that PUA-Eu
exponential decay mode by the equation

\[ I(t) = I_0 \exp(-t/\tau) + \gamma_0 \]

where \( t \) is the time and \( \tau \) is the lifetime of decay. From the
fitting curve \( y = 4657.327 \exp(-x/0.41718) + 3.24749 \), the
fluorescence lifetime of the Eu complex is 0.41718 ms. Because
of the good level-matching of crotonic acid and Eu3+, the Eu
complex has a long fluorescence emission lifetime.

Structure of PUA-Eu Nanowires. FTIR spectra of PUA-
Eu nanowires containing the 1 wt % Eu(III) complex with
different diameters after removing the AAO template are
shown in Figure 4. It can be clearly seen that PUA-Eu
nanowires with different diameters have the same absorption
peaks. The absorption peak at nearly 2270 cm\(^{-1}\) disappears,
indicating that the isocyanato-bonds (–NCO) of the systems
reacted completely. FTIR spectra of the PUA-Eu nanowires
showed the urethane structure demonstrated by the absorption
bands at around 3351 cm\(^{-1}\) (N–H stretching), 1533 cm\(^{-1}\)
(C–N stretching, combined with N–H out-of-plane bending),
1107 cm\(^{-1}\) (–O– asymmetrical stretching), and 1704 cm\(^{-1}\)
(C–=O stretching). A shoulder band at a lower wavenumber
than that around 1704 cm\(^{-1}\) can be detected. This may be
because the absorption peak of the carbonyl groups shifts to a
low wave number after some carbonyl groups in the urethane
bond form the hydrogen bond. Moreover, the absorption peak
about 1600 cm\(^{-1}\) (–C–=C–) disappears, implying that the
double bonds of hydroxethyl methacrylate (HEMA) and the
Eu(III) complex were reacted entirely. The results confirm that
the structure of the PUA-Eu nanowires fully accords with that
of design.

Influence of Wetting Time on the Formation of PUA-
Eu Nanowires. In order to explore the formation mechanism
of nanowires in the pores of the AAO template, we adopt
physical immersion AAO template method. First, PUA-Eu
prepolymers were directly dropped onto the AAO templates.
Second, the AAO templates were placed for 1, 3, and 12 h at
room temperature, respectively, and then transferred into the
oven for curing. Curing conditions and removal approach of
the template were the same as the experiment.

Field-emission scanning electron microscopy (FESEM)
images of PUA-Eu nanowires, which are wetted in the AAO
membrane for 1, 3, and 12 h respectively, are shown in Figure
5a–c. Surface and internal morphology of the AAO template is
shown in Figure 5d,e. The pore size of the AAO template is
uniform. The PUA-Eu nanowires have formed, but the
nanowires arrange closely after removing the AAO template.
The reasons are that PUA-Eu nanowires are so soft and long
that they cannot stand upright. Hence, they present the held-
together phenomenon. In Figure 5a, the bottom ends of arrays
are slender. Extending wetting time for 3 h, PUA-Eu nanowires
become disorder in diameter, big head, and small and smooth
body. For wetting 12 h, the shape of nanowires is extremely
close to cylinder. When the wetting time of the PUA-Eu
prepolymer increases, the morphology of PUA-Eu nanowires
tends toward perfection in the pore of the AAO template. The
lengths of PUA-Eu nanowires are consistent with the thickness
of the AAO membrane template, and the diameters of the
PUA-Eu nanowires are close to the pores of AAO templates.
All the above results indicate that the experimental wetting
time is an important factor to the morphology of the PUA-Eu
nanowires array in preparing PUA-Eu nanowires. In the follow-
up experiments, the long wetting time (12 h) was chosen to
fabricate PUA-Eu nanowires.

Based on the above research results and pioneer
contributors, the processes of forming nanowires in
nanochannels are speculated by wetting method. Schematic
illustrations of the experimental processes to prepare PUA-Eu
nanowires in the nanochannel of AAO template is shown in
Figure 6. Because of the presence of Brønsted and Lewis acidic
sites on the surface of alumina, it is favorable for adsorption
of electron-pair donor solvents or prototypical basic polymers.33
At first, the PUA-Eu prepolymer solution was dropped on the
template with open-through pores, which will spread along the
pore walls to form a precursor by the adhesion force. The
solution will stuff the pore walls in the initial stages of wetting
because the cohesion force of molecule chains in PUA is much
bigger than the adhesion force between polymeric solution and
A nanoporous wall. Hence, when the wetting time is relatively short, nanowires with small head and big body are formed. With the increase of wetting time, the solution fills the nanochannel and forms nanowires, and length increases. The reasons are as follows: first, the flow rate of PUA-Eu prepolymer is faster than wetting rate in the nanochannels. Second, the adhesion force is much weaker than the cohesive driving forces. As the wetting time continues to increase, due to the high viscosity of the prepolymer, the flow rate is slow, and under the effect of the gravity, the nanowires present a big head and small body. When the wetting time is long enough, the prepolymer totally fills the pore of the AAO template and forms cylinder nanowires. It can be seen that when the wetting time is 12 h, nanowires with a uniform diameter are formed. The above results show the diameter, length, and shape of nanowires can be accurately controlled by the time of prepolymer solution passing through the pore. If prepolymer solution passes through the pore, the length of the nanowire can be as long as the thickness of the AAO template. Experiments demonstrate that wetting 12 h in the AAO template can prepare excellent nanowires via wetting method. The mechanism described in this study is not the same as those previously described.44,45

**Morphology of PUA-Eu Nanowires with Different Nanometer Sizes.** Figure 7 shows the PUA-Eu nanowires in AAO membrane with 160–200 nm nanochannels. As we know, ordered porous alumina templates have high surface energy and consist of ordered vertical pores with uniform pore size distribution. It can be clearly noticed that each pore was almost filled with PUA-Eu nanowires, and the diameters of PUA-Eu nanowires are smaller than the pores of AAO template because PUA-Eu nanowires produced certain volume shrinkage after curing in the nanochannels. The phenomenon is consistent with Zou’s research results.46 Because of polishing, the bottom surface of PUA-Eu nanowires is a little out of shape. The results indicate that PUA-Eu nanowires have been successfully formed in the AAO nanochannels.

**Luminescence Properties of PUA-Eu Nanowires.** To further understand the effect of the Eu complex content on the photoluminescence performances, the PUA-Eu nanowires with different diameters. It also can be found that the microscopic appearance of PUA-Eu nanowires array is regular and without defect. The TEM images of single PUA-Eu nanowire are shown on the right-hand side of Figure 8, which reveal that the diameter of a single PUA-Eu nanowire corresponds to that of the pore of AAO template. The outer surface of the PUA-Eu nanowires is smooth and the inner is solid. The diameters of the PUA-Eu nanowires are uniform from the top to the bottom, which confirmed that the formation of the PUA-Eu nanowires is uniform along the pores of the template. Moreover, with an increase of the diameter of the PUA-Eu nanowires, the color deepens because the electron beam through the PUA-Eu nanowires decreases.

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the different Eu complex content were prepared and the effects of Eu complex content on emission were investigated (shown in Figure 9a). The emission spectra of PUA-Eu nanowires are similar to those of the Eu complex (Figure 3a). The characteristic emission peaks at 591 and 616 nm correspond to the $^{5}D_0 \rightarrow ^{7}F_1$ and $^{5}D_0 \rightarrow ^{7}F_2$ transitions of the Eu$^{3+}$ ion, respectively. The luminescence intensity of the complex at 616 nm is distinctly stronger than the other emission wavelength and exhibits bright red light with good monochromaticity, which is in accordance with the Eu complex. The luminescence intensity of PUA-Eu nanowires increases gradually with the increase of Eu complex content, and there is no fluorescence concentration quenching within the range of Eu complex contents from 0.4 to 2.00 wt %. The reasons are as follows: (a) the content of the Eu complex is too little to induce the luminescence concentration quenching and (b) the Eu complex has been copolymerized with the macromonomer of PUA and is evenly distributed in the PUA. In addition, the relative intensity ratio of $^{5}D_0 \rightarrow ^{7}F_2$ and $^{5}D_0 \rightarrow ^{7}F_1$ increases as the amount of the Eu complex increases. In general, the intensity ratio is related to the symmetry of the coordinated geometry around Eu(III) ions. The results indicate that the copolymerization of the Eu complex and macromonomers has changed the local environment of Eu$^{3+}$ and lowers the degree of symmetry of the local environment.

In order to elucidate the origin of increasing intensity by increasing content of the Eu complex, the luminescence lifetime of the $^{5}D_0$ excited state has been studied. Figure 9b shows the excited state decay curves of the emission at 616 nm, under 395 nm excitation. The luminescence decays of PUA-Eu nanowires are well fitted by a bi-exponential function $I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, and the average lifetime values are calculated using the equation $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$, where $A_1$ and $A_2$ are the amplitudes of the two exponentials, that is, the fast and slow components, respectively. The obtained values for the average lifetimes are 0.499, 0.667, 0.698, 0.923, and 0.970 ms, respectively, for 0.4, 0.5, 0.8, 1.0, and 2.0 wt % of the Eu complex (listed in Table 2). The decay time gradually increases with increasing content of Eu complex. Moreover, the fluorescence lifetimes of all the PUA-Eu nanowires are longer than that of the Eu complex.
The fluorescence lifetime of nanowires is 133% higher than that of the Eu complex when the content of the Eu complex is 2.0 wt %. The results obtained show that the Eu complex is uniformly bonded onto the PUA without agglomeration.

In order to further research the influence of the material state on the fluorescence lifetime, PU-Eu plates and PU-Eu nanowires containing the 1.0 wt % Eu complex were synthesized under the same polymerization conditions. Figure 9c shows the fluorescence decay curve of PU-Eu plate (the thickness of the plate is 3.5 mm) and nanowires containing 1.0 wt % Eu complex under the same synthetic conditions. The luminescence decays of PU-Eu plate are well fitted by a bi-exponential function, and the obtained fitting curve equation is \( I(t) = 4008.428 \exp(−t/0.713) + 2.244 \exp(−t/0.004) + 3.544 \). The value obtained for the average lifetimes is 0.713 ms. Compared with the PU-Eu plate, the fluorescence lifetime of the PU-Eu nanowires (0.923 ms) increased by about 30%. This may be due to the small size effect of PU-Eu nanowires, which can increase the specific surface area of the material and make the Eu complex more uniformly dispersed in the nanowires, which is not easy to cause agglomeration. Therefore, the probability of fluorescence quenching is relatively small. In PU-Eu materials, the fluorescence property of PU-Eu nanowires is better than that of PU-Eu plates.

**CONCLUSIONS**

The aligned, vertical, and large-scale PUA-Eu nanowires were fabricated through in situ copolymerized PUA macromonomer and the Eu complex inside the AAO template. The morphology of PUA-Eu nanowires can be tuned by wetting time and the nanopore diameters. The diameters of PUA-Eu nanowires are smaller than the pores of AAO template for the reason of volume shrinkage. The PUA-Eu nanowires exhibit the characteristic emission of Eu\(^{3+}\) ion, and luminescence intensity can be strongly improved by increasing the Eu(III) complex amount. The change of luminescent properties of nanowires can be strongly improved by increasing the Eu(III) complex amount. The change of luminescent properties of nanowires can be strongly improved by increasing the Eu(III) complex amount. The change of luminescent properties of nanowires can be strongly improved by increasing the Eu(III) complex amount. The change of luminescent properties of nanowires can be strongly improved by increasing the Eu(III) complex amount. The change of luminescent properties of nanowires can be strongly improved by increasing the Eu(III) complex amount. The change of luminescent properties of nanowires can be strongly improved by increasing the Eu(III) complex amount. The change of luminescent properties of nanowires can be strongly improved by increasing the Eu(III) complex amount. The change of luminescent properties of nanowires can be strongly improved by increasing the Eu(III) complex amount.

**MATERIALS AND METHODS**

**Materials.** 2,2-Azo-bis-iso-butyro-nitrile (AIBN) was recrystallized from alcohol and dried by vacuum distillation. All the other reagents, including crotonic acid, Eu₂O₃, isophorone diisocyanate (IPDI), poly(ethylene glycol) 400 (PEG400), and 2-hydroxyethyl methacrylate (HEMA), dibutynil dilaurate (DBTL), and ethyl ether, were used as received.

**Characterization.** FTIR spectra were measured on a Tensor 27 FTIR (Bruker) spectrometer in the range of 400–4000 cm⁻¹. Excitation and emission spectra and fluorescence lifetime were obtained using a time-resolved and steady-state fluorescence spectrometer (FLS 980, Edinburgh Instruments, UK). The morphologies of PUA-Eu nanowires were investigated by FESEM (JSM-7001F) and TEM (JEM-2100). For FESEM, before measurement, samples were coated with a Au layer. For TEM, PUA-Eu nanowires were dispersed in ethyl alcohol and dropped onto copper grids. Single-crystal X-ray diffraction measurement was carried out with an Oxford diffraction Gemini E CCD equipped with a graphite crystal monochromator situated in the incident beam for data collection at 294 K.

**Synthesis of the Eu Complex.** The Eu(III) complex \([\text{[Eu}_3(\text{MeCH/CHCO}_2)_9(\text{H}_2\text{O})_4]/\text{H}_2\text{O}/\text{EtOH}]_n\) was fabricated according to the literature method. Briefly, 5 mmol of Eu₂O₃ and 40 mmol of crotonic acid was dissolved in 60 mL of distilled water, stirred, and heated under reflux at 90 °C, till the reaction was complete and filtered. The filtrate was heated to remove distilled water by vacuum distillation. The obtained powder was carefully washed with deionized water and ethyl ether at least 5 times and followed by drying in a vacuum desiccator for 6 h and then stored in a dryer. In order to research the structure and properties of the Eu(III) complex, the obtained powder was dissolved in a mixture of water/ethanol solution with different ratios at room temperature. Then, transparent crystals were separated out and characterized by single-crystal X-ray diffraction.

**Synthesis of the Prepolymer of PUA-Eu (PUA-Eu).** IPDI (0.04 mol, 8.8916 g) and PEG 400 (0.02 mol, 8.0000 g) were placed in a 100 mL round-bottomed flask and kept stirring 15 min at 25 °C. Then, 0.35 mmol (0.2210 g) of DBTL was added and the system was kept stirring at 25 °C for 20 min. A mixture of 0.04 mol (5.2056 g) of HEMA and 0.40 mmol (0.0663 g) of AIBN were subsequently added to the system and continue stirring below 20 °C for 30 min, and the PUA macromonomer with carbon–carbon double bonds was obtained. Then, a certain amount of the Eu(III) complex was added in the PUA macromonomer and stirred for 30 min. The prepolymer of PUA-Eu was synthesized. The experimental scheme for preparing the prepolymer of PUA-Eu is shown in Figure 10. The other relevant PUA-Eu prepolymer with different contents of the Eu(III) complex were obtained according to the same procedure. The mass percentages of the Eu(III) complex are 0, 0.4, 0.5, 0.8, 1.0, and 2.0% of the total mass of IPDI, PEG400, and HEMA.

**Fabrication of PUA-Eu Nanowires.** The PUA-Eu nanowires were fabricated by in situ free radical polymerization of prepolymer of PUA-Eu in the AAO nanomembranes. The experimental scheme for preparing nanoarrays is shown in Figure 10. The porous alumina template was covered on the top surface with a large drop (about 0.5 mL) of the PUA-Eu prepolymer. By means of capillary action, the prepolymer gradually entered the nanochannels of AAO and was left for 1, 3, and 12 h, respectively, to study the detailed growth process of nanowires in the nanochannels. Then, the PUA-Eu prepolymer was cross-linked and cured in the AAO nanocavities under different temperatures, 40, 50, 60, and 70 °C for 1 h, respectively, and 80 °C for 24 h. After removing the nanotemplate by dipping in NaOH solution (3 mol L⁻¹).
several times, the sample was washed with deionized water followed by drying in oven at 60 °C for 2 h, and the PUA-Eu nanoarrays were obtained. Other PUA-Eu nanoarrays were fabricated with different ratios of the Eu complex and different AAO nanotemplates by the same procedure.

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