Synthesis, Characterization, and Self-Assembly of Cationic Coumarin Side-Chain Polymer

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ABSTRACT: In this study, the synthesis of a novel cationic coumarin-containing polymer (C-CPA) was presented. C-CPA was examined optically using photoluminescence (PL) spectroscopy. The optical data suggested that they were promising blue-emitting materials mainly due to the coumarin chromophore on the side chain. Moreover, the synthesized cationic polymer was suitable for layer-by-layer electrostatic self-assembly thin film deposition from dilute polymer solution and multilayers were fully characterized by UV–vis spectroscopy, PL spectroscopy and atomic force microscope. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2667–2673, 2008

Key words: coumarin; fluorescence; polyelectrolytes; self-assembly; thin films

INTRODUCTION

Coumarin compounds are well known as fluorescence materials, laser dyes,[1] and nonlinear optical materials because of their high photons stability and photoluminescence (PL) efficiency.[2] They are of great interest in emerging applications including transmission, storage and display of information, antifake marks and especially molecular apparatus field.

It makes great sense that coumarin compound is connected to polymer via grafting reaction to produce nanoscale composite films with excellent luminescence properties, and further to prepare thin film luminescence apparatus from the former.

It is essential to select an appropriate polymer as main chain for the synthesis of these novel coumarin-containing functional polymers. Polymer matrices whose sides could graft small molecules mainly are polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), etc. In this study, with the purpose of connecting with novel coumarin's chloromethyl functional group, there must be a reactive group in the polymer matrix, such as hydroxyl or amino-group. A copolymer (CPA), synthesized with methyl methacrylate (MMA), 2-(dimethylamino) ethyl methacrylate (DM), 2-hydroxyethyl acrylate (HEA), *n*-butyl acrylate (BA), and styrene (ST), was chosen to be the grafting main chain because modified coumarin could be connected on it by quaternization and

PMMA has well film-forming characteristic, and the flexibility of the film could be good too. Moreover, hydroxyl, amino-group and ester group in CPA could act with indium-tin oxide electrode and enlarge their attach force so as to improve fastness of the film.

Since Decher and his coworkers[3] successfully synthesized the polyelectrolyte multilayer composite flat panel films based on molecular static adsorption by opposite charges firstly in 1991, electrostatic self-assembly (ESA)[4] techniques have attracted huge interest in nearly 2 decades due to the advantages of simpler procedure, higher stability of the resultant films, achieving molecular-level control for the deposition process and film structure, and realizing functionalization[5–13] to the films, etc. Therefore, ESA is one of the fastest developed techniques for obtaining nanoscale composite films, and has hitherto been used to make various functional thin film materials, such as systems of biomacromolecules,[14,15] inorganic nanoparticles,[16,17] dyes,[18,19] and luminescent polymers.[20–22]

In this study, to make use of the excellent luminescence properties possessed by coumarin compound, 3-(2-benzothiazolyl)-6-chloromethyl-coumarin was grafted on the main chain of CPA by a quaternization reaction to form positive-charged quaternary ammonium luminescence polymers with different proportions of coumarin on the side-chain. The coumarin-containing polymer (C-CPA) was then used as luminescence layer along with nafion 117 as negative-charged cavity transfer layer to make flexible and high luminescent efficiency nanoscale composite films based on ESA technique directly.

To our knowledge, little work has been reported in this filed up to now. Research was conducted in our laboratory for the fabrication of luminescent

ultrathin films, which were built by ESA of couma-rin side-chain polymers. It is make great sense for the studying on luminescent materials.

Scheme 1 Synthesis route of coumarin side-chain poly-mer (C-CPA).

EXPERIMENTAL

Materials

Reagent-grade samples of acrylic resin monomers including MMA, DM, HEA, BA, and ST were pur-chased from Beijing East Chemical Industry Factory (Beijing, China) and distilled before use. 2-amino-thiophenol was purchased from New Jersey, USA. Analytically pure 2,2′-azobisisobutyronitrile (AIBN), tetrahydrofuran (THF), 2-hydroxybenzaldehyde and malononitrile were supplied by Chengdu Kelong Chemical and Technology Reagents (Chengdu, China). Nafion 117 Solution was obtained from Fluka (Switzerland). Quaternized poly-2-(dimethyl-amino) ethyl methacrylate (PDM) was chemically synthesized using DM and bromoethane.

Instruments

A XRC-2 microscopic melting point apparatus (Sichuan University Plant, Chengdu, China), a differ-ential scanning calorimeter (DSC) (200 PC, netzsch, Germany), a high performance liquid chromatogra-phy (HP1100, Agilent, USA), a Nicolet 1700SX Fou-rier transform infrared spectrometer (all samples grounded in KBr), a UV–vis spectrometer (TU-1901, Bejing Puxi General Instruments, China), a Fluores-cence spectrophotometer (Hitachi F-4500, Japan), and a atomic force microscope (AFM) (Seiko SPA-400, Japan) were employed in our work.
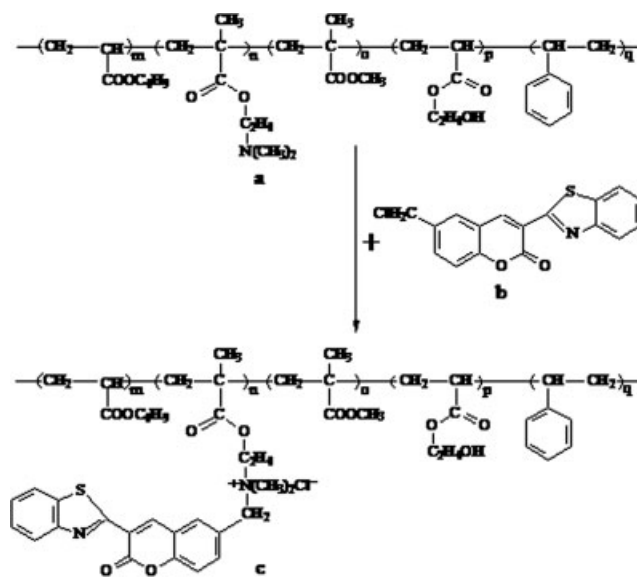
Synthesis

Synthesis of the Copolymer (CPA)

Isopropanol was added into a 250-mL three-neck flask as solvent. When circumfluence just began, a mixture of monomers (MMA, DM, HEA, BA, and ST) and ini-tiator (AIBN) confected in projected proportion was fed continuously into the flask using dropping funnel and finished in 6 h. The resultant products were spilled when temperature cooled off to 40–50°C. The details of the process refer to literature.[23] Red–brown and sticky CPA was synthesized in this way corre-spond to 16.29% of DM added as starting material. The products have well film-forming characteristic. The molecular structure is given in Scheme 1(a).

Synthesis of 3-(2-benzothiazolyl)-6-chloromethyl-coumarin

The title compound was synthesized from 2-hydroxy-benzaldehyde, 2-aminothiophenol and malononitrile according to the previous literatures procedure.[24]

m.p.: 236–237°C; IR (KBr): 3042.20 (Ph-H), 2921.19 (CH_3), 1718.59 (versus, C=O), 1614.68, 1572.48 (C=C), 1456.39 (C—H), 1165.82 (C—O), 765.68, 692.29 cm^{-1} (δ Ph-H). The molecular structure is shown in Scheme 1(b).

Synthesis of cationic luminescent polymers (C-CPA)

CPA (1.0 g), 3-(2-benzothiazolyl)-6-chloromethyl-cou-marin (0.1 g) and absolute THF (50 mL) were put into 100-mL flask equipped with a stirrer, a condenser and a drying tube. 0.4 g anhydrous Na_2CO_3 was fed into the mixture after the solids were dissolved by mixing round. Then the system was submerged in a water bath carefully controlled at 67°C. The resulting mixture was refluxed for 36 h, cooled down, and then filtrated. Fifty milliliters of petroleum ether was added into the filtrated stock solution with continu-ous stirring. Some brown–yellow precipitates were formed as preform. The rough products were then purified by means of dissolution/deposition in THF/ petroleum ether by turns. The resultant brown–yellow product (C-CPA) was dissolved in THF with the concentration of 2 mg mL^{-1}. The molecular struc-ture is given in Scheme 1(c).

Fabrication of multilayer films

About 2 mg mL^{-1} of PDM [see Fig. 1(a)] solution was prepared with ammonia solution as solvent and 2 mg mL^{-1} of Nafion 117 [see Fig. 1(b)] solution was made with distilled water.

Cleaned quartz template (45 mm × 12 mm × 1 mm) was immerged into Piranha solution [V(H_2O_2) : V(H_2SO_4) = 3 : 7], heated and seethed until no bubbles
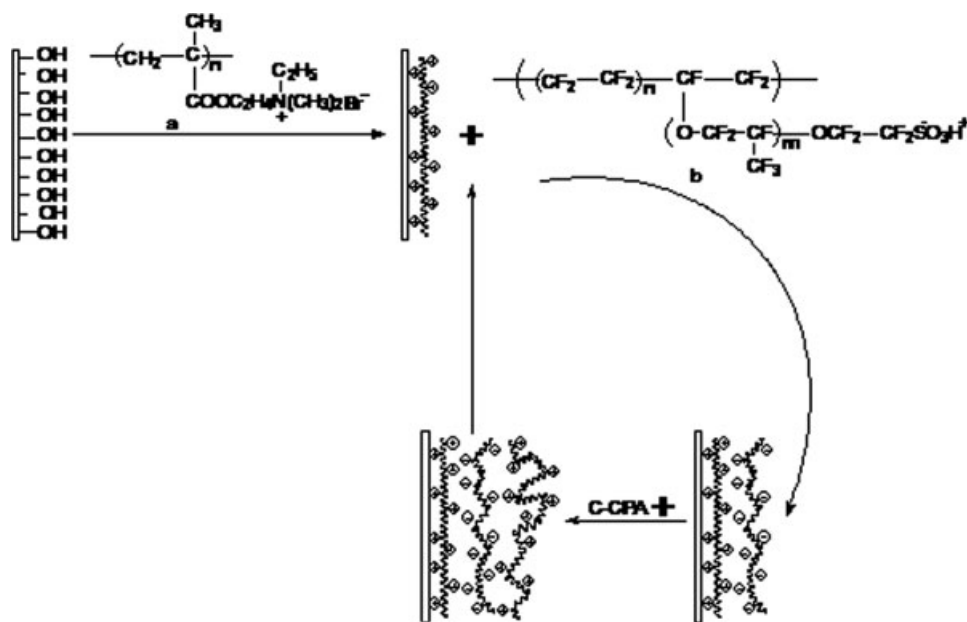
Figure 1 Scheme of constructing nanoscale composite films by ESA technique.

overflowed to make the surface of quartz template rich of —OH groups. Then washed with deionized water three times and dried at 100°C in vacuum for 1.5 h. Nanoscale composite films were then built by ESA technique under steps below. (The process is shown in Fig. 1).

1. A flexible substrate was obtained by immersing the quartz template dealt with by steps above into 2 mg mL^{-1} PDM solution for 20 min. In this process, PDM molecules having positive charges were adsorbed onto the surface of the quartz template due to electrostatic force, then took out the substrate and immerged into deionized water for 3 min to wash away the attachments on its surface, and then dried at 45°C in vacuum oven for 1.5 h.
2. Sequentially, the flexible substrate was immerged into Nafion 117 solution for 20 min, retrieved and immerged into deionized water for 3 min to scour off the attachments on its surface, then dried at 45°C in vacuum oven for 1.5 h.
3. Again, the treated flexible substrate was immersed into C-CPA solution for 20 min, then took out and immerged into deionized water for 3 min to remove the attachments on its surface, and dried in the same way mentioned above.

As a result, the first bilayer film was assembled in this way. The two to three steps were repeated, until 10 bilayers film was built.

In each circulation of preparation processes of the films, UV–vis absorption spectra were used to track and analyzed the growth processes of self-assembly films. PL spectra of the resrltant materials were mensurated by fluorescent spectrum apparatus. Atomic force microscopy was used to observe morphologies of the composite films and analyze the microcosmic process of the ESA.

RESULTS AND DISCUSSION

Characterization of CPA and C-CPA

Purification of C-CPA

C-CPA can dissolve in many common solvents, so it is of importance to select appropriate solvent for purification with method of dissolution/deposition. THF/petroleum ether system was chosen to purify primary C-CPA. The results of control experiments showed that no fluorescence was found on the simple mixture of 3-(2-benzothiazolyl)-6-chloromethyl-Coumarin and CPA after five cycles of dissolving and depositing with THF/petroleum ether system. However, very strong fluorescence of C-CPA could be observed even after 10 such cycles used for rough C-CPA products. It is proved that coumarins have already been grafted on the main chain of the polymer.

FTIR spectra of CPAand C-CPA

The FTIR spectra of CPAand C-CPAare presented in Figure 2. CPA (a) IR (KBr): 3403.85 (versus, OH), 2964.43 (versus, CH$_3$), 1731.83 (versus, C=O), 1603.97 (C=C), 1455.25 (C—H), 1163.52 (C—O), 761.94, 702.74 cm^{-1} (δ Ph-H); C-CPA (b) IR (KBr): 3532.08 (OH), 2957.20 (s, CH$_3$), 2873.81, 2772.19 (N—C), 1731.95 (versus, C=O), 1601.21 (C=C), 1453.82 (C—H), 1166.20 (C—O), 761.79, 702.40 cm^{-1} (δ Ph-H).
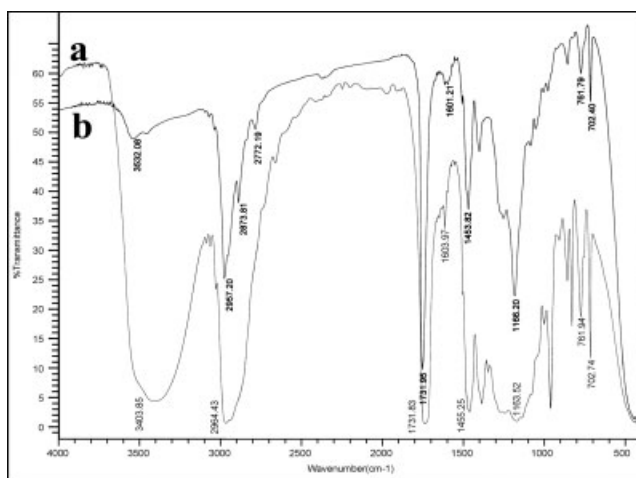
**Figure 2**   FTIR spectra of CPA (a) and C-CPA (b).

It is clear that C-CPAshows a stretching vibration mode of quaternary ammonium salt groups at around 2772 and 2874 cm^{-1}, whereas such peaks are absent from the spectrum of CPA. It is well known that there is a big lactone ring in coumarin compound. As shown in Figure 2, after the introduction of coumarin onto CPA, a strong characteristic peak of lactone appears at around 1731 cm^{-1}. All these facts reflect that the coumarins have already grafted on the copolymer through quaternization reaction.

Molecular weight and molecular weight distribution of CPA and C-CPA

The number-average molecular weight ($\overline{M}_n$), the weight-average molecular weight ($\overline{M}_w$) and distribution of the polymers were determined by gel permeation chromatography (GPC, Agilent 1100 chromatograph) at 35°C. THF was used as the eluent at a flow rate of 1.0 mL min^{-1} and standard PS as the reference. (cf. Table I). The results indicated that either number-average molecular weight ($\overline{M}_n$) or weight-average molecular weight ($\overline{M}_w$) of C-CPA was larger than that of CPA due to the grafting of coumarin. The distribution index D remained at 2.5 around, which implied the same molecular weight distribution before and after grafting reaction for CPA and C-CPA, respectively. From the results of calculation, average number of coumarin grafting on a CPA molecule in this work should be $(1.63 \times 10^4 - 1.31 \times 10^4)/327.5 = 9.77$, and the relevant theoretical grafting data is $(1.31 \times 10^4$

TABLE I
The GPC Results of CPA and C-CPA

	$\overline{M}_n$ ($\times 10^4$ g mol^{-1})	$\overline{M}_w$ ($\times 10^4$ g mol^{-1})	D ($\overline{M}_w / \overline{M}_n$)
CPA	1.31	3.41	2.59
C-CPA	1.63	4.18	2.57
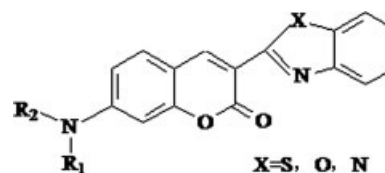
Scheme 2   Molecular structure of coumarin used as laser dye.

$\times$ 16.29%)/157 = 13.59, where 16.29% is the DM content in CPA, and 157 is the molecular weight of DM. So it is convinced that the coumarins have already been grafted on the main chain of CPA and the grafting rate was roughly 71.89%.

Glass transition temperature (T_g) of CPA and C-CPA

Glass transition temperature (T_g) was determined by DSC for CPAand C-CPA, respectively: $T_g = 52.9$°C for CPA; $T_g = 77.7$°C for C-CPA. The results show that T_g will go up because of the weakened flexibility of the polymer chain after introducing of the rigid conjugated system of coumarin.

Fluorescence of 3-(2-benzothiazolyl)-6-chloromethyl-coumarin and C-CPA

Usually, coumarins used as laser dyes have different functional groups like benzoxazolyl and amino-group located at c-3 and c-7, respectively, in the host. These functional groups can conjugate with lactone ring on the coumarin to form a push–pull electronic system (Scheme 2). Its PL commonly is blue–green to yellow–green. To obtain modified blue-emitting PL materials, a benzothiazolyl was introduced into c-3 and the amino-group in c-7 was removed from the system to reduce the conjugated degree, so that its PL spectrum could shift to the blue band. Figure 3 shows the emission spectra peaks of the coumarin and C-CPA in different states: 455.0 nm for solution of the
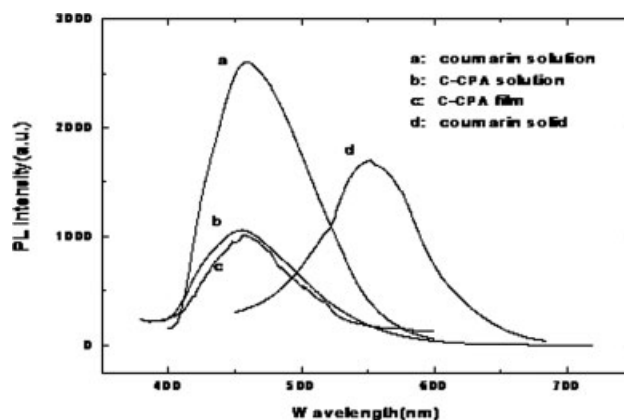

Figure 3   PL spectra of coumarin and C-CPA.

coumarin; 551.8 nm for solid of the coumarin; 457.8 nm for C-CPA solution, and 459.2 nm for C-CPA solid films. The results suggest the achievement of the purpose mentioned above.

Multilayer assembly

Growth of self-assembly films

As the self-assembly films of C-CPA/NAFION-117 were being formed, the growth process of the films was tracked by UV–vis absorption spectra [cf. Fig. 4(a)]. The peak appeared at 365.0 nm is caused by coumarin group grafted on C-CPA, because N, S, O atoms along with the double bonds form a large conjugated structure in coumarin leading $n \rightarrow \pi^*$ electron transitions and bring about an R band absorption, which results in the emergence of the strong and wide peaks in UV–vis patterns. Figure 4(a) gives the linear relationship between the maximum UV absorbance (365.0 nm) and the number of bilayers in their growth processes, which shows clearly that C-CPA/NAFION-117 actually has realized the layer-
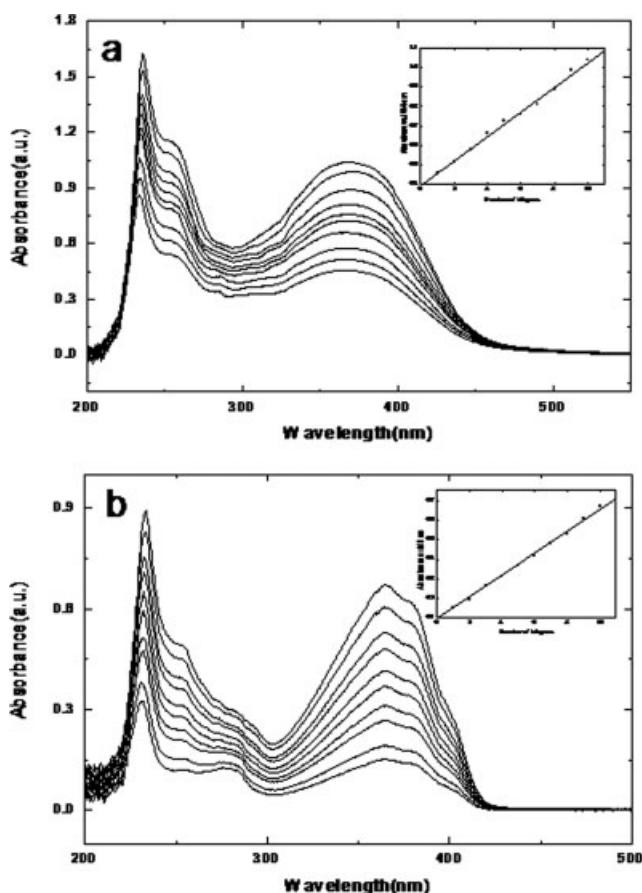
Figure 4 UV–vis absorption spectra of multilayer films of C-CPA/NAFION-117 [(a) 16.29% DM and (b) 9.69% DM] and the relationship between absorbance at 365 nm and bilayer number.
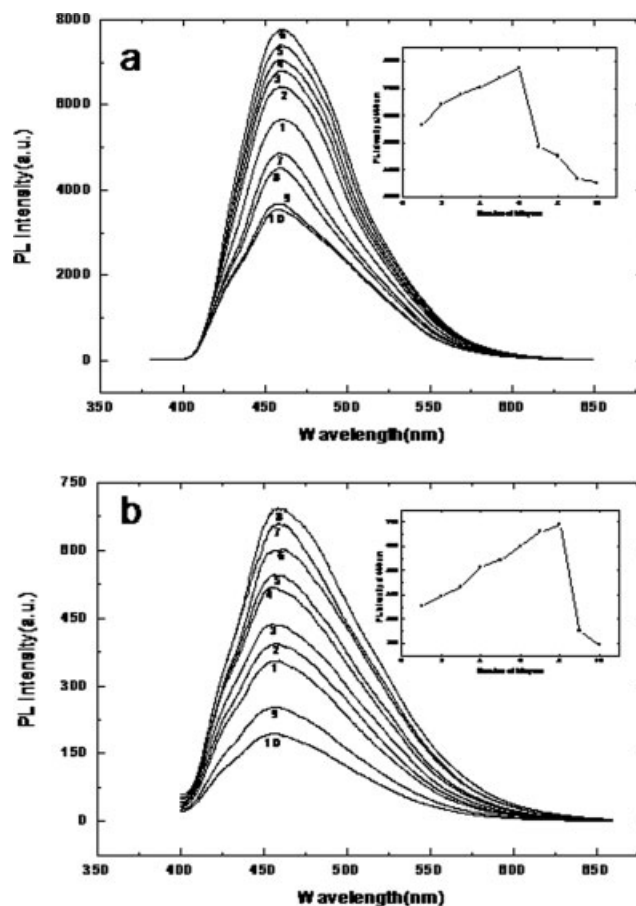
Figure 5 PL spectra of multilayer films of C-CPA/NAFION-117 [(a) 16.29% DM and (b) 9.69% DM] and the relationship between PL intensity at 459 nm and bilayer number.

by-layer ESA. The same result appears in Figure 4(b), in which C-CPA was synthesized corresponding to 9.69% of DM added as starting material, and these results indicate the repeatability as expected.

Fluorescence properties of self-assembly films

The fluorescence spectra of the self-assembly films of C-CPA/NAFION-117 are shown in Figure 5(a). All of the wavelengths corresponding to the strongest PL intensity locate at 459 nm around. In Figure 5(a), when the bilayer number of the film of C-CPA/NAFION-117 increases from 1 to 6, the fluorescence intensity increases, but when the number is larger than 6, the intensity sharply decreases. This may attribute to fluorescence quenching mechanism.[25–27] Possibly, when the bilayer number reaches 7, the amount of the coumarin containing in the film are too high, and fluorescence intensity drops instead. To illustrate this phenomenon, the polymer main chain structure was changed, that is, C-CPA was
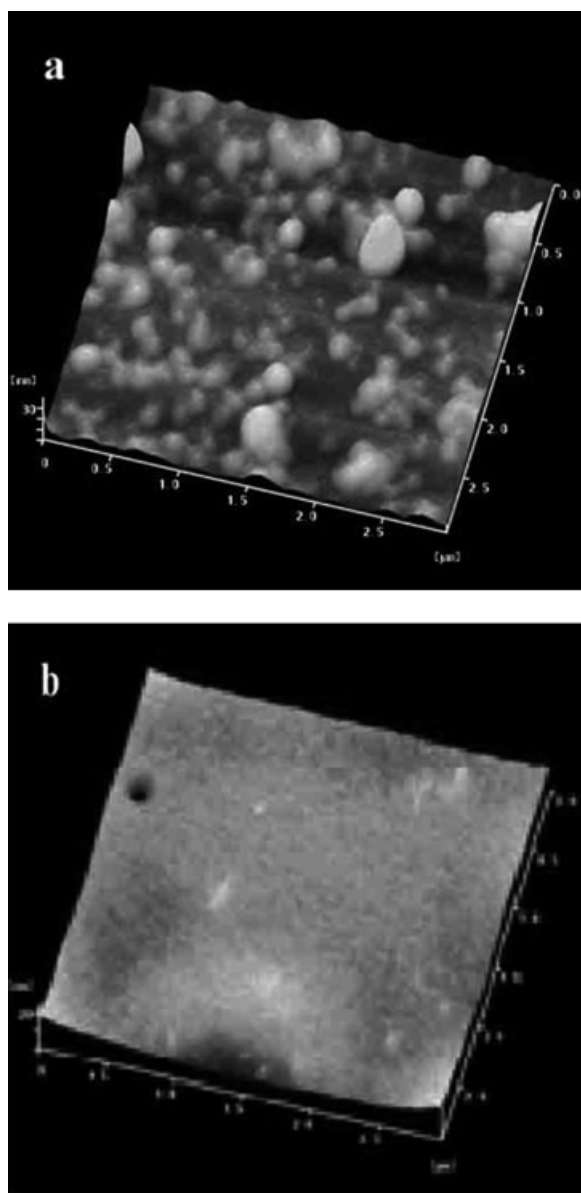
Figure 6 The appearance of assembled films. (a) one bilayer film and (b) 10 bilayers film.

synthesized corresponding to 9.69% of DM added as starting material. The results of control experiments show that as the bilayer number of the film increases from 1 to 8, the fluorescence intensity is increasing, then when the number increases further, the fluorescence intensity decreases instead [cf. Fig. 5(b)]. The details suggest that the fluorescence quenching is delayed in comparison with that shown in Figure 5(a) due to the less amount of coumarin in C-CPA as the content of DM changed from 16.29 to 9.69%. In Figure 5(b), the wavelengths corresponding to the strongest PL intensity also locate at 459 nm around, which means that the amount of the coumarin containing in the film are irrelevant with the wavelength corresponding to the strongest PL intensity.

Morphology of self-assembly films

AFM observations are presented in Figure 6. The morphology of the first bilayer film of C-CPA/NAFION-117 is given in Figure 6(a). There are some obvious disfigurements existing on the surface of the film. However, the surface becomes smoother on the 10 bilayers film sample [Fig. 6(b)]. This is attributed to the reason that ESA process can repair the disfigurements automatically. Regardless of the disfigurements arising from rough substrates, chemical noneven surface or occasional defects caused in the adsorption process, the self-assembly film could be gradually repaired as the adsorption process continued.

CONCLUSIONS

A novel cationic luminescent polymer (C-CPA) was synthesized by grafting the modified coumarin compound on CPA. UV–vis absorption spectra were employed for the composite films to track the process of ESA, and the absorbance intensity increased linearly with the number of bilayer on the substrate. The fluorescence spectra proved that the self-assembly films were blue-emitting materials, and the fluorescence quenching would appear when the number of bilayers increased to some extent. The disfigurements of the film could be repaired automatically in the process of constructing nanoscale composite films by ESA technique.

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