Luminescent Rare-Earth Multilayer Chelates from Segmented Poly(urethane ureas)

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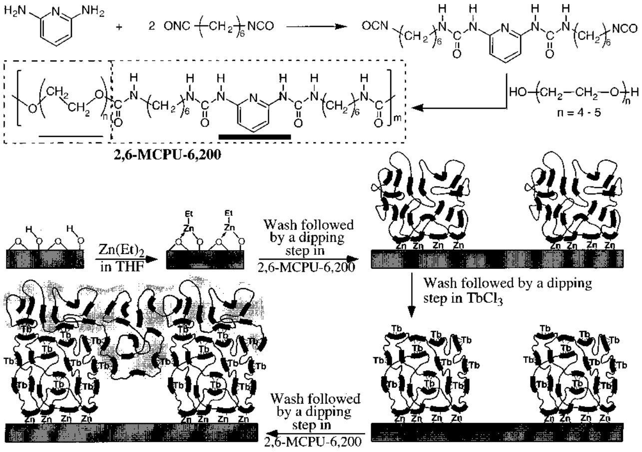
Self-organization of block copolymers on surfaces has been a topic of intense scientific and technological interest.[1−4] Thermodynamic considerations usually favor placement of the lowest surface energy block in contact with air, pushing the remaining block(s) below the interface.[5,6] Utilizing the ability of block copolymers to phase separate, in conjunction with the versatile growth realized through alternative self-assembly, construction of 2-D quantum-confined structures and nanosized microelectronics/storage media can be greatly simplified.[7,8] In an effort to realize polymeric systems that could potentially exhibit such complex surface architectures, this paper describes the use of metallorganic self-assembly[9,10] of a poly(urethane urea)−*(block)*−poly(ethylene glycol)) copolymer with Tb^{3+}, a rare earth-metal fluorescent cation.

Scheme 1. Synthesis of the 2,6-MCPU-6,200 Segmented Poly(urethane urea) and Its Subsequent Metal-Chelating Self-Assembly Process[a]



[a] This simplified illustration is further elaborated in the text.

Scheme 1 illustrates the synthesis and self-assembly methodology utilized in this study. The self-assembly technique uses terbium chloride and a *m*etal-*c*helating segmented *p*oly(*u*rethane urea) (2,6-MCPU-6,200) based on 2,6-diaminopyridine and 1,6-diisocyanato hexane that has been chain-extended with α,ω-hydroxy-terminated poly(ethylene glycol) of 200 molecular weight. Both synthesis and self-assembly were performed in organic solvents. The polymer molecular weight was determined via size exclusion chromatography to be 61 kDa with respect to polystyrene standards in dimethyl formamide (DMF), with a polydispersity of 1.5. Pre-cleaned quartz or silicon (with native oxide) substrates were activated with diethyl zinc in inert atmosphere.[11] The self-assembly consisted of 5 min alternating immersions in a 10^{-6} M solution of 2,6-MPCU-6,200 in a mixture of pyridine and chloroform (40/60 v/v) and a 10^{-3} M solution of $TbCl_3$ in THF. Excess reagents were removed by rinsing these assemblies in freshly distilled chloroform for 10 min between each dip. This 30 min sequence (dip cycle) was repeated to form multilayers.

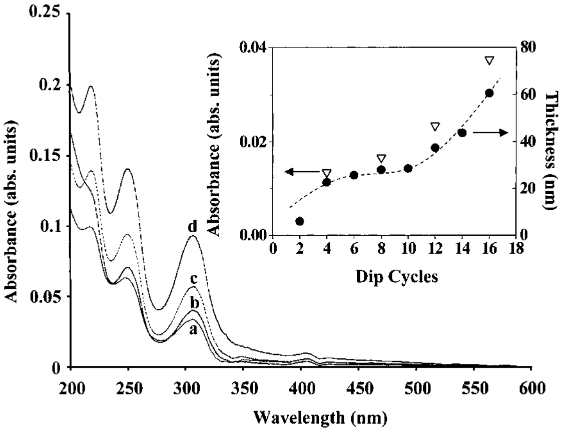


Figure 1. UV−vis spectra of Tb^{3+}/2,6-MCPU-6,200 self-assembled chelate films on quartz substrates; (a) 4, (b) 8, (c) 12, and (d) 16 dip cycles. Inset: Ellipsometrically determined film thickness and UV−vis absorbance at 309 nm, plotted as a function of dip cycles.

The inset in Figure 1 illustrates film thickness as a function of dip cycles as determined by spectroscopic ellipsometry. This is in agreement with the increase in absorbance, as shown in Figure 1, which is also indicated in the inset by plotting the first absorption maxima with respect to dip cycle. This growth pattern appears to be slightly more complex than in previously reported assemblies, where initial slow growth rates have been attributed to poor surface anchoring.[11] Figure 2 depicts the typical surface topographies for 2-, 4-, 6-, and 8-dip cycle films. After 2 dip cycles, small globules of polymeric metal chelate dominate the surface terrain of the silicon substrate. The average globule size (ellipsoids ~20 × 50 nm in lateral size and ~6 nm in height) appears to be approximately that of individual 2,6-MCPU-6,200 polymer coil, assuming an average density of 1.25 g/cm^3.[12]

Optimizing the concentration and solvent strength of the 2,6-MCPU-6,200 solution was necessary to keep the polymer in solution but not dissociate the Tb^{3+}/2,6-MCPU-6,200 complex as it assembles on the substrates. Pyridine/chloroform is a good/bad solvent mixture, which is optimal for deposition of this polymer at 40% (vol.) pyridine. Increasing the chloroform content resulted in slow precipitation of the polymer from the solution. Alternatively, increasing the pyridine content resulted in slower growth of the assembled chelate with Tb^{3+}. Thus, it is likely that this solvent mixture is close to the θ-solvent condition, where

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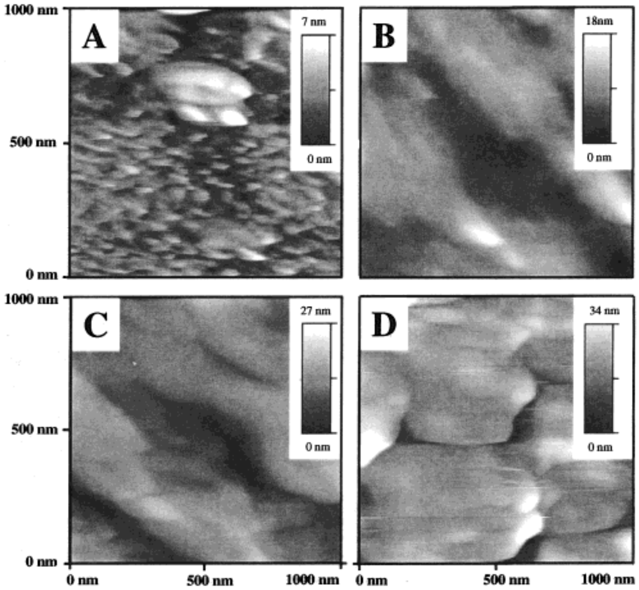

Figure 2. Representative atomic force micrographs of the 2 (A), 4 (B), 6 (C), and 8 (D) dip cycles films on siliconsubstrates.

interactions with the solvent are minimal and the polymer exists in a globular configuration. This could explain, in part, the morphology witnessed in Figure 2A. As more dip cycles are carried out, these globules grow in both the lateral and vertical directions, to form diffuse islands, as illustrated in Figure 2(B and C). This growth pattern further proceeds to the point where the islands begin to fuse and attempt to seal up the defects (Figure 2D), with additional layers growing more rapidly, as indicated in Figure 1.

Room temperature (25 °C) contact angle measurements were performed by means of the sessile drop technique[13] on 2-, 4-, 6-, 8-, 10-, and 12-dip cycle films. Terminating the film deposition with 2,6-MCPU-6,200 (last dip), resulted in highly hydrophilic surfaces, with contact angles of less than 30°. This is consistent with the block copolymer organized in such fashion that the soft hydrophilic PEO segments are pushed to the film surface (see Scheme 1).[14] On the other hand, terminating the film deposition with $TbCl_3$ resulted in contact angles $40 \pm 2°$. Spin-casting films of 2,6-MCPU-6 (a polymer with only the hard segments) from DMF resulted in films exhibiting contact angles $43 \pm 4°$, with or without Tb^{3+} chelation. The latter suggests that the dipping step in the THF solution of $TbCl_3$ reorganizes the adsorbed polymer by placing the chelating hard segments at the outer surface (see Scheme 1). Thus, the surface is prepared for the next layer, where 2,6-MCPU-6 finds ample Tb^{3+} sites to chelate. The initial $ZnEt_2$-stimulated growth however, is effective only for the first immersion in 2,6-MCPU-6 solution that takes place in the glovebox. Upon exposure to atmospheric conditions, the unchelated Zn−Et sites are transformed to chelation-inert Zn−OH sites, offering an explanation to the island type of growth pattern observed in Figure 2.

Due to their characteristically bright and narrow-band fluorescent emission, rare-earth metal chelates have found many important applications.[15] Figure 3 illustrates the fluorescence of the Tb^{3+}/2,6-MCPU-6,200 assemblies as a function of dip cycle. The strong green emission with narrow maxima at 490, 546, 585, and 620 nm arises from the $^5D_4 \rightarrow {}^7F_j$ ($j = 6, 5, 4, 3$) electronic transitions of Tb^{3+} respectively.[16] This involves intersystem crossing from the singlet excited state to the lowest triplet state on the ligand, followed by intramolecular energy transfer from the ligand to the highly localized 4f orbital levels of the rare-earth metal ion.[17] The presence of carbonyl moieties in the chelate ligands has been proven to be instrumental for facile intersystem crossing.[18,19]

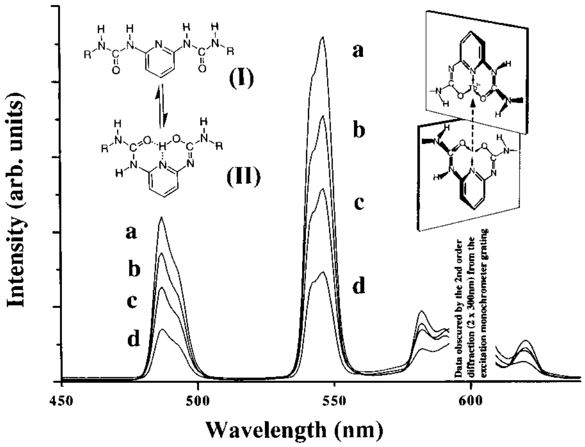

Figure 3. Photoluminescence spectra of the 4 (a), 8 (b), 12 (c), and 16 (d) dip cycles films. Inset illustrates two isomeric states of the 2,6-diamino-urea pyridine moiety, along with a three-dimensional representation of the chelation center.

A broad absorption peak at 310 nm was visible in the UV−vis spectrum of the unchelated 2,6-MCPU-6,200 in DMF. Over the course of approximately 2 days, this peak gradually resolved into two distinct absorbance peaks with maxima at 283 and 322 nm. This could be the result of enolization of the diurea moiety, as shown in the left inset of Figure 3. Intramolecular H-bonding stabilizes the more highly conjugated enol **(II)** isomer. Polar aprotic solvents such as DMF, gradually disrupt the intramolecular H-bonding to yield the keto **(I)** isomer during solvation. Chelation of terbium results in the disappearance of the 283 nm absorption peak, suggesting that the chelating moiety is in its enolized form.[20] Empirical molecular simulations[21] suggest that the most energetically favorable geometry involves two ligands in their enolized form **(II)**, interacting with terbium as depicted in the right inset of Figure 3. X-ray photoelectron spectroscopy provided further evidence for this stoichiometry, revealing a 1:1 atomic ratio of Tb to Cl in the self-assembled film. Although chelation of Tb^{3+} with the PEO segments cannot be excluded at present, control experiments with mixtures of PEO and $TbCl_3$ suggest that such chelations do not contribute to the photoluminescence spectra in Figure 3. More work is underway to elucidate the growth and extent of phase separation in these assemblies via the use of copolymers of varying composition and molecular weight.

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