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Study on self-assembly properties of aryl-alkyl hyperbranched polyesters with carboxylic end groups

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Summary

Carboxylic ended aryl-alkyl hyperbranched polyester poly(5-hydroxyethoxyisophthalic acid) (PHEIA) was synthesized and employed for an electrostatic layer-by-layer self-assembly procedure, in which poly(diallydimethylammonium chloride) (PDAC) was used as the polyanion while PHEIA acted as the polycation. From both aqueous solution and water-THF mixture of PHEIA, self-assembly films have been successfully formed as monitored by UV-Vis spectroscopy and contact angle measuring device. In the self-assembled surface where PHEIA acted as outmost layer, sphere-like particles with uniform diameter was observed by Atom Force Microscope (AFM). This phenomenon should be attributed to the aggregation of PHEIA. Furthermore, the layer-by-layer self-assembly procedure provided a favorable method for adjusting the hydrophilicity of the substrate without much interpenetration between these two polyelectrolyte layers.

Introduction

Layer-by-layer (LBL) adsorption process was firstly developed by Decher in 1991 to prepare ordered thin films[1]. By alternately dipping a substrate into dilute solutions of polyanions and polycations, uniform multilayers can be self-assembled on a charged substrate[2,3]. As a simple and powerful technique, LBL has several important advantages, such as the high film stability and inexpensive processing. Thus this technique has potential application for preparing ordered nano-composite multilayer films.

With special three dimensional architectures and plenty of functional end groups, dendritic polymers, including dendrimers and hyperbranched polymers, have attracted great attention during these years[4]. It is suggested that these highly branched polymers could be applied as a new kind of polyelectrolytes in preparing self-assembly films through LBL technique. By this process, the assembly films have been effectively prepared from dendrimers [5]. However, the complexity in the preparation of dendrimers would become a problem for their application.

Compared with dendrimers, hyperbranched polymers have many similarities in structure and properties but is much more easily to be prepared. Traditionally, hyperbranched polymer can be synthesized by one-step polymerization. The addition of core monomer and the careful control of the reaction condition may give out a product with more perfect structure. In a recent study, hyperbranched polymers have been applied as surface modified materials [6]. However, to our knowledge, the utility of hyperbranched polyelectrolytes in preparing assembly films by LBL technique were seldom reported [7].

In the present study, an aryl-alkyl hyperbranched polyester with carboxylic endgroups was synthesized and used to prepare assembly films by LBL technique. The preliminary study on the properties of the films was undertaken.

Experimental

All solvents were used directly as purchased without further purification unless otherwise indicated. 5-Hydroxy isophthalate was purchased from New Jersey, USA. 20% solution of poly (diallydimethylammonium chloride) (PDAC, MW: 200,000-350,000) was received from Aldrich. ^{1}H-NMR spectra were recorded by UNITY-200 spectrometer using the DMSO/solvent signal as an internal reference. Differential scanning calorimetric (DSC) measurements were carried out by DuPont-2400 DSC plus module. Thermogravimetry analyses (TGA) were done by TGA-2050 module. Viscosity measurements were made by an Ubbelohde viscometer in a constant temperature bath at 30°C. The growth of polyanion/polycation bilayers was recorded with UV-vis spectrometer (Perkin-Elmer Lambda Bio-40). The contact angle of water on the films was measured with a contact angle measuring device (Dataphysics, OCA-20). The surface of the film was observed by AFM (NanoScope IIIa, tapping mode).

Preparation of 5-hydroxyethoxyisophthalic acid (HEIA)

HIA was esterified by propanol in the presence of H_2SO_4 in 94% yield. The reaction of the product dipropyl (5-hydroxy) isophthalate with 2-chloroethanol in the presence of anhydrous potassium carbonate and potassium iodide gave out dipropyl (5-hydroxyethoxy) isophthalate in 35% yield. After hydrolyzed in the mixed solvent of THF and water, 5-hydroxyethoxyisophthalic acid (HEIA) was obtained in 88% yield. mp: 200~203°C. ^{1}H-NMR (in ppm): 3.75(2H, $CH_2C\underline{H}_2OH$), 4.05(2H, $C\underline{H}_2CH_2OH$), 4.85 (1H, OH), 7.6(2H, aromatic), 8.0(1H, aromatic), 13.0(2H, COOH).

Polycondensation of HEIA

With $Zn(OAc)_2$ as catalyst, the melt polycondensation of HEIA was taken place at 225~228°C under vacuum (<2mmHg). The ^{1}H-NMR(in ppm) for PHEIA: 4.5(2H, $PhOC\underline{H}_2CH_2$), 4.8(2H, $PhOCH_2C\underline{H}_2$), 7.8 (2H, aromatic), 8.1 (1H, aromatic), 9.8(1H, COOH). T_g was determined to be 176°C by DSC. By TGA analysis, the decomposition onset temperature was found to be 414°C.

Titration of PHEIA

PHEIA was dissolved in NaOH aqueous solution with the repeat unit concentration of 0.5mmol/L and pH=11. The titration curve of PHEIA was obtained by rightly dropping of 10mmol/L HCl according to the change of pH of the solution with the amount of HCl used.

Multilayer Fabrication

PDAC was diluted to a 0.1 mmol/l concentration (repeat unit) with Milli-Q water (resistance>18MΩcm) and used as polycations. Carboxylic ended PHEIA was used as polyanions and was dissolved in Milli-Q water with a 0.1 mmol/l concentration (repeat unit). Suitable amount of NaOH was added to increase the solubility of the polyanions. The pH values of PHEIA solutions were adjusted with the addition of HCl and NaOH.

Quartz slides(50 mm×14 mm×0.8 mm) were used as adsorption substrates and were treated as follows. The slides were sonicated in 98% H_2SO_4/30% H_2O_2 solution (piranha solution) for 1 h and washed with excess Milli-Q water for several times and then sonicated in H_2O/ H_2O_2/NH_4OH (5:1:1) solution for 1h followed with thorough rinsing and dried with air stream.

A freshly treated quartz slide was alternately dipped in PDAC and PHEIA solutions each for 10 min. After each dipping, the slide was washed with excess Milli-Q water for 2 min and dried with air stream. The formed assembly films were determined with UV-vis spectrometer and a contact angle measurement meter (Dataphysics, OCA-20).

Results and discussion

Synthesis of PHEIA

Monomer 5-hydroxyethoxy isophthalic acid (HEIA) was firstly synthesized starting from 5-hydroxy isophthalic acid (HIA) with 2-chloroethanol as alkylating agent[8,9]. The thermal polycondensation of HEIA was performed under vacuum at 225~228°C for a desire period[10].The reaction time was found to affect the properties of the products considerably. As shown in table 1, longer reaction time gave out products with higher molecular weight and consequently lower solubility both in organic and alkali aqueous solution. Considering the solubility, the sample of No. 1 was selected for the following investigation.

Table 1. Effects of the reaction time on the properties of the products

No.	Time ^{a}/hr	$[\eta]^b$/ $(dL \cdot g^{-1})$	M_η^c $/10^4$	solubility		
				THF	DMF	NaOH solution
1	2	0.12	1.3	slowly	slowly	easily
2	3	0.15	2.0	slowly	slowly	normal
3	4	0.24	8.0	partially	partially	slowly

[a] reacted at 225~228□ under vacuum

[b]. measured in DMF at 30.0□

[c] according to the relationship between [η] and M_η developed by Turner et al[10]

Measurement of PHEIA solution

With plenty of terminal carboxylic acid groups, PHEIA was dissolved completely in NaOH aqueous solution. The titration curve in Figure 1 implied that the acidity of the carboxylic groups in PHEIA was relatively the same as the system reported by Kim and Webster [11]. PHEIA was stable in the solution and no precipitate was found during the titration course.

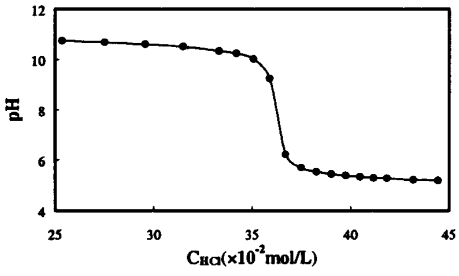


Figure 1. The titration curve of PHEIA

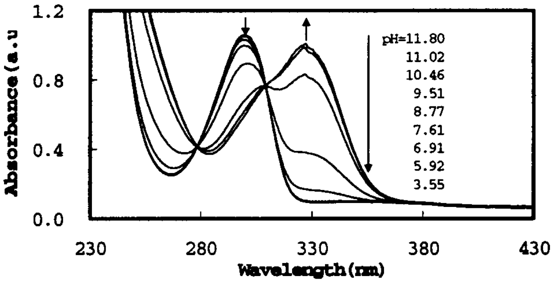


Figure 2. The UV-vis spectra of PHEIA solution

Figure 2 showed the UV-vis absorption spectra of PHEIA in aqueous solution. In addition to the absorption peak of phenyl ring at about 200nm, a strong absorbance between 300 and 350nm was also observed, which would be attributed to the conjugation between the carbonyl groups at 3 and 5 positions and the phenyl ring. This conjugated absorption band was sensitive to the pH of the solution and theλ_{max} at 300nm in acidic media would red-shift to 330nm in basic solution. With increase of the solution pH, the absorption intensity at 300nm became weaker and weaker while that at 330nm increased stepwisely. This result revealed the ionization process of the carboxylic acid groups in PHEIA. With increasing the pH value of the solution, more carboxylic acids was ionized, which makes the conjugated π-electrons more easily to be excited and subsequently results in the red-shift of theλ_{max} in the conjugated band. However, even all the carboxylic acid being ionized at the pH of 11.28, the absorption peak at about 300nm would not disappear thoroughly but red-shifted to about 310nm.

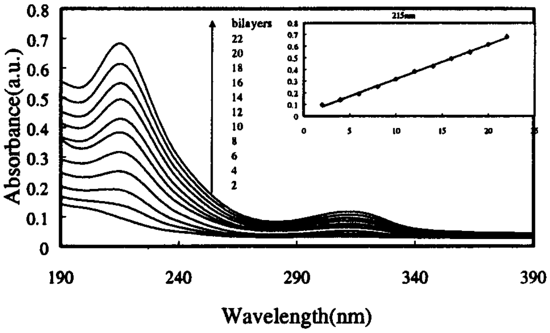


Figure3. The growth of bilayers in aqueous solution

The Assembly of PHEIA/PDAC

Polyanionic PHEIA was further used to form assembly film with polycationic PDAC by LBL technique. Since PHEIA showed strong absorption in UV-vis spectrum but PDAC did not, the building course of the assembly film on quartz substrate can be monitored by UV-vis

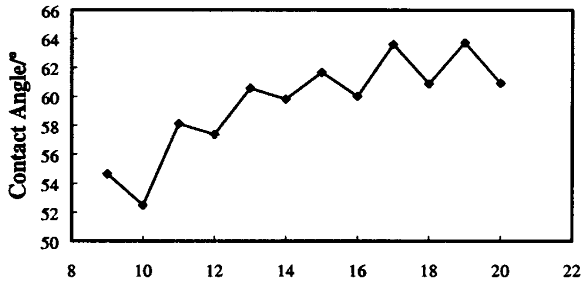


Figure 4. The contact angle of the each layer of the assembly film

spectroscopy. As shown in Figure 3, the increase of the absorbance at 215 nm indicated the growth of the thickness of the film. The linear relation between the absorbance and the number of bilayers indicated that the thickness of every bilayer was nearly the same. The contact angle of the surface of each monolayer was measured to study the surface wettability. The surface of treated quartz glass was very hydrophilic with the contact angle at about 10~20°. But after four cycles of dipping procedure, the contact angle of the surface increased to about 55°, indicating of the drastically change in the hydrophilicity of the surface, although the thickness of the film was only several decades of nanometers[12]. This indicated the high efficiency to change the surface properties by LBL technique. The relationship between the hydrophilic property of the surface and the increase of the number of multilayers was shown in Figure 4 beginning from the ninth monolayer of PDAC. At the beginning, the contact angle of the surface was increased with increasing the thickness of the film, but then it came to a steady value. So it was suggested that the hydrophilic property of the film surface could be controlled by varying the number of monolayers. Furthermore, the zigzag curve alternating with the monolayer of PDAC and PHEIA indicated that the intersection between PDAC and PHEIA was not serious, which should be due to the ionization of carboxylic groups. The ionized carboxylic acid groups was adsorbed to form bond when deposited on the surface of the opposite-charged PDAC and could not intersection freely, i.e. the combination of PDAC and PHEIA was preferential to happen on the outmost of PHEIA.

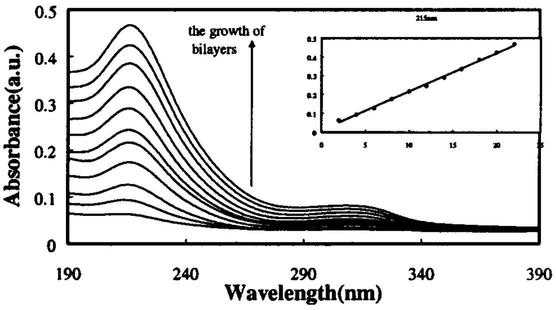
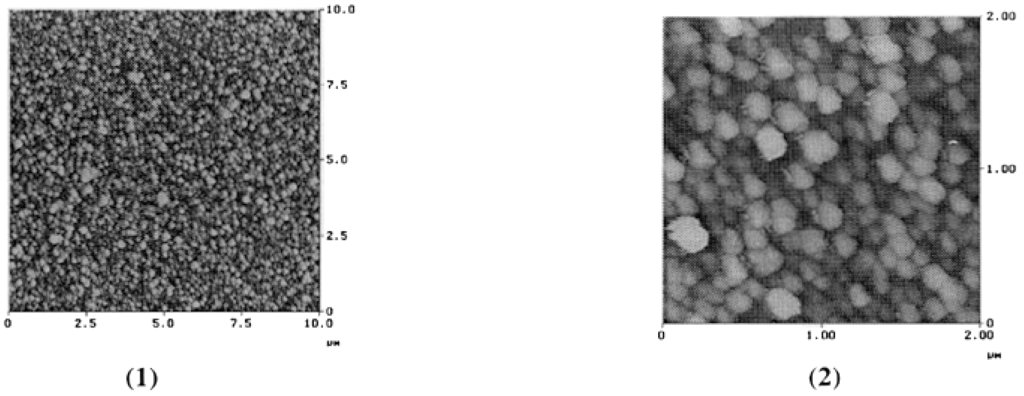


Figure 5. The growth of bilayers in mixed solution

Most of the recent studies on LBL process were focused on aqueous solution. Here PHEIA showed the same desirable assembly properties even in THF-H_2O (1:20,v/v) mixed solvent

(Figure 5). The surface of PHEIA monolayer in the PHEIA/PDAC assembly film was observed by AFM. The result in Figure 6 clearly showed that the surface formed by LBL was fairly regular which indicated again that PHEIA has desirable assembly properties in mixed solvent. Furthermore the hyperbranched moleculars aggregated into uniform spheroid paricles with the diameters ranged from 100~200 nm. So it was proved that the entanglement among these molecules existed in the thin film.



(1) (2)

Figure 6. The morphology of the PHEIA surface observed by AFM

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