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Photoisomerization of amphiphilic azobenzene derivatives in Langmuir Blodgett films prepared as polyion complexes, using ionic polymers

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Abstract

Polyion complexation in mixed Langmuir and Langmuir Blodgett (LB) films of photochromic amphiphilic azobenzene carboxylic acids, 11-[4-(4-hexylphenyl)azo] phenoxyundecanoic acid, 11-(4-phenylazo)phenoxyundecanoic acid, and diamine grafted poly(methylmethaacrylate) polymers has been studied. Monolayer behaviour of the pure components and mixed films was studied through pressure–area isotherms and LB films were characterized by spectroscopic, X-ray diffraction and Atomic force microscopy techniques. Aggregation (H-type), often observed in LB films of pure amphiphilic azo acids, was partly avoided in the mixed LB films as indicated by absorption spectral studies. Photoisomerization of the polyion complexed LB films was also studied. The results altogether demonstrate that amine grafted polymer enter into a polyion complexation with azo acid carboxylate group. LB films could be obtained by transfer of the composite monolayers and these LB films exhibited different levels of aggregation of the azo acids. Reversible photoisomerization was observed in LB films with unaggregated azo acid.

Keywords: Polyion complexes; Azobenzenes; Langmuir-Blodgett films; Photoisomerization

1. Introduction

Photochrome containing Langmuir Blodgett (LB) films have been explored as media for photochromic reactions aimed at constructing molecule based information storage or switching devices [1–3]. In this context LB films of azobenzene derivatives have attracted increasing attention in recent years due to their diverse photofunctional applications [4–8]. These derivatives undergo facile *cis*–*trans* photoisomerization in solution, however isomerization is inhibited [9–12] in pure LB films due to insufficient 'free volume' in the higher order structure of LB films. Photoisomerization not only involves electronic changes but also involves changes in the molecular conformation and cross-sectional area due to difference in the shape of the *cis* and the *trans* isomers. Changes in the cross-sectional area and molecular conformation that are associated with azobenzene isomerization necessitate availability of adequate 'free volume' within the two dimensional LB film structure since the cross-sectional area of the *cis* isomer is larger than that of the *trans* isomer. Another factor limiting many potential applications of LB films is the poor chemical and thermal stability.

Amongst various strategies [13–21] used to provide additional 'free volume', complexation of azobenzene derivatives with suitable polyions has received much attention partly due its versatility and convenience. This approach obviates the need for synthesis of specially designed complex amphiphilic molecules [22,23]. Polyion complex approach has been investigated extensively in last two decades for enhancing the stability of monolayers and influencing the orientation of the amphiphiles [24]. The polyion complex method is useful in stabilizing monolayers at the air–water interface by the electrostatic interaction between the monolayers and the water-soluble polyions [25–27]. This strategy has the advantage of providing azobenzene a favorable environment for the reversible *cis*–*trans* photoisomerization [25,26]. It has been reported by Nishiyama et al. [26] that polymers with ionic pendent groups are capable of forming complexes with carboxylic acid groups of acid at the air water interface. This

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phenomenon could be used for hooking the azo acids on polymer backbone at a certain intervals thereby breaking the aggregates of azo acid being formed in the monolayer [28]. LB films of azobenzene containing polyion complexes have been shown to exhibit reversible photoisomerization. The photo stationary state *cis* isomer composition and the free volume availability in such films depend on the nature of polyions and the experimental conditions under which the film are prepared [29,30].

In this paper we report investigations on monolayers and transferred multilayers prepared as polyion complexes made from amphiphilic azobenzene carboxylic acids, 11-[4-(4-hexylphenyl)azo]phenoxyundecanoic acid(6A10) and 11-(4-phenyl azo)phenoxyundecanoic acid(0A10), and diamine random grafted poly(methylmetha acrylate) (PMMA) polymers (GP*n*, 6–16% graft) by LB method and study of photoisomerization in LB films. The chemical structures of the azo acids and the amine grafted polymers are shown in Fig. 1. The protonated basic amino centers in the grafts are expected to function as polyions for complexation with the ionized acid. Monolayer behaviour has been examined by detailed pressure–area isotherms (π–A) isotherm studies. π–A isotherm studies of the monolayers essentially indicated absence of aggregation in the monolayers. LB films were obtained by transfer of the monolayers by vertical transfer methodology and characterized by Fourier Transform Infrared spectroscpoy (FTIR), electronic absorption spectroscopy (UV-Vis), X-ray diffraction (XRD) and Atomic Force microscopy (AFM). The results demonstrate that suitable pendent group grafts on polymers enter into complexation with the carboxylate group on azo acid and can serve as a basis for thin film media for reversible photoisomerization of the azo group.

2. Experimental details

2.1. Materials

11-[4-(4-hexylphenyl)azo]phenoxyundecanoic acid [31], and 11-(4-phenylazo)phenoxyundecanoic acid [32], were synthesized by diazotization of respective 4-substituted aniline and coupling of the diazotized product with 11-bromoundecanol followed by its oxidation using PDC (6A10, mp = 106 °C, reported mp = 106–108 °C, 0A10, mp = 116–119 °C, reported mp = 116–118 °C) [31,32]. 4-substituted anilines, 11-bromoundecanol and dodecylbromide were bought from Aldrich. The azo acids were repeatedly recrystallized to achieve a purity of 99.9%. Purity of the azo acids was monitored using high performance liquid chromatography (HPLC) (Shimadzu LC-8A).

Grafted PMMA was prepared by refluxing 1, 2-diaminopropane (10–50% of the PMMA) and PMMA in toluene for 8 h in a Dean–Stark apparatus to remove methanol. Subsequently grafted polymers were precipitated in hexane. The precipitated polymers were purified and freed from unreacted diaminopropane by repeated dissolution in toluene and precipitation in hexane. The levels of grafting achieved were much lower than the attempted graft level. Extent of grafting was determined by amine value method. Grafting achieved and attempted in % for different samples were GP1, 6.7(10); GP2, 8.7(20); GP3, 11(30); GP4, 13.1(40); GP5, 15.3(50), respectively. The grafted PMMA was further characterized by FTIR and Nuclear Magnetic Resonance spectroscopy.

Measurements of surface pressure–area isotherms and the automated deposition of the monolayers were carried out with Langmuir trough (KSV 3000) equipped with an electronic microbalance and a platinum Wilhelmy plate, kept in a clean room, class 10,000. Deionized water with resistivity 18.2 MΩ cm from Millipore system was employed for subphase preparation. Pure azo acid monolayer behaviour and deposition of LB films was studied with water subphase and subphase containing 10^{-4} M $CdCl_2$. Composite monolayers films of azo acids and GP*n* polymers were made by spreading solutions of the azo acid and polymer made by mixing parent solutions of azo acid (0.56 mg ml^{-1}) and GP*n* (0.62 mg ml^{-1}) in HPLC grade chloroform in 1 : 1 M proportion of the presumed graft. 100 μl of the mixed solution of azo acid and GP*n* was spread on the LB trough with water subphase at ambient temperature and chloroform was allowed to evaporate. An equilibration time of 40 min was allowed. The monolayers at the air–water interface were compressed with the help of barriers (barrier speed 3 mm/min). Formation of the condensed monolayer was followed by π–A isotherms. Stability of the monolayers was studied by noting the change in mean molecular area while maintaining the monolayer at a specific pressure.

Monolayers were transferred onto quartz plates of dimensions 1 × 1 in. (and on CaF_2 plates of dimensions 1 × 0.5 in. for FTIR) at a surface pressure of 15 mN/m with a dipping speed of 3 mm/min. For all films either 11 or 22 monolayers were

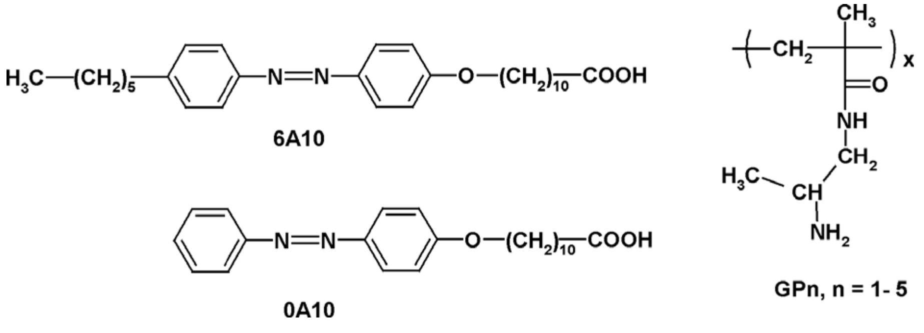

Fig. 1. Structures of azo acids and the grafted polymer.