

Fabrication and Characterization of Multilayer Films from Amphiphilic Poly(*p*-phenylene)s

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Over the past two decades, considerable efforts have been devoted to the development of conjugated polymeric materials for electronic applications due to the tunability of their properties through variation of their chemical structure. The LB technique is one of the most effective and precise methods for controlling the organization and thereby the properties of polymer films at the nanoscale for device fabrication. A detailed study was performed on the Langmuir–Schaefer (LS) monolayer and Langmuir–Blodgett–Kuhn (LBK) multilayer formation of newly designed conjugated poly(*p*-phenylene)s (C_{*n*}PPPOH), incorporated with alkoxy groups with different chain lengths (C₆H₁₃O-, C₁₂H₂₅O-, and C₁₈H₃₇O-) and hydroxyl groups on the polymer backbone. The monolayer formed at the air–water interface was characterized using surface pressure–area isotherms, including hysteresis measurements. The films were then transferred to different hydrophilic solid substrates and analyzed using surface plasmon resonance spectroscopy, UV–vis spectroscopy, fluorescence spectroscopy, and AFM measurements. The results showed that the polymer with a short alkoxy chain (C₆PPPOH) forms uniform monolayers at the air–water interface and can be transferred as multilayer films compared to C₁₂PPPOH and C₁₈PPPOH. The observed film thicknesses measured by SPR and AFM studies were similar to the theoretical value obtained in the case of C₆PPPOH, whereas this was not the case with the other two polymers. The present study shows that the polymer C_{*n*}PPPOH with short alkoxy chain can be transferred onto different solid substrates for device fabrication with molecular level control.

Introduction

The role of conjugated polymers in emerging electronic, sensor, and display technologies is rapidly expanding owing to their interesting electrical, luminescent, and photoconducting properties.^{1–6} To fabricate devices, the preparation of nanostructured thin films of the conjugated polymer with good optoelectronic properties is needed. However, the development of effective and precise methods for controlling the organization of the polymer in the solid state has been limited because polymers often fail to assemble into organized structures due to their amorphous character and large molecular weight. Although there are limitations in the structure and properties of the films formed, Langmuir–Blodgett–Kuhn (LBK),^{7–10} spin-coating, or organic molecular beam epitaxy (OMBE) techniques have been com-

monly used for the deposition of thin films.¹¹ However, LBK or Langmuir–Schaefer (LS) techniques are useful tools for the fabrication of ultrathin polymeric films with controlled structures and enhanced electronic and optical properties.¹² In addition, organized LBK/LS assemblies are particularly attractive as they allow for a very high control of the layer thickness, and require a very small amount of polymer material in contrast to solution casting or spin coating techniques. Furthermore, the functional properties of films prepared by the LBK techniques are closely related to their micro/nano-structures since long-range ordering provides new insights on the electron-transfer reactions at the interface.¹³ Thus, design and synthesis of functional conjugated polymers as well as the fabrication of LBK/LS films has been particularly interesting for the preparation of a highly ordered structures of ultrathin polymeric films.

Substituted poly(*p*-phenylene) (PPP) molecules are an interesting class of conjugated polymers which can form linearly conjugated π orbital systems and display interesting electronic properties.¹⁴ These polymers have potential applications in photo- or electroluminescence devices. Despite the widespread interest,

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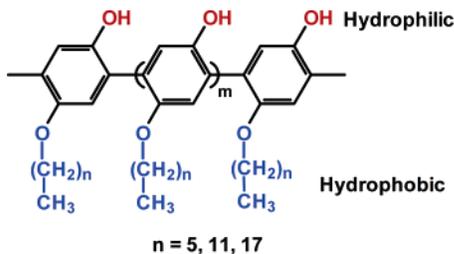


Figure 1. Molecular structure of C_n PPPOH polymers.

only a few studies on PPPs with substituents which give rise to amphiphilicity and ultrathin film formation properties have been reported.¹⁵ Recently, Bo et al. demonstrated the synthesis and monolayer film formation at the air/water interface of amphiphilic PPPs substituted with alkyl side chains with hydrophobic or hydrophilic dendrons.¹⁶ In our previous studies the synthesis and characterization of a new class of rigid planar amphiphilic poly(*p*-phenylene) (C_n PPPOH) were reported.¹⁷ Due to incorporation of alkoxy chains and hydroxyl ($-OH$) groups to the phenylene backbone, these polymers are planar and amphiphilic in nature. Indeed, the introduction of the functional groups imparts the ability to form ordered thin films and self-organizing properties to PPP polymers.¹⁸ The present work investigates the influence of three different alkoxy side chains incorporated on to the polymer backbone, such as C_6 PPPOH, C_{12} PPPOH, and C_{18} PPPOH (Figure 1) to control the formation and characterization of optical properties of LS monolayer and LBK multilayer films.

Experimental Section

Synthesis of Polymers. The amphiphilic poly(*p*-phenylene)s C_6 -PPPOH, C_{12} PPPOH, and C_{18} PPPOH were synthesized by a transition metal catalyzed Suzuki polycondensation method as reported earlier.¹⁷ Molecular structures were characterized using NMR, mass spectrometry, FTIR, and elemental analysis. Number-average and weight-average molar masses of the three polymers were obtained using gel permeation chromatography (GPC) – C_6 PPPOH ($M_n = 10\,450$, $M_w = 23\,524$, PDI = 2.2), C_{12} PPPOH ($M_n = 3083$, $M_w = 4139$, PDI = 1.3), and C_{18} PPPOH ($M_n = 6851$, $M_w = 8937$, PDI = 1.3). The end to end distance of the monomer repeat unit of the polymers C_6 PPPOH, C_{12} PPPOH, and C_{18} PPPOH were theoretically calculated using HyperChem Lite molecular modeling systems. Optimization was carried out using the Polak-Ribiere conjugate gradients algorithm.

Preparation of Substrates. The quartz substrate was cleaned using ultrasonication in hot chloroform (15 min), followed by a hot solution of $H_2SO_4/H_2O_2/H_2O$ (1:1:5, 30 min), and rinsed with copious amounts of distilled water to get hydrophilic substrates. The silicon wafers used were cleaned with a similar procedure as that of the quartz substrates. Gold-coated LaSFN9 glass substrates were prepared by thermal evaporation. Each glass slide was pre-cleaned using ultrasonication in 2% Hellmanex solution, water, and ethanol followed by drying in a stream of N_2 . Gold (~ 47 nm) was deposited onto the substrates by thermal evaporation in a vacuum chamber (Biemtron

Co. Inc) at $\sim 1 \times 10^{-5}$ Torr at a rate of 0.1 nm/s. The Au substrates were modified using 16-mercaptohexadecanoic acid solutions (Aldrich Chemical Co.) to form hydrophilic surfaces. The thiol SAMs were assembled from ethanolic solutions at a concentration of 1 mM. The surface modification was carried out by immersion of a freshly evaporated gold substrate into a freshly prepared thiol solution for 14 h at room temperature in order to ensure the formation of a high quality film. The substrate was then removed from the solution and immediately rinsed with absolute ethanol and dried in a stream of N_2 .

Multilayers were deposited onto different hydrophilic substrates such as quartz using a vertical deposition (Z-type) method for investigating optical properties (e.g., absorbance and photoluminescence), and on gold-coated LaSFN9 glass ($n = 1.845$) at $\lambda = 633$ nm for the SPR spectroscopy measurements.

Preparation and Characterization of Langmuir Monolayers and LBK Films. The experiments for monolayer spreading were performed on a KSV-2000 Langmuir–Blodgett system (KSV Instruments, Helsinki, Finland) equipped with computer controls. A Wilhelmy plate was used as the surface pressure sensor placed in the middle of the trough. Two barriers compress or expand symmetrically at the same rate from two ends of the trough. Monolayers were obtained by spreading 100 μ L of a chloroform solution composed of the C_n PPPOHs with a concentration of 0.5 mg/mL onto pure Milli-Q water at a neutral pH. After this, solvent was allowed to evaporate, and the monolayer was compressed at a typical rate of 50 mm/min. The interfacial properties of the films at the air/water interface was studied by π - A isotherm. Isotherms of surface pressure, π , versus the mean molecular area/repeating unit, A , are measured at $T = 22 \pm 0.2$ °C. Isobaric creep measurements and compression expansion cycles were also investigated.

The UV measurements were performed on a Shimadzu SPD-10A spectrophotometer. Different layers were transferred to hydrophilic quartz substrates via Z-type deposition and the dependence of the film absorption on the number of transferred layers was investigated. Fluorescence emission of the polymer in solution and as a multilayer film was collected on a Shimadzu RF-5301PC spectrofluorometer. Various deposition parameters influence the microstructure and the growth rate of the deposited films. Based on the monolayer behavior, the parameters used for the deposition were as follows: surface pressure of $\pi = 15$ mN/m for C_6 PPPOH, $\pi = 12$ mN/m for C_{12} -PPPOH, and $\pi = 10$ mN/m for C_{18} PPPOH. Films transferred onto hydrophilic Au substrates were used for angular scan SPR measurements. The thickness of the LBK film was calculated by curve-fitting the data from the angular scans on the films and bare gold as a reference in air. The SPR set up was based on the configuration introduced by Kretschmann and details of the set up were described elsewhere.¹⁹ Briefly, a 90° high refractive index glass (LaSFN9, $n = 1.845$ at $\lambda = 633$ nm) prism was used as the plasmon coupler. The light of a p-polarized HeNe laser ($\lambda = 632.8$ nm) mechanically chopped for lock-in detection was reflected off the metal-coated base of the prism. The intensity of the beam reflected at the gold surface was monitored by a photodiode detector and recorded as a function of the incident angle for “angular scan” measurements. The angular scan data were fit into an optical model that accounts for the thickness and the complex dielectric constants of the deposited material at the interface.

Results and Discussion

A series of amphiphilic PPPs, C_6 PPPOH, C_{12} PPPOH, and C_{18} PPPOH, have been synthesized using Suzuki polycondensation of the respective monomers (see the Supporting Information for details on the polymer synthesis, SI1) and used for the present study.¹⁷ The incorporation of alkoxy chains on one side and hydroxyl groups on the other side of the rigid polymer backbone improves the solubility and provided the desired amphiphilicity (Figure 1). Thermogravimetric analysis of the three polymers showed good stability in nitrogen or in air up to 325 °C, with

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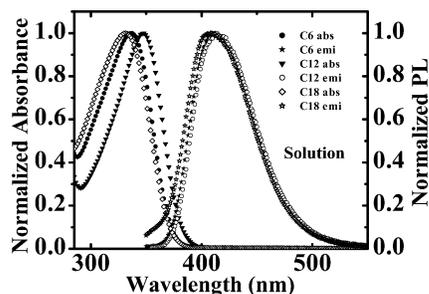


Figure 2. Absorbance and emission spectra of the polymers C_n -PPPOH in chloroform solution.

a mass loss of less than 2%. The polymers C_6 PPPOH, C_{12} PPPOH, and C_{18} PPPOH, showed a strong absorption ($\lambda_{\text{abs}} = 335, 345,$ and 331 nm) and intense blue emission in solution ($\lambda_{\text{emis}} = 415, 414,$ and 418 nm; Figure 2).

In general, conjugated polymers with tunable emission wavelengths in a wide range of color and good solubility are of great interest. Specific functional groups modify the electroactive properties or enhance the usually poor solubility of the rigid conjugated backbone, e.g., by grafting flexible chains to the polymer backbone. Even if these requirements are achieved, it is necessary to optimize the quality of the emitting layer by an appropriate deposition technique to significantly influence the film morphology, carrier mobility, and emission yield of the film for device applications. To this respect, the LBK technique is promising as it provides self-organized films with good molecular order and alignment, which are also indispensable features to obtain polarized light. First, the properties of Langmuir monolayers of the polymers C_6 PPPOH, C_{12} PPPOH, and C_{18} PPPOH at the air–water interface were examined. The surface pressure–area (π – A) isotherm and hysteresis curves of different alkoxy substituted PPPs are summarized in Figure 3. It is interesting to note that the observed isotherm of the polymer C_6 PPPOH is very different compared to that of the polymer with the longer alkoxy side chains, C_{12} PPPOH and C_{18} PPPOH, respectively. The isotherm of C_6 PPPOH exhibits a liquid expanded region. In contrast, C_{12} PPPOH and C_{18} PPPOH showed a steep rise in surface pressure without a phase transition. These results are similar to that of typical amphiphiles such as a simple long chain fatty acid, in which increasing the length of the hydrocarbon chain causes the expanded state to disappear with a direct transition from a gas to a condensed phase.²⁰ The observed low compressibility of the monolayers from C_{12} PPPOH and C_{18} PPPOH indicates the stiffness and rigidity of the monolayer. The area per repeat unit calculated by the extrapolation of the solid region in the surface pressure–area isotherm to zero pressure in all three cases is $A_0 = 0.2 \pm 0.02$ nm², which is close to the cross-sectional area of the alkyl chain. From the observed data, the orientation of the alkyl side chains relative to the phenylene backbone is mainly in an up-right standing position with the OH groups facing to the water surface.

The compression–expansion experiments (hysteresis) were carried out in order to evaluate the stability of the monolayer at various surface pressures. The isotherm of each polymer is summarized in Figure 3 and the hysteresis of the π – A isotherm of the different C_n PPPOH monolayers during compression–expansion cycles is depicted in the inset in the figure. In the case of C_6 PPPOH, the isotherm was reversible until the collapse pressure is reached where as in the other two polymers, the first cycle showed a clear hysteresis with the next π – A isotherm

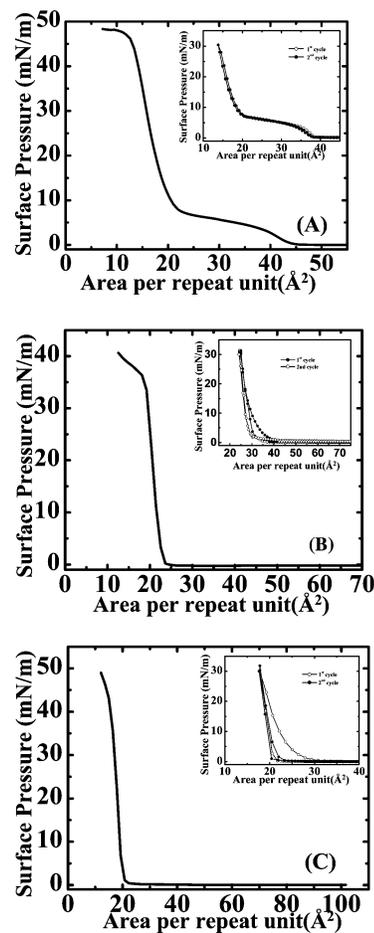


Figure 3. Surface pressure–area (π – A) isotherm and hysteresis curves (inset) of C_6 PPPOH (A), C_{12} PPPOH (B), and C_{18} PPPOH (C).

curve displaying a smaller area per repeat unit than the foregoing cycle. However, the monolayers showed a relatively small hysteresis during the repeated compression–expansion cycles. The large hysteresis of the first cycle may be due to the influence of domain formation during the solution spreading and by the solvent evaporation process. This indicates that the initial states of the monolayers are slightly different and reorganization takes place during the compression–expansion cycles with C_{12} PPPOH and C_{18} PPPOH.

The stability of the monolayer on the trough was also investigated by compressing the thin layer with a constant surface pressure (about 15 mN/m) and allowing the barrier to move freely to keep the surface pressure constant over a long period (60 min). Compared to C_{12} PPPOH and C_{18} PPPOH (~ 15 min), the equilibrium surface pressure was reached very quickly in the case of C_6 PPPOH (~ 5 min). After reaching the equilibrium surface pressure, only a minor decrease in the surface area per repeating unit was observed for all three polymers. This indicated that the monolayers of all three polymers are stable at the air–water interface.

To understand the differences in the molecular level orientation as well as the morphology of C_n PPPOH as monolayers, the Langmuir films were horizontally transferred (LS) to a freshly cleaved mica substrate at different surface pressures and morphologies of these thin films were examined using AFM. The AFM images of the monolayers transferred at different target pressures starting from 0 mN/m at 50 Å² to the collapse pressure are shown in Figure 4. The morphology of the monolayer changes with smooth topology at low pressures (Figure 4, panels a,b; f,g;

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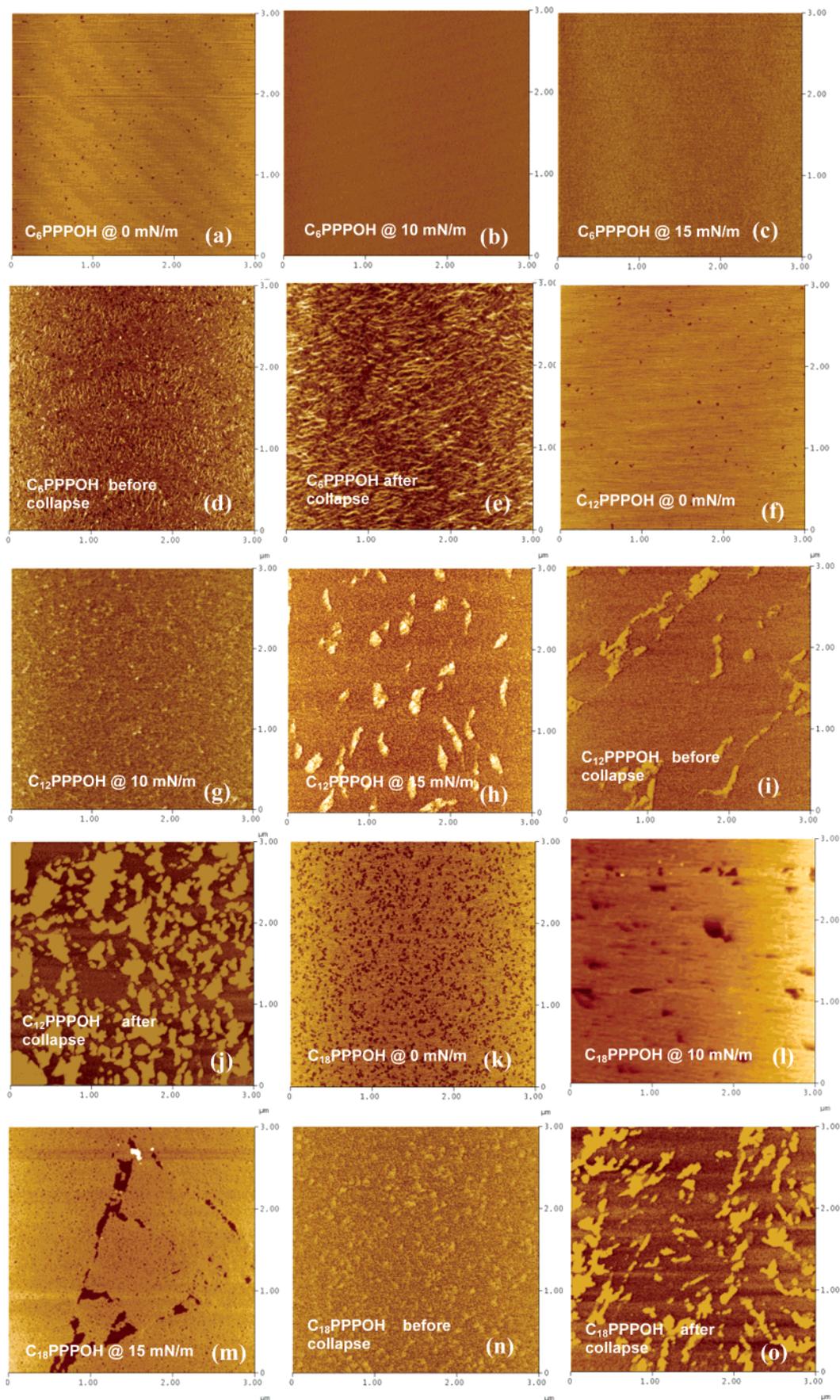


Figure 4. AFM topography image of LB monolayer of C₆PPPOH (a–e), C₁₂PPPOH (f–k), and C₁₈PPPOH (k–o) horizontally transferred to a freshly cleaved mica surface at five different target pressures such as 0 mN/m at 50 Å² per repeat unit, 10 mN/m, 15 mN/m, just before collapse pressure, and after collapse pressure in each cases.

Table 1. Calculated Roughness of the LB Monolayer of C₆PPPOH, C₁₂PPPOH, and C₁₈PPPOH Horizontally Transferred to a Freshly Cleaved Mica Surface at Five Different Target Pressures Such as 0 mN/m at 50 Å² Per Repeat Unit, 10 mN/m, 15 mN/m, and Just before Collapse Pressure

polymer	surface pressure			
	0 mN/m	10 mN/m	15 mN/m	before collapse
C ₆ PPPOH	0.125 nm	0.135 nm	0.172 nm	0.341 nm
C ₁₂ PPPOH	0.109 nm	0.336 nm	0.383 nm	0.476 nm
C ₁₈ PPPOH	0.240 nm	0.220 nm	0.385 nm	0.350 nm

and k,l) to a bumpy rough layer at higher pressure (Figure 4, panels d,e; i,j; and n,o). In the case of C₆PPPOH, the characteristic topography of the collapse was observed only at higher surface pressures (35 mN/m) as compared to C₁₂PPPOH (~15 mN/m). Also a uniform coverage was observed for C₆PPPOH both at 10 (Figure 4b) and 15 mN/m (Figure 4c), whereas the transferred monolayer seems to have discontinuous features with cracks in the case of C₁₈PPPOH even at lower surface pressures of 10 and 15 mN/m (Figure 4l). In the case of C₁₂PPPOH, the observed multilayer aggregate formation at a surface pressure of 15 mN/m may be due to the collapse of the monolayer due to the low stability imparted by the long alkyl chain. To study the monolayer film quality i.e., the difference in roughness with the surface pressure, we quantified the roughness using AFM over a representative area (Table 1). The observed results are in agreement with the anticipated increase in roughness as the surface pressure increases for the polymer which shows good transfer ratio.

To study the differences in transferring monolayers and to get multilayers, the monolayers were transferred to different hydrophilic substrates by the Z-type deposition at a surface pressure of $\pi = 15$ and 12 mN/m for C₆PPPOH and C₁₂PPPOH, respectively. Y-type deposition was not successful with any of these polymers owing to the peeling of deposited layers during down stroke. The multilayer thickness was found to be linearly related to the number of layers deposited as monitored by UV-vis absorption (Figure 5) in the case of C₆PPPOH and C₁₂PPPOH, respectively, but was erratic in the case of C₁₈PPPOH. Multilayers comprising 40 layers were deposited in the case of C₆PPPOH with a uniform transfer, as seen by the linear increase in absorbance intensities with the number of layers (Figure 5). However, the UV absorption was found to decrease after 12 layers for C₁₂PPPOH, and after 7 layers for C₁₈PPPOH. This demonstrated again that amphiphilic PPPs incorporated with short alkoxy chain (C₆) transferred more uniformly than the longer ones. This may be due to the fact that the hydrophobicity was increased as the alkoxy chain length was increased and this in turn reduced the amphiphilic character of C_nPPPOH. Another factor is the inability of the long-alkyl chains attached to the rigid polymer backbone to pack uniformly in contrast to straight chain fatty acid amphiphiles.

The AFM surface topography section analysis yielded the molecular layer thickness $d = 1.32$ nm for the monolayer of the polymer C₁₈PPPOH at a surface pressure of 15 mN/m measured across a crack in the film. The theoretical value for the molecular length of the repeat unit of each polymer in the upright standing position were calculated using HyperChem Lite molecular modeling systems. The calculated values are 1.29 nm, 2.03 nm, 2.79 nm for C₆PPPOH, C₁₂PPPOH, and C₁₈PPPOH, respectively. Thickness obtained from AFM measurements in the case of C₁₈PPPOH was much lower than the theoretical value. This may be due to the low transfer ratio as well as the disordered orientation of the alkyl chain in the case of polymer with a long alkyl chain compared to a shorter one. The thickness of the monolayer of

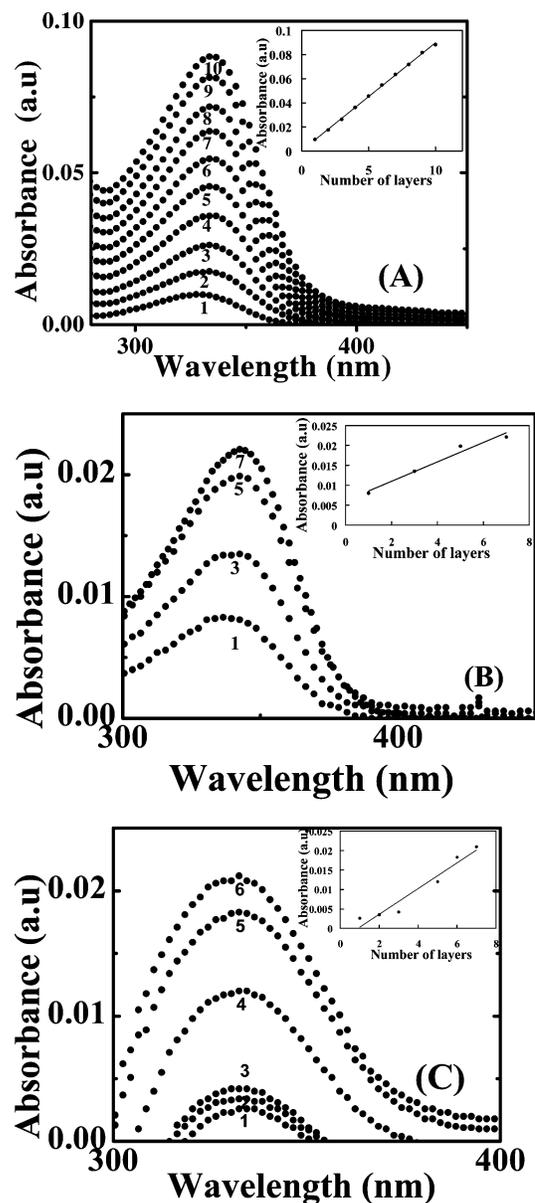


Figure 5. Absorption spectra of LBK films of the three polymers (A) C₆PPPOH, (B) C₁₂PPPOH, and (C) C₁₈PPPOH with different number of layers transferred onto quartz substrate. The dependence of the film absorption on the number of transferred layers are indicated in the inset.

C₆PPPOH and C₁₂PPPOH transferred at higher surface pressure could not be measured, since the transferred film was more or less uniform and no cracks were observed.

To get further insight into the structural properties of the multilayer assemblies, surface plasmon reflectivity scans were taken from LBK films of different thicknesses. A similar result as in the UV-vis studies was observed with SPR measurements of the LBK films of C₆PPPOH and C₁₂PPPOH prepared on hydrophilic Au/LaSFN9 substrates at a lateral pressure of $\pi = 15$ mN/m with the Z-type deposition. In the case of C₁₂PPPOH, the transfer was found to be successful only to chemically modified hydrophilic gold-coated LaSFN9 substrates. C₆PPPOH monolayers were transferred uniformly to both bare and hydrophilic gold coated LaSFN9 substrates, whereas C₁₈PPPOH monolayers were difficult to transfer onto bare gold or to the modified gold substrates. The peak shifts ($\Delta\theta$) seen in the angular scans of the plasmon resonance curves of the LBK multilayer assemblies on the hydrophilic Au surface relative to the bare

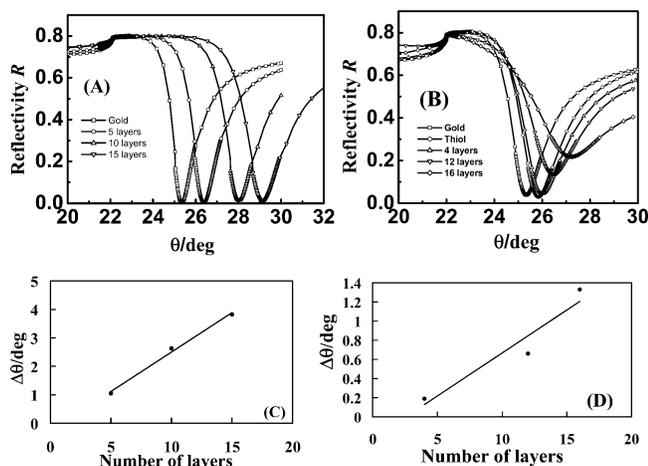


Figure 6. SPR curves of the multilayers of C₆PPPOH (A) and C₁₂PPPOH (B) and plot of the shift of the resonance minimum for LBK films from C₆PPPOH (C) and C₁₂PPPOH (D) obtained from the SPR angular scans.

gold, increased linearly with the number of layers (Figure 6) for C₆PPPOH and C₁₂PPPOH. Furthermore, the observed results showed that in the case of C₁₂PPPOH, the width of the peaks broaden asymmetrically with increasing thicknesses. This indicates an increasing surface inhomogeneity whereas for the C₆PPPOH multilayers, the width of the peaks measured was more or less constant. The observed monolayer thickness as obtained from the SPR data was $d = 1.25 \pm 0.1$ nm for C₆PPPOH and $d = 0.5 \pm 0.1$ nm for C₁₂PPPOH using a refractive index value of $n = 1.6$ for both polymers. In the case of C₆PPPOH, the observed monolayer thickness is close to the theoretically calculated value of $d = 1.29$ nm, using HyperChem Lite molecular modeling systems.

All the aforementioned observations were supported by the uniform LB film deposition of up to 40 layers in the case of the polymer with the shorter alkyl chain (C₆PPPOH). The film morphology studies (Figure 7) confirmed that a continuous and uniform thin film from C₆PPPOH (40 layers) was obtained in contrast to the irregular rough film from C₁₂PPPOH (10 layer). Next, the absorbance and emission properties of multilayers of C₆PPPOH transferred to hydrophilic quartz substrate were measured. The observed UV–vis absorption maximum of the film is $\lambda_{\text{abs}} = 335$ nm, which is identical to the absorption maximum observed for the polymer in chloroform solution. Interactions between polymers or polymer segments strongly influence the electronic properties of conjugated polymer films and lead to large spectral shifts measured in aggregates or thin films.²¹ Since no shift in absorption maxima was observed for C₆PPPOH in solution and the LBK multilayers, it is believed that the polymer retains its electronic nature and conjugation in the polymer film prepared by LBK technique. Contrary to the absorption, a slight blue shift of $\Delta\lambda = 10$ nm of the emission maximum of the film ($\lambda = 405$ nm) compared to solution ($\lambda = 415$ nm) was observed. This may be due to the reduced conjugation or enhanced H aggregation in the excited state of C₆PPPOH. Emission from C₁₂PPPOH and C₁₈PPPOH films was relatively weak and this may be due to the low amount (10–15 layers) of the polymers on the substrate as well as disorder in the packing.

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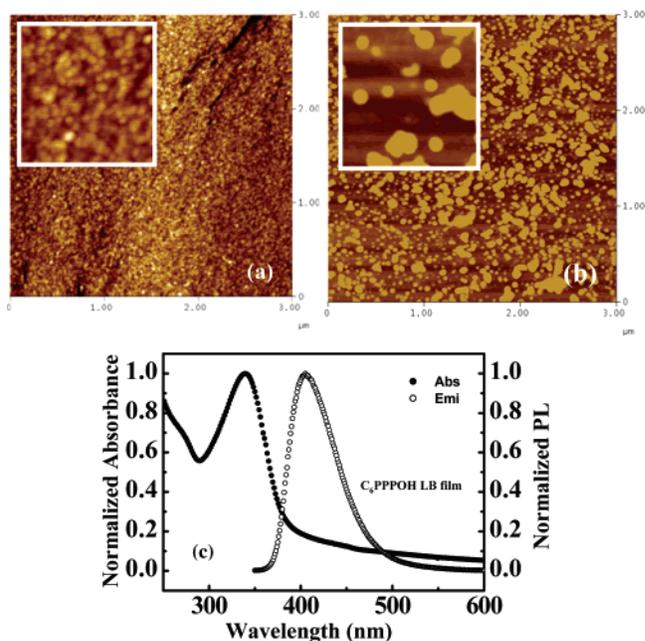


Figure 7. AFM images of (a) 40 layers of C₆PPPOH and (b) 10 layers C₁₂PPPOH deposited on a silicon wafer at $\pi = 15$ mN/m and $\pi = 10$ mN/m, respectively. The magnified image is shown in the inset. (c) Absorbance and emission spectrum of 40 layers of C₆PPPOH transferred to quartz at a surface pressure $\pi = 15$ mN/m.

Nanoscale control of the organization of polymer film can be achieved using the LBK or the self-assembly techniques,²² rather than by spin casting which leads to randomly oriented polymer chains and disordered monomer units.²³ Earlier studies demonstrated that the LBK technique can precisely control the thickness and the order of the film at the molecular scale and that such organization at the nanoscale level might have a great influence on the optical and electrical properties of the polymer film and the corresponding devices.²⁴ Thus, the LBK deposition technique is considered to be a powerful method for molecular processing and organization of rigid-rod conjugated polymers with nonpolar “hairy-rod” structures.^{22a,25} However, not all molecules can be processed into single-component multilayers, which requires a proper balance between hydrophilic and hydrophobic properties and between rigid and flexible moieties that control the formation of stable monolayer phases at the air/water interface. In the present study, a series of new amphiphilic PPPs, C_nPPPOH, bearing alkoxy tails and phenolic headgroups were chosen to induce the required amphiphilicity and planarization of the PPP backbone. Our experimental studies highlight that the polymer bearing a short alkyl chain, C₆PPPOH, is a typical amphiphile with excellent monolayer forming properties at the air/water interface. The comparison of the molecular thickness from theoretical predictions ($d = 1.29$ nm) and the value measured using SPR ($d = 1.25$ nm) are in good agreement with each other in the case of C₆PPPOH polymer.

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The SPR and AFM studies demonstrated that stable well organized multilayers were formed with the plane of the π system perpendicular to the air–water interface. The monolayer is apt to be deposited onto a substrate in the Z-type fashion using LBK technique. The UV absorbance increased uniformly for C₆PPPOH, whereas the absorbance intensity was found to decrease after 12 layers for C₁₂PPPOH, and 7 layers for C₁₈PPPOH. Comparison of the UV–vis spectra of C₆PPPOH in solution and LB multilayer gave no shift in λ_{max} , indicating that there is no change in the electronic structure even after many layers of polymer were deposited. Furthermore, the results from the SPR studies indicated that in the case of conjugated main chains of C₆PPPOH, multilayer LB films are aligned in a side-by-side parallel fashion and packed with the plane of its π system approximately perpendicular to the layer plane. These results indicated that, among the three polymers chosen, the layer-by-layer deposition of C₆PPPOH films at molecular level is successfully controlled using the LB technique. This manipulation at the molecular level offers many potential advantages in device applications.

Conclusion

In the present study, three amphiphilic poly(*p*-phenylene)s were studied to investigate the influence of a hydrophobic long alkoxy side chain and hydrophilic phenolic headgroup on the organization of the film at the air/water interface and in multilayer assemblies. A new series of PPP derivatives (C_{*n*}PPPOH) was synthesized using Suzuki polycondensation and characterized. The LB monolayer studies were performed by analyzing the π –A isotherm, hysteresis, and film stability. In addition, the morphology of the film and efficiency of the film transfer to various substrates were investigated for the LS monolayer which

was transferred at different surface pressures. The morphology of the monolayer films was characterized using AFM, which indicated that the polymer C₆PPPOH formed stable and defect-free monolayer and multilayer films. UV–visible, fluorescence spectra, and SPR data confirmed the above observation and highlighted the influence of alkoxy groups on the PPP backbone toward the organization of polymer chains in thin films. Long alkoxy groups on the PPP backbone appear to induce hindrance for effective transfer of monolayers as well as providing a defect free monolayer. Thus, we conclude that the LB films of C₆PPPOH are well ordered in the layer-by-layer structure. Stiff aromatic polymer backbone and the flexible alkoxy chains provide the polymer C_{*n*}PPPOH, a hairy-rod nature and optimum length of the alkoxy group on the polymer backbone imparts the desired amphiphilicity for the film formation.

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Supporting Information Available: Details on the polymer synthesis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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