Ordered Self-Organizing Films of an Amphiphilic Polymer by Slow Evaporation of Organic Solvents

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ABSTRACT: An ordered self-organizing film of amphiphilic polymer composed of hydrophilic ethyldiamine−epichlorohydrin slightly cross-linking networks and hydrophobic stearoyl side chains was fabricated by slow evaporation of organic solvents. The self-assembling film has a well-ordered, partially interdigitated layer structure which is different from that of the bulk material confirmed by X-ray diffraction, polarized ATR-IR spectra, and DSC.

Introduction

Due to potential applications in molecular and supramolecular devices, fabrication of ordered organic ultrathin films in designed ways is attracting considerable attention. Significant progress has been achieved.[1,2] Ultrathin films can be achieved by self-assembly, Langmuir−Blodgett techniques, organic molecular beam epitaxy, and many other methods.[3] Among these, self-assembly has been attracting increasing interest since Sagiv first succeeded in fabricating a self-assembling monolayer and multilayers using octadecyltrichlorosilane (OTS).[4] Polymers with functional groups have been used to fabricate polymeric self-assembled monolayers, in most cases via gold−alkane thiolate bonds. Compared with that of the self-assembled monolayer made by small, individual molecules, polymeric self-assembled monolayers show improved thermal and mechanical stability and so may be found to have wider potential for application.[5] Recently, a new self-assembling technique based on electrostatic interaction has been introduced, first by Decher and then further developed by many other groups.[6] Along the same lines, Kunitake and his co-workers studied the self-assembly of bilayers from amphiphiles in aqueous media and protic and aprotic media and further developed a new molecular assembly technique by which ordered cast films were fabricated by slow evaporation of water from aqueous bilayer dispersions.[7]

In previous work, we developed a new kind of amphiphilic polymer composed of a hydrophobic microgel and hydrophilic grafting chains, and vice versa. By using this kind of amphiphilic polymer, we fabricated a new kind of polymeric Langmuir−Blodgett film, we termed the "duckweed" and "reversed duckweed" type of polymeric LB film. These materials combined properties of order with structural stability.[8] Recently, we synthesized another amphiphilic polymer composed of hydrophilic ethyldiamine−epichlorohydrin cross-linked microgel and hydrophobic stearoyl side chains. It was found that this amphiphilic polymer can form a highly ordered "reversed duckweed" type polymeric LB film,[9] and moreover, based on the film as a matrix, functional complex LB films can be realized.[10] Furthermore, possibly due to some semirigid rods formed by the collective strong interactions between the polymer's alkyl chains, this amphiphilic polymer lacking mesogens exhibits an interesting thermotropic smectic liquid crystalline phase.[11] In this contribution, we report on the self-assembling film of this amphiphilic polymer by slow evaporation of organic solvent from its solution.

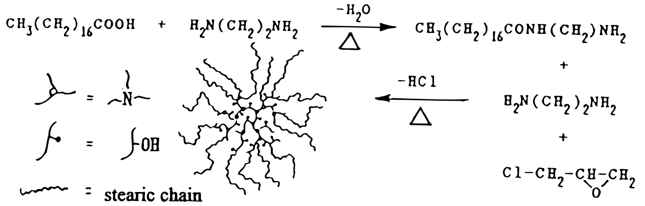

Figure 1. Schematic chemical structure of the amphiphilic polymer.

Experimental Section

An amphiphilic polymer composed of hydrophilic ethyldiamine−epichlorohydrin slightly cross-linking networks bearing hydrophobic stearoyl side chains (chemical structure shown in Figure 1) was synthesized as described in detail in our previous paper.[11] This polymer has M_n 7840 and an alkyl chain content of 75.8%; one molecule contains 20.8 stearoyl side chains on average. The number average molecular weight was determined by membrane osmometry (KUAUER Model), ethanol as the solvent at 40 °C. The alkyl chain content of the amphiphilic polymer was determined by weighing the amount of stearic acid obtained by thorough hydrolysis of 0.5 g of polymer in HCl solution. The stearic acid obtained was washed with water and dried in vacuum for 24 h at 50 °C.

The amphiphilic polymer was slightly cross-linked, and the cross-linking degree can be controlled by the feed ratio of ethyldiamine to epichlorohydrin to assure the polymer's solubility. In this amphiphilic polymer, the tertiary amine group (=N−) is the cross-linking position, and the cross-linking degree is defined as the content of tertiary amine (=N−) unit in the polymers' hydrophilic part:

$$\text{cross-link degree} = \text{tertiary amine } (-\mathrm{N}{=})\%/[\text{tertiary amine } (-\mathrm{N}{=})\% + \text{primary amine } (-\mathrm{NH_2})\% + \text{secondary amine } (-\mathrm{NH}-)\%]$$

We have tried some methods including ^{1}H NMR and ^{13}C NMR to determine the cross-linking degree. However, we cannot resolve the different nitrogen contributions due to the large amount of alkyl chains. Here, we try to use N1s XPS to determine the cross-linking degree using the following method: the polymer contains four types of nitrogen units,

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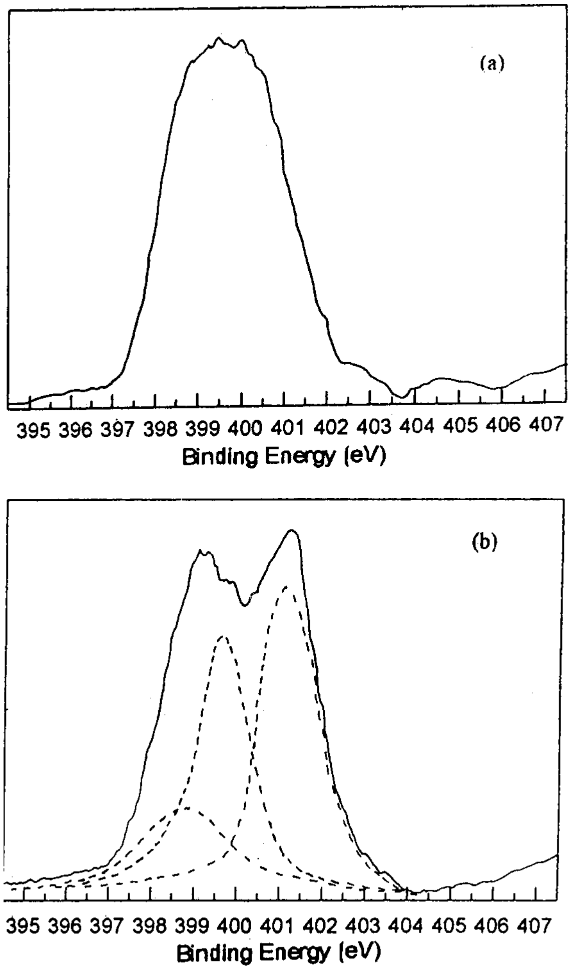

Figure 2. N1s XPS spectra of the polymer (30 scans for each spectra): (a) pure polymer; (b) reacted with excess *p*-toluenesulfonyl chloride (deconvoluted into the =N− (398.9 eV), amide (399.60 eV), and sulfonamide (401.3 eV)).

$-NH_2$, $-NH-$, $=N-$, and amide group. The binding energies of $-NH_2$, $-NH-$, and $=N-$ are all approximately 398.9 eV, so we react the polymer with excess *p*-toluenesulfonyl chloride to assure that all of the −NH and NH_2 are completely converted to *p*-toluenesulfonamide. The binding energy of *p*-toluene sulfonamide is approximately 401.3 eV, so we can resolve the different nitrogen contributions by deconvoluting the N1s XPS; then we can get the content of =N− and the contents of $-NH_2$ and −NH− and further calculate the cross-linking degree. The results are shown in Figure 2: The =N− units constitute 25% of the total nitrogen content in the hydrophilic network, as calculated from conventional integration of the XPS N1s signal. XPS was performed on a VG-ESCA MKII instrument with a monochromatic Mg Kα source, 30 scans, and the operating pressure was approximately 3 × 10^{-9} Torr. The binding energy scales for all spectra were referenced to the Au ($4f_{7/2}$) peak at 84.00 eV. Peak fitting of the spectra was done using Gaussian peak shapes with commercial software supplied by VG Co.

The polymer was dissolved in $CHCl_3/C_2H_5OH$ (volume ratio 7:3) at a concentration of 2 mg/mL and cast onto a clean Si substrate (for X-ray diffraction experiments), a CaF_2 window (for FTIR experiments), or a Si-ATR crystal (for FTIR-ATR experiments; the Si-ATR crystal was purchased from Perkin-Elmer Co., its size is 50 × 18 × 2 mm, its face angle is 30°, and the IR beam can be reflected 51 times). Under saturated vapor pressure at room temperature for more than 48 h the solvent was slowly evaporated, producing the self-organized polymer films on these substrates, and then dried under vacuum at room temperature to remove residual solvents.

The cast polymer films were characterized by X-ray diffraction carried out on a Rigaku X-ray diffractometer (D/max rA, using Cu Kα radiation of a wavelength 1.542 Å), by differential scanning calorimetry with a heating rate of 5 K/min (Perkin-Elmer DSC 2c), and by FTIR-ATR (Bruker IFS66V spectrometer equipped with a MCT detector at 25 °C, 200 scans, resolution 2 cm^{-1}).

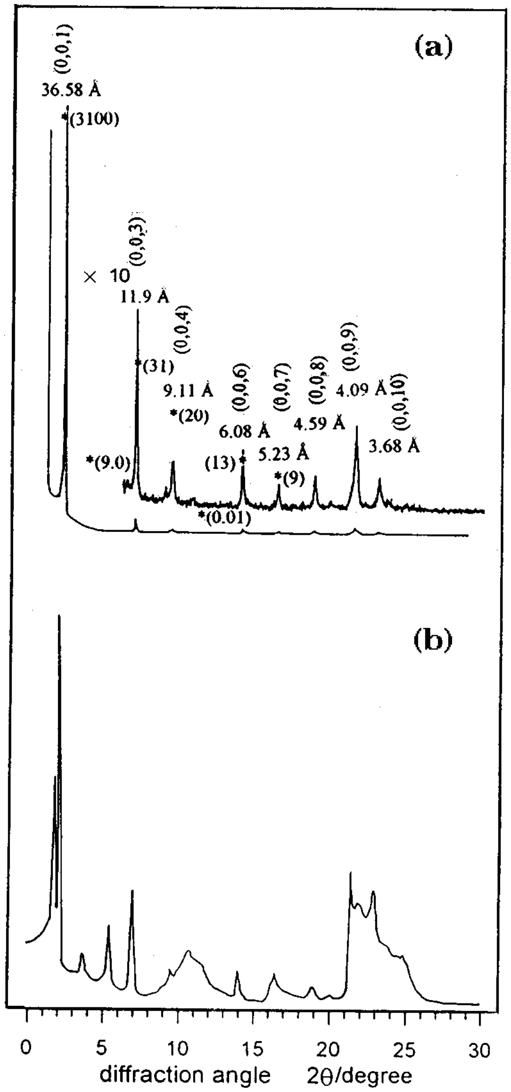

Figure 3. X-ray diffraction patterns for (a) the self-organizing polymer film by slow evaporation of solvent and (b) the polymer bulk powder: (*) theoretic calculation of the intensity of the diffraction peak.

Results and Discussion

Figure 3 a shows the X-ray diffraction pattern for a self-organizing polymer film generated by slow evaporation of organic solvent. Bragg diffraction peaks, even up to the tenth order with a layer spacing of 36.6 Å, are observed, suggesting a highly ordered film with a well-defined layer structure fabricated by slow evaporation of organic solvent. It is well-known that intensities of X-ray diffraction peaks show odd−even alternation in common layer structure such as cadmium arachidate LB multilayer. However, this odd−even alternation phenomenon is not observed here. Moreover, it is noted that the second- and fifth-order diffraction peaks disappear; hence, we infer that the structure of the self-organizing film is different from a common lamellar structure. On the contrary, by the natural evaporation of solvent at room temperature, the film product was more like the bulk powder than film, with a structure similar to that of the bulk polymer crystal, as shown in

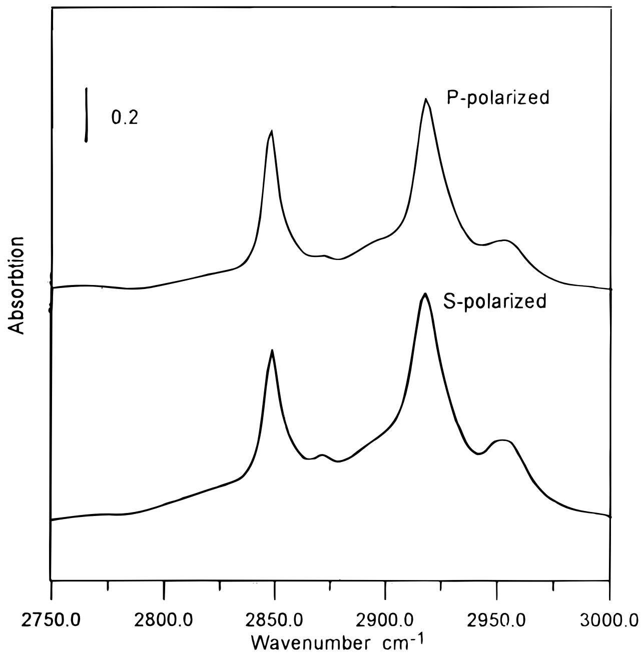

Figure 4. Polarized FTIR-ATR spectrum for the CH_2 stretching bands of the self-organizing polymer film.

Figure 3b. This indicates that the evaporation rate of the solvent greatly influences the structure of this amphiphilic polymer.

We used the FTIR-ATR technique to study the order and orientation of the alkyl chains in the self-organizing film. Frequencies for CH_2 antisymmetric and symmetric stretching bands are sensitive to the conformation of the alkyl chains: If the alkyl chains are highly ordered (all trans conformation), the bands appear near 2918 and 2850 cm^{-1}, respectively. However, if the alkyl chains are highly disordered, the frequencies may shift upward to near 2927 and 2856 cm^{-1}. Hence, the frequencies of CH_2 antisymmetric and symmetric stretching bands can be used as practical indicators of the degree of order for alkyl chains.[12] From the FTIR spectrum of the cast polymer film, we can see that the symmetric and antisymmetric stretching bands for CH_2 appear near 2918 and 2850 cm^{-1}, respectively, indicating that the alkyl chains in the organized film are well-ordered. The polarized FTIR-ATR spectra for the CH_2 stretching bands are shown in Figure 4. The dichroic ratio was defined as the ratio of the absorbance intensity of S-polarized light to that of P-polarized light, using the uniaxial orientation modes (which means all molecular chain axes are uniaxially oriented around the film surface normal) and the transition moment of the CH_2 group stretching vibration perpendicular to the alkyl chain axis.[13] We calculated the average tilt angle of the alkyl chains in the multilayer as $\gamma = 30°$, according to eq 1.

$$D(\gamma,\theta{=}90°) = \frac{E_y^{\,2}(2 - \sin^2\gamma)}{E_x^{\,2}(2 - \sin^2\gamma) + 2E_z^{\,2}\sin^2\gamma} \qquad (1)$$

The layer spacing 36.6 Å of the self-organizing polymer film is anomalously small, since the thickness of the ES-3 monolayer is about 25 Å,[9] and the tilt angle of 30° is still not sufficient to account for this low layer spacing. We propose a partially interdigitated model to fit these data for the cast polymer films, as shown in Figure 5. Since we have obtained the thickness of the network as about 6 Å in our previous work,[9] an approximate 14.4 Å interdigitated length between alkyl chains on adjacent layers is easily calculated to fit this model.

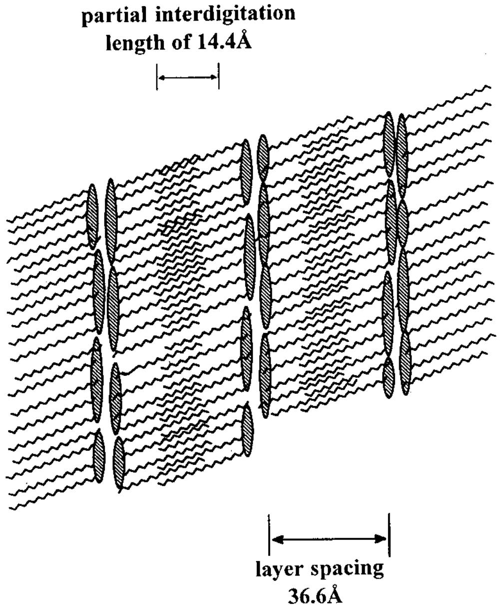

Figure 5. Plausible model of the self-organizing film based on the collected data.

Considering that the local electron density maximum in the layer's middle between the hydrophilic regions resulted from partial interdigitation, we can calculate the intensities of the X-ray diffraction peaks using eq 2.[14] While we have used several structural models with different interdigitation lengths, only the 14.4 Å interdigitation length (equal to double the $^{1}/_{5}$th layer spacing 36.6 Å) provides reasonable results. This is strengthened by results confirming this structural model shown in Figure 3. The disappearance of the fifth-order diffraction and relatively lower intensity of the second-order diffraction peak are clearly evident here. The calculation is very consistent with the experimental results and thus indicated that the schematic model of partial interdigitation is reasonable.

$$I_k(S) = \frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta}\Big|\sum_{j=1}^{m} F_j e^{isx_j}\Big|^2 |G|^2 e^{-2m} A(\theta) \qquad (2)$$

where I is the intensity of the diffraction, k is the diffraction order, S is $4p \sin q/l$, F_j is the structural factor of the j layer, $|G|^2$ is the interference function, and $A(q)$ is the absorption factor.

From the structural model for the cast polymer film, we deduce that the polymer bulk thermal behavior may differ from that of the thin film. Figure 6 represents the DSC thermograms comparing the self-organizing film and its bulk material. As predicted, the thermobehavior of the self-organizing film is quite different from that of its bulk material. As we reported, for this amphiphilic polymer (powder), three thermal transitions corresponding to the melting and liquid crystalline transition processes exist.[11] However, for the self-organizing polymer film only two thermal transitional peaks appeared near 348 and 408 K, respectively. The enthalpy change of the self-organizing film at the first transition was 32 J/g (7 kJ/mol alkyl chains), which was much smaller than that of the bulk material (75.5 J/g) at the first transition but similar to the typical enthalpy

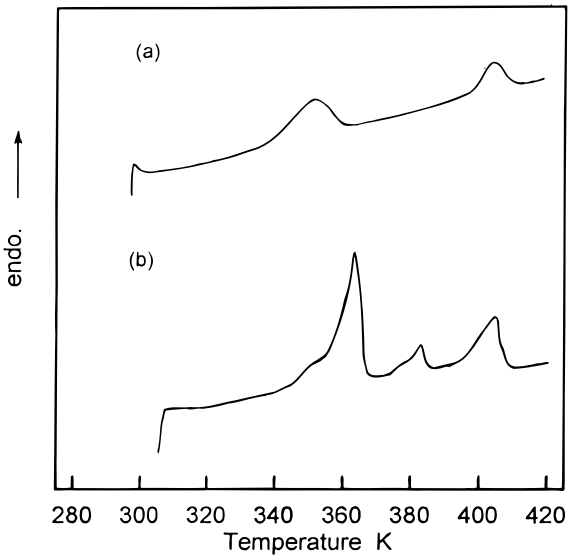

Figure 6. DSC thermogram of (a) the self-organizing polymer film by slow evaporation of organic solvent and (b) the polymer bulk precipitated powder.

of melting for stearic chains. We may attribute the first thermal transition to the transition from ordered lamellar phase (similar to the gel phase in the bilayer) to fluid lamellar phase. The second transition may correspond to the transition from the fluid lamellar phase to the nonlamellar phase. Temperature dependent X-ray diffraction also supports this attribution: when heating above the second transition region, the X-ray diffraction pattern indicates the existence of an isotropic phase.

From the above results, we conclude that ordered self-organizing polymer films have been fabricated by slow evaporation of organic solvents. The cast film has a partially interdigitated layer structure quite different from the bulk material. Slow evaporation of the organic solvents plays an important role in the fabrication of self-organizing polymer films. A similar effect of solvent evaporation rate on the self-organized polymer films with honeycomb morphology has also been observed by Francois.[15] We think that the organic solvents provide the amphiphilic polymer with a special microsurrounding. The solute alkyl chains have strong cohesive forces for each other, but smaller than those of medium molecules.[7g] Therefore, the alkyl chains dissolve in the medium and, at the same time, the solvophobic network self-associates to repulse the solvent. In the case of the natural evaporation of solvent, the alkyl chains simply align as the solvent is removed. During this process, there does not exist a self-organizing process of alkyl chains to form an interdigitated structure since the long spacing of the products is 51 and 49 Å.[11] So products behave the same as the polymer crystal, which is just like the case of precipitation from solution. However, in the case of the slow evaporation of solvent under saturated vapor pressure, the solvophilic alkyl chains have enough time to undergo a self-organizing process which may be responsible for the partial interdigitation. At the same time, the solvophobic network also tends to associate and repel the alkyl chains. So, these cooperative effects could be responsible for the formation of this highly ordered stratified polymer film. Furthermore, the balance between the hydrophilic and hydrophobic parts may also play an important role. As we reported before,[8] for this amphiphilic polymer with an alkyl side chain content of 75.8%, the balance between the hydrophilic and hydrophobic parts appears to be well balanced. However, for an amphiphilic polymer with a low alkyl chain content (e.g. 48.5%), it has a stronger hydrophilicity than hydrophobicity, and it cannot form an ordered cast film even by slow evaporation from an organic solvent. This means the balance between the hydrophilic and hydrophobic polymer parts plays an important role in the film-forming (organizing) process.

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