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LB film structure of poly(2-methoxy,5-(8-methoxy-3,6-dioxa-1undecoxy)-*p*-phenylene vinylene) studied by spectroscopy

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Abstract

A PPV derivative, poly(2-methoxy,5-(8-methoxy-3,6-dioxa-1-undecoxy)-*p*-phenylene vinylene), has been synthesized by the Gilch route to study the influence of a long alkyl side chain and a di(ethylene oxide) methyl ether group on the multilayer structure obtained by Langmuir–Blodgett (LB) technique. UV–visible, PL, and FTIR spectra are applied to study the conformation and orientation of the MMDU-PPV molecules in multilayer organization. MMDU-PPV is apt to form a transferable monolayer film, in which the plane of its π system is perpendicular to the air–water interface. The adjacent conjugated main chains of MMDU-PPV in LB films are aligned in parallel fashion and packed with the plane of its π system approximately perpendicular to the layer plane and not organized to compact π -stacking structure for introducing di(ethylene oxide) methyl ether (DEOM) side chains to conjugated main chains. The long alkyl side chains are characterized by all trans-zigzag conformation and average tilt angle of $36\pm1.5^\circ$. The layer-by-layer multilayer of MMDU-PPV obtained by Langmuir–Blodgett technique exhibits some in-plane anisotropy and more pure photoluminescence than that of the dilute MMDU-PPV solution. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: PPV and its derivative; LB film; Layer-by-layer structure; Anisotropy

1. Introduction

Conjugated polymers have been the subject of great interest in the recent literatures from both fundamental point of view and applied science perspective [1,2]. Among the several types of conjugated polymers in the present investigations, poly(p-phenylene vinylene) (PPV) derivatives

stand out for being able to combine a reasonably good environmental stability to high optoelectronic properties [3], and they are presently developed as active components for organic electroluminescent (EL) device. At present, active layers in lightemitting devices (LEDs) are made mostly via simple spinning cast technique [4], which leads in principle to randomly oriented polymer chains and monomerie units. It appears that controlling over the organization of polymer film in nanoscale might have a great influence on the optical and electrical properties of EL device [5]. Recently,

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highly anisotropic optical properties have been obtained in stretched layers [6], as in LEDs with polarized emission with an intensity ratio up to 3:1 between light emitted parallel and perpendicular to the stretching direction [7]. Such a film can also be strongly birefringent with different refractive indexes taken at the preferential directions [8].

Nanoscale control of the organization of polymer film can be obtained when the Langmuir-Blodgett (LB) technique, or self-assembly techniques, is used instead of the spinning cast technique. The LB technique can precisely control the thickness and order of a film to molecular scale, and allow the study and modeling of polymeric devices [9]. Using the LB deposition technique in molecular processing has represented a powerful method for organizing rodlike polymers [10]. Previous LB studies of rigid-rod polymers with a. nonpolar 'hairy-rod' structure have established that the flow induced in transferring monolaver film to substrate is responsible for the formation of anisotropic polymer film [11]. Unfortunately, not all molecules can be processed into single-component multilayers by this technique. The appropriate materials must have the proper balance between hydrophilic and hydrophobic properties and between rigid and flexible moieties to facilitate the formation of a stable monolayer phase at the air-water interface. So far, most LB films of PPVs have been prepared by using heat treatment of LB films of a precursor polymer [12,13], which is so called tailoring precursor route of PPV in soluble form. Upon heat treatment, a large volume fraction of the multilayer is eliminated from the film, probably causing the disruption of film structure. Synthesis of regioregular head to tail coupled amphiphilic PPV derivative is another way to be suitable to LB technique. However, the reports of LB films of these PPV's derivatives are few. The LB layers of poly(2-methoxy,5-(2'-ethylhexyloxy)*p*-phenylene vinylene) (MEH-PPV), a typical EL material produced commercially, have been built up on quartz and ITO substrates, but it seems not a monolayer film at the air-water interface [14].

A synthesis of a PPV derivative (see Scheme 1) carrying long hydrophobic *n*-hexadecyloxy side chains and hydrophilic di(ethylene oxide) methyl ether (DEOM) side chains is reported in this

article. Such a PPV derivative is soluble in many organic solvents and apt to form a stable and transferable monolayer at the air-water interface. The characteristics of Langmuir films of the poly(2-methoxy,5-(8-methoxy-3,6-dioxa-1-undecoxy)-*p*-phenylene vinylene) (MMDU-PPV) formed at the air-water interface is investigated and the results of UV-visible polarized spectroscopic studies and preliminary linear dichroism infrared analysis for molecular orientation of polymeric chains deposited via LB transfer on solid substrates are presented. The peak width at the half height of the photoluminescence spectra of MMDU-PPV LB films is smaller than that of its dilute solution. It is expected that further work on these compounds could in fact corroborate their potential as anisotropic thin films for use in optoelectronic devices.

2. Experimental

2.1. Synthesis

MMDU-PPV and its intermediates were prepared in accordance with the methods proposed in the literature [15–17]. All the reaction steps are described in Scheme 1 and the intermediates were characterized by FT-IR and ¹H-NMR (no shown here)

2.1.1. Synthesis of 1-bromo-2-(2inetlioxyethoxy)ethane (1)

To a round-bottom flask were added di(ethyleneglycol)methylether (12.0 g, 0.10 mol) and dry THF (30 ml). To this solution was slowly added phosphorus tribromide (10.0 g, 0,04 mol). The reaction was then heated to 65 °C for 8h. After allowing the reaction to cool to ambient temperature, 30 ml CHC1₃ and 50 ml water were poured into the reaction and the layers were separated followed by extracting of the organic layer with water. The organic layer was dried with MgSO₄ and then concentrated under vacuum to yield the desired product in 93% (17.0 g) yield as colorless oil.



(MMDU-PPV, 56% yield)

Scheme 1. Synthesis of MMDU-PPV.

2.1.2. Synthesis of 4-(n-hexadecyloxy) phenol (2) To a round-bottom flask were added hydroquinone (14.5 g, 0.13 mol), NaOH (4.0 g, 0.10 mol) and ethanol (100 ml). To this solution was added 1-bromohexadecane (30.5 g, 0.10 mol), and a N₂ atmosphere was established. The reaction was then heated to reflux for 6 h. After allowing the reaction to cool to ambient temperature, the precipitate was suction-filtered and washed with hot water five times., and dried in a vacuum oven at 50 °C for 24 h. The product was purified by recrystallization twice from ethanol to give 27.0 g (81%) of **2**.

2.1.3. Synthesis of 1-(n-hexadecyloxy), 4-(8methoxy-3,6-dioxa-1-undecoxy) benzene (3)

To a round-bottom flask were added 2 (6.7 g, 0,02 mol), KOH (1,3 g, 0.022 mol), and ethanol (50 ml). To this solution was added **1** (3.86 g, 0.02 mol), and a N_2 atmosphere was established. The

reaction was then heated to reflux for 12 h. After allowing the reaction to cool to ambient temperature, the precipitate was suction filtered and washed quickly with ethyl ether several times, and dried in a vacuum oven at 50 °C for 24 h, A white plate crystals were recovered in ethanol, dissolved in CHCl₃, again, recovered in ethanol and dried in a vacuum oven at 50 °C for 24 h. The yield of **3** was 76% (6.7 g)

2.1.4. Synthesis of 1,4-bis(bromomethyl)-2-(nhexadecyloxy), 5-(8-methoxy-3,6-dioxa-1undecoxy) benzene (4)

To a round-bottom flask were added **3** (5.2 g, 0,012 mol), paraformaldehyde (2.5 g, 0.08 mol), acetic acid (20 ml), and 30% HBr in acetic acid (20 ml). A N_2 atmosphere was established followed by heating the reaction firstly to 70 °C for 1.0 h, a while precipitate appeared in the solution, the

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precipitate was dissolved again with heating to 85 °C, and then keeping reaction at the temperature of 85 °C for 2.0 h. After allowing the reaction to cool to ambient temperature, the reaction was neutralized by Na₂CO₃ (aq). The precipitate was suction filtered and washed with water until the water tested natural, and dried in a vacuum oven at 50 °C for 24 h. The product was purified by recrystallization twice from hexane to give 4.73 g (63%) of **4**.

2.1.5. Polymerization of 1,4-bis(bromomethyl)-2-(n-hexadecyloxy),5-(8-methoxy-3,6-dioxa-1undecoxy) benzene (MMDU-PPV)

To a round-bottom flask, well flushed with N₂ and equipped with a rheostat as the mechanical stirrer, was added a solution of potassium tertbutoxide in THF (20 ml, 1.0 M), 4-methoxyphenol (1.0 mg), and dry THF (20 ml). The solution of 4 (2.5 g, 4.0 mmol) in dry THF (60 ml) was then added at a rate of 15 ml h^{-1} with syringe. After complete addition of the monomer, the reaction was stirred for an additional 18 h and poured into rapidly stirred methanol, and the resulting polymer was collected by suction filtration. The polymer was purified by two additional precipitations, from THF into methanol. Then the polymer was collected and dried under a reduced pressure to give 1.08 g (56%) of MMDU-PPV. IR (KBr), cm⁻¹; 3058, 2920, 2850, 1598, 1504, 1468, 1422, 1388, 1355, 1256, 1206, 1050, 966, 851, 822, 721, 697. ¹H-NMR (500MHz, CDC1₃): 7.10–7.43 (m, 2H, PhH), 6.80-7.01 (m, 2H, vinyl protons), 3.87-4.20 (m, 7H, OCH₂CH₂O, OCH₂ and OCH₃), 1.81 (m, 2H, OCH₂CH₂), 1.48-0.80 (m, 29H, CH_2 and CH_3).

2.2. Monolayer characterization

The experiments for monolayer spreading were performed on a KSV-5000 LB system (KSV Instruments, Helsinki, Finland) equipped with computer controls. A Wilhelmy plate was used as the surface pressure sensor and situated in the middle of the trough. Two barriers compress or expand symmetrically at the same rate from two sides of the trough. Monolayers were obtained by spreading 300 μ l chloroform solution composed of MMDU-PPV with a concentration of 160 μ g ml⁻¹ onto pure water without the adding of acid (pH ~ 6.0). After this, 15 min were allowed for solvent evaporation and then the monolayer was compressed at a typical rate of 20 mm min⁻¹. Isotherms of surface pressure versus mean molecular area/repeating unit are measured at 12± 0.2 °C. The molecular weight/repeating unit of 460.0 g mol⁻¹ was adopted for all calculations.

2.3. Fabrication of Langmuir-Blodgett films

LB films were fabricated onto both CaF₂ crystals and quartz plates by vertical dipping method at a surface pressure of 20 mN m⁻¹ and a dipping speed of 2.0 mm min⁻¹. The substrate surface was set to be parallel or perpendicular to the moving direction of the barrier. Prior to deposition, the CaF₂ crystals were washed with hot CHC1₃, for 24 h in a Soxhlet apparatus and the quartz plates were treated with saturated K₂Cr₂O₇/concentrated H₂SO₄ solution for 6 h and then carefully washed with ultrapure water. In course of deposition, after each cycle of the upward and downward stroke, the substrate was kept dry completely in air for at least 15 min, so that the following monolayer could be favorably transferred. The transfer ratio for Z-type of films was of the order of 0.8 ± 0.1 for both CaF₂ and quartz plates, respectively. The forward (backward) speed of the barriers was set to be 10.0 mm \min^{-1} .

2.4. Spectra measurement

UV-visible absorption spectra were obtained on a Shimadzu UV-3100-VIS-NIR spectrophotometer, and PL spectra were obtained on a Aminco Bowman series 2 Luminescence Spectrometer (USA). Fourier transform infrared (FTIR) transmission spectra were collected through a IFS66V FT-IR spectrophotometer (Bruker, German) equipped with a DTGS detector, 20 scans for those KBr pellets and 300 scans for those LB films on CaF₂ substrates. An edualite polarizer (USA) was employed for UV-visible polarization and a KRS-5 polarizer for IR polarization measurements of LB films. For linear dichroism studies, behind a rotating polarizer the sample frame composed of aluminum strips could be rotated to change the incidence angle in CaF_2 plate. All FTIR spectra were collected for 500 interferograms with the resolution 4 cm⁻¹.

3. Results and discussion

3.1. Behavior of MMDU-PPV monolayer

MMDU-PPV is not a classical surfactant with charged headgroups, but it has structural components that can be ranked as more or less polar. The DEOM groups of MMDU-PPV are the polar portion of the macromolecule, and the hexadecyloxy groups constitute the nonpolar tails, Spreading the chloroform solution of MMDU-PPV onto the air–water interface carefully obtains a uniform dispersion. The corresponding pressure area (π – *A*) isotherm is shown in Fig. 1. In Fig. 1, MMDU-PPV molecules exist three kinds of aggregation states at the air–water interface in the process of compression: the first at about 50 Å² per repeating unit, the second at about 30 Å² per repeating unit, and the third at about 14 Å² per repeating unit.



Fig. 1. Isotherm corresponding to the first compression of a floating film of MMDU-PPV (on water subphase at temperature of 14 $^{\circ}$ C) spread from a dilute solution. Inset is the orientation of repeating unit of MMDU-PPV at the air–water interface.

According to CPK. model [13], the repeating unit: area of 54 $Å^2$ might be accounted for the orientation of the aromatic rings and the alkyl chains tilting to the air-water interface. While the per repeating unit surface area of 30 $Å^2$, close to the value of the related macromolecules at the airwater interface [13,17], suggests formation of a MMDU-PPV monolayer with the plane of its π system nearly perpendicular to the air-water interface (see Scheme 2). The declining slope of the $\pi - A$ isotherm in the second state, characteristic of flexibility of the monolayers, indicates that MMDU-PPV is not arranged in a rigid crystalline π -stacked structure. The repeating unit of 14 Å², which is close to the half of area in the second state, gives that the monolayers of MMDU-PPV have collapsed to the multilayers.

3.2. UV-visible and PL spectra

The UV-visible absorption of conjugated polymers from the $\pi - \pi$ transition is very sensitive to the direction of polarization of an incident light, which enables the use of polarized light to probe the structural anisotropy within the films [18]. LB films were obtained by setting the substrate surface parallel to the moving direction of the barrier at 14 and 30 mN m⁻¹ surface pressure, respectively. P-Polarization is defined so that the electrical field is parallel to the substrate edge (dipping direction). S-Polarization is orthogonal to P-polarization. Both P and S polarization directions are perpendicular to the light transmission direction. Fig. 2 shows UV-vis spectra of LB films, which is prepared at the surface pressure of 14 mN m⁻¹, corresponding to different polarization directions. The absorption under P-polarization mode is the strongest, while that under the S-polarization mode is the weakest. The absorption at any other polarization angle falls between two extremes. Since the absorption of UV light is the strongest when the electric vector of the incident light is parallel to the backbone of a conjugated polymer [19,20], the results indicate that MMDU-PPV backbones preferentially align parallel to the dipping direction. There is a natural tendency of rigid rods to align perpendicular to the direction of compression and parallel to lines of flow between



Scheme 2. Molecular structure and aggregating state of MMDU-PPV monolayer at the air-water interface.



Fig. 2. Polarized UV-visible spectra of MMDU-PPV LB films (15 layers on both sides of the plate, prepared at the surface pressure of 14 mN m⁻¹).

the water and the substrate induced by dipping [11]. Thus, to obtain the films with more obvious anisotropy, optimal deposition geometry can be chosen (in a standard LB trough) to place the substrate plane parallel to the direction of compression. These observations again confirm the preferential order and edge-on arrangement of the polymer backbone in the film [21]. The polarized UV-visible absorption of LB films obtained at the surface pressure of 30 mN m⁻¹ (not shown here) reveals no any anisotropy, which further confirms the results shown by the π -A isotherm that the MMDU-PPV monolayers under the pressure of 30 mN m⁻¹ have collapsed to multilayers.

Interactions between polymers or polymer segments strongly influence the electronic properties of conjugated polymer films. For example, the large absorption spectral shift measured in aggregates of oligo-phenylene vinylene [22] and the rapid spectral diffusion observed in time-resolved photoluminescence spectra of amorphous PPV films [23] are quite related to these interactions. Fig. 3 shows the UV–vis absorption spectra of both LB films and the solution of MMDU-PPV. The maximum peaks of the absorption are found at 489 and 485 nm, respectively. The broad ground-state absorption spectrum for LB films shows a small red shift compared with that for the solution spectrum. This characteristic is in contrast



Fig. 3. Absorption spectra of MMDU-PPV; (a) multilayer on a quartz plate (15 layers on both sides of the plate); (b) solution in chloroform $(1 \times 10^{-5} \text{ mol } 1^{-1})$.

to that of many other soluble conjugated polymers where large solvatochromism) (the spectra in dilute solution show large blue shifts relative to that obtained in the solid state) has been observed [24–26]. Conformational changes of π -conjugated polymers are inherently coupled to the electronic structures of the π -electron system. The broad, longest wavelength absorbance of LB films can be attributed to the $\pi - \pi$ electronic transition associated with the π -conjugated polymer backbones. In the previous literature, polydiacetylenes, poly(thiophene)s and PPVs exhibit color change (chromism), which is solvent (solvatochroinism) and/or temperature (thermochromism) dependent. But the interpretation of these transitions for conjugated polymers has been controversial because of the difficulties in separating the contributions of the conformational changes in the polymer backbone and the aggregation phenomenon of the macromolecules to the observed chromism [27]. However, in MMDU-PPV, the side groups mat render the polymer soluble are well separated from those on the adjacent alternating chromophore units. The steric interaction between side groups, which may twist the conjugated repeating units from planar configuration and cause solvatochromism, is negligible in

MMDU-PPV.Therefore, this negligible red shift in MMDU-PPV films compared with the solution spectrum may be the result of solid-state aggregation [28]. It seems that the introduction of DEOM to the conjugated main chains may favor formation of J-stacking [29] between benzene rings in LB films and avoid the compact H-stacking structure, in which the stronger interaction of the conjugated repeating units can lead to large absorption spectral shift. The absorption edge of MMDU-PPV is about 690 nm, which corresponds to 1.80 eV of optical band gap, smaller than that of the parent PPV (E_{opt} – 2.39 eV). The steric interaction of side groups between the conjugated repeating units and the ordered arrangement of conjugated main chains in LB films of MMDU-PPV might account for the narrowed bandgap.

The PL spectra of MMDU-PPV pumped by UV light (λ_{ex} – 350 nm, Xe lamp) of 5-layer LB films onto the quartz substrate and the solution in CHCl₃ display some similar feature(as shown in Fig. 4). The sharp main peaks for LB films and for the solution sample are at 584 and 586 nm, respectively, indicating that the emission area lies in the region of orange. No obvious shift in the PL spectrum of LB films relative to that of the dilute



Fig. 4. PL spectra of MMDU-PPV: (a) multilayer on a quartz plate (five layers on both sides of the plate); (b) solution in chloroform $(1 \times 10^{-5} \text{ mol } 1^{-1})$.

solution would be an implication that the polymer main chains are separated from each other and excimer emissions are suppressed in both LB films and the dilute solution. In addition, the peak width at the half height of LB films is smaller than that of the dilute solution, suggesting the introduction of DEOM to PPV might improve the monochromalicity of emission light in solid state.

The UV-vis absorption spectra of MMDU-PPV LB films prepared at surface pressure of 14 mN m⁻¹ with various numbers of layers are in Fig. 5. The linear increase in absorbance with the number of layers confirms that the transfer process of Lungmuir films is uniform and the layer-by-layer deposition of MMDU-PPV films at molecular level is successfully controlled.

3.3. FTIR spectra of MMDU-PPV LB films

Fig. 6 shows the FTIR spectrum of 15-layer MMDU-PPV LB films obtained at the surface



Fig. 5. Absorption spectra of MMDU-PPV LB multilayers deposited on quartz. The number of layers deposited is indicated. The absorbance at 489 nm as a function of the number of layers is given in the inset.



Fig. 6. FTIR absorbance spectrum of MMDU-PPV LB multilayers on CaF_2 plate. See the text for the discussion of many characteristic peaks.

pressure of 14 mN m⁻¹. A weak feature near 2955 cm^{-1} is assigned to the CH₃ antisymmetric stretching mode of hydrocarbon tail; two strong bands at 2920 and 2850 cm⁻¹ are attributed to the antisymmetric and symmetric CH₂ stretching vibration of long polymethylene hydrocarbon chains, respectively. The band at 1734 cm^{-1} is attributed to the carbonyl absorption of a ester or carboxylic acid; a weak band at 1678 cm⁻¹ is attributed to C=O stretching vibration of the aromatic aldehydes; a weak peak at 1600 cm⁻¹ can be assigned to the antisymmetric stretching vibration in the aromatic rings due to the formation of carbonyls [30], these peaks suggest that MMDU-PPV has been oxidized in some extent. A band at 1508 cm^{-1} is assigned to the stretching vibration of semicircular phenyl rings; a strong peak at 1467 cm⁻¹ is attributed to the CH_2 scissoring mode of long polymethylene hydrocarbon chains; a band at 1414 cm^{-1} is attributed to the scissoring mode of the CH₂ connected to oxide atom; a band at 1208 cm^{-1} is attributed to the stretching mode of C-O in the benzene rings. It is well-known that the frequency of CH₂ antisymmetric and symmetric stretching vibrations bands are sensitive to the degree of conformational order of alkyl chains [31-33]. When the alkyl chains are highly ordered (trans-zigzag conformation), the

bands appear near 2920 and 2850 cm⁻¹, respectively, and if conformational disorder is included in chain, they shift upward to higher wavenumber depending upon the content of gauche conformers. Therefore, the observations in Fig. 6 suggest that the polymethylene hydrocarbon chains of MMDU-PPV in LB multilayers are ordered. The band pattern and splitting of the CH₂ scissoring mode have been used extensively to characterize subcell packing in LB films since this peak can be spilt by the dimer local crystal field of adjacent methylene groups. Usually the splitting of δ (CH), 1470 cm^{-1} peak, provides an indication of orthorhombic-type packing with two molecules in one unit cell. On other hand, if only a single peak is observed at 1468 cm⁻¹, the crystal packing will be triclinic with one molecule per unit cell or, rarely, hexagonal [34]. A single peak near 1467 cm^{-1} in Fig. 6 assigned to the scissoring mode of alkyl side chain is indicative of triclinic subcell packing of polymethylene hydrocarbon chains in multilayer LB films of MMDU-PPV [35-39].

To evaluate the orientation of the polymethylene hydrocarbon side chains, Chollet's treatment of the linear dichroism of FTIR spectra is extended [34,40-42]. A detailed description of the method will not be repeated here since similar theory has been shown in the literature. The experimentally measured dichroic ratio $\beta(i)$ is related to the angle ϕ , between transition moment u and the surface normal of the substrate (see Fig. 7 inset). $\beta(i) = A_{\parallel}(i) |A_{\parallel}(0)| = A_{p}(i) |A_{\parallel}(0)|$, where $A_{\rm p}(i)$ and $A_{\rm p}(0)$ are measured band intensities in P-polarized absorption spectra with the incidence angle of *i* and normal incidence angle (i = 0) with respect to the film plane, respectively. Base on the assumptions proposed by Hsu et al for extended application of Chollet's treatment [34], equations can be derived directly from the Fresnel equations and Descartes laws:

$$\alpha = \frac{A_{\rm s}(0)}{A_{\rm p}(0)}$$

 $(1-\alpha)/(1+\alpha) = \langle \cos 2\omega \rangle$

 $n_1 \sin i = n_3 \sin T$



Fig. 7. Rotating polarized transmission FTIR spectra of MMDU-PPV LB films (21 layers). A_p (i = 0) (solid line), A_s (i = 0) (dotted line), and A_p (i = 60) (dash-dotted line). Inset is the transition dipolar moment u of a molecule positioned by the angles ω and θ in the trihedral OXYZ in nondegenerate case.

$$n = \frac{2\pi d}{\lambda}$$

$$\beta(i) = \frac{A_{\rm P}(i)}{A_{\rm p}(0)} = \frac{n_1 n_3 (n_1 + n_3)}{(n_1 \cos r + n_3 \cos i)} \\ \times \left\{ \frac{n_1^2}{n_2^4} \sin^2 i \frac{\langle ctg^2 \ \phi \rangle}{\langle \cos^2 \ \omega \rangle} + \frac{\cos i \cos r}{n_1 n_3} \right\}$$

where, $i = 60^{\circ}$, $n_1 = 1$ (air), $n_2 = 1.5$ (LB films), n_3 is the index of calcium fluoride which is 1.42.

The polarization of fine and very intense lines at 2920 cm⁻¹ is well known. This vibration, polarized in the crystal plane ac and perpendicular to the chain axis, is used to study the orientation of chains in acid layers. Fig. 7 shows the polarized infrared transmission spectra for a 21-monolayers MMDU-PPV LB films in the CH₂ stretching vibration region. It is found that $\alpha(2919) = A_s(0)/A_p(0) = 1.41$, then $\langle \cos 2\omega \rangle = -0.066$, the angle ω being measured in the XY plane from the OX axis (Figure 7 inset) which, in all the infrared experiments, coincides with the dipping direction. The fact that $\langle \cos 2\omega \rangle$ is not zero implies a molecular distribution anisotropy in the XY plane. A positive value of this orientation parameters is interpreted by assumption that the polymer layer consists of crystallites with the crystal plane ac oriented preferentially, parallel to the dipping direction.

The tilt angle of chains with the *OZ* axis is then obtained from the $\beta(60^{\circ}) - A_{\rm p}(60^{\circ})/A_{\rm p}$ (i=0)which is found equal to 0.982 for the line at 2920 cm⁻¹. It can be gotten that, knowing $\langle \cos 2\omega \rangle$, $\phi = 54^{\circ}$, which corresponds to a tilt angle of 36° between the polymethylene hydrocarbon side chains and the normal to the plate with an estimated error of $\langle 1.5^{\circ}$. This result is similar to those obtained with stearic acid monolayers in which the tilt angle of the chains is estimated at 30.3° by Bateman [43] and between 27 and 35° by Takenaka [44].

4. Conclusion

A conjugated polymer, MMDU-PPV, is successfully dispersed at the air-water interface to form a long-term stable monolayer, which is organized with the plane of its π system nearly perpendicular to the air-water interface. The monolayer is apt to be deposited on the substrates in Z type structure by LB technique. The conjugated main chains of MMDU-PPV in 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. The long alkyl side chains of MMDU-PPV in multilayer films present all trans-zigzag conformation and have an average tilt angle $(36+1.5^{\circ})$. These results indicate that the layer-by-layer deposition of MMDU-PPV films at molecular level is successfully controlled. This manipulation at molecular level offers many potential advantages in device applications.

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