Interfacial Organization-Induced Supramolecular Chirality of the Langmuir−Schaefer Films of a Series of PPV Derivatives

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ABSTRACT: This paper reports the supramolecular chirality from optically inactive polymers through an interfacial organization at the air/water interface. A series of poly(*p*-phenylenevinylene) (PPV) derivatives with dimethyloctyloxyphenyl substitutents were designed, and their spreading Langmuir monolayers as well as Langmuir−Schaefer (LS) films were investigated. The films were characterized by the $\pi-A$ isotherm, UV−vis absorption, fluorescence, and circular dichroism (CD) spectroscopy. The $\pi-A$ isotherms showed plateau regions for all the polymers. The monolayers of the polymers can be transferred onto solid substrates as multilayer films, in which chromophores exhibited an H-aggregation. Although no CD signal was detected in both chloroform solutions and the cast films, supramolecular chirality was observed for some of the polymers at certain conditions. The larger steric hindrance of the side chain in the PPV polymer and a lateral compression of the Langmuir film over the plateau region in the $\pi-A$ isotherm were necessary to obtain the chiral multilayers. It was suggested that the supramolecular chirality of the films was due to the formation of a stereoregular arrangement of the side chain along the polymer backbone through an interfacial organization.

Introduction

Chirality is of considerable importance in both life and material sciences.[1] Molecular chirality, which describes the handedness of a molecule, is an important basis for understanding complex phenomena in biological systems.[2] It is also a fundamental issue in sterochemistry with crucial importance in crystal growth, asymmetric catalysis, and molecular recognition.[3] Chirality can be observed in various levels from a single molecule to supramoelcualr systems, in which noncovalent interactions such as hydrogen-bonding, electrostatic interactions, hydrophobic interactions, $\pi-\pi$ stacking, and coordination play important roles.[4−6] Besides the chiral components, achiral components can also contribute to the supramolecular chirality through interactions with chiral substrate or matrix. In some particular cases, even complete achiral molecules can form chiral assemblies. For example, some inorganic compounds were reported to form chiral crystals.[7a] Banana-shaped achiral compounds were reported to form chiral liquid crystals.[5j] McConnell et al. recorded the formation of chiral crystalline monolayer domains in Langmuir films of enantiomerically pure lipids by epifluorescence optical microscopy.[7b] Chiral conglomerate crystallization monolayers from chiral molecules have also been observed at molecular resolution by scanning probe microscopy.[7c,d] In forming these chiral assemblies, the cooperative arrangement of the achiral molecules played an important role. We have investigated the supramolecular chirality of a series of Langmuir and LB films from achiral amphiphiles and found that the interfacial organization was one of the effective ways to control the molecular arrangement and obtain the chiral assemblies.[5a−e] Polymer can be regarded as the assembly of the monomers through the covalent bond. If the polymer units were cooperatively connected, chiral polymers can be obtained from the achiral monomers. This is true and was verified in some polymers such as polyisocyanide[8] and poly(phenylacetylene),[9] in which achiral monomer formed a chiral polymer. Moreover, through the introduction of a small amount of chiral unit, the chirality of the polymer can be controlled and the chirality was significantly amplified.[10] In addition, some preformed polymers were found to be induced or controlled by interacting with some small chiral molecules.[11]

In this paper, we report the supramolecular chirality based on a racemic PPV system through the interfacial organization. The π-conjugated PPV derivatives have been extensively studied due to their applications in organic light-emitting diodes (OLEDs),[12] solar cells,[13] field effect transistors (FETs),[14] chemical sensors,[15] and the others,[16,17] most of which are based on the films fabricated by the spin-coating method. However, there are few reports on the Langmuir and Langmuir−Blodgett films of PPV derivatives.[18,19] We have been interested in the chirality of supramolecular systems from achiral molecules in several systems.[5a−e] Here, we synthesized a series of racemic PPV derivatives and studied the supramolecular chirality in the LS films. Although some achiral or optically inactive polymers could show induced chirality upon interaction with chiral molecules in solution,[10,20] to the best of our knowledge, there is no report on the interfacial organization-induced chirality of polymer films. The used polymers are poly(2-methyloxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO−PPV), poly(2-(3′,4′-bis(3″,7″-dimethyloctyloxy)phenyl)-1,4-phenylenevinylene) (BDP−PPV), poly(2-(3′,4′-bis(3″,7″-dimethyloctyloxy)phenyl)-5-methoxy-1,4-phenylenevinylene) (BDMP−PPV), and poly(2-(3′,5′-bis(3″,5″-bis(3‴,7‴-di-

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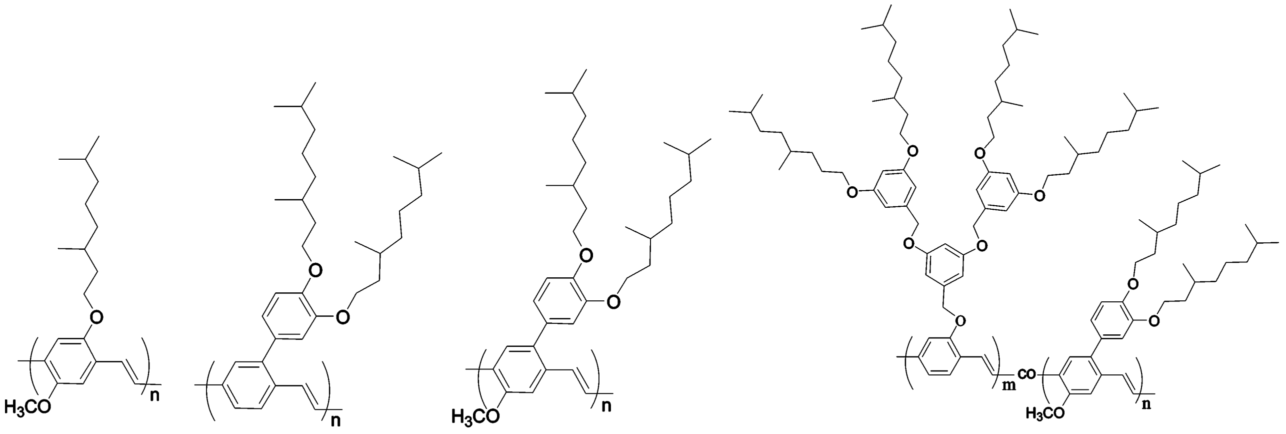
Chart 1. Chemical Structures of Alkylphenyl-Substituted PPV Derivatives



MDMO-PPV **BDP-PPV** **BDMP-PPV** **Co-PPV (m:n=1:2)**

methyloctyloxy)benzyloxy)benzyloxy)-1,4-phenylenevinylene)-*co*-poly(2-(3′,4′-bis(3″,7″-dimethyloctyloxy)phenyl)-5-methoxy-1,4-phenylenevinylene) (Co−PPV), as shown in Chart 1. MDMO−PPV is one of the well-known polymers of PPV derivatives, and the typical feature of BDP− and BDMP−PPV is that they have larger alkyl substitutes with phenyl groups directly connected to the backbones. However, Co−PPV has a small part of flexible substitutes. We have found that all the polymers can form stable monolayers at the air/water interface. Although the chloroform solutions did not show any chirality, supramolecular chirality was detected for the LS films of BDP− and BDMP−PPV, which were transferred at the surface pressures above the plateau region. However, all the films transferred at the surface pressure below the plateau region did not show any chirality. It is suggested that the supramolecular assemblies showing chirality were formed due to the cooperative stereo arrangement of both the large side chains and polymer backbone through an interfacial organization, not by the racemic nature of the polymers, because the LS films of MDMO−PPV and Co−PPV did not show chirality in the same conditions.

Experimental Section

Materials. The chemical structures and the abbreviations of the polymers are shown in Chart 1. They were synthesized via Gilch route[21a,b] and had been characterized by the ^{1}H NMR, ^{13}C NMR, and elemental analysis. The weight-average molecular weights (M_w) were 3.20×10^5, 3.22×10^5, 4.84×10^5, and 1.50×10^5 g mol^{-1}, and the polydispersity indexes (PDI) were 1.36, 1.27, 1.78, and 1.48 for MDMO−PPV, BDP−PPV, BDMP−PPV, and Co−PPV, respectively.[21c]

Procedures. Monolayers were formed by spreading a chloroform solution (~0.25 mg/mL) onto the water (Milli-Q, 18 MΩ cm) surface. After 15 min for the evaporation of the solvent, the surface pressure−molecular area (π−A) isotherms were recorded on a computer-controlled KSV-1100 film balance system with a barrier compression speed of 5 mm/min. After 10 min relaxation at certain surface pressure, the monolayers were transferred onto solid substrates, such as quartz and CaF$_2$, using the Langmuir−Schaefer (LS) method. In transferring the monolayer to the solid substrates by the LS method, the hydrophobic plate was hold parallel to the surface and lowed to touch the monolayer. After touching the film for 30 s, one end of the plate was slowly lifted up to form an angle of about 30°, and then the whole plate was slowly lifted up. After the film was dried in the air for a few minutes, the process was repeated and multilayer up to 70 layers could be obtained.

For UV−vis absorption, fluorescence, and circular dichroism (CD) spectra measurements, the transferred LS films, the cast films, and chloroform solutions were recorded by a JASCO UV-530, Hitachi F4500 fluorescence, and JASCO J-810 CD spectrophotometer, respectively. When measuring CD spectra, all the films were placed perpendicular to the light path and rotated within the film plane to avoid polarization-dependent reflections and eliminate the possible angle dependence of the CD signals.[22] All the experiments were carried out at 20 °C.

Results and Discussions

Spreading Langmuir films at the Air−Water Interface. PPV derivatives with certain alkyl chain substitutions were reported to form well-defined monolayers at the air/water interface.[18,19] The same is true for our newly synthesized polymers. Figure 1 shows the π−A isotherms of Langmuir films of PPV derivatives spread on water surface. MDMO−PPV shows an onset of the surface pressure at 0.28 nm^2/repeat unit and an inflection at 20 mN/m. This point does not appear to be associated with collapse because the area did not show significant changes with the elongation of time in this region. It might be related to the transition of the orientation and/or packing change of the functional groups. The extrapolated limiting molecular area for MDMO−PPV was approximately 0.26 nm^2/repeat unit. Previously, it was reported that poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH−PPV) could not form a true monolayers (extrapolated area of only ~0.027 nm^2/unit),[23] while those of the polymers with long alkyl chains could form a stable monolayer with monomer area of 0.22−0.25 nm^2.[24] The limiting area of MDMO−PPV suggested that our polymer formed a true monolayer.

When a phenyl group with substituted long alkyl chains was introduced to the side chain of the polymer backbone, as in the case of BDP−PPV, the isotherm of the spreading monolayer showed a larger molecular

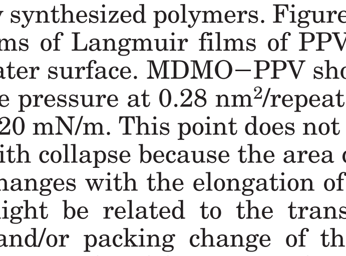


Figure 1. Surface pressure−area isotherms of PPV derivatives on water subphase: a, MDMO−PPV; b, BDP−PPV; c, BDMP−PPV; d, Co−PPV.

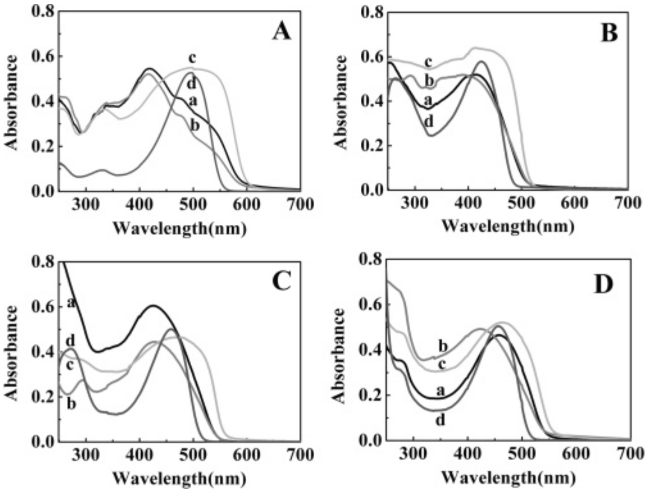


Figure 2. UV–vis absorption spectra of the LS films of PPV derivatives from water subphase: A, MDMO–PPV; B, BDP–PPV; C, BDMP–PPV; D, Co–PPV. a, lower surface pressure (70 layer); b, higher surface pressure (40 layer); c, cast films; d, in $CHCl_3$ solution.

area. Furthermore, a clear and longer plateau region was observed. When an additional methoxy group was introduced to the BDP–PPV, a further increase in the molecular area was obtained. Although the molecular area of Co–PPV was nearly that of BDMP–PPV, the isotherms of them were quite different because of the existence of the flexible substituted groups connected to the polymer backbone. The limiting areas extrapolated from the linear part of the isotherms were 0.35, 0.47, and 0.48 nm^2/repeat unit for BDP–PPV, BDMP–PPV, and Co–PPV, respectively. These data suggested that the phenyl side chain and methoxy group contributed to the molecular area.

On the other hand, when the film was compressed over the plateau region, the limiting areas of the linear became less than half of the limiting areas. This indicated that after the plateau region the aromatic rings were more densely packed, and also a bilayer was suggested to be formed.

UV–Vis Absorption and Fluorescence Spectra. Figure 2 shows the UV–vis absorption spectra of the transferred LS films in comparison with those of the cast films of PPV derivatives as well as those of compounds in $CHCl_3$ solution. Because all the monolayers showed a plateau region in the isotherms, we have transferred the films at a surface pressure below and above the plateau region on the solid substrates. A comparison of the spectra of LS films and those in $CHCl_3$ demonstrated that the major absorption bands, which correspond to $\pi-\pi^*$ transition of PPV derivatives,[18] showed a blue shift. For example, the maxima absorption wavelengths of LS film, $CHCl_3$ solution, and cast film were 416, 495, and 496 nm for MDMO–PPV, respectively. According to the molecular exciton model,[25] the formation of parallel aggregates (i.e., H-aggregate structure[26]) causes the spectrum of the monomer to broaden and blue shift. This indicated that H-aggregates were formed in the LS film of MDMO–PPV. In addition, although both of the films transferred at a higher and lower surface pressure showed a blue shift in absorption spectra, the shifts of the wavelength were different for these films. For example, 8 and 34 nm of the blue shifts were observed for the films of BDP–PPV transferred at 10 and 20 mN/m, respectively. Similar behavior was found for the other polymer films except for BDMP–PPV, where almost the same shift was observed for the films transferred at a lower and higher surface pressures. This indicated that when the films were compressed above the plateau region, the functional groups would be more vertically packed. Table 1 listed the maximum absorption position of all the LS films in comparison with those in $CHCl_3$ solution and the cast films. The spectral results indicated that H-aggregates were formed in the film, in which the chromophores of the PPV took a face-to-face arrangement. Previously, some PPV polymers were also reported to form J-aggregates (head-to-tail mode),[27] and some argued that blue shift may be caused from oxidation of the film. The spectra of the as-prepared films in our cases showed no change at atmosphere for more than 1 day. In addition, when these films were dissolved into chloroform, the same UV–vis spectra as those before spreading were obtained. These data clearly indicated that the blue shift in the organized molecular films was indeed due to the H-aggregation of the functional groups.

Table 1. Comparison of Peak Positions of UV–Vis Absorption and Fluorescence Spectra of Four Polymers

	MDMO–PPV	BDP–PPV	BDMP–PPV	Co–PPV
$CHCl_3$	495 (553)	424 (487)	470 (518)	456 (517)
cast film	496	410	459	465
LS film[a]	419	416	426	459
LS film[b]	416 (557)	390 (522)	428 (554)	424 (551)

[a] Below the plateau of $\pi-A$ isotherms and the surface pressures are 15, 10, 15, and 10 mN/m, respectively. [b] Above the plateau of $\pi-A$ isotherms and the surface pressures are 25, 20, 25, and 17 mN/m, respectively. The peak positions in the fluorescence spectra are in parentheses, and the excitation wavelength is the corresponding peak maximum in UV–vis spectra.

The substitutents in the side chain of the PPV backbone have great influence on the absorption spectra of the polymers in both solution and LS films. These differences could be ascribed to the perturbation of the conjugated PPV backbone by the substituted groups. In chloroform solution, the absorption maximum appeared in the order of MDMO–PPV > BDMP–PPV, Co–PPV, and BDP–PPV, which was a reasonable order regarding the donor–acceptor properties of the substituted groups. However, the extent of the blue shift in the film compared to the solution was greatly different for the PPV derivatives. The largest shift was observed for MDMO–PPV film, and the smallest one was for the Co–PPV film. It is regarded that the blue shift was related to the H-aggregation of the polymer in the films. These data indicated that in MDMO–PPV film the main chains were the most orderly packed in the four polymers, while it was the worst for the Co–PPV due to the existence of the flexible side substitutions. Considering the steric hindrance of the side groups, MDMO–PPV has the smallest substituted group and can freely rotate through the C–O bond; therefore, the backbone can be easily packed. Thus, we obtained the largest shift in the MDMO–PPV film, while the smallest for the Co–PPV.

PPV is typical of fluorescence emission and can be applied to OLED. All of the transferred LS films of these compounds exhibited emission upon excitation at 390–430 nm. Figure 3 shows the fluorescence spectra of the compounds in chloroform solution and in the films. In chloroform solution, main emission bands were observed at 553, 518, 517, and 487 nm for MDMO–, BDMP–, Co–, and BDP–PPV, respectively. The sharpness of the

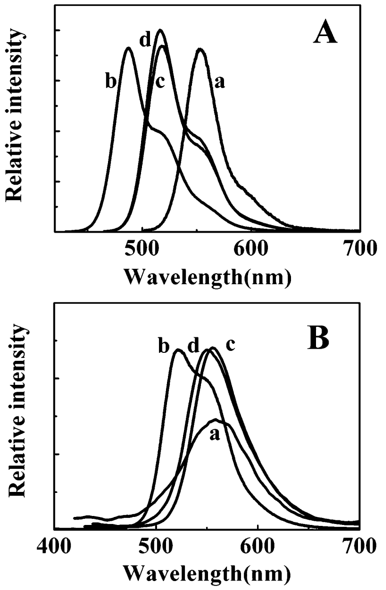


Figure 3. Fluorescence spectra of PPV derivatives: A, $CHCl_3$ solution; B, LS films deposited at higher surface pressure. a, MDMO–PPV (×10); b, BDP–PPV; c, BDMP–PPV; d, Co–PPV.

fluorescence spectra were essentially the same as those reported for the other PPV polymers.[6a,17c,24a] The emission bands of the polymers in the chloroform solution were in the same order as in the UV–vis absorption spectra. In the LS films, broad emission spectra with the red shift of the emission maxima were observed for all the films. The emission maxima appeared at 557, 522, 554, and 551 nm for MDMO–PPV, BDP–PPV, BDMP–PPV, and Co–PPV, respectively. These broad and red-shifted emission in comparison with the corresponding solution might be related to the excimer formation between the aromatic rings.

Supramolecular Chirality of the LS Films of PPV Derivatives. The film properties of the PPV derivatives described above are basically similar to those of other PPV derivatives.[18,19] We have further detected an interesting supramolecular chirality for some of the films although we used the PPV derivatives containing the racemic substituents. It was found that both the cast films and $CHCl_3$ solutions of all the polymers did not show any chiral optical effect. However, it is interesting to find that bisignated CD signals appeared for the LS films of BDP–PPV and BDMP–PPV transferred at the surface pressure over the plateau region, as shown in Figure 4. In the BDP–PPV LS film deposited at a higher surface pressure (Figure 4A), positive and negative Cotton effects were observed at about 440 and 320 nm, respectively, with a crossover at about 390 nm. The position of the crossover was very close to the absorption maximum in the UV–vis spectrum of the corresponding film. On the basis of this, the Cotton effect can be ascribed to the exciton couplet.[1b] In this case, however, the split was asymmetric. PPV is a conjugate polymer and has various conjugate lengths. In the absorption spectra, the shoulder or broaden of the peak at the longer wavelength was observed due to the overlap of the polymer with different conjugate lengths. Therefore, an intense Cotton effect in the longer wavelength was observed. In the case of BDMP–PPV film (Figure 4B), positive and negative Cotton effects are observed at 474 and 399 nm, respectively, with a crossover at 428 nm, indicating the existence of the exciton couplet in the films. However, besides these two kinds of polymers, the LS films of both MDMO–PPV and the Co–PPV did not show any chiral optical effects. In addition, no CD signal was obtained for all the films deposited at a lower surface pressure, i.e., below the plateau region.

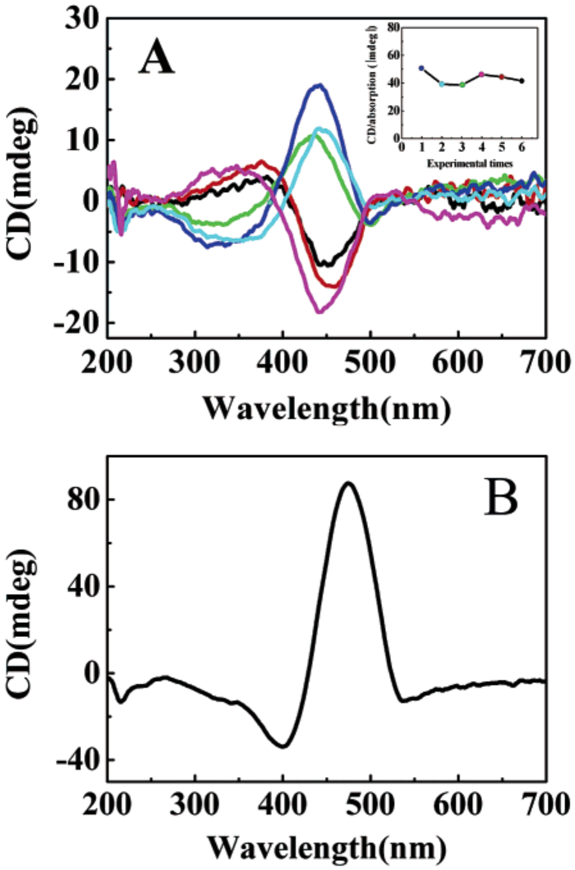


Figure 4. CD spectra of the transferred LS films of BDP–PPV (A) and BDMP–PPV (B) from water subphase. The different spectra in (A) indicate the films transferred from different batches, and the inset is a plot of the relative ratio of CD intensity to the optical density of the corresponding film in the UV–vis spectra against the numbers of the transferred films.

These results were somewhat different from those previously reported on chiral conglomerate behavior on surfaces of biphenyl benzoates[7d] and the formation of chiral smectic phase of banana-shaped achiral molecules[5j] because the chirality of the LS films of BDP– and BDMP–PPV was detected only when the films were transferred at the surface pressures above the plateau region. A possible explanation of the supramolecular chirality of PPV polymers was that a stereoregular stacking of the side chains along the polymer backbone in a helical sense, similar to the case of polyisocyanide.[8] When the PPV polymeric monolayers were compressed over the plateau region, a conformational change occurred, in which all the side chains together with the polymer backbone were suggested to align in a helical sense although the direct evidence for such helical structure still remained to be provided. Such kind of packing contributed to the formation of the supramolecular chiral assemblies, as illustrated in Figure 5. In forming such chiral assemblies, the steric hindrance between the neighboring units and the compact packing of the polymer unit seemed to be very important. Thus, supramolecular chirality was only observed in the films of BDP– and BDMP–PPV. When the polymer at water

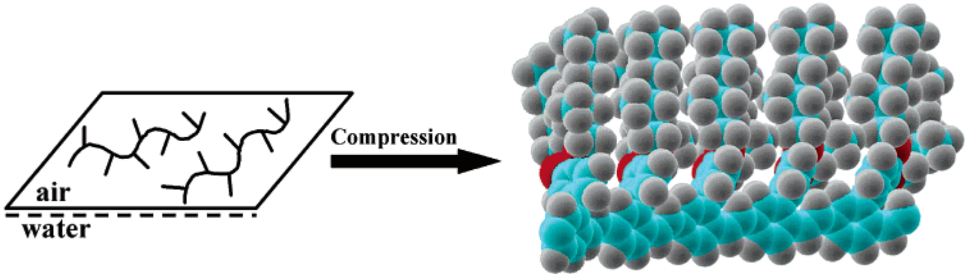


Figure 5. Illustration of the formation of the chiral PPV films induced by interfacial organization.

surface was compressed, an overcrowded stacking of the side chain occurred due to the larger side chain. For MDMO−PPV, the side group was too small to initiate a cooperative arrangement of side chain. For the Co−PPV, the cooperative arrangement of the side chain can be disrupted by the different monomer unit, and therefore, no chiral optical effect was obtained. Furthermore, a lateral compression of the Langmuir film was necessary to form the chiral LS films. When any of the Langmuir films was compressed to a surface pressure below the plateau region, the side chain was not overcrowdedly packed, and no chirality was observed, even for the films of BDP−PPV and BDMP−PPV.

It should be noted that although we can always get the CD signals for the films transferred at a surface pressure over the plateau region, the CD signals with opposite signs could be observed for the films transferred in different batches. Figure 4A shows the CD spectra of the BDP−PPV films transferred from six different batches, and the inset shows a plot of the relative ratio of CD intensity to the optical density of the corresponding film in the UV−vis spectra against the numbers of the experiments. It is clearly observed that opposite signals were obtained. In addition, the same CD intensity could not be obtained for the films with the same absorbance, as verified by the inset. This suggested that enantiomeric polymer assemblies were in fact formed in each compression. However, in each case, one of the enantiomers predominated when the film was compressed over the plateau region, and thus macroscopic chiral assemblies were formed. This is a manifestation of majority rule effect described in the literature for both covalently bound and supramolecular helical arrays.[1b,10] These results indicated that when the optically inactive PPV polymers were organized at the air/water interface, the symmetry could be broken at the point where the polymer unit was compressed to an overcrowded array, and one of the enantiomers was predominantly formed by chance.

Although the supramolecular chirality of the present PPV films is similar to that of polyisocyanide,[8] in which a stereoregular arrangement of the side chain in a helical sense played an important role, the present results are new and different. In the situation of helical polymers,[8−11] the achiral monomer was polymerized into a chiral polymer. In the present case a racemic mixture of a chiral polymer was compressed into a polymer film with an excess of one enantiomer by the help of the interface. Here, the Langmuir technique as well as the lateral compression of the film is very important. To obtain the assemblies with an enantiomeric excess, it seems that both a larger steric hindrance of the monomer unit and the lateral compression of the Langmuir film are very important. Even for the polymers with larger side chains, we could not obtain the assemblies with chiral optical properties at a surface pressure below the plateau region. Only when the Langmuir film was compressed over the plateau region did the chiral optical effect appear. So far, many chiral polymers from achiral molecules via induction by external chiral molecules have been reported,[6,8,10] but here we presented an example in which supramolecular chirality could be obtained from racemic precursor though an interfacial organization.

Conclusion

The newly synthesized PPV derivatives showed good spreading behavior at the air/water interface where a plateau region existed in the isotherms of the monolayers. Typical H-aggregates were formed in all the LS films. Although the cast films and chloroform solutions of these PPV derivatives did not show any chiral optical effects, bisignate CD signals were obtained for the LS films of BDP− and BDMP−PPV transferred at a surface pressure above the plateau region. The supramolecular chirality of the LS films, that is, forming macroscopic regions of the film with an excess of one enantiomer, is ascribed to the stacking of the polymer units in a helical sense in the films. Such kind of stacking can be realized through a molecular design and a lateral compression in the Langmuir film. In molecular design, a side group with larger steric hindrance is expected to form the nonracemaic chiral assemblies. The lateral compression on the Langmuir film played an important role to realize the cooperative arrangement of the polymer. Up to now, many researchers have disclosed that supramolecular chirality can be derived from achiral molecules through noncovalent interactions. However, our results indicated that an interfacial organization using the sophisticated Langmuir method was also effective in inducing the optically inactive polymer to the chiral polymer assemblies. The results provided an important new way to control the supramolecular chirality at interface and deepened the understanding of the supramolecular chirality from achiral components.

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