ABSTRACT

The aggregation of hairy-rod segments in solid films was observed using wide angle X-ray diffraction (WAXD). The films cast by evaporating the THF solvent from MEH-PPV/THF were extremely rigid due to the strong aggregation among the main chains of MEH-PPV and could not be disaggregated by heat. In contrast, aggregations in the films cast by evaporating the toluene solvent from MEH-PPV/toluene could be disaggregated due to the weak interactions among the side chains of MEH-PPV. Accordingly, the MEH-PPV/toluene system exhibits good thermal reversibility between aggregation while cooling and disaggregation when heated. The aggregation of the semi-rigid polymers occurs even at a concentration of well below the threshold lyotropic concentration. This process takes place in semi-rigid polymers with disk-like domains which serve as nuclei for the development of a macroscopic nematic phase as the polymer concentration increases during solvent evaporation. A film with a dominant lyotropic liquid crystalline (LC) phase was formed. As the temperature of the cast polymer film was increased, the thermotropic LC phase, rather than the lyotropic LC phase, was dominant between ca. 100°C and 230°C. However, both thermotropic and lyotropic LCs coexisted and associated with aggregation. The photoluminescence (PL) emission spectra and UV-vis absorption spectra of MEH-PPV in solution were obtained to elucidate the self-organized supramolecular aggregated conformation in various solvents, concentrations, and temperatures. The peaks exhibited a red shift in the PL emission spectra accompanied by a right shoulder when aggregation occurred. The shoulder grew as the concentration was increased.

INTRODUCTION

Liquid crystalline polymers (LCPs) constitute a class of soft materials whose anisotropic optical, electrical, mechanical, and rheological characteristics have led to a wide spectrum of practical applications. LCPs can be classified into at least two groups according to the position of the rigid monomers. One group forms the main chain liquid crystalline polymers (mcLCPs) [1], typically semi-rigid due to the rigid monomer units in their backbone, which PPV is a typical example [2]. The second group forms the side chain liquid crystalline polymers (scLCPs), composed of hairy-rod segments, for which MEH-PPV is a typical example [3]. In solution, these molecules self-organize to form a nematic phase, and the phase transition is a structural...
transformation either parallel to the concentration axis (so-called lyotropic LC) as predicted by the mean-field theory, or parallel to the temperature axis (so-called thermotropic LC).

The mean-field theory is known to focus on one particle and assume that the most important contribution to the interactions of such particle with its neighbouring particles is determined by the mean field due to the neighbouring particles. These aggregates are naturally identified as a nematic phase, formed by the self-organization of rod or disk segments. Moreover, the physical basis of the formation of these aggregates, the self-assembled structure of MEH-PPV and aggregated strands are studied in this work.

Electroluminescent semi-conducting polymers (ELSCPs) have good opto-electronic characteristics because their polymer main chains are composed of alternately conjugated double bonds and because the delocalized $\pi$ electrons can move along each main chain or hop between the adjacent main chains [4]. Therefore, ELSCPs have been widely investigated for their potential applications in light-emitting diodes (LEDs), photovoltaic devices, fluorescent sensors, and electrochromic devices [5-13]. Electroluminescent (EL) polymers that are suitable for application in organic/polymer displays have attracted intense academic and industrial research interests.

The electronic characteristics of conjugate polymers which are based on poly (p-phenylene vinylene) alkoxy derivatives are extremely sensitive to the chemical synthesis conditions, film processing, and photo-oxidation effects. In solid films, these materials aggregate and form excited interchain excitons, which are responsible for approximately 90% of optical excitations. These electronic species act as efficient quenching centres that decrease the quantum luminescent yield. The control of interchain interactions has been examined by varying the molecular conformation in solution and film processing [14-16]. This can be exploited to enhance the electrical and optical properties of polymeric light emission diodes.

Synthesis of MEH-PPV

Scheme I shows the synthesis of MEH-PPV [28-30]. A solution of $\alpha,\alpha'$-dibromo-2-methoxy-5-(2-ethyl-hexyloxy)xylene (1.0 g, 3 mmol) in dry THF (30 mL) was degassed at room temperature. A degassed solution of 95% potassium $t$-butoxide (1.045 g, 9.31 mmol) and 4-(t-butyl)benzyl bromide (0.435 mL, 2.37 mmol) in dry THF (80 mL) was added dropwise to the stirred solution within 30 min at 20°C under argon. The reaction mixture became red and viscous during the addition. The highly viscous reaction mixture was stirred at 20°C for another 16 h. It was then poured into methanol (50 mL) with strong
stirring. The resulting red precipitate was filtered and washed with distilled water. It was then dissolved in THF (100 mL) and reprecipitated by being poured into methanol (1000 mL). The precipitate was dried in vacuum at 20°C to afford MEH-PPV. The polymer yield was ca. 68% after purification. The number average molecular weight ($M_n$) and polydispersity index of MEH-PPV were $4.06 \times 10^5$ g/mole and 2.0, respectively.

Sample Preparation
The thick films used for WAXD measurements were obtained by casting polymer solutions in two organic solvents, THF and toluene, at concentrations ranging from 0.002 to 2.0 w/v%. The thick films were then grinded to a powder and pressed into thick disks (diameter ~15 mm, thickness ~0.5 mm) using a pressing machine which is typically used for preparing FTIR samples. The thick disk films were heat-treated in a vacuum oven at temperatures ranging from 25 to 240°C. Each thick disk film was stuck on the groove of a quartz plate and then examined using X-ray diffraction with a scan speed of 2º/min and a scan angle of 2 ~ 40º.

MEH-PPV was dissolved in four distinct solvents, chlorobenzene, chloroform, THF, and toluene, respectively, for the photoluminescence (PL) experiment. Three concentrations (0.002%, 0.01%, and 0.1%) were prepared. A UV-vis absorption spectrometer was used to determine the maximum absorption wavelength. The temperature was increased from room temperature to the boiling point of the used solvent at a step rate of 10°C, and then PL was used to measure the emitted wavelength.

Instruments
Gel permeation chromatography (GPC) analysis was performed with a Waters 1515 separation module using polystyrene as the standard and THF as an eluent. WAXD experiments were conducted using a Rigaku D/max-2200 X-Ray diffractometer. Ultraviolet-visible light absorption spectra were obtained using a Hitachi U-2000 UV-vis absorption spectrometer and the light source was an incandescent lamp with tungsten filaments. Standard state emission and excitation spectra were obtained using a Hitachi F-4500 PL spectrometer; the light source was a Xe lamp, the scan speed was 1500 nm/min, and the scan range was 400~800 nm.

RESULTS AND DISCUSSION
Supramolecular Structure of MEH-PPV Films Probed by WAXD
Poly(phenylene vinylene)(PPV) is insoluble in most solvents because its backbone comprises of rigid monomer units, but its derivative, the hairy-rod polymer MEH-PPV, is highly soluble in common organic solvents, such as THF, chloroform, chlorobenzene, toluene, and xylene because its backbone is bonded with the short flexible ethereal side chains [5]. The variation in polymer solubility was determined by the aggregation of certain amount of soluble molecular segments in each solvent. Greater aggregation of soluble segments is associated with the longer effective conjugated chain length of $\pi$ electrons in double bonds to hop along a single chain or between two adjacent main chains. Accordingly, aggregation
among the conjugated molecular chains significantly influences the photophysical characteristics. The solvatochromic shifts ultimately lead to either hyperchromism or hypochromism, depending on the effective conjugated chain length due to severe aggregation. When the solvent of the MEH-PPV solution of 0.01w/v% on the glass was evaporated, the concentration was increased and the lyotropic LC appeared before the film was formed and remained for a long time. It can be observed by a polarized optical microscope (POM) as a powerful tool to study the internal supramolecular structures of anisotropic entities. The POM image of lyotropic LC film as-cast from MEH-PPV/THF solution is shown in Figure 1.

WAXD Measurement and Analysis of MEH-PPV Powder

Bragg’s law was applied to evaluate the d-spacing:

\[ 2d \sin \theta = n\lambda \]  

where, \( d \) is the spacing between the layers of the crystal surface, \( n \) is an integer (in general, \( n=1 \)), \( \theta \) is the scan angle, and \( \lambda \) is the X-ray wavelength (1.5405 Å).

Figure 2 shows the X-ray diffraction profile of the PPV film, the inset shows the chemical structure. The backbone of the PPV comprises a co-planar benzene ring and an ethylene group which is a somewhat regular and rigid structure. The main diffraction peaks appear at 21° and 28°, and a diffraction shoulder appears at 22°. The corresponding d-spacings are 4.22 Å, 3.13 Å, and 4.04 Å, respectively. Since PPV does not have side chains, the diffraction peaks are determined only by the arrangement of the PPV main chain. Karasz et al. and Heeger et al. suggested that these three diffraction peaks correspond to a regular stack of two adjacent main chains and the corresponding crystal planes are (110), (200), and (210), respectively, they belong to a monoclinic cell [31-33]. Figure 2 also shows the X-ray powder diffraction profile of MEH-PPV at 25°C and the inset shows the chemical structure. MEH-PPV has diffraction peaks at small angles (2θ = 4~8°) and larger angles (2θ =22~24°).

The shape of the broader diffraction peaks located around larger angles differs from those of traditional amorphous polymer haloline and demonstrates that the polymer molecular chains are somewhat regularly arranged. The diffraction peaks around 2θ =18~24° correspond to the regular stack of the main chains of PPV with a corresponding d-spacing of 4.9~3.7 Å, which is slightly larger than that of PPV (4.0 Å). This suggests that the regular stack of the main chains of MEH-PPV is around larger angles 2θ =18~24° and that the diffraction shoulder is around 2θ =13~18° (d = 6.8~4.9 Å), which corresponds to the regular stack of the short ethereal side chains. The diffraction peak located at the smallest angle is caused by the presence of the long ethereal side chains.
Figure 3. WAXD profiles of MEH-PPV thick films, MEH-PPV was soluble in THF at 25°C at various concentrations (0.002~1.0 w/v%). (The solvent evaporated to form the films, which were then grinded into powder and pressed with a pressing machine into thick disks (15 mm in diameter and 0.5 mm thick). Heat treatment was conducted under a vacuum oven at 230°C for 8 h).

Effects of Solvent and Concentration

Figures 3 and 4 show the WAXD profiles of thick disk films at 230°C and 150°C, respectively. These films as-cast, were from different concentrations in THF and toluene, which demonstrate that different supramolecular structures of the films of MEH-PPV can be afforded at various concentrations and in distinct solvents.

Figure 3 shows the X-ray diffraction profiles of MEH-PPV of thick disk films which were cast from MEH-PPV/THF solution at various concentrations. All the small-angle diffraction peaks are at 5° and independent of the concentrations. This indicates that MEH-PPV exhibits strong aggregation in THF, even in solutions as dilute as 0.002 w/v%. In contrast, Figure 4 shows the small-angle diffraction peaks shift to a lower angle (larger d-spacing) as the concentration decreases, which reveals a strong dependence on the concentration. Table 1 summarizes the 2θ value of the diffraction peaks in Figures 3 and 4. When MEH-PPV is dissolved in toluene, the interval between two zones which are regularly arranged by side chains is increased by dilution. The good affinity of the aromatic solvent (toluene) and the conjugated main chains suggests that the slight aggregation of side chains is associated with the presence of the aromatic solvent (toluene), which has been patrolling among the conjugated main chains to prevent them from aggregation in solution. In contrast, the non-aromatic solvent (THF) has good affinity with ethereal side chains rather than the main chains and allows the latter to aggregate. The structure in the as-cast films exhibits

<table>
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<th>Solvent</th>
<th>Conc. (w/v%)</th>
<th>2</th>
<th>1</th>
<th>0.5/0.3</th>
<th>0.1</th>
<th>0.01</th>
<th>0.002</th>
</tr>
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<tr>
<td>THF (230°C)</td>
<td>N/A</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
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<tr>
<td>Toluene (150°C)</td>
<td>5.7</td>
<td>4.7</td>
<td>4.5</td>
<td>4.3</td>
<td>4.2</td>
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Table 1. Values of 2θ angle of longer ethereal side chains of MEH-PPV soluble in THF and toluene at temperatures 230°C and 150°C.
the memory effect, and therefore, the difference of supramolecular structures between the two solvents in solution is transferred to the films after the solvents have been evaporated.

**Effect of Temperature**

X-ray diffraction experiments on MEH-PPV powder were performed at various temperatures to evaluate the effect of temperature on MEH-PPV film morphology. The experimental temperatures were controlled from 25°C to 250°C because MEH-PPV polymer begins to decompose near 300°C [34]. Figures 5 and 6 show the X-ray diffraction profiles of thick MEH-PPV disk films, which were as-cast from 1 w/v% solution, at various temperatures in THF and toluene, respectively.

Figure 5 demonstrates that the packing of side chains is regular at temperatures from 25°C to 240°C. The index peaks at $2\theta = 5^\circ$ are fixed, showing that strong aggregation remains despite the increase of temperature.

Figure 6 shows that the regular packing of side chains at temperatures from 25°C to 240°C is similar to that in Figure 5. However, the index peaks shift slightly to a lower angle, which shows that the d-spacing is increased. This suggests that the increased spacing of the main chains by heating means that the aggregation is somewhat loosened or disaggregated. In other words, as the temperature increased, the aggregates were disaggregated. This result is consistent with a study on small-angle neutron scattering (SANS) performance reported in 2005 [35]. DeAzevedo et al. [36] studied the temperature dependence in MEH-PPV film and the in situ WAXS experiments revealed that the interchain spacing in the MEH-PPV molecular aggregates increases particularly with temperatures while the molecular relaxations occur. The crystallization of MEH-PPV can be clearly observed around 100~200°C, the $2\theta$ angle of crystallization is approximately 5.2~5.4°, and the corresponding d-spacing is 16.98~16.35 Å, which is due to the regular stacking of the long ethereal side chains. Accordingly, the thermotropic LC phase is formed. In a broad

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**Figure 5.** WAXD profiles of MEH-PPV thick film. MEH-PPV was soluble in THF (1 w/v%). (The solvent evaporated to form a film, which was then grinded into powder and pressed with a pressing machine into thick disks (15 mm in diameter and 0.5 mm thick). Heat treatments under a vacuum oven at temperatures ranging from 25°C to 240°C were then conducted. Each heat treatment took 8 h).

**Figure 6.** WAXD profiles of MEH-PPV thick film. MEH-PPV was soluble in toluene (1 w/v%). (The solvent evaporated to form a film, which was then grinded into powder and pressed with a pressing machine into thick disks (15 mm in diameter and 0.5 mm thick). Heat treatments under a vacuum oven at temperatures ranging from 25°C to 240°C were then conducted. Each heat treatment took 8 h).

**Figure 7.** UV absorption spectra of MEH-PPV dissolved in toluene at room temperature.
sense, the crystallization of the LC phase is another characteristic feature of aggregation.

Solvent, Concentration, and Temperature Effects of Optical Characterization of MEH-PPV Solution

The energy band gap of the conjugated polymer $\pi-\pi^*$ transition can be evaluated from the absorption spectrum. Figure 7 shows the absorption spectra of MEH-PPV dissolved in toluene. The maximum absorption wavelength ($\lambda_{\text{max}}$) at concentrations of 0.002 w/v% and 0.01 w/v% were 486 nm and 502 nm, respectively, and the $\lambda_{\text{onset}}$ values were 555 nm and 562 nm, respectively. As the concentration was increased, the maximum absorption peak exhibited a red shift; the spectrum has a photoluminance (PL) emission shoulder associated with a vibronic transition at 325 ~ 345 nm because the conjugated molecular segments aggregated. Therefore, the $\lambda_{\text{onset}}$ of the UV absorption spectrum can be used to evaluate the energy of the $\pi-\pi^*$ inter-band onset transition [37,38], which is known as the energy band gap ($E_g$):

$$E_g = \frac{1240}{\lambda_{\text{onset}}} \tag{2}$$

Eqn (2) shows that the energy band gap decreases as the maximum absorption wavelength increases. Therefore, when the concentration is increased, the energy band gap is decreased. The conjugated chain length increases with the increase in concentration through segmental aggregation. The conjugated chain

![Figure 8](image_url)

**Figure 8.** PL maximum excited wavelength vs. temperature plots of MEH-PPV dissolved in (a) chlorobenzene, (b) toluene, (c) THF, and (d) chloroform (concentrations are 0.1%, 0.01%, and 0.002%).
chains tend to aggregate and charge carriers undergo energy transportation through the aggregated channel, thus, the energy gap decreased as the concentration was increased [39].

The experimental results demonstrate that the effects of temperature, concentration, and solvent affect the UV-vis and PL spectra of MEH-PPV in solution. MEH-PPV solution exhibits a blue shift at high temperatures (Figure 8). Heat influences the activity of the molecular chains of conjugated polymers. As the temperature decreases the PL emission intensity increases and the PL emitting peak is red-shifted because the aggregated supramolecular structure is composed of the MEH-PPV main chain and the side chain is frozen. As the concentration is increased, the possibility of collision of fluorescent conjugated segments is also increased, thus aggregation occurs naturally in solution [40-42].

Figure 9 shows the fluorescence spectra of MEH-PPV dissolved in four common laboratory solvents: chlorobenzene, chloroform, THF, and toluene, respectively. The concentrations are 0.002, 0.01, 0.1, and 0.5 w/v%, respectively. Figure 9a shows a main emission peak at 560 nm which is accompanied by a small shoulder located at 600 nm. Solvents cause various red shifts. Accordingly, the degree of aggregation is different in various solvents and the extent of the red shift is in the sequence: CB > CF > toluene > THF. When the concentration is increased to 0.01 w/v% (Figure 9b), the red shift is still present. The PL intensity of the shoulder increases from 0.2 to 0.5 due to the increasing aggregation. When the concentration is

Figure 9. PL spectra of MEH-PPV dissolved in various solvents at room temperature. The concentrations (w/v%) are: (a) 0.002%, (b) 0.01%, (c) 0.1%, and (d) 0.5%.
increased to 0.1 w/v% (Figure 9c), owing to the peak location at ca. 590 nm, it definitely belongs to the shoulder rather than the main peak. The main peak is completely replaced by the shoulder. Accordingly, the aggregation is more serious than the case of 0.01 w/v%. When the concentration is further increased to 0.5 w/v% (Figure 9d), the shoulder still appears obvious while the main peak begins to grow at the original location. Accordingly, it seems at this stage there is a concrete conclusion, i.e., with dilute concentration (0.002 w/v%), the aggregation has taken place in solution regardless of the type of solvent. Aromatic solvents such as chlorobenzene and toluene have good affinity for the main chain of MEH-PPV [31-33] and non-aromatic solvents such as chloroform and THF, by contrast, have good affinity for side chains of MEH-PPV. Furthermore, the shoulder grows further as the concentration increases, which implies that the aggregation is also increased. Figure 9c shows that a complete first aggregation stage has been fulfilled and Figure 9d shows that the main peak begins to grow at the original location and the neighbouring peak with the obvious shoulder illustrates that another complicated aggregation stage is still going on.

Figure 10 shows the self-assembled structure of MEH-PPV and aggregated strands. In MEH-PPV/toluene system, as the concentration is increased, the intra-hairy side chains begin to aggregate and then inter-hairy side chains are also involved as shown schematically in Figures 10a and 10b. However, there is no sign of main chain aggregation because the aromatic solvent (the toluene molecules) is patrolling among the aromatic main chains. In contrast, MEH-PPV dissolves in THF, because of the good affinity between THF and the side chains of MEH-PPV, the aggregation takes place mainly among the main chains as shown in Figure 10c.

Since the morphology of aggregation is rather complicated in solution state, an even more complicated supramolecular aggregation structure can be expected in solid film. The aggregation influences the photoelectrical characteristics of the devices. The supramolecular aggregation structure investigations are still in progress.

CONCLUSION

The mechanism of liquid crystalline formation involves the aggregation of main chains before the
formation of mcLCPs as MEH-PPV in THF. If the aggregation originates from the side chains of MEH-PPV in toluene, scLCPs are naturally formed. In the MEH-PPV/toluene solution, toluene molecules are among the conjugated main chains and prevent segment aggregation from the inter-conjugated main chains. In contrast, the degree of aggregation among main chains in the MEH-PPV/THF system exceeds the degree of aggregation among side chains in the MEH-PPV/toluene system. The interactive force causes the aggregation of main chains to be much stronger than the aggregation of side chains. Comparing the aggregation of MEH-PPV/THF with that of MEH-PPV/toluene, the aggregation of MEH-PPV/THF exhibits no temperature effect. The diffraction peaks of the small angle of WAXD corresponding to the packing of long ethereal side chains are all fixed at $2\theta = 5^\circ$ despite increasing temperature. Therefore, there is no tincture of disaggregation with heating. In other words, after aggregation occurs in MEH-PPV/THF, the aggregates cannot be disaggregated through heating but only through dilution. Notably, in the final stage of synthesis of MEH-PPV, the products including MEH-PPV are enriched in THF solvent, resulting in serious aggregation of conjugated molecular chains. Therefore, there is an inherent risk of gelation. In the MEH-PPV/toluene system, the diffraction peaks of WAXD tend to shift to smaller angle, showing that the spacing between the main chains is increased. This suggests that the aggregates are disaggregated by heating. Consequently, the supramolecular structures of aggregations in two systems differ markedly from each other.

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