# Alignment of Conjugated Polymers in a Nematic Liquid-Crystal Host

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A general procedure, solvent-induced homogeneous dispersion, SIHD, is presented to incorporate and align conjugated polymers into a nematic liquid-crystal host. We report the investigation of the dye, N′,N′-bis(2,6 dimethylphenyl)-3,4,9,10, perylenetetracarboxylic dimide (PERY), and a conjugated polymer, poly[2-(2′ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH−PPV), aligned in a low molecular weight nematic liquid-crystal matrix, 4-*n*-pentyl-4′-cyanobiphenyl (5CB). Order parameters obtained for the guests from polarized absorption and fluorescence spectra are 0.46, 0.24, and 0.30 for PERY, MEH−PPV ($M_n = 8.6 \times 10^4$), and MEH−PPV ($M_n = 1.1 \times 10^5$) in 5CB, respectively. The liquid-crystal host provides a unique environment in which to study the conjugated polymer in a highly extended conformation. To this end, we discuss the relationship between polymer conformation and fluorescence, the line shape of the spectra, and the interchromophore/interchain versus intrachromophore/intrachain resonance energy transfer processes.

## Introduction

For the last 30 years, liquid-crystalline materials, including hybrid materials made from liquid crystals, guest−host and polymer-dispersed liquid crystals, have been intensively investigated, mainly owing to their applications in display technologies.[1−3] A guest−host liquid-crystalline system consists of a liquid-crystalline host that has been doped with a small concentration of a guest, often a chromophore such as a dye. In such guest−host dye-doped liquid crystals, a spatially varying refractive index grating can be photoinduced.[4] Polymer-dispersed liquid crystals (PDLCs) consist of liquid-crystal microdroplets dispersed in a polymer matrix.[5−7] PDLC systems have a spatially varying refractive index and efficiently scatter light, making them translucent when an electric field is applied. The inverse of a PDLC, a polymer guest incorporated into a liquid-crystal matrix, is the subject of the present paper. We report the preparation and characterization of a conjugated polymer guest incorporated and aligned in a nematic liquid-crystal matrix via a method we call solvent-induced homogeneous dispersion (SIHD).

Conjugated polymers have been studied intensively owing to the promise of applications, such as in electroluminescent devices and optical switches.[8,9] One important conjugated polymer is poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylevinylene] (MEH−PPV) which is used to make organic light emitting diodes.[10−15] Conjugated polymers are also attractive materials because of their large optical nonlinear responses. The macroscopic nonlinear optical response has an orientation dependence that may be optimized by suitably aligning the polymers. In addition to possible applications, incorporation of MEH−PPV into the nematic LC host opens up the possibility of studying a unique model system in which chain−chain interactions are minimized owing to the highly extended chain conformation.

Nguyen et al.[16] have previously incorporated MEH−PPV into a mesoporous silica matrix, which they suggest aligns part of the chains. Weder et al.[17] have used gel processing to blend a soluble conjugated polymer with ultrahigh molecular weight polyethylene. Subsequent tensile drawing of the film was shown to orient the polymer. A new method for aligning MEH−PPV is presented in this paper, which utilizes a nematic liquid crystal as the matrix. Our results are compared to those for a model dye incorporated into the same liquid-crystal matrix. The standard guest−host preparation[18] was used for the incorporation of a low concentration of the dye, N′, N′-bis(2,6-dimethylphenyl)-3,4,9,10-perylenetetra carboxylic (PERY), into a nematic liquid-crystalline host. The long axis of the dye aligns parallel to the director of the liquid crystal. PERY has been chosen for its solvation properties.[19] The order parameter characterizing the alignment of the host with respect to the liquid-crystal director is determined using linear dichroism and fluorescence anisotropy.

## Experimental Section

Nematic liquid-crystal films were prepared as described by Khoo.[18] A planar alignment was achieved by dip coating a pair of quartz slides using a 0.2% aqueous solution of poly(vinyl alcohol), PVA, (Aldrich) and then unidirectionally rubbing them with lens paper (Kodak). After the sample was deposited between the two slides, it was firmly sandwiched together (separated by an adhesive 76 $\mu$m Mylar spacer). An optically clear, aligned liquid-crystal film was rapidly formed.

Two different procedures were used to prepare the doped LC matrixes: (1) guest−host and (2) SIHD. The guest−host method was used for the dye, while the latter one was developed for the polymer. A small amount of PERY, [N′, N′-bis(2,6-dimethylphenyl)-3,4,9,10-perylenetetra carboxylic], (Aldrich) was mixed with pentylcyanobiphenyl, 5CB, (Aldrich) and left overnight to homogenize. The following day, the orange supernatant was collected and used to prepare an aligned LC sample as described above. The concentration of PERY in 5CB was determined via Beer's law to be $5 \times 10^{-6}$ M. A more dilute sample of $4 \times 10^{-10}$ M was used for the fluorescence measurements. On the other hand, the poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylevinylene], MEH−PPV, was first

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dissolved in chlorobenzene (Aldrich), and 1 mL of that solution was mixed with a small amount of 5CB. This mixture was then set under a medium-slow nitrogen flow for about 20 min to evaporate the solvent. The nitrogen flow was stopped once the phase transition occurred, thereby leaving a homogeneous mixture of MEH−PPV and 5CB.

Two different MEH−PPV samples were investigated in this work, see Figure 1 for structures, MEH−$PPV_A$ (Aldrich) having an average $M_n \sim 8.6 \times 10^4$, and the MEH−$PPV_B$ having an average $M_n \sim 1.1 \times 10^5$. The synthesis and characterization of MEH−$PPV_B$ have been previously reported.[20] The concentrations used for the absorption measurements of the MEH−$PPV_A$ and MEH−$PPV_B$ in the LC were 0.32% w/w and 0.30% w/w, respectively. The concentrations for the fluorescence measurements were considerably lower: $2 \times 10^{-6}$ % w/w and $1 \times 10^{-6}$ % w/w, respectively.

The polarized absorption spectra were recorded at room temperature using a CARY 100 BIO UV−visible spectrophotometer fitted with a Glan−Thompson polarizer and a depolarizer. All of the absorption spectra were baseline corrected. Absorption spectra of an oriented sample were recorded using light polarized parallel, $A_{\|}$, and perpendicular, $A_{\perp}$, to the direction of orientation of the sample. The difference between these absorption spectra is the linear dichroism (LD) spectrum,[21] $LD = A_{\|} - A_{\perp}$. The LD is used to determine the orientation of the transition dipole moment of the sample. A positive LD spectrum indicates that the polarization of the light is parallel to the orientation of the main axis of the sample. On the other hand, when the LD is negative, the polarization of the light is perpendicular to the orientation of the main axis of the sample.[21] The dichroic ratio $D$ is defined as the ratio between the absorption spectrum recorded using light polarized parallel to and perpendicular to the molecular orientation:

$$D = \frac{A_{\|}}{A_{\perp}} \tag{1}$$

The polarized fluorescence spectra were recorded using a Spex Fluorolog 3-22 fluorometer fitted with center slits in both the excitation and emission double monochromators. The emission gratings were blazed at 500 nm (1200 grooves/mm). The reported fluorescence spectra are uncorrected and were collected at room temperature. All fluorescence spectra were recorded in the front-face geometry. The fluorescence anisotropy, $r$, is defined in terms of the fluorescence spectra resolved with vertically polarized excitation and vertical emission analyzer $I_{VV}$, versus horizontal analyzer $I_{VH}$ emission as:[22]

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \tag{2}$$

where $G = I_{HV}/I_{HH}$.

The fluorescence data were obtained using extremely dilute samples of the guest in the liquid-crystal host to avoid energy transfer between the molecules. Energy transfer, observed by depolarization of the fluorescence emission, was particularly efficient between the polymeric chains of the MEH−PPV. At the low guest concentration, the liquid crystal Raman bands shifted from the 500 nm excitation were comparable in intensity to the guest fluorescence. Therefore, a reconstruction of the total fluorescence spectrum as a linear combination of the 5CB background and the guest fluorescence was performed by assuming that the spectrum of the guest emission is invariant as a function of the concentration and is well represented by the fluorescence spectrum measured for the 0.3 % w/w samples. In that way the fluorescence spectra, and hence fluorescence anisotropy of the most dilute samples, could be successfully deconvoluted from the 5CB background.

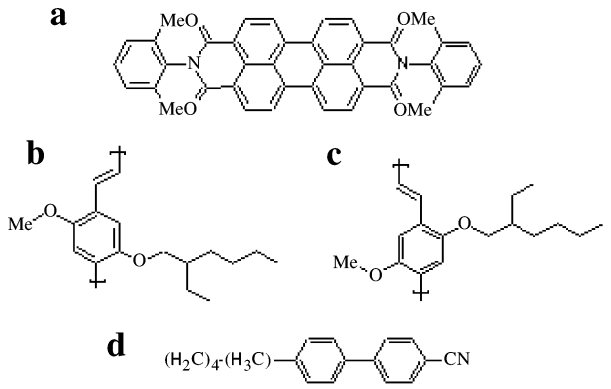


**Figure 1.** Structures of the guests molecules (a) PERY, (b) MEH−$PPV_A$, (c) MEH−$PPV_B$, and (d) of the liquid-crystal matrix 5CB.

All results reported in this paper (e.g., order parameter) are an average of about five measurements from a variety of samples. These values were calculated from the region of maximum spectral intensity.

**Preparation of the Polymer Samples: Solvent-Induced Homogeneous Dispersion (SIHD).** The alignment of small guest molecules in a liquid-crystal host is a well-known procedure: the guest−host technique.[23,24] However, the incorporation of polymeric molecules as a guest has not been explored. On the other hand, polymers as a host for liquid-crystal guests have been extensively studied and are referred to as polymer-dispersed liquid crystals, PDLCs.[25] There are a variety of procedures to fabricate PDLCs, but phase separations are typically employed,[25,26] for example, solvent-induced phase separation, SIPS.[27,28] Also in recent years, evaporation-induced self-assembly has been developed as a technique used to form mesostructured materials on the basis of lyotropic liquid-crystal templating.[29,30] Such techniques have inspired the SIHD technique that we report here.

The fabrication of PDLCs via SIPS involves an excess of polymer compared to the liquid crystal. The polymer and the LC are homogeneously mixed in a common solvent, and then the phase separation is induced as the solvent is evaporated. When the latter occurs, the liquid crystal forms droplets and the polymer solidifies or gelatinates. The size of the liquid-crystal droplets is controlled by the rate of evaporation of the solvent.

In the SIHD method, the polymer is dissolved in a good solvent, and then a small amount of that solution is transferred to a new vial, into which an excess of the LC is added. The overall percentage of MEH−PPV in the LC is kept small to avoid formation of a PDLC. Usually in a PDLC, the polymer can be found at $\geq$60 wt %,[1,31] while in the SIHD technique the polymer is approximately $\leq$2 wt %. The solvent is evaporated from the homogeneous mixture using a stream of nitrogen gas at a moderate-slow rate for about 20 min. The flow rate of the nitrogen is crucial in determining the homogeneity of the polymer guest in the liquid-crystal host. If the nitrogen flow is not uniform, then the mixture will separate owing to aggregation of the polymer.

For the alignment of conjugated polymers such as MEH−PPV, the choice of solvent is important. A good solvent was necessary to prepare the polymer in a more extended conforma-

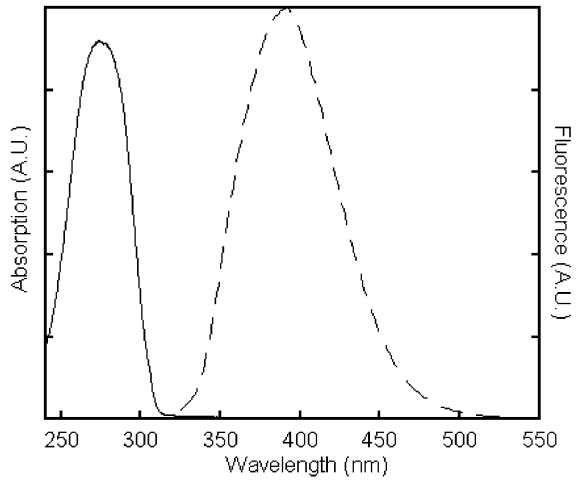


**Figure 2.** Absorption (solid line) and fluorescence (dashed line) spectra of the guest matrix, 5CB, in hexanes. Fluorescence spectrum excitation wavelength was 280 nm, slit widths were 5 and 5 nm, integration at 1 s.

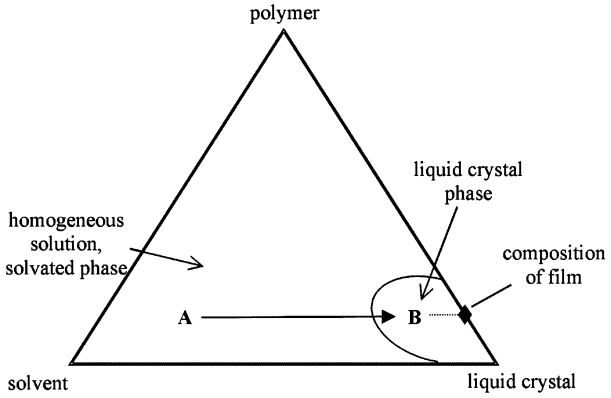


**Figure 3.** A ternary mixture of solvent, polymer, and liquid crystal illustrating the phase transition from solvated phase, A, to the liquid-crystal phase, B, via SIHD. The diamond (◆) indicates the homogeneous mixture of the polymer guest in the liquid-crystal host.

tion. We used chlorobenzene, which has been shown by Nguyen et al.[32] to be a good solvent for MEH−PPV.

The SIHD method is diagrammed in Figure 3. A phase transition is seen traveling through the A−B line where the system starts in a solvated phase and finishes in a liquid-crystal phase. In other words, a low polymer concentration and a high LC concentration dissolved in a common solvent (A) moves along the A−B line as the solvent is evaporated from the system, where B is a homogeneous mixture of the LC and the polymer.

## Results

A series of polarized absorption and fluorescence experiments were performed to confirm the repeatability of the observed phenomena and to verify that the differential absorption and fluorescence were not due to any kind of artifact. The observed alignment of the guest molecule was not credited to the PVA-coated slides, the sample holder, or the solvent but was attributed to the alignment of the LC host.

The nematic phase of a LC can be quantified by an order parameter, describing the degree of directional correlation. The scalar order parameter, *S*, is defined as

$$S = \frac{1}{2}(3\langle\cos^2\theta\rangle - 1) \tag{3}$$

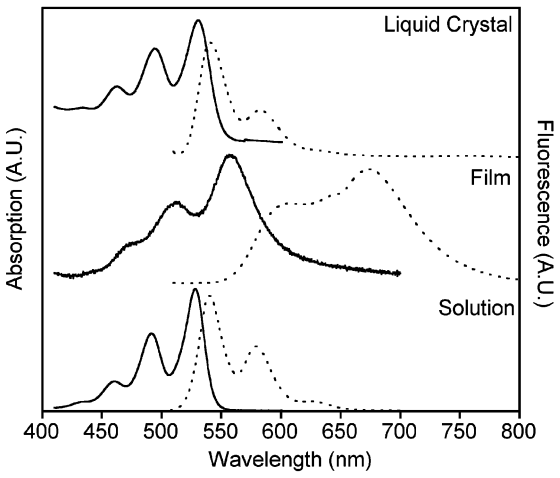


**Figure 4.** Absorption (solid line) and fluorescence (dotted line) spectra of the nonlinear dye, PERY, in a solution of chlorobenzene, a drop-cast film from chlorobenzene solution, and dissolved in the 5CB liquid crystal. All spectra are scaled to the same maximum intensity for ease of comparison. Fluorescence spectra excitation wavelength was 495 nm, slit widths were 7 and 7 nm, and integration time was 1 s.

where $\theta$ is the angle between the long axis of the molecule and the direction of the host orientation.[18,33] The order parameter is an ensemble average quantity and therefore provides a measure of the long-range orientational order. In a perfectly aligned LC, $\langle\cos^2\theta\rangle = 1$ and $S = 1$. On the other hand, in a perfectly random (isotropic) system $\langle\cos^2\theta\rangle = 1/3$ and $S = 0$.[18] We can determine the order parameter from either absorption anisotropy, $S_A$, or fluorescence anisotropy, $S_F$ . The polarized absorption spectra are used to determine the order parameter $S_A$ according to

$$S_A = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} \cdot \frac{2}{3\cos^2\beta - 1} \tag{4}$$

where the parameter $\beta$ is the angle between the absorption transition moment of the chromophore and its long axis.[4] The order parameter is determined from the polarized components of the fluorescence spectra via[4]

$$S_I = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \tag{5}$$

To establish a basis for comparison of the alignment of the conjugated polymer, we first consider the PERY dye.

**PERY Doped Liquid Crystal.** The PERY dye was chosen as a reference owing to its planar and symmetric structure, which facilitates its alignment in the LC matrix. In Figure 4, the absorption and fluorescence spectra of the PERY dye in chlorobenzene, cast as a film, and incorporated in the 5CB host have been plotted. For all of the fluorescence measurements, the excitation wavelength was 495 nm. The absorption and fluorescence spectra of the PERY film sample are clearly much broader and redshifted compared to both the solution and the LC spectra, owing to aggregation of the dye. The absorption and fluorescence spectra of PERY in the LC matrix are seen to be slightly broader and redshifted compared to those of the solution.

The dichroic absorption spectra, shown in Figure 5, indicate that PERY is aligned in the LC. The alignment is indicated by the difference between the parallel and perpendicular absorption spectra and is quantified by the dichroic ratio, which was 2.9. This indicates that the parallel spectrum is almost 3 times more intense than the perpendicular spectrum suggesting that PERY

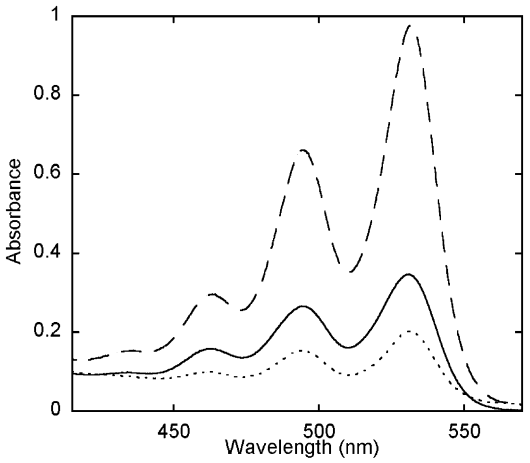


**Figure 5.** Dichroic absorption of PERY dissolved in 5CB. The unpolarized spectrum (solid line) is shown for reference. The parallel spectrum (dashed line) is much more intense then the perpendicular spectrum (dotted line).

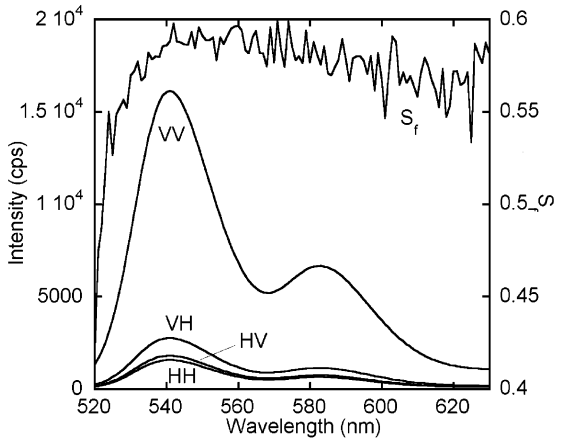


**Figure 6.** Fluorescence anisotropy of PERY dissolved in 5CB. The four contributing spectra are shown, VV, VH, HV, and HH. The fluorescence spectra excitation wavelength was 495 nm, the slit widths were 7 and 7 nm, and the integration time was 1 s. The fluorescence order parameter, $S_F$, was averaged over the wavelength range of 520−630 nm. All the fluorescence data were deconvoluted from the 5CB background.

is aligned parallel to the LC director. This was verified by the LD spectrum, which was positive (average value of 0.22).

In Figure 6, the four polarized fluorescence spectra are plotted. Owing to alignment of the dye, it can be seen that the VV spectrum significantly differs from HH spectrum. In these experiments, the director of the liquid crystal is vertically (V) oriented. In this figure, the fluorescence anisotropy has also been plotted. The average fluorescence alignment parameter for PERY was $S_F = 0.57 \pm 0.09$, while from absorption anisotropy it was calculated that $S_A = 0.35$. The average of these order parameters is ≈0.46 indicating that the dye molecules were well aligned compared to the 5CB liquid crystal, which has a typical order parameter of 0.48.[34]

In Figure 7, the VVV and VVH fluorescence spectra are shown. The first two letters denote the orientation of the fluorometer polarizers, while the final V or H indicate vertical or horizontal alignment LC director. The VVV spectrum is 1.7 times more intense than the VVH spectrum, verifying that the PERY sample is aligned parallel to the director of the liquid crystal.

**MEH−PPV Doped Liquid Crystal.** The key to aligning the conjugated polymer, MEH−PPV in 5CB is the evaporation of

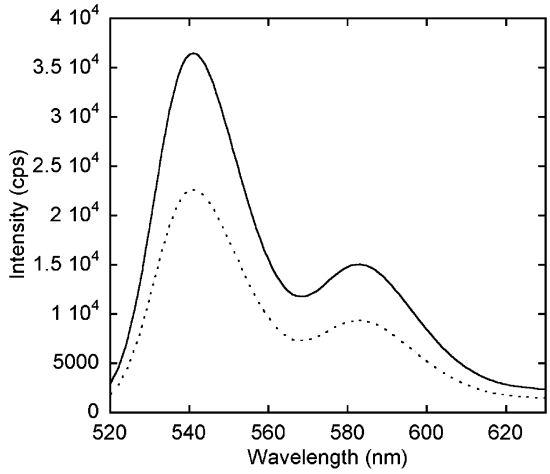


**Figure 7.** The directional difference of the fluorescence spectra of PERY in 5CB, VVV (solid line), parallel to the director of the LC, and VVH (dotted line), perpendicular to the director of the LC.

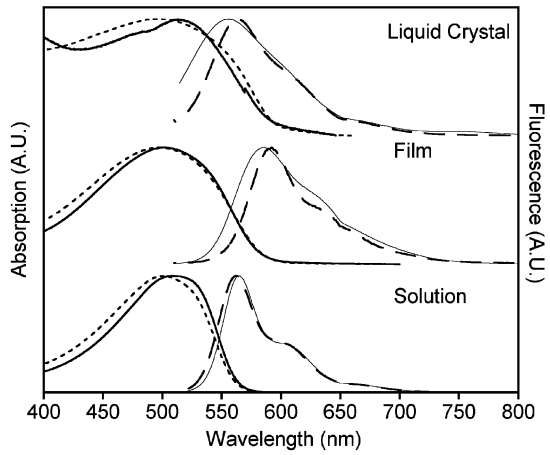


**Figure 8.** Absorption (dark solid line) and fluorescence (light solid line) spectra of the MEH−$PPV_A$, in a solution of chlorobenzene, a film casted from a chlorobenzene solution, and in the 5CB liquid crystal. Absorption (dotted line) and fluorescence (dashed line) spectra of the MEH−$PPV_B$, in a solution of chlorobenzene, a film cast from a chlorobenzene solution, and in the 5CB liquid crystal. All spectra are scaled to the same maximum intensity for ease of comparison. Fluorescence spectra excitation wavelength was 500 nm, slit widths were 7 and 7 nm, and integration time was 1 s.

the solvent. This creates a homogeneous mixture that enables the LC to solvate and to align the polymer chains along its director.

In Figure 8, absorption and fluorescence spectra of MEH−$PPV_A$ and MEH−$PPV_B$ in solution, film, and in liquid crystal have been plotted. All fluorescence data were collected using 500-nm excitation. It is evident that the absorption and fluorescence spectra are broader for the film than those for the solution, as is well known.[35,36] Interestingly, the absorption and fluorescence spectra for the polymer in the liquid crystal are broader than those for the film. In the MEH−$PPV_A$ film sample, in addition to the broadening, there is a significant redshift in the fluorescence spectrum and a small redshift in the absorption spectrum, when compared to the solution spectra.

The alignment can be inferred from the polarized absorption data shown in Figure 9. The unpolarized spectra of both MEH−PPV in LC are shown for comparison. The MEH−$PPV_A$ has a dichroic ratio of 1.7 indicating that the parallel spectrum is almost twice as intense as the perpendicular one. The LD spectrum has an intensity of 0.14, indicating a parallel alignment

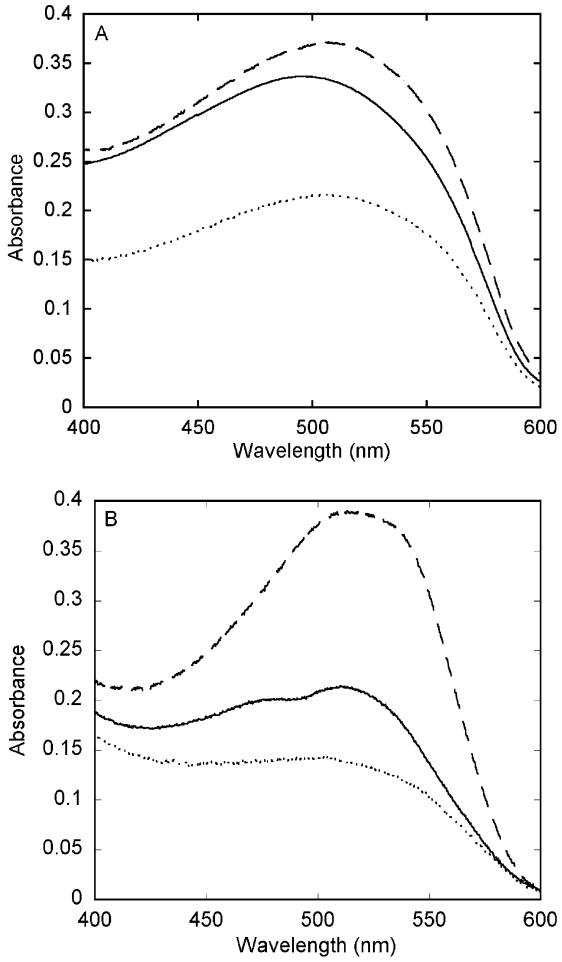


**Figure 9.** Dichroic absorption of MEH−$PPV_A$ (A) and MEH−$PPV_B$ (B) in the 5CB liquid crystal. The unpolarized (solid line) is shown for reference. The dashed line indicates parallel alignment of the MEH−PPV guest along the director of the 5CB host, while the dotted line shows the perpendicular alignment.

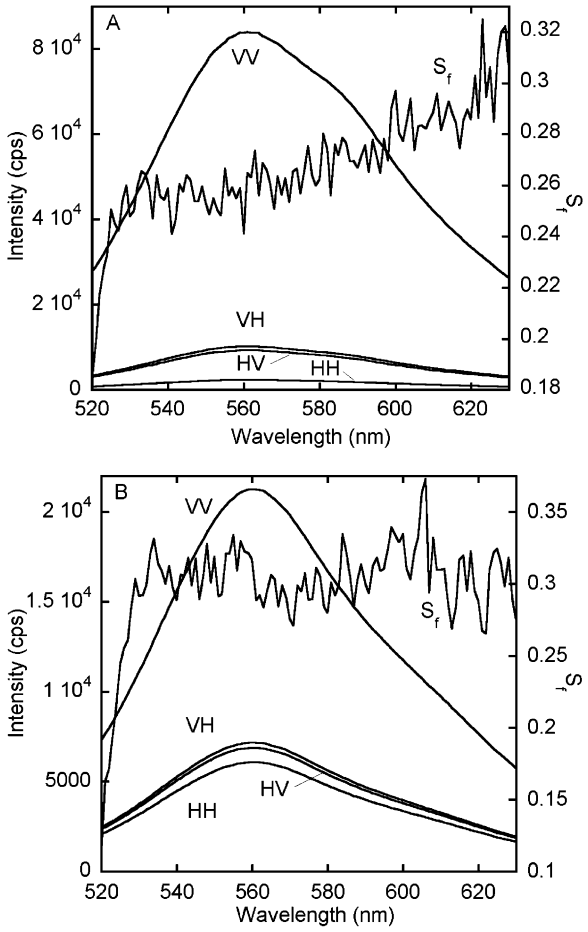


**Figure 10.** The fluorescence anisotropy of MEH−$PPV_A$ (A) and MEH−$PPV_B$ (B) in the 5CB liquid crystal. The four contributing spectra are shown, VV, VH, HV, and HH. The fluorescence spectra excitation wavelength was 500 nm, the slit widths were 7 and 7 nm, and the integration time was of 1 s.

of the polymer backbone with respect to the director of the LC. The dichroic ratio of MEH−$PPV_B$ has a value of 2.6 and the LD was 0.14.

In the MEH−$PPV_A$ sample, the order parameters $S_A$ and $S_F$ were 0.20 and 0.27 ± 0.03, respectively. On the other hand, for MEH−$PPV_B$ $S_A$ is 0.29 and $S_F$ is 0.30 ± 0.02. The fluorescence anisotropy is plotted in Figure 10. In Figure 11, the difference between the VVV and VVH for both MEH−PPV is evident. These spectra confirm that the samples are aligned parallel to the director of the LC.

## Discussion

The dye molecule PERY incorporated in the 5CB host was found to have an order parameter similar to that typical of 5CB, which will ultimately limit the alignment of the guest. MEH−$PPV_A$ and MEH−$PPV_B$ had order parameters of 0.24 and 0.30, respectively. This suggests that they are remarkably well aligned considering that these conjugated polymers are, on average, 330 and 420 repeat units long, respectively. Comparing the order parameters obtained from the fluorescence and absorption data it can be seen that the order parameter deduced from fluorescence is greater than that determined by absorbance. The discrepancy is attributed to the different concentrations of the MEH−PPV in the liquid crystal. The samples for the fluorescence data were extremely dilute compared to the samples for the absorption data. These observations suggest that the dilute polymer sample may align more effectively than the concentrated sample. Also, the concentrated samples might contain MEH−PPV aggregates, thus inhibiting homogeneous dispersion and hence the alignment.

It was necessary to prepare extremely dilute ($<10^{-6}$ % w/w) MEH−PPV/LC and PERY/LC samples to record polarized fluorescence spectra, since the emission was depolarized in the more concentrated samples. Peterson and Fayer[37] found from fluorescence depolarization studies of aromatic polymers that when a short pulse of polarized light excites a sample of randomly oriented chromophores, the main source of depolarization of the fluorescence arises from resonance energy transfer (RET) among the chromophores. Similarly, it is RET that caused the depolarization of the fluorescence emission from the concentrated samples in the present study.

The concentration dependence of the fluorescence anisotropy suggests that the primary RET process is interchromophore (in PERY/LC) and interchain (in MEH−PPV/LC). In an ensemble *isotropic* system, one RET hop from the initially excited chromophore is sufficient to completely depolarize the ensemble emission. Beljonne et al.[38] have shown that in solutions of polymeric complexes, intrachain processes dominate RET, while in films, where there is more close contact between chains, interchain transport is favored. At this point, it is worth mentioning that by intrachain energy migration we mean hopping of electronic excitations along a single polymer chain, in the absence of any chain−chain contact that may derive from

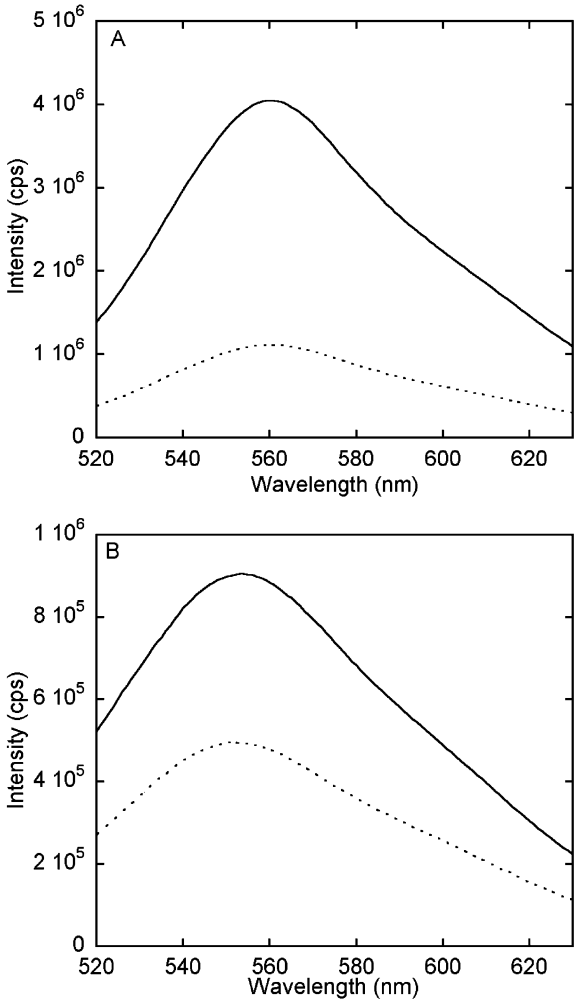


**Figure 11.** The direction difference of the fluorescence spectra VVV (solid line) and VVH (dotted line) of MEH−$PPV_A$ (A) and MEH−$PPV_B$ (B) in the 5CB liquid crystal.

contacts between polymers, or from one polymer chain folding back on itself.[38] Conjugated polymers are generally thought of as long conjugated chains, on which each chain has smaller localized conjugations that are separated by kinks or other defects. In other words, the polymer chain consists of a sequence of segments—conformational subunits—with different conjugation length, or number of monomer repeat units, in each segment.[39] Barbara et al.[40,41] have suggested that MEH−PPV adopts cylindrical conformations in the presence of tetrahedral chemical defects, in which case energy transport may occur in multiple dimensions. Thus, our observation of significant steady-state anisotropy in the fluorescence of isolated MEH−PPV polymer indicates that chain segments of the polymer must be fairly parallel to each other; otherwise, intrachain RET would lead to depolarized emission. A corollary to this is that each polymer should have an intrinsic anisotropy owing to intrachain RET, which means that the actual order parameter of the polymer may be higher than that suggested by our measurements.

It is not obvious why the fluorescence is completely depolarized by interchromophore or interchain RET in systems that, according to the polarized absorption spectra, are macroscopically ordered along the LC director. In an isotropic system, it is clear that RET randomizes the emission transition dipole relative to the absorption transition dipole, thus leading to zero anisotropy in the emission. In a system such as this nematic LC, the emitting transition dipole, whether directly excited or sensitized via RET, lies within a distribution of angles about the director. In such a case, the emission will not be completely depolarized by one RET step. This suggests that the energy is undergoing more than one hop during the excited-state lifetime in order that the emission from the more concentrated MEH−PPV samples is completely depolarized. Considering the order parameter of MEH−PPV/LC was ≈0.3, this would lead to complete depolarization of the ensemble emission. In the dilute samples, the distance between the molecules is sufficient to prevent interchain transport in the polymer system, yet intrachain transport is not precluded. If intrachain transport leads to some depolarization of the emission, then the polymer could be even more aligned than suggested by the measured anisotropy.

In solution, the photophysics of conjugated polymers is sensitive to solvent quality.[42,43] In this regard, the liquid-crystal host serves as a special kind of solvent environment. The conjugated polymer is likely to be an extended defect cylinder when it is imbedded into the LC.[44] Thus, spectral diffusion, resulting from resonance energy transfer among the conformational subunits of the polymer, is multidimensional. So, we would expect the polymer to have an intrinsic anisotropy that we have not accounted for in our estimation of the order parameter. The high-steady-state fluorescence anisotropy we have observed in this study provides evidence that the chain segments folded into the defect cylinder are largely parallel. This represents a unique model system in which to study the ramifications of conformational disorder.[45−53] In the present report, we have focused only on the steady-state spectroscopy.

It has been recognized previously that there are significant differences between the absorption and fluorescence spectra of MEH−PPV in solution compared to a cast film.[35,54] Usually, the spectra are redshifted and broader for a film compared to a solution. In solution, the relatively narrow, structured emission spectrum is thought to arise because, regardless of the distribution of conformational subunits that are initially excited, RET rapidly transfers the excitation to a narrow distribution of longer conformational subunits, which subsequently fluoresce. Such a model explains the large Stokes' shift between absorption and emission spectra maxima. According to Rothberg, the redshift of the film spectra may be caused by an increased average conjugation length of the chains owing to suppression of torsional motion.[35] Rumbles attributes the redshift to interchain interactions that arise when the polymers are cast in the film.[54]

A quantitative comparison of the absorption spectra of the MEH−PPV samples in the LC host with those of films and solutions is encumbered by the underlying absorption tail from 5CB in the blue side of the spectrum. However, the fluorescence spectra, shown in Figure 8, can be compared. Interestingly, it is observed that the fluorescence spectra of MEH−PPV in the LC host are broad, like in the films, but are not appreciably shifted with respect to the solution spectra. The lack of shift in both MEH−PPV/LC fluorescence spectra is believed to be due to the exclusion of interchain interactions.[54] Both the MEH−PPV/LC and film spectra of MEH−$PPV_A$ are significantly broader than those of MEH−$PPV_B$, which may be indicative of a greater defect concentration.[55] The broad emission spectra of MEH−PPV/LC compared to in solution can be attributed to inefficient intrachain resonance energy transfer along the extended polymer chain, which results in fluorescence emission deriving from a broader distribution of conformational subunits. In that case, the emission is not derived from such a narrow distribution of "red" conformational subunits as in solution,

**TABLE 1: Summary of All the Measured Alignment Data for the Three Samples, PERY, MEH−PPV$_A$, and MEH−PPV$_B$**

| guest in LC | LD | D | $S_A$ | $S_F$ |
|---|---|---|---|---|
| PERY | 0.22 | 2.9 | 0.35 | $0.57 \pm 0.09$ |
| MEH-PPV$_A$ | 0.14 | 1.7 | 0.20 | $0.27 \pm 0.03$ |
| MEH-PPV$_B$ | 0.14 | 2.6 | 0.29 | $0.30 \pm 0.02$ |

where presumably intrachain energy transfer is more efficient owing to the folded conformation adopted by the polymer chain.

## Conclusion

We have described a simple, room-temperature procedure to align polymers in a liquid-crystal matrix, which we call SIHD. This technique is successful for a polymer concentration of approximately $\leq 2$ wt % compared to the liquid crystal. We have reported order parameters of 0.46, 0.24, and 0.30 for PERY, MEH−PPV$_A$, and MEH−PPV$_B$ in 5CB, respectively. We have observed efficient interchromophore/interchain RET in samples with chromophore/polymer to 5CB concentrations even as moderate as 0.3% w/w. Interchain RET in MEH−PPV/LC samples was excluded at polymer concentrations of $2 \times 10^{-6}$ % w/w in the LC.

The liquid-crystal host was shown to serve as a special kind of solvent environment, wherein the conjugated polymer is likely to be an extended defect cylinder. Thus, the spectral diffusion resulting from resonance energy transfer along the conformational subunits of the polymer is multidimensional but occurs between reasonably parallel chain segments. This represents a unique model system in which to study the ramifications of conformational disorder.

It was observed that the fluorescence spectra of MEH−PPV in the LC host are broad, like in thin films of MEH−PPV, but are not appreciably shifted with respect to the solution spectra. This is caused by the suppression of interchain energy transfer along the extended polymer chain.

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