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ABSTRACT: Conjugated polymers in solution exhibit interesting photophysical behavior, which is dictated by their molecular conformation. The conformations and resulting photophysics can be altered by deformational flows such as simple shear. Solutions of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) in dimethylformamide (DMF) show large decreases in fluorescence intensity as a function of shear rate, combined with significant spectral shifts upon exposure to shear. The excitation and emission spectra shift toward shorter wavelengths, indicating a change in conformation with shortened conjugated segment lengths attributed to compressive hydrodynamic forces in flow. Addition of poly(methyl methacrylate) to the solutions is shown to alter the fluorescence emission spectral behavior, which we ascribe to energy transfer from the higher energy, short segments to a small population of lower energy conjugated segments. The measured fluorescence changes were not reversible upon cessation of shear, demonstrating that permanent conformational changes are induced by flow.
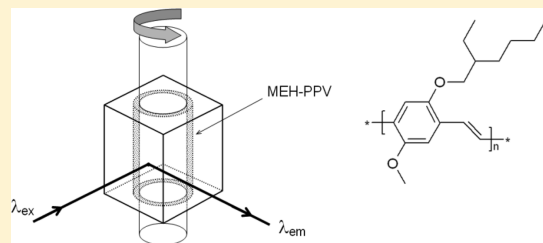
■ INTRODUCTION

The field of polymer electronics is rapidly expanding to become very important in consumer electronics and other applications. Optical devices which employ polymer films and smaller molecule compounds, such as organic or polymeric LED devices, provide many benefits such as improved durability and efficiency combined with low manufacturing costs[1−3] compared with conventional materials. Conjugated polymers are a class of polymers capable of conducting electrons along their molecule backbones and are often capable of exhibiting photoluminescence and/or electroluminescence.[1−3] These polymers can be soluble in a wide variety of organic or aqueous solvents, enabling a range of solution processing techniques to tailor the properties of the polymers to specific applications and simplifying manufacturing. The manufacture of conjugated polymer films from solution, including inkjet printing,[4] involves a range of flow processes where the polymer solutions may be exposed to both shear and extensional flow. The light absorption and emission properties of the conjugated polymers are dependent on the molecular conformation of the polymer,[5,6] and the conjugated segment lengths and interchain proximity of the polymer molecules determine the photophysical properties.[2,7,8] These can be altered by shear and flow conditions, thereby affecting processed film products, so it is important to study the effects of mechanical forces acting on the polymer molecules during solution processing, such as shear and extensional hydrodynamic forces. To date, however, little appears in the literature pertaining to optimization regarding the processing- and flow-induced structural changes in these systems. In this paper we investigate the shear-flow-induced photophysical solution behavior of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), a commonly used conjugated

polymer for light-emitting duties due to its optical properties and solubility in a range of organic solvents (see Figure 1).[9−11] MEH-PPV has been widely studied, with particular emphasis on film formation or film processing mechanisms.[7,12−14] The objective of this study is to understand the effects of shear forces on the optical properties of MEH-PPV solutions by undertaking fluorescence measurements in Couette flow in order to quantify the effects of hydrodynamic forces on polymer conformation in flow.

Previous researchers have shown that conjugated polymer films often reflect the processing history of the polymer molecules, such as the film casting technique used or the solvents used in the process.[11,15] A key to the optimized use of these conjugated polymers in applications is the ability to process solutions to effect self-assembly at the molecular level. Understanding the flow-induced structural and spatial organizational changes is therefore critical for optimized applications.

Despite the importance of understanding the process-induced changes in MEH-PPV conformation in flow, there remain relatively few reports on the effects of shear forces on MEH-PPV conformation and photophysics.[16,17] Several prior studies by Hill et al.[16,17] using Couette flow have shown that the flow-induced rheofluorescence exhibits polarization (orientation) and spectral shifts with increased shear exposure. In dilute xylene solutions no measurable conformational changes of MEH-PPV were observed. However, in polystyrene polymer solutions an irreversible red shift was observed.[16] The reasons for the red-shifted emission were not fully understood. Furthermore, the water-soluble polymer,
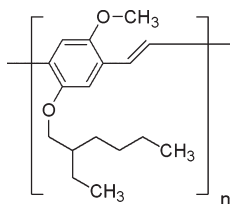
Figure 1. Chemical structure of the monomer in the MEH-PPV polymer.

poly[2,5-dipropoxysulfonato-*p*-phenylenevinylene] (DPS-PPV), showed an irreversible shear-induced aggregation in flow.[18] In summary, MEH-PPV was shown to undergo an irreversible red shift in the polystyrene matrix, while the aqueous solutions aggregated in flow. In order to further understand these effects we performed the experiments reported here in background PMMA polymer solutions.

EXPERIMENTAL DETAILS

The MEH-PPV polymer samples were purchased from Sigma Aldrich, with a reported molecular weight of 133 kg/mol with a polydispersity index of 1.06 as determined by GPC-MALLS. The polymer was dissolved into dimethylformamide (DMF), sourced from Sigma Aldrich, at a concentration of 0.1 mg/mL. Poly-(methyl methacrylate), PMMA, also sourced from Sigma Aldrich, molecular weight of 130 kg/mol and polydispersity index of 1.49 with $C^* = 6.0\%$, was also added to some samples at concentrations of up to 5 wt % to increase the viscosity and alter solution behavior. Concentrations of 2.5% and 5.0% PMMA were used as they increased the viscosity without causing concentration-induced conformation changes in the MEH-PPV. Solutions were continuously agitated for at least 48 h to ensure full solubilization, and undissolved matter was filtered using a 2 μm syringe filter. These solutions were inserted into a custom-built Couette rheofluorescence cell,[18] which was mounted inside a Varian Cary Eclipse 2E fluorimeter. Fluorescence measurements were conducted at excitation and emission wavelengths of 490 and 554 nm, respectively, at 25 °C. Light-scattering measurements were also performed simultaneously in the fluorimeter by exciting at 800 nm (outside the absorption band of the sample) and selecting an appropriate monitoring emission wavelength, 803 nm in this experiment, to observe light scattered at the same settings as the fluorescence measurements. The sensitivity of the scattered light intensity measurements is readily adjusted by selection of wavelength. The rheofluorescence cell enabled measurement of real-time fluorescence signals from polymer solutions exposed to constant shear.

RESULTS

The MEH-PPV/DMF solutions were exposed to constant shear rates between 154 and 616 s^{-1}. All samples showed decreasing fluorescence intensity over time, down to steady state values between 3% and 10% of the initial intensity. Figure 2 shows the results for 0.1 mg/mL MEH-PPV in DMF at various shear rates. The rate of fluorescence intensity decrease is dependent on shear rate, with higher shear rates having a larger rate of intensity decrease initially and reaching an intensity plateau earlier than low shear rates. The sample exposed to shear at 154 s^{-1} took more than 60 min to reach a constant value, while under 616 s^{-1} shear conditions the intensity plateaued after approximately 30 min.
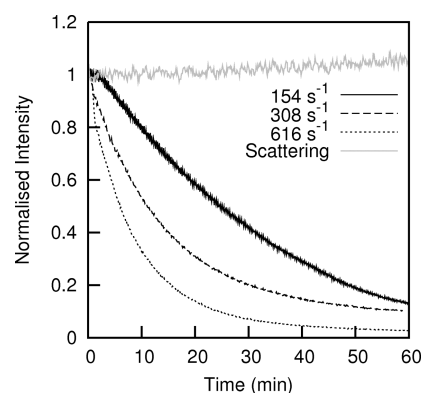

Figure 2. Fluorescence intensity as a function of time of 0.1 mg/mL MEH-PPV/DMF solutions exposed to various values of constant shear, and light scattering response at shear rate of 154 s^{-1}, normalized to initial fluorescence intensity.
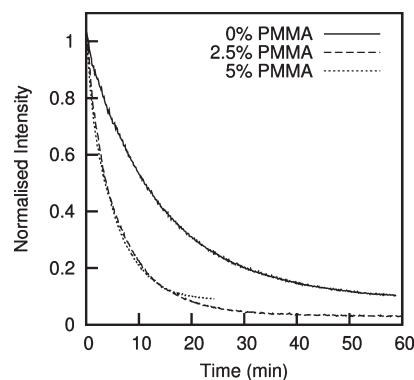

Figure 3. Fluorescence intensity as a function of time of 0.1 mg/mL MEH-PPV/DMF with 0%, 2.5%, and 5% PMMA solutions exposed to constant shear at 308 s^{-1}, normalized to initial fluorescence intensity.

The mechanics of the process that causes the reduction in fluorescence intensity were investigated further by performing a light-scattering measurement in order to detect any particle aggregation in the polymer solutions. Light of 800 nm was introduced into the sample, and the scattered light intensity was monitored at 803 nm with a spectrometer bandwidth of 5 nm. The comparison of light-scattering response to fluorescence intensity at a constant shear of 154 s^{-1} is also shown in Figure 2. The light-scattering response showed a small gradual increase over time, suggesting either slow evaporation of the solutions or some very small degree of aggregation of polymers over time. However, it is clear that this minor change in the scattered light signal does not correlate with the dramatic decrease in fluorescence intensity with time. The scattering data shown is typical of all the shear rates measured, which showed a very slight increase in intensity with time. This is strong evidence that exposure to shear flow is not causing any significant aggregation to occur in this case. In contrast, the DPS-PPV solutions measured previously show a pronounced increase in scattering on the order of 20% over the same time.[18]

Addition of PMMA into the DMF solutions affected the rate of fluorescence intensity change observed. Figure 3 shows the normalized fluorescence intensity of the solutions at a constant shear rate of 308 s^{-1}, with added concentrations of 2.5 and 5 wt %
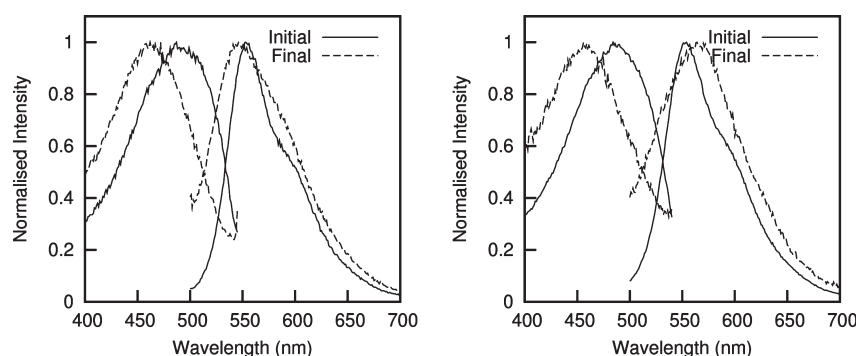
Figure 4. Normalized fluorescence excitation and emission spectra of (a) 0.1 mg/mL MEH-PPV/DMF solution before and after exposure to constant shear at 154 s^{-1} and (b) 0.1 mg/mL MEH-PPV/DMF with 5 wt % PMMA solution before and after exposure to constant shear at 308 s^{-1}.

Table 1. Fluorescence Intensity and Wavelength Changes of 0.1 mg/mL MEH-PPV/DMF Solutions before and after Exposure to Constant Shear Rates

sample	maximum excitation wavelength (nm)	maximum emission wavelength (nm)	steady-state fluorescence intensity (%)
initial	490	554	
154 s^{-1}	458	540	12.8
308 s^{-1}	462	547	10.0
616 s^{-1}	448	532	2.7

PMMA. Addition of PMMA increases the rate that the fluorescence intensity decreases. However, the amount of added PMMA did not seem to affect any of these phenomena, with the 2.5% and 5% samples showing identical responses.

In addition to the marked decrease in fluorescence intensity with the duration of the applied shear, significant changes in the fluorescence spectral behavior were also detected, as shown in Figure 4. Both the excitation and the emission spectra of the MEH-PPV shift to lower wavelengths after exposure to shear. The maximum excitation wavelength shifted from 490 nm before shear was applied to approximately 458 nm, and the maximum emission wavelength shifted from 554 to 540 nm after exposure to shear at 154 s^{-1} for 60 min.

Addition of PMMA to the polymer solutions also resulted in changes in the fluorescence excitation and emission spectra after exposure to shear, as seen in the spectra of the 5% PMMA sample shown in Figure 4b. The fluorescence excitation maximum blue shifts in a manner very similar to that observed in pure solvent. The emission spectral maximum, however, red shifts, opposite to the behavior observed for the solvent alone as shown in Figure 4a.

Results for the other shear rates used are shown in Table 1, where the steady-state fluorescence intensity is given as a percentage of the initial intensity. All shear rates caused a similar shift in excitation and emission wavelengths, with no clear trend in the magnitude of the spectral shift observed. The steady-state fluorescence intensity provided is the final intensity measured at the end of each experiment at fixed wavelengths of 490 and 554 nm for excitation and emission, respectively. Higher shear rates resulted in a more pronounced decrease in fluorescence intensity. Control samples monitored in the absence of shear for time periods up to 3 h show no significant change in fluorescence intensity and fluorescence spectra. The spectral shift in the excitation spectra

will result in a reduction in the light absorbed at 490 nm, which alone would account for a ~30% reduction in fluorescence emission intensity. A similar shift in the emission spectra results in a smaller but additional reduction in intentsity at the measured wavelength of 554 nm on the order of 10% (see Figure 4). The resulting overall change in intensity resulting from spectral shifts is on the order of 40%, which is significantly less than the 80−90% reduction observed with time as seen in Figure 2. The observed decrease in fluorescence intensity with increasing shear rate is therefore partially due to the shift in maximum fluorescence excitation and emission spectra and an overall decrease in fluorescence intensity attributed to an increase in the dominance of nonradiative relaxation processes occurring in the polymers, assuming the radiative rate constant, k_r, remains unchanged.

Samples of the sheared solutions were recovered and heated at 60 °C for 20 min. Blue shifts of a further 5−10 nm were observed when the samples were exposed to heat, but the spectra returned to the original after-shear form upon a return to ambient temperature. The spectral shifts that resulted from the affects of shear, however, were somewhat surprisingly irreversible and remained permanently.

■ DISCUSSION

The large decreases in fluorescence intensity of the polymer solutions as a function of shear would most easily be explained by the occurrence of aggregation of polymer molecules or phase separation, as previously reported for the polymer poly[2,5-dipropoxysulfonato-p-phenylenevinylene], DPS-PPV.[18] However, aggregation of particles would be expected to cause significant changes in both the fluorescence intensity and the light-scattering behavior of the solutions. Aggregation of conjugated polymer molecules typically causes a red shift in the fluorescence emission with an increase in the intensity of the secondary emission peak, which is associated with intermolecular energy transfer to the lowest energy (longer) segment lengths.[19] In the current experiments, the final polymer solutions appeared to be homogeneous and did not show localized areas of variable concentration and particulate matter was not observed, in contrast to the behavior seen for DPS-PPV aggregation.[18] Phase separation and aggregation are therefore discounted as the major cause of the observed intensity changes. The gradual increase in scattered light intensity observed in Figure 2 is possibly associated with slow evaporation of the solution leading to a slight increase in the concentration of polymer. Chain scission is also considered a possible mechanism for the permanent fluorescence changes in the polymer molecules; however,

the shear rates used and magnitude of the spectral changes do not correlate with this mechanism. Studies examining the effect of extensional shear on polystyrene and polyethylene oxide chain scission show effects at significantly higher shear rates than used here.[20,21]

The fluorescence of all samples, both excluding and including added PMMA, showed significant spectral shifts after exposure to shear. The excitation spectra of all samples were blue shifted compared to the initial (quiescent) state, which suggests an overall decrease in the average length of the conjugated polymer segments. This phenomenon may be caused by compressive hydrodynamic forces acting on the polymer molecules while the solutions are exposed to shear, leading to a reconfiguration of the molecule conformations resulting in an overall reduction in the average segment lengths. The fluorescence emission spectra of the samples without added PMMA are also consistent with this mechanism, where the shorter wavelength emission is characteristic of reduced average conjugated segment lengths. A bias toward emission at shorter wavelengths could also be attributed to a reduction in intramolecular energy transfer to low-energy (long conjugation length) segments, which could be caused by reorganization of the polymer chains into a conformation that reduces intrachain contacts. No trend was observed in the magnitude of the wavelength shift as a function of exposure shear rate; therefore, this reconfiguration appears to be a discrete process rather than one that becomes incrementally more dominant proportional with shear rate. No reversibility in the shear-induced fluorescence changes was observed. The conformational changes caused by shear flow therefore appear to result in permanent deformation of the molecules, with coupling of chain segments within individual molecules, leading to increased vibrational energy dissipation in the polymer chains. Other mechanisms that could account for permanent changes observed include aggregation, phase separation, or chain scission in the shear flow; however, arguments presented above indicate that aggregation and phase separation are not dominant. Chain scission is also discounted as the principal cause for the observed emission behavior, based on the observation that shorter conjugation length segments exhibit higher emission quantum yields than the longer (low-energy) segments.[22] If chain scission were dominating as a result of the applied shear, an increase in emission intensity would be expected rather than the observed decrease. Furthermore, chain scission would result in a permanent blue shift of both the excitation and the emission spectra, and the same behavior would be expected with and without PMMA added. Modeling the chains using the bead—spring model enables an approximate calculation of the maximum hydrodynamic force on the middle of the chain. Dynamic light-scattering measurement of the hydrodynamic radius gave a value of 4 nm. Modeling the chain as two beads of 2 nm radius in a solution of 10 mPa·s viscosity (5% PMMA solution) at a shear rate of 1000 s^{-1} yields a maximum extensional force of 2 fN on the chain. The work done on the chain over the bond length is then 2.4 J/mol (assuming that the bond length is 0.2 nm). Obviously this is well below the required scission energy of the carbon—carbon bond of order 350 kJ/mol. The activation energy associated with the conformational changes related to the so-called "tetrahedral defects" proposed by Barbara et al.[23] is approximately 1.5 kJ/mol. The energy imparted by the flow field is relatively small compared to this conformational barrier. However, the total power dissipated in the solution over the time scales associated with the observed shear-induced conformational changes (30—60 min) may result in an increased rate of conformational change of the polymer in flow. This change would then be irreversible on cessation of
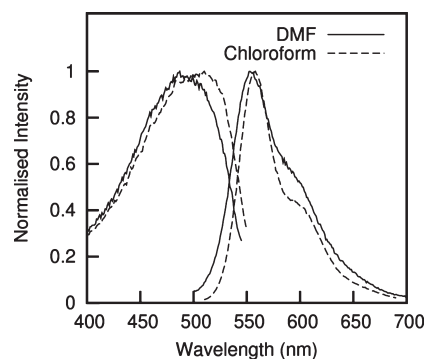

Figure 5. Comparison of excitation and emission spectra for MEH-PPV/DMF solution and MEH-PPV/chloroform solution, normalized to maximum intensities.

shear. Tetrahedral defects would, however, also result in shorter average conjugation segment lengths and, as with chain scission, increased emission intensity.

The emission spectra of the samples with added PMMA showed a different response to that in the absence of added PMMA. The emission wavelength maximum red shifted following exposure to shear, whereas the excitation spectral maximum blue shifted. This creates an apparent contradiction in the interpretation since both the excitation and the emission wavelengths should depend in the same way on the conjugated segment lengths, particularly if the change in average conjugation length were the sole reason for the spectral shifts. A possible explanation for this observation is that in addition to the compressive forces acting on the polymer, reducing the average conjugation length and therefore the wavelength of the excitation maximum, an increase in the efficiency of energy migration pathways is also occurring prior to emission in the presence of PMMA. The PMMA molecules could have either integrated themselves into the MEH-PPV polymer chain conformation/morphology or altered the viscosity of the solutions in such a way that the reconfiguration of the molecules in shear results in more efficient energy transfer pathways, causing fluorescence to be emitted more predominantly from the small population of lower energy (longer) conjugation segments. This is consistent with the reduced intensity of emission observed after shear. Recent reports suggest that conformational collapse may lead to more efficient exciton migration to trap sites on the MEH-PPV chain.[24] The rod-like collapsed state shows a red shift in emission consistent with reduced emission due to increased nonradiative mechanisms.[6] Rothberg et al.[6] have shown that the red shift for shorter chains is due to their greater efficiency in transferring energy to the longer emissive segments. In toluene the chains are more collapsed than better solvents and show improved energy transfer to the red emissive states.

The decrease in fluorescence intensity is partly explained by the shifts in maximum wavelength, since the data are recorded increasingly further from the maximum wavelength as the spectrum shifts. This accounts for approximately 40% of the overall decrease observed. Phase separation, particle aggregation, and chain scission are ruled out as the dominant reasons for the fluorescence decrease, as discussed above. The primary cause of the reduced fluorescence intensity is most likely molecular-level quenching of the fluorescence, due to the reconfiguration of the molecular conformation. This may enhance nonradiative energy dispersion pathways for the conjugated polymer molecules. The shear-induced changes observed in the polymer solutions were nonreversible.

The changes in the molecular conformations observed in these experiments were measured only in DMF solutions. Figure 5 shows the comparison of the initial fluorescence spectra for the polymer in DMF compared to chloroform before exposure to shear. It is seen that in chloroform the excitation peak of the polymer is shifted to the red compared with in DMF, suggesting a tendency for the polymer to adopt conformations with longer conjugated segments on average. There also appears to be a small red shift in the emission spectrum maximum of the polymer in chloroform compared with DMF and an increase in the prominence of the secondary peak to the red in the emission spectra at around 600 nm. These two observations are associated with an overall sharpening of the emission bands of the polymer in chloroform compared with DMF, which may be due to a reduction in a broad red emission associated with aggregates, underlying the emission band. Similar shear experiments performed with the chloroform solutions showed no change in fluorescence spectra, although they did still show some overall decrease in fluorescence intensity with time of shear. The unperturbed conformation the molecules adopt in solution is therefore an important factor in the deformation processes when solutions are exposed to shear.

Changes in the photophysical behavior of conjugated polymers due to configurational changes in the molecular conformation have been observed in other work, such as in the deformation of polymer films[7,12,25] or in the film casting process.[26,27] In previous work with casting conjugated polymer films under an electric field, spectral shifts in the absorption and emission were also observed, largely attributed to altered aggregation efficiency and chain alignment when the films were cast under strong electric fields.[26]

CONCLUSIONS

Solutions of the conjugated polymer, MEH-PPV, in DMF have been exposed to uniform shear fields in Couette flow where changes in the photophysical behavior were measured using a custom-built rheofluorescence cell. Real-time fluorescence measurements show a reduction in fluorescence intensity over time as a function of shear rate with spectral shifts of the fluorescence excitation and emission maximum observed after exposure to shear. The excitation spectra of all samples showed a shift toward blue wavelengths, suggesting an overall compressed molecular conformation favoring shorter conjugated segment lengths. The emission spectra for samples embedded in a PMMA background red shifted, which suggests an increase in the energy migration pathways in the compressed conjugated polymer molecules leading to a red-shifted emission. In DMF alone, the chains extend, leading to a blue shift in the emission due to reduced efficiency of the energy transfer. We have shown shear-induced changes and effects from matrix polymers in the photophysical behavior of these polymers.

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