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Aggregation of Water-Soluble Conjugated Polymers in Couette Shear Flow

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Aqueous solutions of the conjugated polymer poly(2,5-disulfopropoxy-1,4-phenylene vinylene) (DPS-PPV) blended with poly(vinyl alcohol) (PVA) have been exposed to Couette shear flow and studied using fluorescence techniques. Significant aggregation of the DPS-PPV and PVA molecules occurred during shear exposure, resulting in an 80% decrease in solution fluorescence intensity and formation of visible polymer particles. The aggregation process caused a separation of the DPS-PPV molecules where the fluorescence of the aggregated particles had a red-shifted emission peak at a wavelength of 594 nm, and the remaining solution had a blue-shifted emission at 513 nm, as compared to an initial emission peak at 574 nm. The fluorescence excitation spectra of the aggregated particles became broadened while the excitation peak of the remaining solution narrowed. This has great implications for the processing of aqueous conjugated polymer systems in various polymer blends, because aggregation could cause significant problems for device manufacture.

Introduction

Conjugated polymers are a class of macromolecules in which electron mobility within and between the chains occurs to emulate properties similar to those found for classical semiconducting materials.^{1–3} Conjugated polymers are often capable of photoluminescence and electroluminescence, combining light-emitting properties with the desirable mechanical and processing properties of polymers.^{1–5} This makes them suitable for a wide range of applications, such as light-emitting devices in the form of polymeric light-emitting diodes¹ or flexible display screens,⁶ and in photovoltaic cells.⁷

In particular, members of the poly(phenylene vinylene) (PPV) group of polymers are commonly used for their light-emitting capacity in a range of devices, including polymer light-emitting diodes.¹ The PPV polymers can be modified by the inclusion of various side groups to induce solubility in a range of solvents (or other desired properties); for example, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), which has alkoxy side chains that allow the polymer to be soluble in common organic solvents,^{8,9} and poly(2,5-disulfopropoxy-1,4-phenylene vinylene) (DPS-PPV), which is soluble in aqueous solutions.¹⁰

The manufacture of conjugated polymer films from solution involves a range of flow processes during which the polymer solutions are exposed to both simple shear and extensional flow. The photophysical properties of the conjugated polymers depend on the molecular conformation of the polymer, such as the length and orientation of conjugated segments and interchain proximity of the polymer molecules.^{2,11,12} To optimize processing conditions for product performance, it is important to understand the effect of shear forces on the conformation of the polymer

molecules. Conjugated polymers can be blended with other polymers to optimize mechanical properties, aid molecule dispersion, affect molecule orientation, or alter optoelectronic properties.^{10,13–15} Previous studies of polymer solution systems have shown a wide range of phase separation, precipitation, and aggregation phenomena.^{16,17} In particular, Yamaura and co-workers investigated the aggregation of PVA in aqueous solution and found fractionation of components based on molecule structure and density after exposure to shear.¹⁷ Aggregation behavior of MEH-PPV in organic solutions has been studied in detail,^{18,19} but little work has been found on aqueous DPS-PPV solution behavior and mechanisms of the aggregation.

The current study involves studying the fluorescence response of a semidilute solution of DPS-PPV blended with poly(vinyl alcohol) (PVA) in water exposed to constant shear in a Couette flow cell, which allows the real time steady state fluorescence and light scattering to be measured.

Experimental Details

The DPS-PPV was synthesized in our laboratory.¹⁰ The molecular weight distribution of the DPS-PPV as measured by fluorescence-based analytical ultracentrifugation showed the presence of three components, two of which had molecular weights of ~24.8 kg/mol and ~82.5 kg/mol, and a third with a smaller contribution of 185 kg/mol material.²⁰ The DPS-PPV powder was dissolved into solutions of 3% or 6% (by weight) poly(vinyl alcohol) (PVA, $M_w = 130\,000$, Aldrich) in pure water at a concentration of 0.05 mg/mL. PVA background was added to the DPS-PPV solutions to increase the solution viscosity and minimize DPS-PPV molecule interaction. The DPS-PPV was stirred at room temperature for at least 3 days to ensure full dispersion in the solution. Thin films of the DPS-PPV/PVA solutions were also drop-cast onto glass slides for comparison purposes. These samples were dried at room temperature for a period of 5 days.

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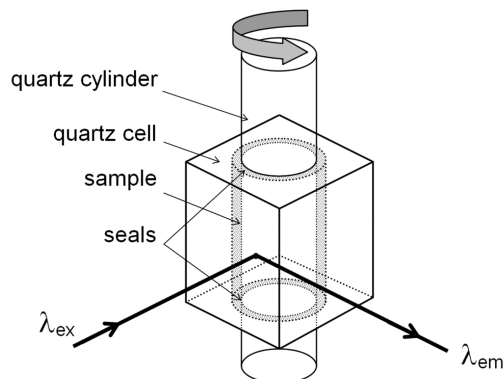


Figure 1. Schematic diagram of the Couette rheofluorescence cell.

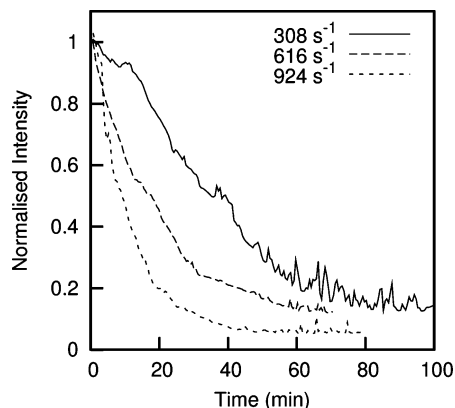


Figure 2. Fluorescence intensity response over time of DPS-PPV/PVA solutions at 3% PVA exposed to constant shear rates of 308, 616, and 924 s^{-1} , normalized to initial intensity.

Polymer solutions were inserted into a custom-built quartz Couette rheofluorescence cell, shown in Figure 1.¹² The cell was placed in the beam of a Cary Eclipse 2E fluorometer with excitation $\lambda = 369$ nm and emission monitored at $\lambda = 415$ nm at a temperature of 25 °C. Light scattering measurements were also performed simultaneously in the fluorometer by exciting at a wavelength outside the absorption band of the sample and selecting an appropriate monitoring emission wavelength to observe light scattered at the same settings as the fluorescence measurements. The Couette cell enables measurement of the real time fluorescence and light-scattering signal from the solution exposed to constant shear.

Results

The DPS-PPV solutions were exposed to constant shear rates ranging from 308 to 924 s^{-1} . The real time fluorescence response was monitored, and the shearing was ceased once the fluorescence had reached a constant intensity. No reversibility in the shear-induced emission intensity changes was observed.

Figure 2 shows the normalized fluorescence response over time of the DPS-PPV solutions at three measured shear rates. All samples show an immediate decrease in fluorescence intensity over time when exposed to shear, with an increased response rate for higher shear rates. Final steady state fluorescence intensities were reduced to less than 20% of the original value. At the end of each experiment, aggregated particles of polymer were clearly visible to the naked eye in the solutions. Figure 3 shows the shear response at 308 s^{-1} for background PVA concentrations of 3% and 6%. It can be seen that the increase in the shear rate or PVA polymer concentration increases the rate of fluorescence decrease.

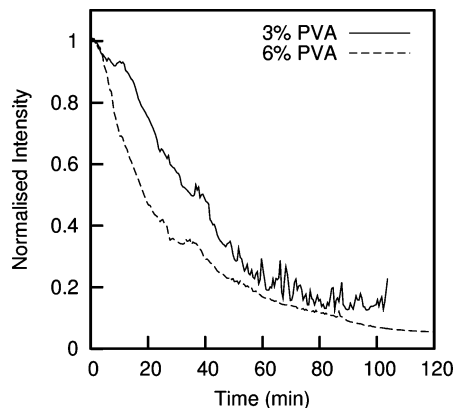


Figure 3. Fluorescence intensity response over time of DPS-PPV/PVA solutions at concentrations of 3% and 6% PVA exposed to a constant shear rate of 308 s^{-1} , normalized to initial intensity.

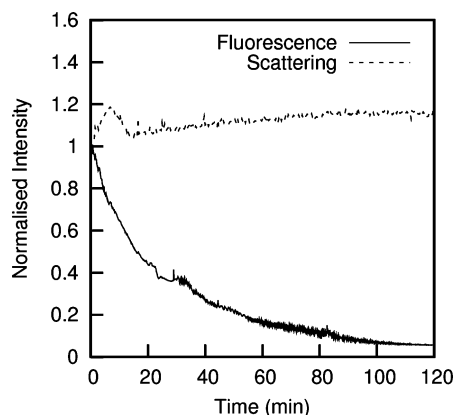


Figure 4. Fluorescence intensity and light scattering response over time of DPS-PPV/PVA solution at 6% PVA concentration exposed to constant shear rate of 308 s^{-1} , normalized to initial intensity.

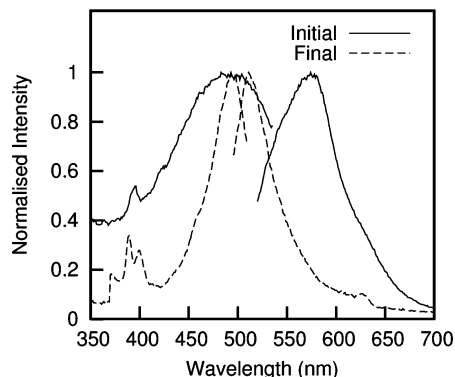


Figure 5. Fluorescence excitation and emission spectra of initial sample of DPS-PPV/PVA (3%) solution and final DPS-PPV/PVA (3%) solution after shear, normalized to maximum intensity.

Light scattering measurements were performed simultaneously with the fluorescence measurements to confirm the effects observed, as shown in Figure 4. The scattered light intensity was measured at 713 nm when the sample was excited at 700 nm with a spectrometer bandwidth of 5 nm for both excitation and emission.

Figure 5 shows the normalized fluorescence excitation and emission spectra of the initial sample and the final sample after shear, and Figure 6 shows the normalized spectra of a DPS-PPV/PVA drop-cast film compared to the aggregated particles found at the conclusion of experiments. The fluorescence spectra of the initial sample show a wide excitation peak at 490 nm

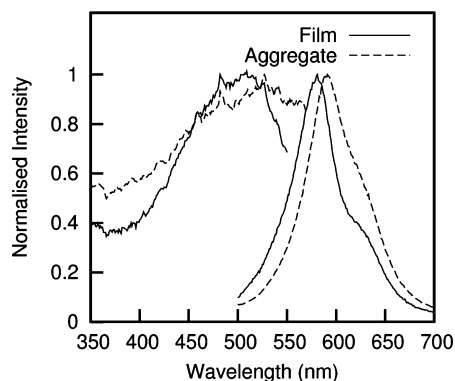


Figure 6. Fluorescence excitation and emission spectra of drop cast film of DPS-PPV/PVA (3%) and the DPS-PPV/PVA (3%) aggregate, normalized to maximum intensity.

and an emission peak at 574 nm. After shearing, the excitation and emission peaks red-shift to 496 nm and blue-shift to 513 nm, respectively, with much narrower peak widths. The fluorescence excitation and emission spectra of the solid polymer particles formed after shear show a broadened excitation peak at 528 nm, and the emission peak red-shifts to 594 nm, as compared to 514 and 580 nm excitation and emission maxima, respectively, for the drop-cast film. Spectral shifts and particle spectra were similar for experiments conducted at all shear rates and PVA concentrations.

Discussion

The fluorescence intensity response curves in Figure 2 and the changes in fluorescence spectra as seen in Figures 5 and 6 show that the shear forces from Couette flow have caused polymer molecules to aggregate and precipitate. Control solutions of the same polymers stored in the dark at room temperature did not show any change over time. The large decrease in fluorescence intensity of the bulk solution is partially due to the reduction of the polymer concentration as the aggregates settled out of solution. The apparent blue shift in the emission spectra is also due to sedimentation of the red-shifted aggregates.

After exposure to shear, the emission peak of the polymer solution blue-shifts significantly from 574 to 513 nm, as compared to the aggregated particles, which have an emission peak red-shifted to 594 nm. The aggregated particles show a red-shifted emission compared to the drop-cast films and a more pronounced shoulder in the emission spectrum at 625 nm. The higher wavelength emissions are characteristic of longer-segment-length conjugated polymers, whereas the shorter wavelength emissions are characteristic of short conjugated segment lengths.²¹ It is proposed that the larger molecules in the polymer solution have aggregated, leaving smaller molecules in the bulk solution. This result agrees with the observed polydispersity of the DPS-PPV sample, in which three molecular weight components were observed.²⁰

The light scattering results shown in Figure 4 confirm this behavior, showing an increase in light scattering and, therefore, evidence of an increase in the aggregated matter in the solution as a function of time under shear. There is an initial spike in the scattering signal that is attributed to the formation of aggregates that consequently settle out of solution.

In previous work by Yamaura and co-workers, aqueous systems of PVA were fractionated into 16 distinct fractions by the application of a shearing force, with trends of decreasing syndiotacticity and lower molecular weight in later fractions.¹⁷

This result is in agreement with the current experiments, in which the higher-molecular-weight species of DPS-PPV have aggregated, leaving low-molecular-weight species in solution.

The aggregated particles resulting from the shear were stable and did not redissolve into solution over a period of 5 days. The mechanisms for the aggregation process are not clear. It is postulated that the shear forces impart deformation and rotation on the molecules, which increases the number of molecule collisions. The aggregation of colliding molecules reduces the overall free energy, resulting in stable aggregate particles that do not resolubilize.²² Michele et al. have shown that shear flow has the ability to induce aggregation in model suspensions of spherical particles. This has great implications for processing of water-based conjugated polymers, since aggregation of polymer molecules could cause significant problems in the manufacture of devices. The mechanisms of aggregation formation and methods to reduce or prevent aggregation will require further investigation. Dynamic light scattering measurements to estimate the size of aggregate particles over time will aid understanding of aggregation mechanisms. Time-resolved fluorescence measurements may identify changes in the conformation of DPS-PPV molecules in solution after shearing.²³ The DPS-PPV synthesis process results in a high polydispersity with three molecular weight components, as shown by analytical ultracentrifugation work. Fractionation of the DPS-PPV by molecular weight should be considered in future work, although this is inhibited somewhat by problems associated with the choice of columns. Ideal processing for DPS-PPV/PVA solutions would be minimization of exposure to shear forces or reduction of exposure time. Blending of other polymer species to reduce aggregation could be considered for future work.

Conclusions

Polymer solutions of DPS-PPV and PVA blends at semidilute concentrations were found to undergo significant aggregation when exposed to constant shear rates in the range of 308–924 s⁻¹, with the final fluorescence intensity being less than 20% that of the initial samples. The larger polymer molecules precipitated out of solution, leaving the short-chain molecules in the bulk solution and, therefore, causing a significant blue-shifting of the emission spectra of the solution from 574 to 513 nm, whereas the aggregated particles had a peak emission at 594 nm. This phenomenon needs to be fully investigated, since it could have major implications for the processing of water-based conjugated polymers.

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