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The effect of solvent quality on the chain morphology in solutions of poly(9,9′-dioctylfluorene)

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Abstract

The thermodynamics of the alpha (α) phase to beta (β) phase transition was investigated in solution of poly(9,9′-dioctylfluorene) in a variety of solvents with UV–vis absorption spectroscopy, differential scanning calorimetry, fluorescence spectroscopy, atomic force microscopy, and near-field scanning optical microscopy. The results show that the solvent quality has a strong affect on the α- to β-conformational change. The trend in enthalpies and transition temperatures indicates that the transition results from an increase in intramolecular interactions upon chain collapse at lower temperatures. This transition leads to subsequent gelation and/or aggregation that stabilizes the β-phase at higher temperatures and leads to a large hysteresis in the transition temperature. The enthalpy for the transition from an aggregated β-phase to a fully solvated α-phase is found to be 21.04 kJ mol^{-1} of monomer for toluene solutions. Differences between the measured heat and those previously reported are discussed.

Keywords: Poly(9,9′-dioctylfluorene); β-Phase; Differential scanning calorimetry

1. Introduction

Conjugated polymers have become an area of increasing interest because of their optical and electrical properties [1–8], making them promising materials for inexpensive, flexible light emitting devices [2,9–13], transistors [14], and photovoltaics [15,16]. One of the advantages offered by polymer electronics is the ease of solution processing. While this offers potential for rapid production, spin casting yields films whose morphology is not governed by equilibrium. Different morphologies lead to films with different properties [9,17–23]. Morphology can vary for films casted at different speeds or from different solvents. Moreover, the treatment of the solution prior to casting can affect the properties of the films, such that the chain conformation of the polymer in solution can be partially retained when casted into a film. Studies of light emitting devices of MEH-PPV cast from different solutions have shown how solvent quality can affect polymer conformation and subsequent properties of both films and devices [9,18]. Given these issues it is important to understand polymer conformations in both dilute and concentrated solutions to better control subsequent properties of films.

Polyfluorenes present an excellent model system for such studies as the polymer has two conformations with distinct absorption spectra. Polyfluorenes have shown promise because of their high quantum yield and thermal stability [24–26]; specifically, poly(9,9′-dioctylfluorene) (PFO) which has been studied for its blue-emitting spectral properties. PFO's thin film morphology has been shown to affect both the photoluminescence and electroluminescence of PFO films [8,17,27,28] because changes in the structure of the polymer backbone will lead to changes in the conjugation of the π electron system

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[29]. In both films and solutions, PFO has exhibited two distinct conformations denoted simply as the α- and β-phases. The α-phase has been characterized as amorphous and is the only phase present in dilute polymer solutions and in a good solvent [30–32]. The β-phase is thought to have a more planar structure with extended conjugation that results in a distinct red-shifted absorption band at 437 nm [28,29,31,33]. It is this unique absorption that makes the PFO system an excellent candidate for studying how solvent processing affects the polymer conformation. There have been numerous studies of PFO β-phase formation in thin films. It was first noted that the 437 nm absorption could be increased in thin films by low temperature processing [34]. The increase in β-phase was observed to remain even when the films were re-heated to room temperature. Subsequent studies demonstrated that the β-phase could be removed by heating at much higher temperature, although these changes were always gradual rather than exhibiting a distinct transition temperature [32–34]. β-Phase formation could also be induced by solvent swelling of films, leading to the conclusion that stressing the film either by low temperature cycling or swelling with incompatible solvents would lead to an increase in β-phase [33].

β-Phase formation has been associated with aggregation in concentrated solutions. Previously, researchers have speculated that in poor solvents, the polymer chains tend to aggregate to avoid contact with the solvent and form small ‘‘crystals’’ that were dominated by the β-phase conformation [34,35]. In films and in concentrated solutions, intermolecular forces, either between polymer chains or the polymer and a matrix, have been postulated to be the driving force for the β-phase formation. A recent study by Monkman et al. examined β-phase formation in dilute solutions [30], where aggregation and intermolecular forces could be minimized. Monkman et al. concluded that the formation of the β-phase at low temperatures was the result of the polymer adopting a more stable but lower entropy conformation. They showed that β-phase formation was a reversible equilibrium process in dilute solutions, and that aggregation proceeded after the formation of the β-phase. In other words, the aggregation was the result of β-phase formation rather than aggregation being the cause of β-phase formation [30].

In this paper we will examine how solvent quality affects dissolution of polymer aggregates and the hysteresis of the β-phase formation in both dilute and concentrated solutions. The β-phase is present when PFO is initially dissolved into many organic solvents and will not dissipate over time even with vigorous stirring. The β-phase can be converted completely to the α-phase by heating the solution above room temperature. The polymer will remain in the α-conformation even after the solution has returned to room temperature. The α-phase can be subsequently converted back to the β-phase by cooling the solution well below room temperature, and will remain until heated again. Concentrated solutions behave similar to dilute solutions upon heating; however, when cooled below room temperature, gelation occurs. The gelation is concurrent with the appearance of the β-phase. This now suggests that the β-phase regions of the polymer serve as cross-linking points in the network causing a gel to form. The aggregate dissolution and the gel formation thermodynamics are explored using UV–vis spectroscopy and differential scanning calorimetry (DSC) in a variety of different solvents. Other spectroscopic and scanning probe techniques were utilized to characterize the β-phase. The transition temperatures for the dissolution and reformation of the β-phase vary with solvent quality. Furthermore, the trend with solvent quality implies a collapse of the polymer chain leads to the formation of the β-phase and subsequent gelation or aggregation, and that a conformational change in the polymer chain is responsible for the conformational change of the polymer backbone.

2. Experimental

The polymer, poly(9,9′-dioctylfluorene) (PFO), was used as purchased from American Dye Source, Inc ($M_n \approx 34{,}800$ with a polydispersity of 2.9). All polymer solutions were made by diluting a 1 wt% PFO stock solution in toluene, tetrahydrofuran (THF), chloroform ($CHCl_3$), or cyclohexane. Heated solutions were prepared in a similar fashion by diluting a portion of the stock solution and applying mild heat until the solution changed from yellow to clear. Cooling was accomplished by either placing the solution in a temperature controlled refrigerator or by immersing the solution in a solvent ice bath (e.g. an acetone/dry ice bath, −78 °C). PFO films were made by spin casting an aliquot of the 1 wt% solution onto a glass coverslip at 3000 rpm for 30 s.

Absorption spectra were obtained using a Beckman DU 7400 UV–vis Diode-array spectrophotometer. Absorption spectra of the 1 wt% PFO stock solution were collected using a Hellma quartz cuvette with a path length of 10 μm; while absorption spectra of diluted polymer solutions were taken using standard quartz cuvettes with a path length of 1 cm. Diluted solutions were prepared to yield an optical density (OD) between 0.4 and 1 at 390 nm. Kinetic experiments were performed using the same UV–vis spectrophotometer as for steady state absorption spectra. The kinetics of dissolution were monitored by measuring the absorbance at a fixed wavelength, 437 nm, every 0.1 s. The spectrometer contained a cuvette holder with a heating mantle. A blank of toluene was placed in a cuvette (3 mL volume) and allowed to equilibrate to the desired temperature. Once the solvent had reached thermal equilibrium, a 25 μL aliquot of the 1 wt% PFO stock solution was added and the kinetic trace was started. The large volume of the solvent compared to the added stock solution, ensured a rapid temperature equilibration. An external digital thermometer was utilized to ensure the calibration of the temperatures as well as monitor the temperature stability.

Fluorescence and anisotropy measurements were acquired using a Photon Technologies International Quanta Master Model C Cuvette based scanning fluorometer. Samples were excited at 400 nm (polymer peak) and 440 nm (aggregate peak). Bandpass filters of appropriate wavelength were used to ensure a monochromatic excitation beam. Long pass filters were used in the emission path to help eliminate scattered excitation light.

Atomic Force Microscopy (AFM) images were taken on a Nanoscope II (Digital Instruments/Veeco) multimode scanning probe microscope in tapping mode. Near-Field Optical Microscopy (NSOM) images were collected using an Aurora system (Thermomicroscopes/Veeco). A frequency doubled Ti-Sapphire laser was utilized to excite the sample at either 400 or 440 nm. Near-field probes were manufactured in-house and mounted on piezo-electric tuning forks for shear-force feedback. The fluorescence was collected through a 455 nm long pass filter on an Avalanche Photo-diode (APD).

Differential Scanning Calorimeter (DSC) measurements were acquired using a Perkin Elmer DSC 7 and/or a TA Instruments Q100 DSC. Two empty large volume stainless steal pans (max volume 60 μL) were used for baseline subtraction. An aliquot of the 1 wt% PFO solution in toluene or THF was used as the sample and for the PFO gel samples, a portion was placed in the pan. DSC data were collected from 20 to 90 °C and/or 20 to −90 °C at a rate of 5 °C/min for both the baseline and the sample.

3. Results

Steady state absorption spectra were used to quantify the β-phase in the PFO solutions. Fig. 1 shows the absorption spectrum of a dilute PFO solution in toluene before heating, after heating above 60 °C, and after cooling to −78 °C. All three spectra were taken after the samples had re-equilibrated to room temperature. The spectrum of the unheated solution exhibits two distinct absorption peaks, one at 390 nm and one at 437 nm. The absorption peak at 390 nm is assigned to the standard morphology or α-phase, while the red-shifted peak at 437 nm is assigned to the β-phase. When the solution is heated, the absorption spectrum shows an increase in the 390 nm peak and no peak at 437 nm, indicating an absence of polymer in the β-phase. The heated solutions remain free of any absorbance at 437 nm even after many months at room temperature. When the sample was cooled to −78 °C for 40 min and then allowed to re-equilibrate to room temperature, the β-phase peak was observed; however, in toluene the size of the peak had greatly diminished when compared to the original solution spectrum.

Table 1
Summary of the transition temperatures of PFO in different solvents with the percent β-phase before heating and after cooling past the transition temperature

Solvent	% β-Phase present	Heat transition temperature (°C)	% β-Phase reformed	Cool transition temperature (°C)	Gel (y or n)
$CHCl_3$	11.52	45	N/A	N/A	n
Toluene	24.71	53	3.61	−55	y
THF	20.59	50	37.43	−25	y
Cyclohexane	46.18	73	18.21	10	y

Comparable results were observed in PFO solutions made with different solvents. Heating the solutions above 50 °C resulted in the dissolution of the β-phase which did not return upon subsequent cooling to room temperature. The only notable difference between the solutions in different solvents was that the β-phase returned at different temperatures. The transition temperatures from the UV–vis are shown in Table 1. These are rough estimates of the temperature obtained by systematically increasing the solution temperature and taking an absorption spectrum at each temperature until the β-phase was gone. The temperature at which the β-phase disappeared was the approximate transition temperature.

Another characteristic of the PFO solutions is that the initial solution is noticeably cloudy, indicating aggregated polymer present in the solution, but after heating the solution becomes clear and remains so indefinitely. In addition to heating, the solution can be either filtered or centrifuged to remove some of the larger aggregates. After filtration or centrifugation, there is a reduction in the β-phase absorption peak (data not shown). The total amount of β-phase also varies with solvent quality. The interconversion between the α- and β-phases can be more clearly seen in Fig. 2, where several absorption spectra were taken at 47 °C at different time intervals as the β-phase slowly disappeared. The spectra reveal a clear isosbestic point at 405 nm, which is characteristic of two

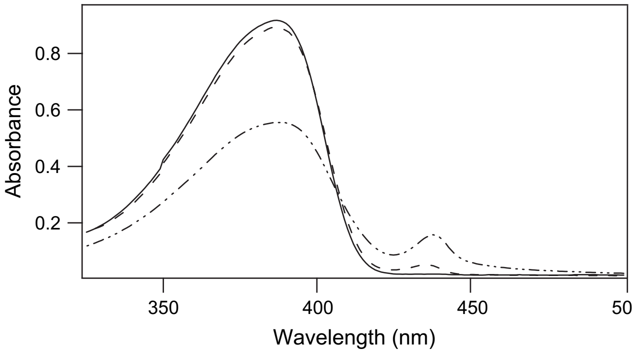

Fig. 1. Absorption spectra of PFO in toluene. The dotted and dashed line is the absorption spectrum of the aggregated PFO solution, the solid line is the absorption spectrum of the PFO solution after heating, and the dashed line is the absorption spectrum of the PFO solution after it had been cooled for 40 min at −78 °C. All absorption spectra were taken using the same PFO solution.

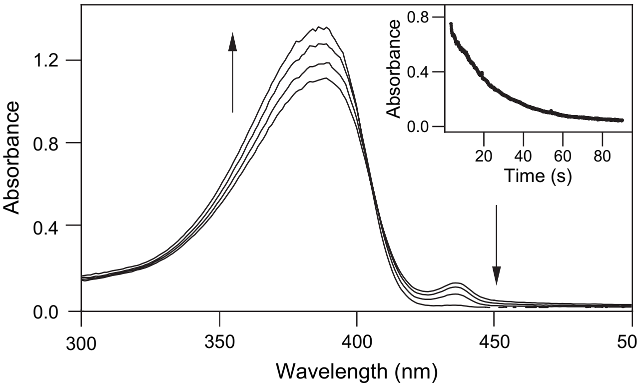

Fig. 2. Absorption spectra of PFO in toluene at 47 °C at different time intervals showing the decay of the aggregate peak with time. The inset is an absorption decay of the 437 nm peak at 52 °C. Exponential fit overlaid by the data yielded a rate constant of 0.045 s^{-1} ($\tau = 22$ s).

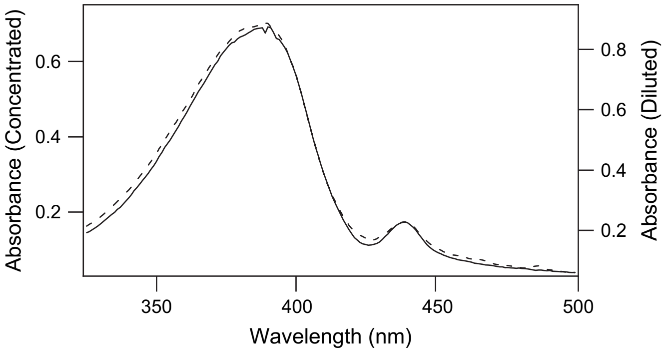

Fig. 3. Absorption spectra of aggregated PFO solutions; a comparison of a concentrated solution versus a dilute solution. The solid line is the absorption spectrum of the concentrated PFO solution (1 wt%) collected using a 10 μm path length cell. The dashed line represents the dilute PFO solution that was collected using a standard 1 cm path length cuvette.

inter-converting species. The increase in the α-peak was found to be directly proportional to the disappearance of the β-phase peak. For all spectra, the total integrated area of both peaks remained constant.

Concentrated solutions exhibited a slightly different behavior. The absorption spectrum for a 1 wt% PFO solution in toluene has a similar absorption spectrum as the dilute PFO solution. When the concentrated solution is heated the 437 nm peak converts into a larger absorption at the α-peak in the same way the dilute solution does. However, when the 1 wt% PFO solution is cooled to −78 °C the solution completely gels. An absorption spectrum of the PFO gel reveals a reformation of the β-phase as indicated by a return of the 437 nm absorption. When the gel returns to room temperature it remains in the gel state and does not melt into an aggregated solution. It will not return to solution until heated again. Similarly concentrated PFO solutions in other solvents have slightly different heating and cooling transitions (see Table 1 for summary) and all formed gels except for $CHCl_3$.

In the best solvent, the fraction of β-phase was found to be independent of concentration. Fig. 3 shows the absorption spectrum of two toluene solutions with very different concentrations. The solid line is the absorption of the 1 wt% stock solution in a cuvette with a path length of 10 μm, while the dotted line shows the spectrum of a solution that has been diluted by a factor of 1000 in a 1 cm cuvette. The product of the concentration and path length for both samples was constant. The ratio of the α-peak to the β-peak (6:1) is identical in both cases despite a three order of magnitude difference in the total concentration of the solutions. Slight differences in the total absorbance of the two samples were likely the result of variation in the thickness of the small path length cuvette and/or slight dilution errors.

The kinetics of the disappearance of the β-phase can be monitored by measuring the absorption at 437 nm as function of time after a temperature jump. Kinetic measurements showed that the peak at 437 nm is apparently infinitely slow at room temperature with the rate becoming finite as the temperature increases. Then the rate increases rapidly when the temperature approaches 50 °C. A typical kinetic transient is shown in Fig. 2 inset. The decay can be well characterized by an exponential fit; however, the final absorbance at 437 nm is not zero indicating a residual amount of polymer still in the β-form, or that the kinetics are extremely slow for the conversion of the remaining polymer.

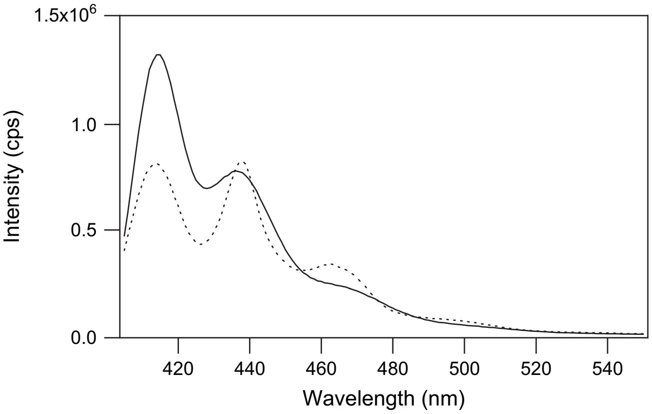

Fig. 4. Fluorescence spectra of PFO solution in toluene excited at 400 nm. The dotted line is the fluorescence spectrum of the aggregated solution and the solid line is the fluorescence spectrum after the solution had been heated.

Similar effects to those observed in absorbance could be seen in the emission spectra of PFO solutions in toluene. When an aggregated PFO solution was excited at 400 nm, the emission spectrum demonstrated three vibrational peaks, with the most predominant peak at 438 nm. After heating the PFO solution, the emission spectrum still had three vibrational peaks, except the first peak had increased dramatically in intensity while the second peak showed little change in intensity (Fig. 4). Since the original aggregated solution was excited near the isosbestic point (405 nm), the emission spectrum was a sum of both α- and β-phase species. However, when the aggregated solution was excited near the β-phase peak (440 nm) only the β-phase emission was excited (data not shown). In order to confirm this, the heated emission spectrum was subtracted from the original aggregated emission spectrum, yielding a spectrum of only the aggregate emission. The subtracted spectrum was then compared to the aggregate emission spectrum excited at 440 nm and when plotted together, the subtracted spectrum and aggregated spectrum overlaid one another exactly.

Scanning probe microscopy was utilized to directly probe the polymer aggregates. AFM images were acquired of films cast from PFO aggregated, aggregated and filtered, and heated solutions in toluene. The AFM image of the film cast from the aggregated solution clearly showed small polymer clumps, roughly 20 nm in height. The film cast from a filtered aggregated solution showed a reduced number of aggregates present on the film, while the film cast from a heated solution had no visible aggregates present.

NSOM [36,37] was used to probe the aggregates in order to see if they can be directly excited at the 437 nm absorption peak. A film cast from a filtered aggregated solution was imaged with an excitation wavelength of 440 nm. The aggregates are clearly present in the topography image as 20 nm clusters (Fig. 5a). The fluorescence image shows that the aggregates

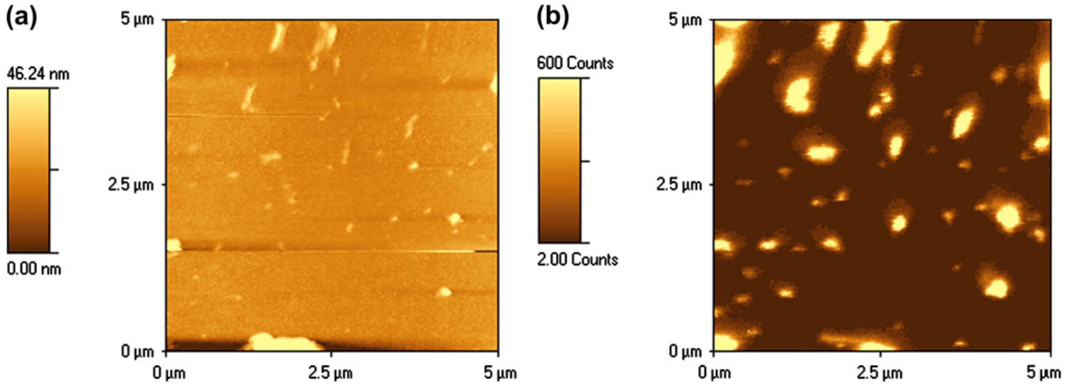

Fig. 5. NSOM images of a filtered PFO solution in toluene spin cast into a film. (a) The topography image of the film. (b) The fluorescence image of the film excited at 440 nm.

are fluorescent at this excitation wavelength (Fig. 5b). Moreover, the rest of the film exhibits almost no fluorescence indicating that nearly all the polymer with the β-phase morphology is in the aggregates. Previous studies of conjugated polymer aggregates have shown that they can have a lower fluorescence quantum yield due to a variety of interchain electronic interactions [17,19]. Previous NSOM images of PFO films with small aggregates having a decrease in emission were observed for the aggregates seen in the topography [38], but these studies did not look at direct excitation of the β-phase. When the β-phase is excited directly it is clear that the polymer aggregates are more fluorescent than the film. Although, this is likely due to the concentration of the β-phase rather than the relative quantum yields of the aggregates versus the film.

DSC measurements were taken to probe the thermodynamics of the aggregate dissolution and the gelation phenomena. Fig. 6a shows the DSC scan of an initially unheated solution from 20 to 90 °C. A clear endothermic peak is observed at ∼53 °C, which is the same temperature where the kinetics become too rapid to record. However, upon cooling from 90 °C to 20 °C, no exothermic peak at 53 °C was seen. Then after the initial heating run, the same sample was allowed to equilibrate to 20 °C and rescanned to 90 °C, and no transition peak was observed. As was the case with the absorption spectra, the changes that were observed were not reversible. The enthalpy for the endothermic transition observed in the initial DSC scan was measured to be 0.1353 J g^{-1} of solution. Subsequently, when an aggregated PFO solution in toluene was heated and then cooled down to −90 °C, an exothermic peak was observed at −56 °C (Fig. 6b). The enthalpy for the transition was calculated to be −0.1518 J g^{-1} of solution (−5.90 kJ/mol of monomer). The sample was then re-heated past the transition temperature and another endothermic peak was observed at approximately the same temperature as before. This suggests that the aggregates are indeed reforming when the sample is cooled off.

The DSC scan of PFO gel in toluene when heated from 20 to 90 °C has a large endothermic transition at ∼46 °C, with an enthalpy of 0.4299 J g^{-1} of gel. When the sample was cooled to −90 °C, there was an exothermic transition at ∼−54 °C with an enthalpy of −0.1834 J g^{-1} of gel. Upon re-heating the sample to 90 °C, another endothermic peak was observed near the same temperature. However, the enthalpy of the second heat transition does not have the same value, which indicates that the β-phase does reform but the sample does not have the time to fully gel. Nonetheless, this extreme hysteresis in transition temperature is often observed in gel formation [39–41].

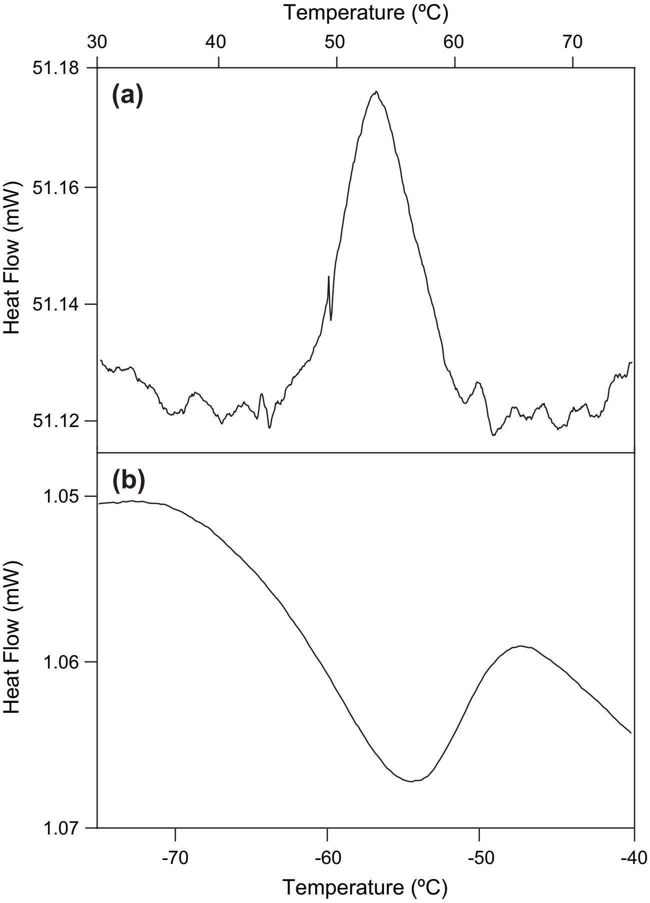

Fig. 6. The DSC data: (a) PFO solution in toluene heated from 20 °C to 90 °C. The transition temperature was measured to be 53.3 °C and Δ*H* was calculated to be 24.37 kJ mol^{-1} of monomer. (b) The same solution as in (a) cooled to −90 °C. The exothermic transition was at −56 °C and the Δ*H* was calculated to be −5.90 kJ mol^{-1} of monomer.

Table 2
Summary of the enthalpies obtained from the DSC results for PFO solutions and gels in either toluene or THF and their transition temperatures

Solvent	Solution or gel	Dissolution transition temperature (°C)	Heating Δ*H* (kJ mol^{-1} of monomer)	Reformation transition temperature (°C)	Cooling Δ*H* (kJ mol^{-1} of monomer)
Toluene	Solution	51	21.04	−56	−5.90
THF	Solution	48	31.70	−25	−12.37
Toluene	Gel	46	167.10	−54	−7.13
THF	Gel	51	40.04	−21	−23.80

DSC measurements were also taken of PFO solution and gel in THF. The DSC scan of an aggregated 1 wt% PFO solution in THF heated from 20 °C to 60 °C showed a clear endothermic peak at ~48 °C. The enthalpy of the aggregate dissolution was 0.1631 J g^{-1} of solution. As in toluene, when the solution was cooled past the transition temperature, no exothermic peak was observed. However, upon cooling down to −90 °C, an exothermic peak occurred at −25 °C. The enthalpy of the reverse transition was −0.3182 J g^{-1} of solution. The reverse transition enthalpy was calculated using the total polymer in the solution, since the fraction of β-phase that reforms is unknown. Upon heating the solution again, an endothermic peak at 47 °C was observed, indicating that in fact the β-phase did reform. Similar results were seen in the DSC scan of the PFO gel in THF. All DSC results are summarized in Table 2.

4. Discussion

It is clear that in the initial aggregated solution the majority of the PFO in the β-phase is in the remnants of larger aggregates that did not dissolve at room temperature. As previously described in other solvent systems, concentrated solutions of cyclohexane, THF, and toluene exhibit a substantial absorbance peak at 437 nm. This absorbance can be greatly reduced upon filtration indicating that the large aggregates contain much of the β-phase PFO. This is confirmed through absorption spectra and AFM images. After filtering, a decrease in the β-phase absorption peak is observed, while the AFM images show a decrease in the number of aggregates present on the film. The NSOM fluorescence image also confirms that the aggregates have a strong 437 nm absorption. Finally, as seen in methyl cyclohexane (MCH) [30], the fluorescence anisotropy of the emission excited at 438 nm shows a large anisotropy value of 0.35 compared to 0.16 when excited at 406 nm, indicating that the β-phase is associated mostly with large, slowly rotating aggregates. There is no doubt that the β-phase is strongly associated with aggregation.

The aggregates that will not dissolve are vestiges of polymer chains with large β-phase regions formed during the drying of the polymer powder. They are not in equilibrium with the solvated α-chains in solution. If the aggregates were the result of the association between solvated chains, then the aggregation would display a strong concentration dependence. In contrast, the number of aggregates as monitored by the β-phase absorbance is concentration independent even over three orders of magnitude (Fig. 3). The aggregates also do not seed the formation of the β-phase. Mixing a fully heated solvated α-phase solution with a portion of the original aggregated solution did not change the amount of β-phase present, even after a couple of days. Given this, the polymer aggregates are clearly not simple π-stacked chains like molecular dye aggregates. While polymer and molecular aggregates both demonstrate a red-shifted absorption spectrum, the physical nature of these two species is found to be dramatically different. Molecular aggregation is an equilibrium process in which the formation and dissolution of the aggregates is a strong function of monomer concentration [42]. In this case the PFO aggregates remain in a similar ratio of α- to β-phase over a wide range of concentrations. The results indicate that the β-phase fraction in the polymer at room temperature is in a meta-stable state stabilized by the aggregates and suspended in the solution regardless of concentration or solvent quality [10,43].

The disappearance of both the aggregates and the β-phase occurs only upon solution heating above a transition temperature. The extent of polymer in the β-phase can be quantified from the magnitude of the 437 nm absorption peak. To quantify the amount of β-phase the absorption spectra were fit with two model spectra of the α- and β-phase. The model spectra were generated from a singular value decomposition (SVD) [44,45] of the kinetic spectra acquired as a time series at 47 °C shown in Fig. 7. The SVD produced only two basis spectra with significant amplitude verifying the hypothesis that the overall spectrum was the result of two inter-converting species. The spectra for the α and β species were produced from a linear combination of the two significant basis spectra. The α-phase spectrum was one of the basis spectra and it exactly matched with that of the fully heated solution. The β-phase was based primarily on the second basis spectrum. A small portion of the first basis was added to the second such that it had no negative amplitude. A linear combination of

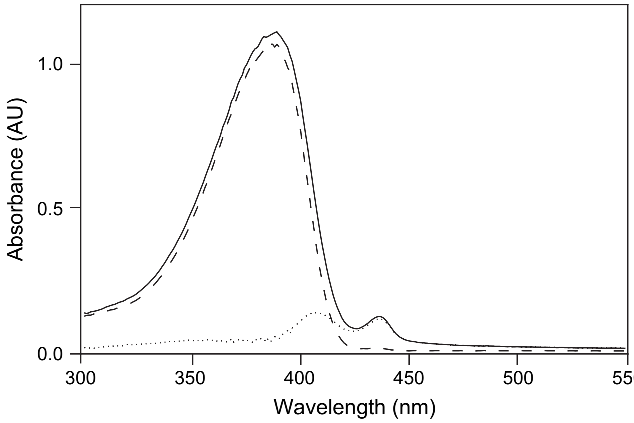

Fig. 7. Singular value decomposition calculation of an aggregated and heated PFO solution in toluene. The solid line is original absorption spectrum of the aggregated solution. The dashed line is the absorption spectrum of the α-phase and the dotted line is the calculated absorption spectrum of the β-phase.

these two spectra could be used to fit all the spectra in the kinetic decay. A representative fit is shown in Fig. 7, which is of an unheated PFO solution in toluene. The dashed line is the α-component and the dotted line is the β-component. The solid line is the actual data and the composite fit is indistinguishable. The portion of the sample in the β-phase could then be calculated from the amplitude of the β-component in the fit of any given spectrum. The fraction of the sample in the β-form was estimated to be ∼25%. Similar analysis showed only 3.6% of this original fraction of β-phase returned upon cooling to −78 °C for 40 min, these results are summarized for all the solvents in Table 1.

The fraction of this maximum β-phase component can be measured as a function of temperature upon heating the original solution. The β-phase component can be determined by fitting spectra at each temperature. Fig. 7 shows the absorption spectrum of PFO in the β-phase for a toluene solution. At temperatures around room temperature, the solution maintains its maximal β-phase component. As the solution is heated the β-phase component disappears sharply at around 53 °C. The rapid change is reminiscent of a phase transition or a collective polymer transition. Previously, Monkman et al. quantified the β-phase formation at lower temperatures in a similar fashion treating the change as an equilibrium process between the α- and β-phase segments. Such a treatment yields a ΔH of $-74.48\ \mathrm{kJ\,mol^{-1}}$ and a ΔS of $-284.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$ in MCH at ∼−18 °C for the formation of the β-phase [30]. However, such an analysis is very difficult to interpret. It is not clear what constitutes an α- or β-phase in this "reaction". Is it a monomer, several monomers, or a polymer chain? Without this knowledge it is impossible to interpret the "per mol" in thermodynamic quantities. The study by Monkman et al. implied these quantities are per mole monomer, but this is only one limit. As the absorbance results from the extended conjugation across several monomer units this would be a more natural choice. However, given that it is not clear exactly how many units make up a "chromophore"; this leads to an ambiguity in what is defined as a mole of the α- and β-phases.

Like the formation, the disappearance of the β-phase could be interpreted as an equilibrium process, but unlike the formation the dissolution is found to have a large hysteresis in the transition. If the solution is heated until all the absorbance at 437 nm has gone to zero and then cooled to room temperature, none of the β-phase absorbance returns unless the sample is cooled to extremely low temperatures. The same is true if the sample is heated until only half of the 437 nm absorbance is gone, and once this solution returns to room temperature the amount of β-phase does not change and the remaining β-phase does not cause more to form. This would indicate that the thermodynamically stable state at room temperature is the fully solvated chain in the α-phase, and that any polymer that remains in the β-phase is trapped in the polymer aggregates.

However, we can learn something about the enthalpy of the β- to α-transition from the calorimetry. The total heat from converting the polymer from the β-phase in the aggregates to the α-phase in solution can be measured. The total heat measured using the DSC was $0.1353\ \mathrm{J\,g^{-1}}$ of solution. The PFO solution is 1 wt% polymer, yielding an enthalpy of $13.53\ \mathrm{J\,g^{-1}}$ of polymer. Using the estimate that 25% of the polymer is in the aggregated form, the transition energy is $54.12\ \mathrm{J\,g^{-1}}$ of aggregated polymer. This number can be converted to an enthalpy that is per mol monomer with the molecular mass of the monomer unit. This yields a transition enthalpy of $21.04\ \mathrm{kJ\,mol^{-1}}$ of monomer. The transition at 53 °C does not correspond to any transition for solid PFO itself, since the lowest temperature transition observed was an endothermic transition at 157 °C. This enthalpy is three times less than that extracted from the equilibrium measurement for the β-phase formation [30]. In addition, the total enthalpy measured in the DSC is not simply the α- to β-transition, but includes the break up of the aggregates and the solvation of the polymer chains. The enthalpy of this transition was also measured in THF solutions, yielding an enthalpy of $31.70\ \mathrm{kJ\,mol^{-1}}$ monomer. This transition is more endothermic as would be expected given that THF is a worse solvent for PFO. The transition will require more heat because there is a less favorable solvation energy for the polymer chains in THF. This β- to α-transition is at the same temperature despite the differences in the solvent quality.

Solvent quality has the strongest affect on the β-phase formation. In all the solvents except $CHCl_3$, if the sample is cooled to a much lower temperature the β-phase was observed to return. In concentrated solutions (1 wt%) this leads to gelation whereas in dilute solutions the PFO concentration is not high enough to sustain a gel. The temperatures at which the β-phase are observed to return in the UV–vis are tabulated in Table 1. For the two solvents measured in the DSC, the α- to β-phase transition temperatures are nearly identical to the gelation temperature measured in the calorimeter, indicating that a common process is associated with both the return of the β-phase and the gelation. The transition temperature for different solvents for the formation of the β-phase demonstrates a clear trend with solvent quality. For the poorest solvent, cyclohexane, the transition is at the highest temperature, 10 °C; however, this transition temperature is just above the solvent's freezing point (7 °C). For the best solvent, chloroform, the β-phase does not reform at any temperature, though, the cooling range is limited by $CHCl_3$'s freezing point, −65 °C. The intermediate solvents show that the better solvent, toluene, reforms at −55 °C and THF at −25 °C. The total amount of β-phase reformed also depends on the solvent quality. The poorer solvents exhibited a greater amount of β-phase returning upon cooling to the transition temperature. This is likely due to greater aggregation in the poor solvents. By simply looking at the Hildebrandt parameters it would appear that if $CHCl_3$ is the best solvent, and then THF should be a better solvent than toluene [34,35]. However, one can just as easily argue the opposite trend for THF and toluene, utilizing a three dimensional solvation parameter such as the Hansen parameters. Toluene and THF are clearly both moderately poor on either solvation scale placing them between the best solvent chloroform and the worst solvent cyclohexane. The trend in solvent quality can be seen in the cooling transition in Table 1. The worst solvent converts to β-phase at 10 °C, the intermediate solvents at −25 °C and −55 °C, and in the best solvent it never returns. As the β-phase is not stable in any solvent at room temperature, it requires stabilization by either a meta-stable gel or aggregates to prevent it from converting back to the alpha phase. Cooling the solutions at a low temperature for longer generally produces more β-phase, while a larger fraction of β-phase could also be reformed if the solvent was cooled significantly below the transition temperature. This was possible in only THF as the other solvents had freezing points close to the polymer phase transition. If the THF was cooled to −78 °C a full 37% of the α-phase could be converted to the β-phase.

The calorimetry of the gels exhibited similar trends to the aggregated solutions. Both gels were formed from concentrated solutions outside the calorimeter and their melt and β-phase reformations were studied in the calorimeter. The gels exhibited an endothermic peak associated with the melting of the gel upon initial heating. The first heat cycle of the gel melt transition occurs at a slightly lower temperature as the β- to α-phase transition in the aggregated solutions. However, the enthalpy of the transitions was larger as it includes both the gel melting and β- to α-transition. Previous studies examining the melting of the PFO gels in cyclohexane did not observe this sharp melting transition [35]. However, this study followed the β-phase in thin films cast from a gel that was heated to 190 °C, and considering that the boiling point of cyclohexane is 81 °C, this indicates that a significant portion of the solvent would evaporate before the β- to α-transition. The evaporation of cyclohexane would greatly slow the transition and eliminate the sharp temperature response.

The dilute and concentrated solutions both show the appearance of the β-phase at the cooling transition temperature, but only the concentrated solution gels. Therefore, it is reasonable to conclude that the gelation is not responsible for the β-phase, but instead the β-phase forms and then gelation occurs. In a similar fashion, aggregation was found not to be responsible for the β-phase in dilute solutions of MCH [30]. The appearance of the β-phase in dilute solutions in the absence of aggregation has been interpreted to indicate that intermolecular interactions are not responsible for the formation of the β-phase. While this rules out interactions from other chains, it does not rule out intramolecular interactions of the chain with itself. As the temperature is lowered the solvent quality decreases until at some temperature the chains collapse on themselves to reduce solvent contact. For poorer solvents the point where the chains collapse on themselves will occur at higher temperatures than for good solvents [46]. This is the same trend that is observed for the solvent effects for the β-phase formation. This implies that the polymer chain collapse leads to stronger interactions between the chain and itself, and it is these interactions that lead to the change in backbone conformation. Theoretically such a collapse could be monitored by light scattering. Unfortunately the propensity for the polymer to aggregate after collapsing precludes the effective measurement of the hydrodynamic radius of the polymer as the measurement is dominated by the large aggregates.

In the absence of a change in the polymer chain conformation, it is unclear why solvent quality would have such a dramatic affect on the α- to β-transition. The two conformations should have very similar interactions with the solvent. A good solvent for the α-phase should be a good solvent for the β-phase. It is not clear why one phase would exhibit a dramatically different preference for one solvent over another. However, if the chain collapses, the polymer backbone experiences two distinct environments: one dominated by solvent–polymer interactions, and one in which there are significantly more interactions of the chain with itself. It is reasonable to deduce that the polymer in the collapsed state has more intramolecular interactions and this is the source of the α- to β-transition. When two chain segments are in close proximity, they prefer the β-phase conformation. This idea of the PFO chain folding back on itself is consistent with the sheet like model observed by Knaapila et al. [47].

5. Conclusion

This research has demonstrated that PFO solutions have a rich phase diagram with different conformations of both the polymer chain and the polymer backbone. The chains can be either in a freely solvated α-phase or in a collapsed state with a large β-phase component. The β-phase segments tend to aggregate at lower concentrations while in more concentrated solutions, they lead to gelation. The thermodynamics of the β- to α-phase transition are complicated by meta-stable aggregates and the gelation, both of which cause a large hysteresis in the transition. The calorimetry reveals that the enthalpy of the transition from an aggregated β-phase to a fully solvated α-phase chain is 21.04 kJ mol^{-1} monomer in toluene and 31.70 kJ mol^{-1} monomer in THF. This is significantly lower than the enthalpy reported for the reverse transition in MCH [30]. This discrepancy could be due to a difference in the per mole quantity of the enthalpy. The ambiguity in the enthalpy derived from the calorimetry arises from the quantification of the fraction of the polymer originally in the β-phase. The ambiguity in the number extracted from the equilibrium constant is the definition of per mole α- or β- phase. Those experiments measured the concentration from the lowest energy electronic absorption in the polymer, which results from a delocalized π state conjugated over several monomers. Taking six monomer units as the conjugation length [48], the enthalpy Monkman et al. [30] calculated would be converted to 12.5 kJ mol^{-1} monomer. This is significantly closer to the current measurements of 25–30 kJ mol^{-1} monomer (depending on solvent quality). The current measurement is an upper limit of the β-phase to α-phase transition since it also includes the energy for the break up of the aggregates. The toluene enthalpy of 21.04 kJ mol^{-1} monomer is likely closer to the α- to β-transition as it has a smaller solvation enthalpy. If the previous equilibrium numbers obtained by Monkman et al. [30] are assumed to be per mole conjugated segment, the seemingly large entropy change will also decrease by a factor of six on a per monomer basis. This could be easily understood with a collapse of the polymer chain giving the α- to β-phase change. These ideas will be examined further with experiments that look at the dilute equilibrium in different solvents as well as how molecular weight shifts the transition. If the polymer collapse is the source of the α- to β-transition a clear reduction in the transition temperature should be observed for lower molecular weight polymers.

Polymer devices often utilize spin-cast films in which the polymer conformations are kinetically trapped in states similar to which they were in solution. The rich phase space, solvent dependence, and strong hysteresis observed in the polyfluorene system implies that a large variety of different morphologies can be made from processes that seem to be similar. The fact that subtle changes will arise from molecular weight and polymer defects in addition to solvent choice and processing history complicates matters. In conclusion, the results indicate that great care should be taken in reproducing studies of conjugated polymer films and solutions as the properties of solutions are easily changed by their processing conditions.

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