Intermolecular Association and Supramolecular Organization in Dilute Solution. 1. Regioregular Poly(3-dodecylthiophene)

S. Yue,† G. C. Berry,* and R. D. McCullough

Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

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ABSTRACT: Static and dynamic polarized and depolarized light scattering characterization of dilute solutions of regioregular poly(3-dodecylthiophene) is described to study intermolecular association as a function of the thermal history of the solutions. It is shown that metastable aggregation obtains under all of the conditions studied, including temperatures as high as 65 °C. Under some conditions, the aggregated moiety appears to have a disklike shape at room temperature, with appreciable depolarized scattering, attributed to an extended chain structure, consistent with the formation of the lamellar suprastructure characteristic of the bulk, with the polythiophene chains adopting an extended conformation and forming a nematic phase in a polythiophene lamella faced by lamellae rich in alkyl chains. Under other conditions, especially at low temperature, elongated supramolecular structures are formed, with the polythiophene chains in an extended conformation. The reversible thermochromic effect is associated with enhanced order of the alkyl side chains with decreasing temperature, facilitating coplanar conformers in the polythiophene backbones, with the attendant enhancement in the π-π* transitions of the thiope ring electronic absorption spectra. This behavior is analogous to the events in the thermochromatic event in the bulk. Such supramolecular structures could intervene in normal film casting solution processing, with effects on the electronic or optical properties of the cast film. This interpretation of the light scattering data suggests strategies to enhance or suppress lamella formation in solvent-cast films.

Introduction

Electronic delocalization in the thiophene rings makes polythiophenes of interest for novel optical and electronic applications. Rodlike conformations have been proposed as a source of extended delocalization, with resultant enhanced electronic and optical behavior. A thermochromic effect observed for poly(3-alkylthiophene)s has sometimes been attributed to a coil-to-rod conformational transition,1–6 In this study, static and dynamic light scattering measurements were undertaken on dilute solutions of poly(3-dodecylthiophene) (PDDT) to evaluate its conformation over a range of temperature and to learn whether a reversible thermochromic effect is associated with any conformational change. The PDDT used in the study was prepared by a novel synthesis that provides a high specificity of head-to-tail configuration of the repeat units (≥98% H–T addition).8,9 In older polymerizations, the head-to-tail configuration is mixed with substantial fractions of head-to-head and tail-to-tail configurations. The regularity of the head-to-tail addition is expected to improve packing in the solid state and is implicated in enhanced electronic conduction,10 Thermochromism has been observed in a number of polymers, both in solution and in the bulk, and has been studied by a variety of methods. Although the thermochromism is ultimately related to factors such as the rotational states of a chain and the environment of the chromophore, the question remains as to whether any rotational transition associated with thermochromism is driven by intermolecular interactions, or is intramolecular in origin, e.g., by a coil-to-helix transition. Thus, intermolecular effects have been cited in chronic transitions in poly(diacetylene),11–14 polysilanes,15 and a heterocyclic polymer,16 but in other work, the same transitions are attributed to intramolecular effects in poly(diacetylene)17–22 and polysilanes.23,24 The thermochromic effect in solutions of poly(3-alkylthiophene)s has been attributed to an intramolecular conformational transition to an extended chain conformation, principally on the basis of an observed isosbestic point,2,7 but evidence for supramolecular aggregates was noted.2 Conformational analysis confirms the expected availability of an extended state.25 It will be found that the thermochromism observed here with PDDT is intermolecular in origin, abetted by intermolecular order in supramolecular aggregates. The supramolecular structure observed in this study may have relevance in the development of structure and properties in solvent-cast films of PDDT.

Experimental Section

Methods. All solvents were reagent grade, used as received except for chloroform and tetrahydrofuran (THF), which were distilled under vacuum over CaH2 and stored over CaH2 in the dark until use. Polymers were evacuated (∼10−4 torr) for several days at 60 °C. Solutions were prepared by weighing the appropriate amount of polymer and about two-thirds of the desired solvent(s) into a centrifuge tube with a screw top cap (Teflon gasket), containing a Teflon-coated stirring bar. After several days, the solution was gently agitated by occasional swirling. After the solution was apparently uniform, the remainder of the solvent was added, and the solution was slowly stirred with the stirring bar for an additional 1–2 weeks. Chloroform solutions were held at 25 °C, but solutions in THF were heated to 65 °C for 2 h to facilitate dissolution. Static and dynamic light scattering experiments were carried out using instruments described elsewhere,19 with incident light with wavelength 647.5 nm from a krypton ion laser (Lexel, Model 95). Solutions in chloroform were filtered into light scattering cells through 0.45 μm Teflon filters, degassed, and sealed on a vacuum line. Cells were centrifuged for 24 h at 7000 rpm in a swinging bucket rotor. Electronic absorption spectra were obtained using a Hewlett-Packard spectrometer (Model 8451A), equipped with a photodiode array detector to permit measurement of a spectrum within 5 s.  

* To whom correspondence should be addressed.
† Present address: Hewlett-Packard Co., San Diego, CA 92127-1899.
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Samples were placed in a sealed cell and cooled by immersion in a 2-propanol/dry ice bath. After being held at a low temperature for the desired time, the cell was transferred to the spectrometer, and spectra were measured as the cell slowly warmed (~2 °C/min) to room temperature; residual 2-propanol on the cell surface served to suppress fogging of the cell face by moisture condensation.

The differential refractometer on a Waters size exclusion chromatograph was used to determine the refractive index increment \( \text{dn/dc} \), bypassing all columns, so that samples were fed directly into the refractometer cell. Standardized volumes (20 μL) of solutions of polystyrene with known concentration were injected into the refractometer to determine the proportionality constant \( k = \Delta n/\Delta N_{\text{polystyrene}} \), where \( \Delta N_{\text{polystyrene}} \) is the integrated instrument response under the elution peak, and \( \Delta n \) is calculated from the concentration and \( \text{dn/dc} \) of the polystyrene solution (\( \text{dn/dc} = 0.198 \text{ mL/g in THF} \)). In subsequent determinations of \( \text{dn/dc} \) for solutions of PDPT, \( \Delta n \) was calculated from measurements of \( \Delta N_{\text{polystyrene}} \) as \( \Delta n = k \Delta N_{\text{polystyrene}} \) for solutions of known concentration and standard injection volume. The solution of PDPT in THF did not dissolve completely at 25 °C and was heated to 65 °C to facilitate preparation of a solution apparently stable at 25 °C for SEC analysis. Large particles were observed on cooling to produce the thermochromic effect; the particles did not redissolve on heating to 25 °C. This solubility behavior dictated the use of chlorof orm for this study to study intermolecular association in dilute solution. By contrast, dilute solutions of nonregioregular poly(3-hexylthiophene) have been shown to be free of intermolecular association at 25 °C in both THF and chloroform by light scattering studies similar to those reported here (thermochromic effects were not reported in the study cited).

Data Analysis. Light scattering results were analyzed according to the model for anisotropic scatterers.

This model provides expressions for the dependence of vertical and horizontal components of light scattered with vertically polarized incident light, denoted \( R_{V V}(q, c) \) and \( R_{H V}(q, c) \), respectively, on the concentration \( c \) and modulus \( q = (4 \pi n_{0} \sin \theta_{0}/2) \) of the scattering angle vector, where \( n_{0} \) is the refractive index of the sample, \( \theta_{0} \) is the angle between the incident and scattered beams. The polarized scattering \( R_{H V}(0, c) \) extrapolated to zero scattering angle provides information on the molecular weight \( M \) and the second virial coefficient \( A_2 \):

\[
\left( \frac{Kc}{R_{HV}(0,c)} \right)^{1/2} = \left( \frac{1}{M(1+4\delta^{2}/5)} \right)^{1/2} \times \left\{ 1 + \frac{1 - \delta^{2}/10}{1 + 4\delta^{2}/5} A_2 M c + \ldots \right\} \tag{1}
\]

where

\[
K = \frac{2\pi^{2}N_{A}n_{0}^{2}}{\text{dn/dc}^{2}} \text{ and } \delta = \text{the molecular anisotropy of the chain.} \]

\[
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Figure 1. Effect of temperature on the absorbance of a dilute solution of poly(3-dodecylthiophene) in chloroform; c = 3.0 g/L. The temperature is indicated on the figure; the cell was 0.2 cm thick.

Table 1

<table>
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<td>T$_{\text{q2}}$ &lt; 0</td>
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For depolarized scattering, the first cumulant is related to rotational dynamics as well as to translational dynamics that dominate the polarized scattering. In general, the concentration dependence of the depolarized scattering will be small (excepting effects of association that change with c). Thus, at infinite dilution,36

$$R_{\text{HLS}} = (\delta^2 M_H \chi_{\text{LS}}) \sum w_M \delta^2 (R_H^{-1})_c.$$  (16)

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$$\lim_{i=0} K^{(1)}_{\text{Hv}}(q, c) = (\delta^2 M_H \chi_{\text{LS}})^{-1} \sum w_M \delta^2 \left\{ (6D_R)_c + (D_T)_c \right\}.$$  (17)

Results

The electronic absorption spectra for a sample of PDPT in chloroform over a range of temperature are given in Figure 1. A reversible thermochromic effect is seen, with an isosbestic point for $\lambda \approx 465$ nm. Consequently, the spectrum may be considered to be the sum of the spectra from two components, with relative concentrations that vary monotonically with temperature.

The refractometry measurements gave $\text{in/nr} = 0.124$ mL/g for PDPT in THF, the solvent used on the SEC. Use of the Dale–Glade stone approximation $\text{in/nr} \approx (n_0 - n_m)\rho_p$ gives $\rho_p \approx 1.0$ g/mL.40

Several thermal histories were utilized in the study, both to characterize the solution under conditions for the thermochromic effect and in an attempt to obtain a state free of association. Six different histories may be distinguished, differing in the thermal history following degassing to room temperature (T$_1$) from the rapidly frozen state used in the degassing to the temperature of the light scattering measurements (Table 1). As shown in Figure 2, the functions KC/R$_{\text{VV}}$(q, c) versus $\sin^2 \theta/2$ generally were neither linear nor parallel over the concentration range studied for samples with history A. The data at the lowest concentration studied, 0.5 g/L (history B), show typical behavior for a solution with a small fraction of a large aggregated species mixed with unassociated or very weakly associated chains.16,34 The data for q greater than some value $q_m$, corresponding to linear behavior at the higher angles ($\sin^2 \theta/2 > 0.5$) may be analyzed to give apparent values (M$_V$)$_{\text{app}}$ and (R$_{G, V}$)$_{\text{app}}$ of the molecular weight and root-mean-square radius of gyration, respectively, on the assumption that the large species contain a negligible fraction of the mass. Thus, for the polarized and depolarized scattering at arbitrary concentration c,

$$(M_V)^{\text{app}} = (Kc/R_{\text{VV}}(0, c))^{-1} \approx \frac{M_w}{1 + 2A_{2LS}M_w c}$$  (18)

$$\left(R_{G, V}^2\right)^{\text{app}} = \left(3Kc/R_{\text{VV}}(0, c)\right)^{-1} \left(\frac{\partial Kc/R_{\text{VV}}(q, c)}{\partial q^2}\right) \approx \frac{R_{\text{GLS}}^2}{1 + 2A_{2LS}M_w c}$$  (19)

neglecting terms involving $\delta c$ for convenience since they are small, and

$$(\delta^2 M_H)^{\text{app}} = \left\{ 3Kc/5R_{\text{H}}(0, c) \right\}^{-1}$$  (20)

$$\left(R_{G, H}^2\right)^{\text{app}} = \left\{ 7/3 \right\} \left(3Kc/5R_{\text{H}}(0, c)\right)^{-1} \left(\frac{\partial Kc/R_{\text{H}}(q, c)}{\partial q^2}\right) \approx f_2^2 \left(R_{G, S}^2\right)$$  (21)

Based on extrapolation of the higher angle data, (M$_V$)$_{\text{app}}$ $\approx$ 95 000 and (R$_{G, V}$)$_{\text{app}}$ $\approx$ 18 nm for the solution with c = 0.5 g/L. By contrast, for the data with c = 1.97 g/L, as shown in Figure 2, appreciable depolarized scattering was observed, revealing the presence of orientational order in the scattering species. The polarized scattering gives (M$_V$)$_{\text{app}}$ $\approx$ 4.5 $\times$ 10$^6$ and (R$_{G, V}$)$_{\text{app}}$ $\approx$ 56 nm, and the depolarized scattering gives (M$_H$)$_{\text{app}}$ $\approx$ 50 000 and (R$_{G, H}$)$_{\text{app}}$ $\approx$ 67 nm. The depolarized scattering was sufficiently intense to permit dynamic scattering, with the result given in Figure 3. As may be seen, the first
cumulant is linear in \(q^2\), with a positive value at zero scattering angle. Analysis with eq 17 gives \(D_R \approx 150\) s\(^{-1}\) and \(D_T \approx 8.55 \times 10^{-8}\) cm\(^2\)/s.

As shown in Figure 4, the scattering behavior is markedly dependent on temperature, with heating to 65 °C tending to loosen the structure observed on subsequent cooling to 25 °C (history C). Further, as shown by the data on the sample with \(c = 3.0\) g/L in Figure 4, annealing at a low temperature for a prolonged period changed the structure to promote association that persists even after heating to 65 °C (history E), with the results \((M_V)^{\text{app}} \approx 10^6\) and \((R_G,V)^{\text{app}} \approx 170\) nm for the polarized scattering; the depolarized scattering was weak in this case. Polarized dynamic scattering for this solution gave the results in Figure 3, with \(a_s(c) = 33\) nm.

The solution with \(c = 3.0\) g/L was studied in more detail with thermal history D. As shown in Figures 5 and 6, both the polarized and depolarized scattering changed slowly on annealing at −16.5 °C, with measurement at −16.5 °C. The change of the depolarized scattering at 45° scattering angle is compared with the change in the transmission \(T(t)\) for \(\lambda = 647.5\) nm as a function of time at the same temperature in Figure 7. Values of \((M_V)^{\text{app}}\) and \((R_G,V)^{\text{app}}\) are given in Figure 8 along with data on the ratio \([R_{Vv}(0,c)/c]^\gamma[R_{Vv}(0,c)/c]^\gamma\) of the reduced intensities at zero scattering angle and the ratio \((R_G,V)^{\text{LS}}/(M_V)^{\text{LS}}\).

**Discussion**

The thermochromic behavior in Figure 1 is similar to that reported for solutions of other poly(3-alkylthiophene)s\(^2\) and for solvent-cast (dry) films of PDDT and other poly(3-alkylthiophene)s.\(^5\) The absorption peak at longer wavelength in Figure 1 is attributed to a \(\pi - \pi^*\)
A function of the transmission diagram for semiflexible molecules, which predict that be understood using concepts embodied in a Flory phase diagram for semiflexible molecules, predict that a semiflexible chain may experience extension in conformation and transition to an ordered phase with increasing concentration. At still lower temperatures, the alkyl side chains order, with approximately coincident enhanced coplanarity of the thiophene rings along the chain backbone and thermochromic transition in the visible absorption spectrum. In addition, the thiophene rings from adjacent (parallel) chains stack parallel to each other in the plane formed by the chain backbones, with an interplanar stacking distance of \( \approx 0.38 \) nm. The intermolecular separation, which is fixed by the length of the alkyl side chains and the extent of their packing, is about 2.3 nm for solvent-cast films of the regioregular polymer studied here; a dimension of 2.7 nm was reported from the diffraction from a drawn fiber of a nonregioregular PDDT sample. Especially well-ordered films have been prepared with regioregular poly(3-alkylthiophene) of the type studied here, such that the 2.3 nm interlamellar spacing is strong in the forward diffraction with an incident ray in the plane of the film but absent in the diffraction with an incident ray perpendicular to the film, and vice versa for the 0.38 nm thiophene inter-ring spacing. Although the chain alignment may tend to be defined over a region of some reasonable length (e.g., in a “domain”), there does not appear to be any long-range correlation in the alignment among domains in solvent-cast films. On heating such a (dry) film from below its glass transition temperature, only one exotherm is observed, near the temperature of the thermochromic event. This is associated with disordering of the alkyl side chains. By contrast, solvent-cast films of the same polymer with less well-defined diffraction behavior may exhibit an additional isotherm at a lower temperature, perhaps due to alkyl chains in less well-organized regions of the sample, similar to behavior reported for nonregioregular PDDT.

The intermolecular association observed in this study under all conditions studied could either abet or frustrate the formation of supramolecular order in a solvent-cast film described above. Thus, premature entrapment of chains into irregular structures might frustrate attainment of the thermodynamically stable supramolecular organization. For example, the scattering profile observed in Figure 4 for the solution with 3.0 g/L with history C (cooled to 25 °C after being heated to 65 °C) exhibits an unusual upward curvature, characteristic of a scattering moity with the symmetry of a sphere or an oblate spheroid of revolution (disklike). The parameters obtained for a spherical shape give a monomer concentration in the aggregate that is less than the average solution concentration, making that model untenable. Consequently, the shape is considered to be disklike and relatively thin. The appreciable depolarized scattering indicates that the polythiophene backbone may be highly extended in the aggregate structure. This suggests that a partially ordered precursor structure to the ordered planes in the solvent-cast film may have been formed under the thermal conditions used. As with the behavior in the bulk, this behavior can be understood using the concept embodied in a Flory phase diagram for semiflexible molecules. Although the solutions studied here were dilute, the local concentration is high in the aggregates and could be sufficient to induce a phase transition to an ordered state, with extended conformations for the polythiophene chains.

Although the principal features of the absorption spectrum change rapidly as a solution is quenched to \(-16.5 ^\circ C\), the results in Figure 7 show that full attain-
ment of the thermochromic transition at longer wavelength (647.5 nm) occurs over a prolonged period, as does a corresponding increase in the depolarized scattering. The change in the scattering profiles shown in Figures 5 and 6 suggests that the disklike shape contracts, with increasing depolarized scattering, on annealing at a low temperature. The parameters given in Figure 8 reveal that following the temperature quench to induce the thermochromic event, both (R_{G,V})_{app} and (R_{G,H})_{app} initially decrease on cooling, with corresponding increase in (\delta M_{H})_{app}/(M_{V})_{app}, but only almost increase in (M_{V})_{app}. Consistent with the corresponding change in the scattering profiles, this behavior corresponds to a change from the oblate spheroidal shape of the aggregate prior to the quench to a more prolate spheroidal shape, with little change in molecular weight or particle volume. Thus, for a spheroid of revolution with unique axis L and transverse axes L, (see below), the square radius of gyration of a spheroid of revolution with volume V is given by \[^{35,48}\]

\[
R_{G}^{2} = \frac{2 + \epsilon^{2}}{20} L^{2} = \frac{2 + \epsilon^{2} (3V/20)^{2/3}}{4 \pi (\epsilon^{2})^{1/3}},
\]

(22)

with \(\epsilon > 1\) for an oblate ellipsoid. Thus, \(R_{G}^{2}\) is expected to decrease as \(\epsilon\) decreases toward unity as the shape of the aggregate transforms from an oblate toward a more extended form at approximately constant particle volume, consistent with the behavior observed here in the early stage of thermal annealing. The increasing order reflected in the increase in \((\delta M_{H})_{app}/(M_{V})_{app}\) may drive this structural change, and may, in fact, be implicated in the thermochromic event itself, since the change in the depolarized scattering begins quickly. The increase in \((\delta M_{H})_{app}/(M_{V})_{app}\) can be attributed to either or both of two effects: increasing persistence length \(\alpha\) of the polythiophene backbone chain, and increasing order among the alkyl side chains. Developing order among the alkyl side chains may be the dominant effect, similar to the change in the order among the alkyl chains at the thermochromic event in the bulk, with the aggregate becoming needlelike, with an ordered polythiophene interior surrounded by a sheath of ordered alkyl chains. If this interpretation is correct, then whereas the original disklike aggregates might provide desirable precursors to a lamellar structure in a solvent-cast film, the extended aggregates may be undesirable, being too well formed in a supramolecular structure that will not pack well to give a global order.

At longer times, \((R_{G,V})_{app}\) and \((\delta M_{H})_{app}/(M_{V})_{app}\) tend to stabilize, whereas \((M_{V})_{app}\) continues to increase slowly, as \(R_{G,V}^{2}/M_{w}\) increases. This behavior suggests agglomeration of the elongated aggregates to form still larger structures. The slow decrease in \(R_{G,V}^{2}/M_{w}\) as \((M_{V})_{app}\) increases is attributed to increasing particle volume of the elongated particles. Thus, for the ellipsoidal model, \(R_{G}^{2}M_{w} = (2 + \epsilon^{2})/20 \epsilon (4\pi V/\eta M)^{2/3},\) with \(\eta M_{w}^{2}\) expected to be approximately constant. Growth of the ordered aggregates by agglomeration of already formed elongated aggregates in parallel arrays to give supramolecular structures that increase more rapidly in diameter than length, so that \(\epsilon\) remains small, would produce the observed decrease in \(R_{G,V}^{2}/M_{w}\).

The data on the solution with \(c = 1.97\) g/L with thermal history A (simple dissolution at 25 °C) are of particular interest since both polarized and depolarized scattering measurements were possible, the latter permitting estimation of both \(D_{R}\) and \(D_{T}\.\) The electronic absorption spectrum for this solution at 25 °C was typical of that for a solution cooled from high temperatures to about 4°C, thus revealing metastable conformational states. As remarked above, the static scattering data indicate a large moiety, with high (apparent) molecular weight: \((M_{V})_{app} \approx 4.5 \times 10^{6},\) \((R_{G,V})_{app} \approx 56\) nm, and \((R_{G,H})_{app} \approx 67\) nm. These supramolecular structures may be remnants of the organization in the solid prior to dissolution or may have been formed as metastable structures during the dissolution of the ordered bulk. The data on \(D_{R}\) and \(D_{T}\) were interpreted by the use of an ellipsoidal model using the relations\[^{39}\]

\[
\psi(\epsilon) = (1 - \epsilon^{2})^{-1/2} \ln \left( \frac{1 + (1 - \epsilon^{2})^{1/2}}{\epsilon} \right), \quad \text{for} \ \epsilon < 1 \quad (25a)
\]

\[
\psi(\epsilon) = (\epsilon^{2} - 1)^{-1/2} \arctan((\epsilon^{2} - 1)^{1/2}), \quad \text{for} \ \epsilon > 1 \quad (25b)
\]

\[
\frac{\partial(\epsilon)}{\partial(\epsilon)} = \frac{3 (2 - \epsilon^{2}) \psi(\epsilon) - 1}{(1 - \epsilon^{4})},
\]

(26)

where \(\psi(\epsilon) = \psi(1) = 1\) for a sphere (\(\epsilon = 1\)) of diameter L. With these relations, \(\psi(\epsilon) = 3(\pi\eta_{f}kT)^{1/2}D_{T}/D_{L}^{1/2} = \psi_{0}(\epsilon)\psi(\epsilon)\) is a single-valued function of \(\epsilon\) for \(\psi(\epsilon) > 1.18\), permitting an unambiguous assessment of \(\epsilon\), and hence L, in that range (neglecting the effects of particle size heterogeneity, see below). The data on \(D_{R}\) and \(D_{T}\) give \(\psi \approx 2.75\), corresponding to a highly asymmetric prolate ellipsoid shape, with \(\epsilon \approx 0.001\) and L \(\approx 700\) nm. Since the estimate of \(\epsilon\) depends critically on the model with this extreme anisotropy and the effects of heterogeneity have not been considered, the result is only taken to indicate that a moiety with a very asymmetric, extended shape exists under the conditions examined. Consideration of eqs 17, 23, and 24 shows that inclusion of the effects of size heterodispersity in particle length would only increase the estimate for the asymmetry. The root-mean-square radius of gyration of 220 nm calculated with eq 22 is much larger than the observed \((R_{G,V})_{app}\) and \((R_{G,H})_{app}\). The low value for \((R_{G,H})_{app}\) suggests that \(f_{3} < 1\), consistent with the relatively low ratio for \((\delta M_{H})_{app}/(M_{V})_{app}\). Indicating that the chains are not perfectly parallel in the aggregate. Deviation from \((R_{G,V})_{app}\) would be expected if \(A_{2c}M_{w}/c\) is large. For rigid ellipsoids interacting through a hard-core potential, \(A_{2c}M_{w}/c \approx 4N_{A}V_{M}m(\epsilon)/M_{w}\), where \(V_{M}\) is the particle volume and \(m(\epsilon)\) is a function of \(\epsilon\) that tends to 1/4k for small \(\epsilon\). Thus, for the parameters given, \(A_{2c}M_{w}/c \approx 7.5 \times 10^{6}/6M_{w} \approx 100(\epsilon^{2})/g\). Although this is appreciable, it is not large enough to account for the discrepancy between the calculated \((R_{G,V})_{app}\) and the observed \((R_{G,V})_{app}\) suggesting other factors, such as particle size heterogeneity must play a role. In any case, the presence of supramolecular structures of the type deduced here would be expected to be detrimental to the attainment of a well-ordered lamellar structure in a solvent-cast film.

Conclusion

The light scattering characterization of dilute solutions of regioregular poly(3-dodecylthiophene) has shown that metastable aggregation obtains under all of the conditions studied, including temperatures as high as 65 °C, with a range of supramolecular structures...
dependent on solution history. The aggregation may be associated with the chemically disparate character of the polythiophene main chain and the alkyl side chains. Notable among the observed supramolecular structures are disklike aggregates, with appreciable depolarized scattering attributed to an extended conformation of the polythiophene chains, and elongated needlelike aggregates, with very strong depolarized scattering, attributed to organization among the alkyl chains. These structures may intervene in normal film casting solution processing and may account for the observed sensitivity of properties on solution processing. For example, under appropriate film-forming conditions, as-cast films show remarkable order and electronic conductivity after doping with I\(_2\), but these properties may be severely compromised if the processing conditions are inappropriate. In this regard, the disklike aggregates may be consistent with the formation of the lamellar suprastructure characteristic of the bulk, with the polythiophenes adopting an extended conformation and forming a nematic phase in a polythiophene lamella faced by lamellae rich in alkyl chains. The reversible thermochromic effect observed here and in the solid state is associated with enhanced order of the alkyl side chains with decreasing temperature, facilitating coplanar conformers in the polythiophene backbones, with the attendant enhancement in the \(\pi-\pi^*\) transition of the thiophene ring electronic absorption spectra and improvement in electronic conduction of the doped film. By contrast, attempts to cast a film with an abundance of elongated needlelike aggregates could lead to deteriorated order and electronic conduction, as these will not be well incorporated into a macroscopically ordered material. This may, for example, explain the observed marked dependence of the conductivity of I\(_2\)-doped solvent-cast films of regioregular PDPT on the choice of the solvent. A further implication of this study is that not only the solvent but also the temperature and the rate of solvent loss may be important in controlling the order, and hence properties, of solvent-cast films.

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References and Notes