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

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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 $\pi-\pi^*$ transitions of the thiophene ring electronic absorption spectra. This behavior is analogous to the events in the thermochromic 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.[1−8] 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 chromic 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 polysilane.[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 CaH_2 and stored over CaH_2 in the dark until use. Polymers were evacuated ($\approx 10^{-4}$ 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,[26] 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.

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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 $\partial n/\partial c$, 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 $k = \Delta n/\Delta V_{instr}$, where ΔV_{instr} is the integrated instrument response under the elution peak, and Δn is calculated from the concentration and $\partial n/\partial c$ of the polystyrene solution ($\partial n/\partial c = 0.198$ mL/g in THF).[27] In subsequent determinations of $\partial n/\partial c$ for solutions of PDDT, Δn was calculated from measurements of ΔV_{instr} as $\Delta n = k\Delta V_{instr}$ for solutions of known concentration and standard injection volume. The solution of PDDT 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 chloroform 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[28] (thermochromic effects were not reported in the study cited).

Data Analysis. Light scattering results were analyzed according to the model for anisotropic scatterers.[26,29−37] This model provides expressions for the dependence of vertical and horizontal components of light scattered with vertically polarized incident light, denoted $R_{Vv}(q,c)$ and $R_{Hv}(q,c)$, respectively, on the concentration c and modulus $q = (4\pi n_s/\lambda) \sin(\vartheta/2)$ of the scattering angle vector, where n_s is the refractive index of the sample, λ is the wavelength of light, and ϑ is the angle between the incident and scattered beams. The polarized scattering $R_{Vv}(0,c)$ extrapolated to zero scattering angle provides information on the molecular weight M and the second virial coefficient A_2:

$$\left(\frac{Kc}{R_{Vv}(0,c)}\right)^{1/2} = \left(\frac{1}{M(1 + 4\delta^2/5)}\right)^{1/2} \times$$
$$\left\{1 + \left(\frac{1 - \delta^2/10}{1 + 4\delta^2/5}\right)A_2Mc + ...\right\} \quad (1)$$

where $K = (2\pi^2/N_A\lambda^4)[n_0\partial n/\partial c]^2$, n_0 is the solvent refractive index, N_A is Avogadro's number, and δ is the molecular anisotropy of the chain. The latter is a function of the chain conformation and the intrinsic anisotropy δ_0 of the scattering elements making up the chain, see below. The factor $1 - \delta^2/10$ is properly appropriate only for a rodlike chain,[38] but it is applied here as its effect is small otherwise, vanishing for a flexible chain as δ tends to zero.

When extrapolated to infinite dilution (denoted by a super zero), the angular dependence of the scattering provides a measure of the root-mean-square radius of gyration R_G:[29,32,35,36]

$$\left(\frac{Kc}{R_{Vv}(q,c)}\right)^\circ = \frac{1}{M(1 + 4\delta^2/5)}\left\{1 + \frac{1}{3}R_{G,V}^2 q^2 + ...\right\} \quad (2)$$

with $R_{G,V}^2 = J(\delta)R_G^2$, where

$$J(\delta) = \frac{j(\delta)}{1 + 4\delta^2/5} = \frac{1 - 4f_1\delta/5 + 4(f_2\delta)^2/7}{1 + 4\delta^2/5} \quad (3)$$

is unity for $\delta = 0$, and $3/7$ for $\delta = 1$. The functions f_1 and f_2 tend to unity as δ/δ_0 tends to unity and decrease approximately as $\hat{a}/L$ for large $L/\hat{a}$ (coil).[32,35,36] Consequently, f_1 and f_2 may

be approximated as unity for practical purposes, since the effect of molecular anisotropy on $(Kc/R_{Vv}(q))^\circ$ is negligible for small δ/δ_0.

The depolarized scattering $R_{Hv}(0)$ extrapolated to zero scattering angle depends on the molecular weight M, the anisotropy δ, and the second virial coefficient A_2:[36,38]

$$\left(\frac{Kc}{R_{Hv}(0,c)}\right) = \frac{5}{3M\delta^2}\{1 - f_{Hv}A_2Mc + ...\} \quad (4)$$

where $f_{Hv} \approx 0$ for a flexible chain and $f_{Hv} \approx 1/4$ for a rodlike chain; $Kc/R_{Hv}(q,c) \approx [Kc/R_{Hv}(q,c)]^\circ = 5/3M\delta^2$ for typical values of A_2. Further (for $\delta \neq 0$),[35,36]

$$\left(\frac{Kc}{R_{Hv}(q,c)}\right)^\circ = \frac{5}{3M\delta^2}\left\{1 + \frac{3}{7}R_{G,H}^2 q^2 + ...\right\} \quad (5)$$

with $R_{G,H}^2 = f_3^2 R_G^2$, where f_3 is similar in form to f_1 and f_2,[34−36] see below. Thus, $R_{G,H}^2 = R_{G,V}^2/J(\delta) = R_G^2$ in the limit of a rodlike chain, but $R_{G,H}^2 < R_{G,V}^2 = R_G^2$ in the limit of a flexible chain. Comparison of the reduced intensities extrapolated to zero angle and infinite dilution provides a measure of δ:

$$\left(\frac{R_{Hv}(0,c)/c}{R_{Vv}(0,c)/c}\right)^\circ = \frac{3\delta^2}{5 + 4\delta^2} \quad (6)$$

Since the samples studied here are heterodisperse, appropriate averages must be used for the derived parameters. Thus, from the polarized scattering,[26,32,34−36]

$$(M_V)_{LS} = \sum w_\nu M_\nu(1 + 4\delta^2/5)_\nu = M_w + 4(\delta^2 M_H)_{LS}/5 \quad (7)$$

$$(R_{G,V}^2)_{LS} = (M_V)_{LS}^{-1}\sum w_\nu M_\nu(j(\delta)R_G^2)_\nu \quad (8)$$

$$A_{2,LS} = M_w^{-2}\sum\sum w_\nu M_\nu w_\mu M_\mu(A_2)_{\nu\mu} \quad (9)$$

The parameters from the depolarized scattering become[34,36,39]

$$(\delta^2 M_H)_{LS} = \sum w_\nu(\delta^2 M)_\nu \quad (10)$$

$$(R_{G,H}^2)_{LS} = \frac{\sum w_\nu M_\nu(f_3^2\delta^2 R_G^2)_\nu}{\sum w_\nu(\delta^2 M)_\nu} \quad (11)$$

Dynamic light scattering measurements were carried out to give the intensity autocorrelation function $g^{(2)}(\tau;q,c)$ as a function of scattering angle and correlation time τ.[35,36] With a cumulant analysis,[36]

$$\ln[g^{(2)}(\tau;q,c) - 1]^{1/2} = A - K^{(1)}(q,c)\tau + \frac{1}{2!}K^{(2)}(q,c)\tau^2 + ... \quad (12)$$

where A is a constant and $K^{(1)}(q,c)$ is the first cumulant, etc. For the polarized scattering, the first cumulant is used to compute the mutual diffusion coefficient $D_M(c)$ in the limit of small q:

$$\lim_{\tau=0} K_{Vv}^{(1)}(q,c) = D_M(c)q^2 \quad (13)$$

Data on $D_M(c)$ are often linear in c for low c:[35,36]

$$D_M(c) = D_T\{1 + (k_1A_2M - k_2[\eta])c + ...\} \quad (14)$$

where D_T is the translational diffusion constant and k_1 and k_2 are constants of order unity. It is convenient to define a hydrodynamic scaling length $a_{LS}(c)$ by the expression[34,36]

$$a_{LS}(c) = \frac{kT}{6\pi\eta_s D_M(c)} \quad (15)$$

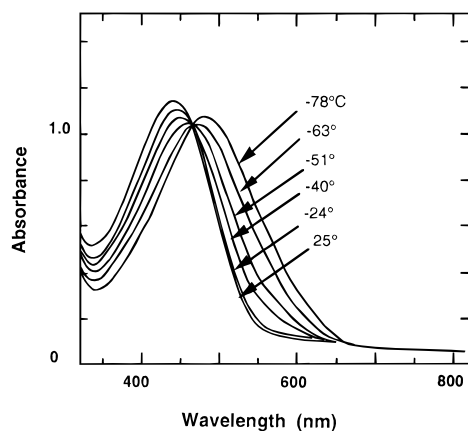with η_s the solvent viscosity; $a_{LS}(c)$ reduces to the hydrody-

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

history	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	T_5 (°C)	T_{meas} (°C)
A	25					25
B	25	65	25			25
C	25	$T_{q1} < 0$	65	25		25
D	25	$T_{q1} < 0$	65	$T_{q2} < 0$		$T_{q2} < 0$
E	25	$T_{q1} < 0$	65	$T_{q2} < 0$	65	65
F	25	$T_{q1} < 0$	65	$T_{q2} < 0$	25	25

namic radius $R_H = kT/6\pi\eta_s D_T$ at infinite dilution. For heterodisperse samples,[35,36]

$$R_{H,LS} = (\delta^2 M_H)_{LS} / \sum w_\nu M_\nu \delta^2 (R_H^{-1})_\nu \qquad (16)$$

For depolarized scattering, the first cumulant is related to rotational dynamics as well as the 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]

$$\lim_{\tau=0} K_{Hv}^{(1)}(q,c) = (\delta^2 M_H)_{LS}^{-1} \sum w_\nu M_\nu \delta_\nu^2 (\{6(D_R)_\nu + (D_T)_\nu q^2\}$$
$$(17)$$

Results

The electronic absorption spectra for a sample of PDDT 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 $\partial n/\partial c = 0.124$ mL/g for PDDT in THF, the solvent used on the SEC. Use of the Dale–Gladestone approximation $\partial n/\partial c \approx (n_p - n_s)/\rho_p$ gives $\rho_p \partial n/\partial c \approx 0.083$ in chloroform, with ρ_p the density of PDDT ($\rho_p \approx 1.0$ 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 dethawing to room temperature (T_1) from the rapidly frozen state used in the degassing to the temperature T_{meas} of the light scattering measurement (Table 1). As shown in Figure 2, the functions $Kc/R_{Vv}(q,c)$ versus $\sin^2(\vartheta/2)$ 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
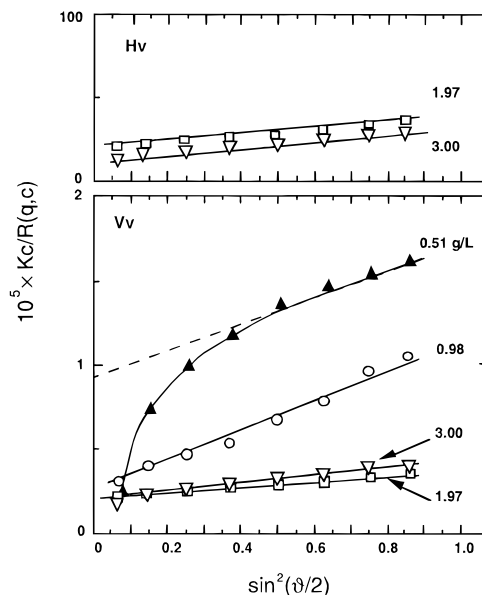

Figure 2. Static light scattering on dilute solutions of poly-(3-dodecylthiophene) in chloroform; upper and lower panels are for the depolarized (Hv) and polarized scattering (Vv), respectively. The concentrations are indicated (g/L); the unfilled and filled symbols are for histories A and B, respectively.

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 ($\sin^2(\vartheta/2) > 0.5$) may be analyzed to give apparent values $(M_V)_{app}$ and $(R_{G,V})_{app}$ 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,

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

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

neglecting terms involving δ for convenience since they are small, and

$$(\delta^2 M_H)_{app} = \{3Kc/5R_{Hv}(0,c)\}^{-1} \quad (20)$$

$$(R_{G,H}^2)_{app} = (7/3)\{Kc/R_{Hv}(0,c)\}^{-1}\left(\frac{\partial Kc/R_{Hv}(q,c)}{\partial q^2}\right) \approx$$
$$f_3^2(R_G^2)_{LS} \quad (21)$$

Based on extrapolation of the higher angle data, $(M_V)_{app} \approx 95\,000$ and $(R_{G,V})_{app} \approx 18$ 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 $(M_V)_{app} \approx 4.5 \times 10^6$ and $(R_{G,V})_{app} \approx 56$ nm, and the depolarized scattering gives $(\delta^2 M_H)_{app} \approx 50\,000=$ and $(R_{G,H})_{app} \approx 67$ nm. The depolarized scattering was sufficiently intense to permit dynamic scattering, with the result given in Figure 3. As may be seen, the first
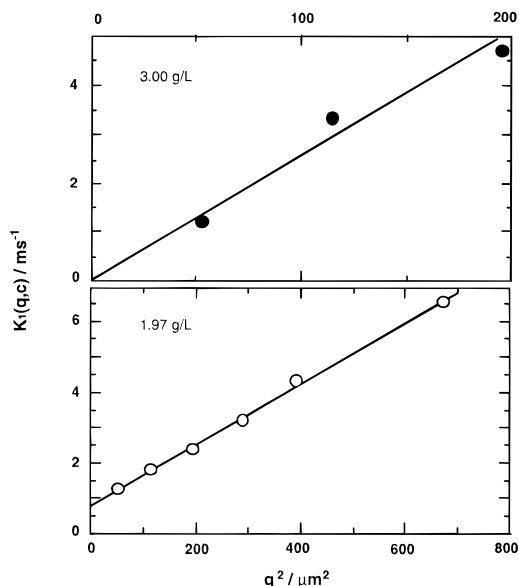
Figure 3. First cumulant from dynamic light scattering on dilute solutions of poly(3-dodecylthiophene) in chloroform. Upper: polarized (Vv) scattering for a solution with $c = 1.97$ g/L, history E; lower: depolarized (Hv) scattering for a solution with $c = 3.0$ g/L, history A.
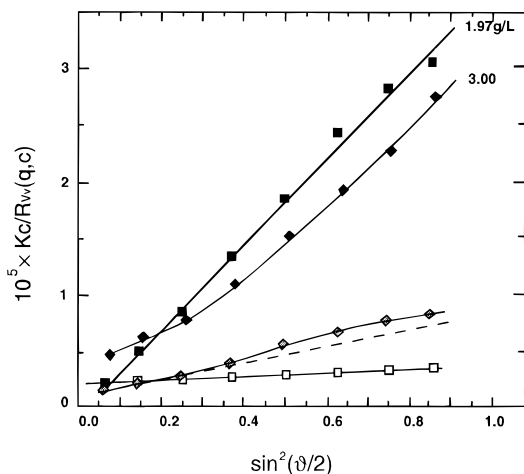

Figure 4. Static polarized (Vv) light scattering on dilute solutions of poly(3-dodecylthiophene) in chloroform. The concentrations are indicated (g/L); the unfilled and filled symbols are for histories A and C ($T_{q1} = -16.5$ °C), respectively, and the shaded symbols are for history E ($T_{q1} = T_{q2} = -16.5$ °C), with the dashed line showing the initial tangent.

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 $(M_V)_{app} \approx 10^6$ and $(R_{G,V})_{app} \approx 170$ 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 $a_{LS}(c) = 33$ 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 mea-
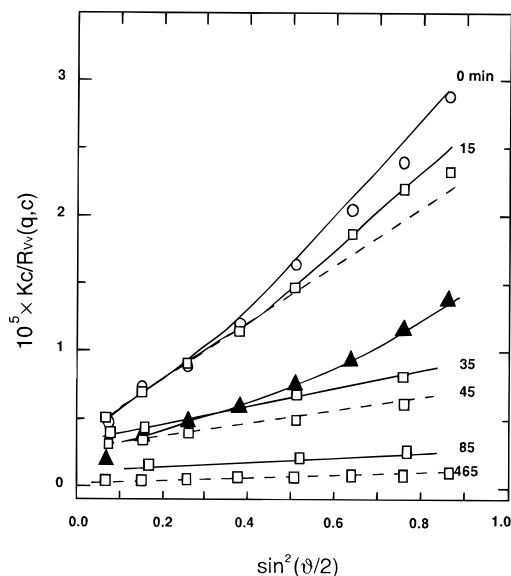

Figure 5. Static polarized (Vv) light scattering on dilute solutions of poly(3-dodecylthiophene) in chloroform; $c = 3.0$ g/L. The unfilled circles and squares are for histories C and D, respectively ($T_{q1} = -16.5$ °C) with the times at $T_{q2} = -16.5$ °C indicated (min), and the filled symbols are for history F ($T_{q1} = T_{q2} = -16.5$ °C).
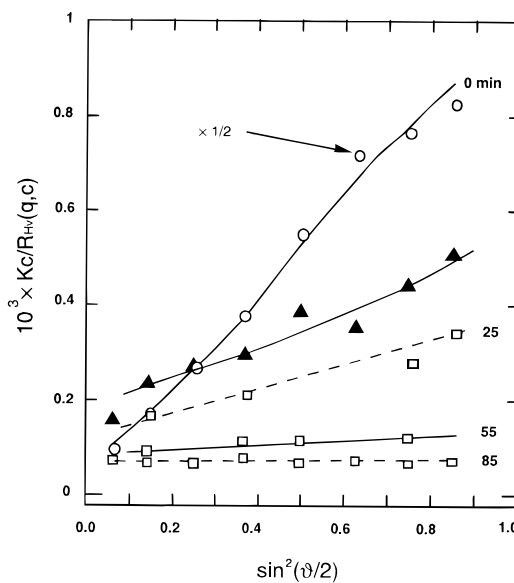

Figure 6. Static depolarized (Hv) light scattering on dilute solutions of poly(3-dodecylthiophene) in chloroform; $c = 3.0$ g/L. The unfilled circles and squares are for histories C and D, respectively ($T_{q1} = -16.5$ °C) with the times at $T_{q2} = -16.5$ °C indicated (min), and the filled symbols are for history F ($T_{q1} = T_{q2} = -16.5$ °C).

surement 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 $(M_V)_{app}$ and $(R_{G,V})_{app}$ are given in Figure 8 along with data on the ratio $[R_{Hv}(0,c)/c]°/[R_{Vv}(0,c)/c]°$ of the reduced intensities at zero scattering angle and the ratio $(R^2_{G,V})_{LS}/(M_V)_{LS}$.

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 $\pi - \pi^*$
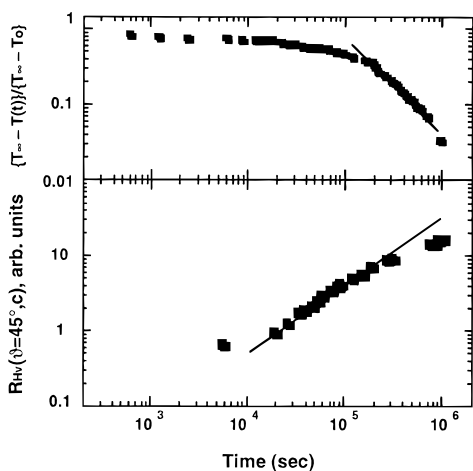
Figure 7. Bilogarithmic plots of the change of two parameters with time for a dilute solution of poly(3-dodecylthiophene) in chloroform for history D, with $T_{q2} = -16.5$ °C; $c = 3.0$ g/L. Upper: a function of the transmission $T(t)$ ($\lambda = 647.5$ nm); lower: the depolarized scattering at 45° scattering angle.
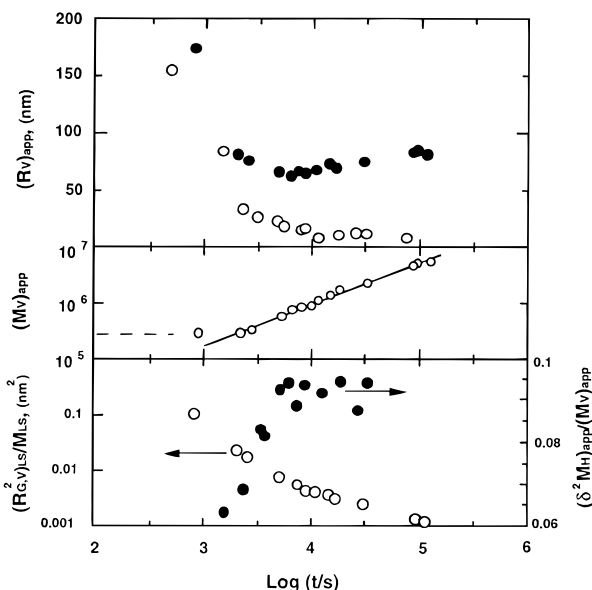

Figure 8. Bilogarithmic plots of the change of several parameters with time for a dilute solution of poly(3-dodecylthiophene) in chloroform for history D, with $T_{q2} = -16.5$ °C; $c = 3.0$ g/L. Upper: the apparent radius of gyration the filled and unfilled symbols are for the polarized (Vv) and depolarized (Hv) scattering, respectively); middle: the apparent molecular weight $(M_V)_{app}$ from the polarized (Vv) scattering; lower: the ratios $(R^2_{G,V})_{LS}/(M_V)_{LS} \approx R^2_{GLS}/M_w$ from the polarized (Vv) scattering (unfilled) and $(\delta^2 M_H)_{app}/(M_V)_{app} = [R_{Hv}(0,c)/c]°/[R_{Vv}(0,c)]°$ of the reduced intensities at zero scattering angle of the depolarized (Hv) and polarized (Vv) scattering.

transition enhanced by coplanar conformers of the thiophene rings in the polythiophene backbone.[2,3,41] X-ray diffraction studies on solvent-cast films of poly-(3-alkylthiophene)s have revealed a lamellar organization,[5,10,42,43] with lamellae of the polythiophene backbones interspersed by lamellae of the alkyl chains. This structure is similar to that typically observed with block and graft copolymers of immiscible polymers.[44] In this case, however, the immiscibility may promote a second phase transition, in which the wormlike polythiophene backbone is induced to form a nematic phase supramolecular order, with the chains in the quasi two-dimensional planes adopting an extended conformation with enhanced persistence length $â$.[45] This behavior can be understood using concepts embodied in a Flory phase diagram for semiflexible molecules, which predict that

a semiflexible chain may experience extension in conformation and transition to an ordered phase with increasing concentration.[16,46] 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 ≈0.38 nm. The interlamellar 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;[10] a dimension of 2.7 nm was reported from the diffraction from a drawn fiber of a nonregioregular PDDT sample.[40] Especially well-ordered films have been prepared with regioregular poly(3-alkylthiophene)s 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.[10] 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.[47] 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.[5]

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 moiety 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.[16,46] 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 °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 $(\delta^2 M_H)_{app}/(M_V)_{app}$, but only a modest increase in $(M_V)_{app}$. Consistent with the corresponding change in the scattering profile, 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 ϵL (see below), the square radius of gyration of a spheroid of revolution with volume V is given by[35,48]

$$R_G^2 = \frac{2 + \epsilon^2}{20}L^2 = \frac{2 + \epsilon^2}{20\epsilon^{4/3}}\left(\frac{3V}{4\pi}\right)^{2/3} \qquad (22)$$

with $\epsilon > 1$ for an oblate ellipsoid. Thus, R_G^2 is expected to decrease as ϵ 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 $(\delta^2 M_H)_{app}/(M_V)_{app}$ 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 $(\delta^2 M_H)_{app}/(M_V)_{app}$ can be attributed to either or both of two effects: increasing persistence length $\hat{a}$ 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, $(R_{G,V})_{app}$, $(R_{G,H})_{app}$ and $(\delta^2 M_H)_{app}/(M_V)_{app}$ all tend to stabilize, whereas $(M_V)_{app}$ continues to increase slowly, as $(R_G^2)_{LS}/M_w$ decreases. This behavior suggests agglomeration of the elongated aggregates to form still larger structures. The slow decrease in $(R_G^2)_{LS}/M_w$ as $(M_V)_{app}$ increases is attributed to increasing particle volume of the elongated particles. Thus, for the ellipsoidal model, $R_G^2/M \propto \{(2 + \epsilon^2)/20 \ \epsilon^{4/3}V^{1/3}\}(V/M)$, with V/M 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 ϵ remains small, would produce the observed decrease in $(R_G^2)_{app}/M_{app}$.

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 −40 °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[49]

$$(\pi\eta_s/kT)D_T = \varphi(\epsilon)/3L \qquad (23)$$

$$(\pi\eta_s/kT)D_R = \vartheta(\epsilon)/L^3 \qquad (24)$$

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

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

$$\vartheta(\epsilon) = \frac{3}{2}\left(\frac{(2 - \epsilon^2)\varphi(\epsilon) - 1}{(1 - \epsilon^4)}\right) \qquad (26)$$

where $\varphi(\epsilon) = \vartheta(\epsilon) = 1$ for a sphere ($\epsilon = 1$) of diameter L. With these relations, $\Psi(\epsilon) = 3(\pi\eta_s/kT)^{2/3}D_T/D_R^{1/3} = \varphi(\epsilon)/\vartheta(\epsilon)^{1/3}$ is a single-valued function of ϵ for $\Psi(\epsilon) > 1.18$, permitting an unambiguous assessment of ϵ, 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 ϵ depends critically on the model with this extreme an 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 $(\delta^2 M_H)_{app}/(M_V)_{app}$, indicating that the chains are not perfectly parallel in the aggregate. Deviation from $(R_{G,V})_{app}$ would be expected if $A_{2LS}M_wc$ is large. For rigid ellipsoids interacting through a hard-core potential, $A_2M = 4N_Av_mf(\epsilon)/M$, where v_m is the particle volume and $f(\epsilon)$ is a function of ϵ that tends to $1/4\epsilon$ for small ϵ. Thus, for the parameters given, $A_2M \approx \pi N_A\epsilon L^3/6M \approx 100$ cm³/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.[47] 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[47] marked dependence of the conductivity of I_2-doped solvent-cast films of regioregular PDDT 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.

References and Notes

(1) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.
(2) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., B: Polym. Phys.* **1987**, *25*, 1071.
(3) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183.
(4) Daoust, G.; Leclerc, M. *Macromolecules* **1991**, *24*, 455.
(5) Chen, S.-A.; Ni, J.-M. *Macromolecules* **1992**, *25*, 6081.
(6) Gustaffsson, G.; Inganäs, O.; Dyreklev, P. In *Electronic Properties of Polymers and Related Compounds*; Kuzmany, H., Mehring, M., Roth, S., Eds.; Springer-Verlag: Berlin, 1992; Vol. 107, p 329.
(7) Roux, C.; Leclerc, M. *Macromolecules* **1992**, *25*, 2141.
(8) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.
(9) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70.
(10) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.
(11) Xu, R.; Chu, B. *Macromolecules* **1989**, *22*, 4523.
(12) Li, Y.; Chu, B. *Macromolecules* **1991**, *24*, 4115.
(13) Wenz, G.; Wegner, G. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 231.
(14) Wenz, G.; Muller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* **1984**, *17*, 837.
(15) Shulka, P.; Cotts, P. M.; Miller, R. D.; Russell, T. P.; Smith, B. A.; Wallraff, G. M.; Bailer, M.; Thiyagarajan, P. *Macromolecules* **1991**, *24*, 5606.
(16) Wei-Berk, C.; Berry, G. C. *J. Polym. Sci., B: Polym. Phys.* **1990**, *28*, 1873.
(17) Patel, G. N.; Walsh, E. K. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 203.
(18) Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Chem. Phys.* **1979**, *70*, 4387.
(19) Lim, K. C.; Fincher, C. R.; Heeger, A. J. *Phys. Rev. Lett.* **1983**, *50*, 1934.
(20) Lim, K. C.; Sinclair, M.; Casalnuovo, S. A.; Fincher, C. R.; Wudl, F.; Heeger, A. J. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 329.
(21) Lim, K. C.; Heeger, A. J. *J. Chem. Phys.* **1983**, *82*, 522.
(22) Taylor, M. A.; Odell, J. A.; Batchelder, D. N.; Campbell, A. J. *Polymer* **1990**, *31*, 1116.
(23) Harrah, L. A.; Ziegler, J. H. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 209.
(24) Rabolt, J. F.; Hofer, D.; Miller, R. D.; Fickes, G. M.; Wenz, G. *Macromolecules* **1986**, *19*, 611.
(25) Brendas, J. L.; Themans, B.; Fripiat, J. G.; Andre, J. M.; Chance, R. R. *Phys. Rev. B* **1984**, *29*, 6761.
(26) Lee, C. C.; Chu, S.-G.; Berry, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1573.
(27) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1989.
(28) Heffner, G. W.; Pearson, D. S. *Macromolecules* **1991**, *24*, 6295.
(29) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(30) Berry, G. C. In *Contemporary Topics in Polymer Science*; Pearce, E. M., Schaefgen, J. R., Eds.; Plenum Press: New York, 1977; p 55.
(31) Wong, C. P.; Ohnuma, H.; Berry, G. C. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 173.
(32) Berry, G. C. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 143.
(33) Metzger Cotts, P.; Berry, G. C. *J. Polym. Sci., B: Polym. Phys.* **1983**, *21*, 1255.
(34) Furukawa, R.; Berry, G. C. *Pure Appl. Chem.* **1985**, *57*, 913.
(35) Berry, G. C. In *Encyclopedia of Polymer Science and Engineering*; Mark, H., Overberger, C. G., et al., Eds.; John Wiley & Sons, Inc.: New York, 1987; Vol. 8, p 721.
(36) Berry, G. C. *Adv. Polym. Sci.* **1994**, *114*, 233.
(37) Sullivan, V. J.; Berry, G. C. *Int. J. Polym. Anal. Charact.* **1995**, *1*, 0000.
(38) Benoit, H.; Stockmayer, W. H. *J. Phys. Radium* **1956**, *17*, 21.
(39) Berry, G. C. In *Encyclopedia of Materials Science and Engineering*; Bever, M. B., Ed.; Pergamon Press: Oxford, U. K., 1986; p 3759.
(40) Moulton, J.; Smith, P. *Polymer* **1992**, *33*, 2340.
(41) Chen, S.-A.; Tsai, C.-C. *Macromolecules* **1993**, *26*, 2234.
(42) Winokur, M. J.; Wamsley, P.; Moulton, J.; Smith, P.; Heeger, A. J. *Macromolecules* **1991**, *24*, 3812.
(43) Prosa, T. J.; Winokur, M. J.; Moulton, J.; Smith, P.; Heeger, A. J. *Macromolecules* **1992**, *25*, 4364.
(44) Brown, R. A.; Masters, A. J.; Price, C.; Yuan, X. F. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: New York, 1989; Vol. 2, Chapter 6.
(45) Tashiro, K.; Ono, K.; Minagawa, Y.; Kobayashi, M.; Kawai, T.; Yoshino, K. *J. Polym. Sci., B: Polym. Phys.* **1991**, *29*, 1223.
(46) Flory, P. J. *Adv. Polym. Sci.* **1984**, *59*, 1.
(47) McCullough, R. D., 1995.
(48) Einaga, Y.; Berry, G. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23* (1), 27.
(49) Zero, K.; Pecora, R. In *Dynamic Light Scattering*; Pecora, R., Ed.; Plenum Press: New York, 1985; p 59.

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