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Molecular Characterization of Poly(3-hexylthiophene)

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ABSTRACT: A complete molecular characterization of poly(3-hexylthiophene) (P3HT) in dilute solution was conducted by using static and dynamic light scattering, gel permeation chromatography, and viscosity measurements. The dependence of the intrinsic viscosity and the radius of gyration upon molecular weight was determined in THF for $40\,000 \le M_w \le 220\,000$ and found to be characteristic of a moderately good solvent. Similar solution characteristics were observed in chloroform. A comparison of the macromolecular dimensions determined by different techniques was made to demonstrate the consistency of the data, which indicate that the P3HT macromolecules exist as isolated flexible-coil chains in dilute THF solution with a persistence length of 2.4 ± 0.3 nm.

Introduction

Although polymers that can be doped to an electrically conducting state were first discovered well over a decade ago,[1] the first examples, which included polyacetylene and polythiophene, were insoluble and nonmelting. Only during the past six years have soluble conducting polymers been synthesized, after it was first discovered that the addition of alkyl side chains to a polythiophene main chain renders it both soluble and meltable while preserving its conductivity.[2] Conductivities of up to 200 S/cm have been measured for these poly(3-alkylthiophenes) (P3ATs),[3] which is 3 orders of magnitude below that of conducting metals, yet sufficient for a number of proposed applications. Furthermore, these polymers have the obvious advantage of being melt- and solution-processible, increasing their potential commercial importance.

An additional advantage of the P3AT's solubility is that standard solution characterization techniques may be implemented to analyze the size, conformation, and molecular weight of these conducting polymers. Although the relative molecular weights of these and other soluble conducting polymers have been estimated by gel permeation chromatography (GPC) using a polystyrene calibration, there are no data obtained by other analytical methods with which to compare these estimates. Indeed, there is still a question as to whether the addition of alkyl side chains renders polythiophene soluble on a molecular level or whether it instead exists as clusters of molecules in solution. Preliminary light scattering experiments on octyl-substituted polythiophene have indicated an increase in hydrodynamic size over time, indicating that aggregation may occur.[4] The degree to which the conjugated P3AT backbone affects chain flexibility is another point of uncertainty which can be determined through more stringent characterization.

In this work we present a complete characterization of poly(3-hexylthiophene) (P3HT) in dilute solution. Static light scattering, GPC, and viscosity measurements were conducted on five P3HT samples of varying molecular weight using THF as a solvent. The largest molecular weight sample (E) was examined in both THF and chloroform. Dynamic light scattering measurements were also performed on this sample so that a comparison could be made of the macromolecular dimensions obtained by several different techniques. The information thus obtained was used to form a complete and consistent picture of the P3HT molecule in dilute solution and how its solution characteristics vary as a function of molecular weight.

Experimental Section

Materials. Four of the P3HT samples studied were provided by Dr. Shu Hotta of Matsushita Electric Industrial Co., while a fifth (sample B) was furnished by Dr. Fred Wudl at the University of California, Santa Barbara. Details of the synthesis using a metal halogenide catalyst are described elsewhere.[3] The as-received polymer formed clear solutions, and no additional fractionation or cleaning was attempted other than that described below.

Degradation. During the course of our investigations it became clear that P3HT in solution degrades upon exposure to light. Figure 1 demonstrates that the specific viscosity divided by concentration, η_{sp}/c (which parallels $[\eta]$ at low c), decreases linearly with time for a solution of P3HT in chloroform subjected to fluorescent room light, representing a drop in molecular weight by approximately a factor of 2 after 48 h. Degradation was also apparent in the THF solutions, although it proceeded at a slower rate. This effect was also observed in light scattering measurements on exposed samples; however, repeated measurements on samples kept in the dark gave reproducible results over several days. Consequently, all solutions were prepared with minimal exposure to light and stored in darkness.

Static Light Scattering. Static light scattering measurements were conducted using a Brookhaven Instruments BI-200SM goniometer and a 15-mW He–Ne laser (Spectra-Physics 124B) as a light source. The goniometer was carefully aligned so that the intensity of an isotropic scatterer, toluene, multiplied by the sine of the scattering angle, θ, varied by only 1% over the angular range $30° \le \theta \le 150°$.

All samples were prepared at concentrations well below the overlap concentration, c^* (calculated as $c^* \sim 1/[\eta]$). At these low concentrations, the polymer solutions did not significantly absorb light at the wavelength of the laser. The solutions were filtered through 0.2-μm PTFE filters (Micron Separations) and subsequently centrifuged at low speed ($\sim$2000g) to remove any remaining particulates. The solutions were maintained at 25.0 ± 0.2 °C during the scattering experiments.

The weight-average molecular weight, M_w, the z-average radius of gyration, $R_{g,z}$, and the second virial coefficient, A_2, were determined by extrapolation of Kc/R_θ to zero angle and zero concentration according to the relation[5]

$$Kc/R_\theta = 1/M_w(1 + q^2 R_{g,z}^2/3) + 2A_2c + ... \tag{1a}$$

where

$$K = 4\pi^2 n^2 (\mathrm{d}n/\mathrm{d}c)^2 / N_a \lambda_0^4 \tag{1b}$$

and

$$q = (4\pi n/\lambda_0) \sin(\theta/2) \tag{1c}$$

R_θ is the excess Rayleigh ratio, c is the polymer concentration,

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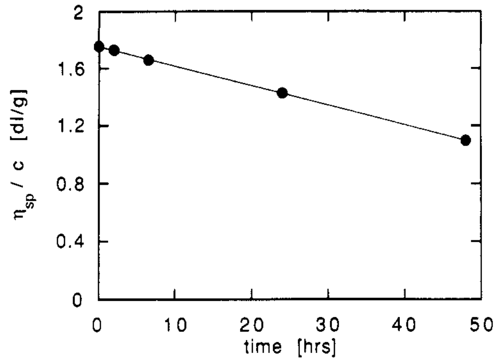

Figure 1. Decrease in η_{sp}/c over time for a dilute solution of P3HT (sample E, c = 0.005 g/mL) in chloroform exposed to fluorescent room light.

n is the refractive index of solvent, λ_0 is the wavelength of light in vacuo, N_a is Avagadro's number, and dn/dc is the refractive index increment. Toluene was used as the calibration solvent; its Rayleigh ratio was taken as 14.02×10^{-6}.[6] Static light scattering measurements conducted on three narrow distribution polystyrene standards (Toya Soda, $M = 1.90 \times 10^5$–1.26×10^6) using our apparatus determined M_w within 2% and R_g and A_2 within 4% of literature values.[7]

The refractive index increment was determined at 25.0 ± 0.2 °C using a differential refractometer of the Brice-Phoenix design[8] (C. N. Wood RF-600). A 300-W tungsten lamp was used in conjunction with monochromatic filters so that dn/dc could be determined for several wavelengths of light. The refractometer was calibrated with aqueous KCl solutions.

Dynamic Light Scattering. Dynamic light scattering measurements were performed by using the apparatus described above and a Brookhaven BI-2030 72-channel correlator. The time correlation function, $\langle I(t)\, I(0)\rangle$, was analyzed by the method of cumulants[9]

$$\ln (\langle I(t)\, I(0)\rangle / \langle I\rangle^2 - 1)^{1/2} = \ln B^{1/2} - \Gamma t + \mu_2 t^2/2 ... \qquad (2)$$

where $\langle I\rangle$ is the average scattering intensity and B is an optical constant. The sample time, Δt, was chosen according to $\Delta t \approx 2/m\Gamma$, where m is the number of channels. A second-order cumulant fit was deemed appropriate since higher order terms typically reduced the RMS error of the data fit by less than 5%. The value of μ_2/Γ^2 is typically much more sensitive to experimental noise than Γ;[9] yet, we found the standard deviation of μ_2/Γ^2 to be less than 10% in our measurements, indicating excellent reproducibility of the data. Agreement between the calculated and measured base-line intensities was always within 0.1%.

The z-average diffusion coefficient, D_z, at each concentration was calculated by

$$D_z = \Gamma / q^2 \qquad (3)$$

and was found to be independent of angle over the range 30° ≤ θ ≤ 75°. Experiments performed with our instrument on narrow-distribution polystyrenes allowed us to calculate the diffusion coefficient within 2% of literature values.[10]

Viscometry and Gel Permeation Chromatography. Viscosity measurements were made by a Ubbelohde viscometer (Cannon) in a constant-temperature bath at 25.0 ± 0.1 °C. The polymer solution was filtered through a 1-μm PTFE filter, and subsequent dilutions were made within the viscometer. The intrinsic viscosity, $[\eta]$, and the Huggins coefficient, k_H, were calculated according to the Huggins equation

$$\eta_{sp}/c = (\eta - \eta_0)/\eta_0 c = [\eta] + k_H [\eta]^2 c + ... \qquad (4)$$

where η is the solution viscosity and η_0 is the solvent viscosity.

The molecular weight and polydispersity of each sample were estimated by GPC using a Waters 150C instrument with μ-Styragel (samples A, B, and E) or Alltech (samples C and D) columns. THF was the carrier solvent at a flow rate of 1 mL/min. The columns were calibrated by a series of narrow-distribution polystyrene standards, and all GPC molecular weights quoted are relative to polystyrene.

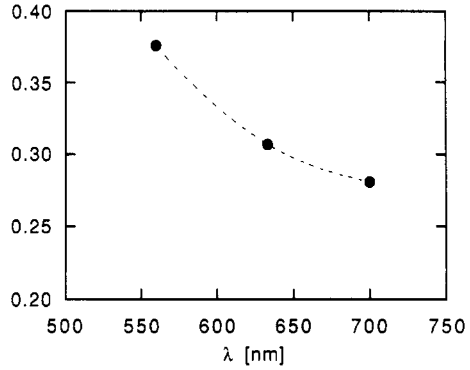

Figure 2. Refractive index increment of P3HT in THF as a function of the wavelength of light (in vacuo).

Results and Discussion

In the absence of absorption, the intensity of light scattered from a polymer solution is proportional to the square of the refractive index increment, dn/dc. The value of dn/dc was found to be independent of concentration (c ≤0.005 g/mL) for P3HT in THF. However, dn/dc varies substantially with the wavelength of light, increasing as the absorption maximum (440 nm[11]) is approached (Figure 2). This resonance-enhanced scattering is characteristic of conjugated polymers in solution.[12] At the He–Ne laser wavelength, λ = 632.8 nm, dn/dc is about 0.3, much larger than most commonly studied polymers. As a result the scattering intensity of extremely dilute solutions can be measured, and absorption, which is often quite strong for conjugated polymer solutions, may be diminished. The concentrations of P3HT solutions used in our static light scattering experiments were on the order of 10^{-4} g/mL. At such low concentrations, the absorption by our light scattering volume was always less than 2%, so no correction of the data was necessary.

The weight-average molecular weight and z-average radius of gyration determined by static light scattering experiments on P3HT in THF are given in Table I. (A_2 was reliably obtained only for sample E.) The five samples cover a molecular weight range of 40 000–220 000, which corresponds to several hundreds of repeat units. The good reproducibility of light scattering measurements on several independently prepared solutions is exemplified by the small standard deviation of the values obtained for sample E (Table II). Typical data in the form of a Zimm plot are shown in Figure 3.

The GPC chromatograms indicated a unimodal distribution of molecular weights for each sample, with polydispersities, M_w/M_n, varying from 2 to 4 according to the polystyrene calibration. The samples having a polydispersity of 2 were found to approximate a logarithmic normal molecular weight distribution (Figure 4), for which $M_z/M_w = M_w/M_n$. This is a not a valid description of the molecular weight distributions of the more polydisperse samples, however, as can be seen from the molecular weight ratios listed in Table I.

A particularly interesting result of the GPC measurements is that the molecular weights determined relative to polystyrene are in remarkable agreement with the absolute values obtained by light scattering (Table I). This suggests that the hydrodynamic volume of P3HT and polystyrene are similar functions of molecular weight in the range of molecular weights studied. As a result, the different moments of the molecular weight can be accu-

Table I
Characterization of P3HT in THF at 25 °C[a]

	light scattering		GPC				viscosity			
sample	M_w	$R_{g,z}$, nm	M_w	M_v	M_w/M_n	M_z/M_w	$[\eta]$, dL/g	k_H	ρ_{LS}, nm	$\rho_{[\eta]}$, nm
A	41 000	[b]	38 900	32 000	3.7	2.2	0.48	0.31		2.1
B	75 400	16.8	75 600	66 200	1.9	1.9	0.73	0.33	2.5	2.2
C	90 300	21.3	86 300	68 600	3.5	2.6	0.73	0.37	2.4	2.1
D	112 000	26.3	113 000	81 800	4.2	3.3	0.87	0.40	2.4	2.2
E	223 000	32.0	225 000	192 000	2.1	2.1	1.35	0.46	2.8	2.4

[a] Estimated uncertainties in the measured values are as follows: M_w(LS), ±5%; $R_{g,z}$, ±1.0 nm; M_v,M_w(GPC), ±5%; $[\eta]$, ±2%. [b] Too small to determine reproducibly.

Table II
Characterization of Sample E in THF and Chloroform at 25 °C

anal. technique	meas quant	in THF	in chloroform
static light scattering	M_w	223 000 (±3%)	207 000 (±6%)
	$R_{g,z}$, nm	32.0 (±3%)	30.0 (±5%)
	A_2, cm^3·mol/g^2	1.04×10^{-3} (±8%)	1.38×10^{-3} (±10%)
	R_T, nm	17.3	18.0
differential refractometry	dn/dc, mL/g	0.307	0.269
dynamic light scattering	D, cm^2/s	2.06×10^7	2.17×10^7
	R_H, nm	21.3	19.6
	k_D, mL/g	200	150
intrinsic viscosity	$[\eta]$, dL/g	1.35	1.38
	k_H	0.46	0.49
	$R_{g,\eta}$,[a] nm	20.1	19.8
GPC (calibrated with polystyrene)	M_n	105 000	
	M_w	225 000	
	M_z	468 000	
molecular size ratios	$R_{g,\eta}/R_{g,z}$	0.63	0.66
	$R_{g,z}/R_H$	1.50	1.53

[a] Using M_w from light scattering.

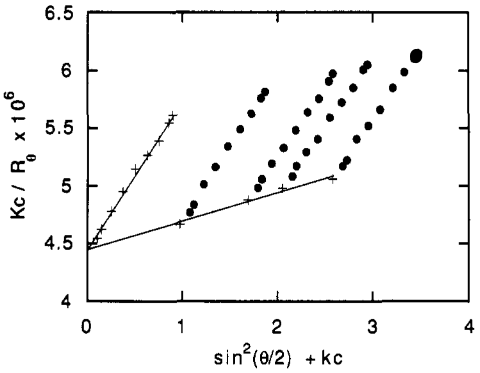

Figure 3. Static light scattering results for P3HT (sample E) in the form of a Zimm plot with a spacing constant $k = 10^4$ mL/g. Filled circles are data; crosses are extrapolations to zero angle and zero concentration.

rately calculated directly from GPC measurements, which is useful in the further analysis of our characterization data.

The viscosity data for P3HT in dilute solution were plotted in the form of η_{sp}/c as a function of concentration, from which the intrinsic viscosity was determined as the value of the y-intercept. The data are shown in Figure 5. A power law relationship exists between the intrinsic viscosity and the molecular weight; for polydisperse samples, the viscosity-average moment of the molecular weight is appropriate. Since the GPC molecular weights are in excellent agreement with the absolute values determined by light scattering, the viscosity-average molecular weight of each sample was determined from GPC data (Table I). From a plot of the data for five different samples (Figure 6), we find that the power law relationship between the intrinsic viscosity and molecular weight is well expressed by[13]

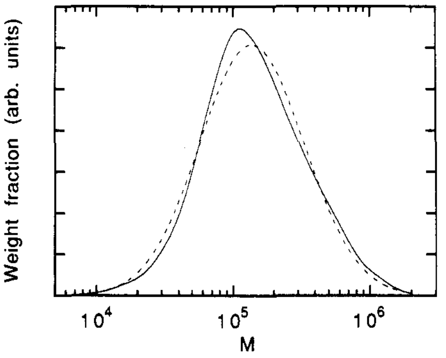

Figure 4. Molecular weight distribution of P3HT (sample E) as determined by GPC in THF using a polystyrene calibration given by the solid line. The dashed line shows a logarithmic normal distribution with M_w = 225 000 and M_w/M_n = 2.1 for comparison.

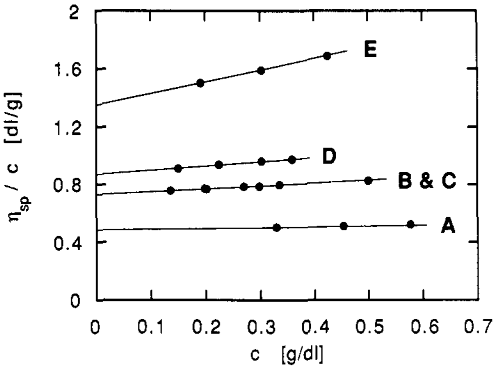

Figure 5. Dilute-solution viscosity results for P3HT (samples A–E) in THF plotted as η_{sp}/c as a function of concentration.

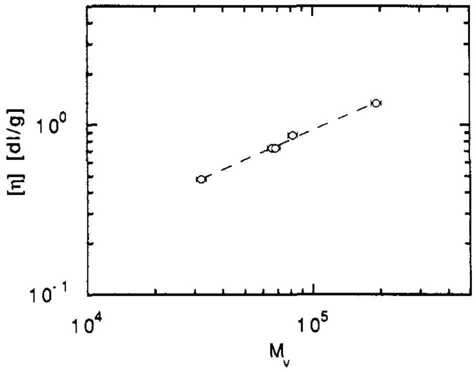

Figure 6. Intrinsic viscosity of P3HT in THF as a function of the viscosity-average molecular weight. The error bars represent the estimated uncertainties given in Table I. (The error in $[\eta]$ is less than the width of the circle.)

$$[\eta] = 1.2 \times 10^{-3} M_v^{0.58 \pm 0.05}\ \mathrm{dL/g} \tag{5}$$

The power law exponent is typically 0.5 for random-coil molecules in a Θ solvent and about 0.75 in a thermody-

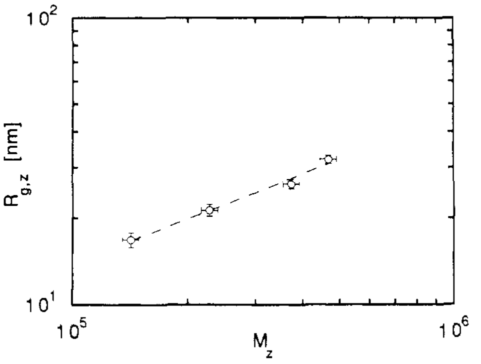

Figure 7. The *z*-average radius of gyration of P3HT in THF as a function of the *z*-average molecular weight. The error bars represent the estimated uncertainties given in Table I.

namically good solvent. The value of 0.58 that we obtain falls in between these two limits, suggesting that THF is what we will term a "moderately good" solvent for P3HT and certainly well above Θ-solvent conditions at which aggregation might occur. The uncertainty in the exponent was determined as ±0.05 based on a linear regression analysis of the data using the method of least squares and a 90% confidence interval.

The magnitude of the Huggins coefficient, k_H, is reasonable for a flexible polymer in a good solvent. This is a further indication that the P3HT exists as isolated molecules in solution, since aggregated molecules often exhibit a greater concentration dependence of the viscosity with $k_H \approx 1.0$.[14] An increasing trend in k_H as a function of molecular weight can be observed (Table I). This suggests a corresponding decrease in solvent quality, since k_H in a Θ solvent is typically larger, between 0.5 and 0.7.[15] Consequently, there may exist a molecular weight limit at which Θ conditions are encountered, and P3HT is no longer soluble at room temperature.

The molecular radius of gyration is also a power law function of the molecular weight, but once again polydispersity effects must be considered. The values of $R_{g,z}$ determined by light scattering are plotted versus the *z*-average molecular weight, M_z, as determined by GPC (Figure 7) to obtain the relation

$$R_{g,z} = 3.6 \times 10^{-2} M_z^{0.52 \pm 0.02}\ \mathrm{nm} \qquad (6)$$

This is an excellent approximation of the relation between R_g and M which would be obtained for monodisperse polymers, with the error in R_g introduced as a result of using the *z*-average values being less than 4% for each of the samples.[16] The power law exponent falls between the values of 0.5 observed for a Θ solvent and 0.6 for a thermodynamically good solvent, confirming our description of THF as a moderately good solvent. The Flory–Fox equation[17] states that $[\eta]M \propto R_g^3$ for a flexible polymer, which predicts an exponent of 0.53 for the molecular weight dependence of R_g from our viscosity data, in good agreement with the observed value.

The largest molecular weight P3HT sample (sample E) was chosen to be the subject of further study using both THF and chloroform as solvents. The objective was to compare the polymer dimensions obtained by three different characterization techniques and demonstrate coherency among the results. The results of this rigorous characterization are given in Table II.

The weight-average molecular weights of the P3HT determined in the different solvents were found to agree within experimental precision. The values of $R_{g,z}$ and A_2 were also similar in each case, suggesting that the solvent properties of THF and chloroform are similar for P3HT.

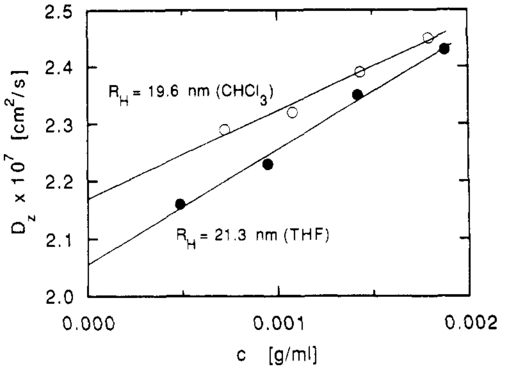

Figure 8. Diffusion coefficient of P3HT (sample E) as a function of concentration. Filled circles are data in THF; open circles are data in chloroform.

A viscosity-average radius of gyration, $R_{g,\eta}$, was calculated from the intrinsic viscosity by the Flory–Fox equation

$$[\eta] = 6^{3/2} \Phi R_{g,\eta}^{\ 3} / M_w \qquad (7)$$

in which $\Phi = 2.5 \times 10^{23}$.[18] This radius can be compared to $R_{g,z}$ from light scattering after correcting for the molecular weight distribution. On the basis of GPC results coupled with eq 5, the expected value of $R_{g,\eta}/R_{g,z}$ can be calculated as 0.63, in excellent agreement with the measured values.

The concentration dependence of the *z*-average diffusion coefficient determined by dynamic light scattering in dilute solution is given by

$$D_z = D_0(1 + k_D c) \qquad (8)$$

D_0 is the diffusion coefficient of a single polymer molecule in pure solvent, which was determined for sample E by extrapolation of the data as shown in Figure 8. The diffusion coefficient can be related to a hydrodynamic radius, R_H, by the Stokes–Einstein equation for hard spheres

$$D_0 = kT / 6\pi\eta_0 R_H \qquad (9)$$

where *k* is the Boltzmann constant and *T* is the temperature. The values of R_H are listed in Table II and are similar for each solvent. We find the ratio $R_{g,z}/R_H$ to be 1.5 in both solvents. This is the same value found experimentally[19] and theoretically[15] for monodisperse flexible polymers; one might expect the ratio $R_{g,z}/R_H = 1.7$ to be more applicable[20] due to the polydispersity of the P3HT, yet this is still in reasonable agreement with our experiments.

An upper limit of the value of k_D is that predicted for a good solvent[15,21]

$$k_D = 2A_2M - 1.66[\eta] \qquad (10)$$

which takes a value of about 300 mL/g according to our results, while k_D in a Θ solvent would be a negative quantity. The experimentally observed values (Table II) are positive but fall short of the good solvent limit, in agreement with our description of THF and chloroform as moderately good solvents for P3HT.

The second virial coefficient obtained by static light scattering is a measure of the polymer's excluded volume and may also be related to a molecular size by thermodynamic arguments. If the excluded volume of a macromolecule in a good solvent is taken as a hard sphere, then[18]

$$A_2 = 4N_a V / M_w^{\ 2} \qquad (11a)$$

where

$$V = 4\pi R_T^3/3 \tag{11b}$$

We find the thermodynamic radius, R_T, to be in reasonable agreement with R_H (see Table II), which is typical of flexible polymers in good solvents.[19] The fact that R_T is slightly less than R_H in each case is consistent with the fact that the excluded volume in a moderately good solvent should be less than that for a thermodynamically good one.

The rigidity of the P3HT macromolecule can be determined by an estimation of its persistence length. The Kratky–Porod model describes the polymer molecule as a Gaussian distribution of equivalent Kuhn segments[22]

$$R_g^2 = n_k a^2/6 \tag{12}$$

where a is the Kuhn segment length and n_k is the number of Kuhn segments, so that $L = n_k a$ is the contour length, which is proportional to the molecular weight. The persistence length, ρ, is defined as half the Kuhn length. A substitution of terms gives

$$\rho = 3R_g^2/L = 3R_g^2 M_0/l_0 M \tag{13}$$

in which M_0 is the monomer molecular weight and l_0 is the monomer repeat length, which is given by Aime et al.[23] as 0.39 nm for poly(3-butylthiophene)(P3BT) and should be the same for P3HT. Since R_g^2 is approximately proportional to M for P3HT in THF according to eq 6, the persistence length should be relatively insensitive to which moment of M and R_g is used to evaluate it, as long as equivalent moments are compared. If the z-average radius of gyration determined by light scattering is inserted into eq 12, the z-average molecular weight should also be used. The persistence length determined in this manner is $\rho_{LS} = 2.6 \pm 0.2$ nm, in good agreement among four different molecular weight samples (Table I). Alternatively, the persistence length can be determined from viscosity data if the Flory–Fox relation is used to determine the radius of gyration, which must be compared to the viscosity-average molecular weight. According to this method, $\rho_{[\eta]} = 2.2 \pm 0.2$ nm for the five samples, in reasonable agreement with that determined by light scattering. These values compare favorably with $\rho = 2.7$ nm as determined by Aime et al.[23] for P3BT in nitrobenzene using small-angle neutron scattering.

Thus, we observe a persistence length of 2.4 ± 0.3 nm, which corresponds to approximately six molecular repeat units. The P3HT molecules in our study are therefore comprised of 50–200 persistence lengths on average, which is in accord with our conclusion that P3HT assumes a flexible-coil conformation in solution.

Conclusion

Four dilute-solution characterization techniques have been utilized to create a coherent and consistent picture of the solution properties of poly(3-hexylthiophene) in tetrahydrofuran. To the best of our knowledge, this is the first time a conducting polymer has been the focus of a complete solution characterization study.

Our results indicate that P3HT exists as nonaggregated flexible-coil molecules in dilute solution. The molecular weight dependence of the intrinsic viscosity and the radius of gyration indicate that THF is a moderately good solvent for P3HT. The solution properties in chloroform appear to be very similar. The molecular weights determined by static light scattering were in the range $40\,000 \leq M_w \leq 220\,000$ and were in remarkable agreement with gel permeation chromatography measurements analyzed by using a polystyrene calibration. This is a fortunate result, since GPC is the most common technique by which the molecular weights of poly(3-alkylthiophenes) have been estimated in the past, and appears to be quite accurate over the range of molecular weights studied.

A comparison of the molecular dimensions as measured by static and dynamic light scattering and viscosity measurements in THF and chloroform follows the expected behavior of flexible-coil macromolecules. An analysis of the radii of gyration and the molecular weights by the Kratky–Porod method indicates a persistence length of 2.4 ± 0.3 nm for all five samples investigated, equivalent to six repeat units. Thus, the rigidity of P3HT is only 2–3 times that of common flexible polymers such as polystyrene and poly(methyl methacrylate), despite its ringed structure and conjugated backbone.

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