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Light Scattering from Solubilized Polyacetylene

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ABSTRACT: A solubilized form of polyacetylene (PA) has recently been created by grafting polyacetylene chains onto a polyisoprene carrier chain. The product of this grafting reaction is stable in toluene solution indefinitely. In the present paper static and dynamic light scattering is used to characterize the particles that exist in solution. Polyisoprene is nearly isorefractive in toluene so that nearly all the scattered intensity is due to the PA part. Also, the scattering from the polyacetylene is strongly resonance enhanced. This allowed PA concentrations near 10^{-7} g/mL to be studied. The excess depolarized (HV) Rayleigh scattering from the solutions is intense. This means that there is a high degree of orientation correlation between PA subunits in the particles. From the angular dependence of the scattered intensity a characteristic length for the polyacetylene part of the particles is calculated (350 Å). This is a lower bound for the radius of gyration for the PA subunits. Dynamic light scattering studies of the depolarized intensity allowed both the translational and rotational diffusion coefficient to be determined ($D_0 = 3.45 \times 10^{-8}$ cm^2/s) ($\Theta = 153$ s^{-1}). The overall shape was determined by solving the Perrin equations and gave a prolate ellipsoid with major axis $a = 1800$ Å and axial ratio $\rho = 0.4$. The present results suggest that the graft copolymer molecules form a micellar aggregate in solution. The polyacetylene subunits are highly ordered in the aggregate, but the degree of order has not yet been quantitatively determined.

1. Introduction

Polyacetylene was first synthesized in 1958 by Natta et al.[1] as an intractable black powder. In 1971 Shirakawa et al.[2] demonstrated that films of polyacetylene could be grown on the surface of a concentrated Ziegler–Natta catalyst solution. In 1978 it was demonstrated[3] that these films could be doped to obtain near-metallic conductivity. These films consist of a mat of insoluble polyacetylene fibers. Characterization of the individual molecules of polyacetylene is still not possible.

Bates and Baker[4] recently reported the first synthesis of a solubilized form of polyacetylene created by grafting the polyacetylene onto a polyisoprene carrier polymer. When the ratio of the polyacetylene molecular weight to the polyisoprene molecular weight was in the right range, the product of the grafting reaction was stable in solution indefinitely. The visible absorption spectrum of the solution was characteristic of *all-trans*-polyacetylene. However, the macroscopic state of the polyacetylene in solution was not determined. In the present work the state of the polyacetylene graft copolymer in toluene solution is examined by static and dynamic light scattering.

2. Theory

The classical theory of light scattering from polymer solutions is well-known.[5] The excess scattered intensity extrapolated to zero angle and zero concentration is proportional to the molecular weight of the polymer. The angular dependence of the scattered light at zero concentration yields the radius of gyration. For polyacetylene, the classical theory is not sufficient to understand the results. For most polymers there is no absorption of visible light so that the excess scattered intensity is simply proportional to the square of the refractive increment dn/dc, where n is the refractive index and c is the polymer concentration. In the case of polyacetylene (PA) visible light is strongly absorbed. This leads to intense scattering even at very dilute concentrations, but the magnitude of the excess polarizability associated with the polyacetylene molecules is not known. Also, at the point when the solution is dilute enough to measure a refractive increment at all there is so little polyacetylene present that a direct measurement of dn/dc is not possible. Since the polyacetylene examined in this work is in fact a block copolymer, the simple theory for homopolymers or random

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copolymers could not be used anyway. However, since the refractive increment for polyisoprene in toluene is very small, almost all the excess scattering does in fact originate in the polyacetylene part of the molecule. This result is propitious because the product of the grafting reaction is still primarily free polyisoprene chains. Only a small fraction (5%) of the carrier chains contain a PA block[4] (see accompanying paper).

For most polymers in dilute solution the excess depolarized (HV) light scattering is negligible. This means that anisotropic scattering can be ignored in the analysis of the polarized (VV) scattering. For PA this is not the case. The excess depolarized scattering (even in toluene) was very strong. The consequences of this result will be discussed in more detail below. The theory of light scattering by anisotropic molecules will be presented here. The intensity of scattered light from an independent assembly of molecules or aggregates in solution is proportional to

$$I(q) \propto \mathrm{Tr}\ \langle \sum_{i,j} \alpha_i \alpha_j \exp(i\vec{q}\cdot\vec{r}_{ij}) \rangle \tag{1}$$

where $q = (4\pi n/\lambda) \sin(\theta/2)$ is the magnitude of the scattering vector $\vec{q}$ for light of vacuum wavelength λ traveling in a medium of refractive index n scattered through an angle θ in the scattering plane, α_i is the excess polarizability tensor associated with the ith subunit of the molecule or aggregate, $\vec{r}_{ij}$ is the vector from unit i to unit j, Tr denotes the trace of the tensor, the brackets denote an ensemble average, and the sum is over all pairs of units.

The polarizability tensor can be separated into a mean scalar part $\bar{\alpha} = (1/3)\ \mathrm{Tr}\ \alpha$ and a symmetric traceless part called the anisotropy tensor $\hat{\alpha} = \alpha - \bar{\alpha}E_3$, where E_3 is the unit tensor. Consider first the scattering due to the mean scalar part. If all the units are identical, the angular (q) dependence of the intensity is entirely determined by the sum over the phases of the constituent subunits. If the exponential is expanded to lowest order in q, the familiar result is obtained

$$I(q) \propto 1 - q^2\langle s^2 \rangle/3 \tag{2}$$

where $\langle s^2 \rangle$ is the mean-squared radius of gyration. The intensity due to optical anisotropy depends on both the correlation in orientation between subunits and the vector distance between them. The correlation in orientation between subunits i and j often becomes negligible long before the distance between the units becomes large enough to affect the phase factor. As a result an angular dependence might not be expected for the depolarized scattering. However, if there is long-range correlation in orientation between the subunits such as in a rod, it is possible to see an angular dependence to the anisotropic intensity. If all the units were identical and if the correlation in orientation extended over the entire molecule or aggregate, then the angular dependence would again be determined entirely by the sum over the phase factors and eq 2 would be obtained. If there were only a finite persistence length to the correlation in orientation, then the correlation length instead of the radius of gyration would determine the angular dependence. The detailed theory of light scattering by chain molecules composed of anisotropic units has been presented,[6,7] but the results are exceedingly complicated.

Another consequence of the correlation in orientation between subunits is the large depolarized intensity relative to the scattering due to the excess scalar polarizability. The intensity of the scalar part depends on $\bar{\alpha}^2$ and hence on the number of subunits squared N^2. If the subunits are oriented randomly or if there is only short-range order, the depolarized intensity will only increase as N. This explains why there is negligible excess depolarized scattering from a dilute solution of a random coil polymer relative to the polarized scattering. With a highly oriented system the depolarized scattering also scales as N^2 and becomes comparable in magnitude to the scalar part. In solubilized PA the anisotropic scattering is even larger than the part due to scalar polarizability.

The theory of dynamic light scattering from particles in solution is also now well-known.[8] In the limit of infinite dilution and small q the relaxation function for the scattering is given by

$$\phi(t) = \exp(-D_0 q^2 t) \tag{3}$$

where $D_0 = k_B T/6\pi\eta R_h$ is the self-diffusion coefficient for the particles, k_B is Boltzmann's constant, T is the absolute temperature, η is the viscosity of the solvent, and R_h is the hydrodynamic radius of the particle. Again, this theory assumes that the scattering is all due to the mean scalar part of the polarizability tensor for the particle. If there is significant anisotropic scattering, the observed relaxation function for the VV scattering will also include a contribution from this source. Since the quantity that is observed in homodyne light scattering is the square of the relaxation function, analysis of the polarized scattering can become very complicated. The relaxation function for depolarized scattering by independent particles is

$$\phi(t) = \exp(-(D_0 q^2 + 6\Theta)t) \tag{4}$$

where $\Theta = k_B T/6\eta V_h$ is the rotational diffusion coefficient and V_h is the hydrodynamic volume of the particle. Both the translational self-diffusion coefficient and the rotational diffusion coefficient can be obtained by measuring the depolarized relaxation function as a function of angle (q).

It is important to note that while almost all the intensity is due to the PA part of the block copolymer, the hydrodynamics are determined by the entire entity. If the sedimentation coefficient could also be determined, the molecular weight could be determined for the whole entity. However, the partial specific volume of the copolymer is not yet known because the product of the reaction is not just pure copolymer and the large excess of homopolymer has not been successfully separated.

If both the translational and rotational diffusion coefficients are known, the general shape of the particle can in principle be determined.[9,10] If the particle is represented by an ellipsoid of revolution with major axis a and axial ratio $\rho = b/a$, then the translational diffusion coefficient is given by

$$D_0 = \frac{k_B T}{6\pi\eta a} G(\rho) \tag{5}$$

and the rotational diffusion is given by

$$\Theta = \frac{3k_B T}{16\pi\eta a^3}\left(\frac{(2-\rho^2)G(\rho) - 1}{1-\rho^4}\right) \tag{6}$$

where the function $G(\rho)$ is given by

$$G(\rho) = \frac{\ln\left(\dfrac{1 + (1-\rho^2)^{1/2}}{\rho}\right)}{(1-\rho^2)^{1/2}} \tag{7}$$

for the prolate ($\rho < 1$) case and

$$G(\rho) = \frac{\tan^{-1}(\rho^2 - 1)^{1/2}}{(\rho^2 - 1)^{1/2}} \tag{8}$$

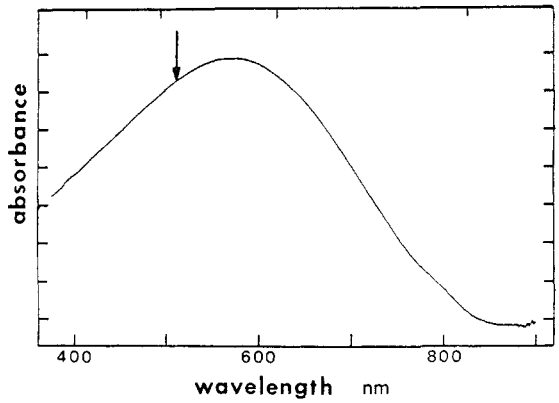

Figure 1. Visible absorption spectrum of solubilized polyacetylene in toluene. The arrow indicates the incident wavelength used in the light scattering experiments (5145 Å).

for the oblate ($\rho > 1$) case. The two equations can then be solved simultaneously for a and ρ.

3. Experimental Section

Polyisoprene (85% cis, 15% trans, 5% vinyl-3,4) was prepared by standard anionic polymerization techniques.[11] The carrier polyisoprene was subsequently treated with *m*-chloroperbenzoic acid in benzene so that approximately 2% of the repeat units were epoxidized. A solution containing epoxidized polyisoprene (100 g/L), $Ti(OC_4H_9)_4$ (6×10^{-3} M), and acetylene ($\approx$1 g/L) was prepared in toluene under purified argon at 25 °C. Triethylaluminum ($\approx 9 \times 10^{-3}$ M) was added dropwise with vigorous stirring. The reaction mixture turned dark purple and continued to deepen in color over a 15-min period. The reaction was quenched with a methanol/acetic acid solution. For further details see the accompanying paper. A visible absorption spectrum of the reaction mixture diluted with toluene is presented in Figure 1.

The quenched reaction mixture was stored under a purified helium atmosphere until use. An aliquot was removed and diluted in toluene until only a slight purple color was visible. The approximate concentration of the PA based on visible spectroscopy data was 10^{-7} g/mL. This meant that the polyisoprene concentration was less than 10^{-5} g/mL so that the total solution was dilute in all species. The light scattering from the polyisoprene was negligible compared to that from the PA, and the solution was dilute enough that the hydrodynamics were dominated by the pure solvent viscosity. The solution was filtered through a 0.45-μm membrane filter directly into the cylindrical scattering cells. Polyacetylene degrades in air, but the capped cells gave identical results over times of several hours. Further dilutions were also studied but the results were identical. This assured as that the measured diffusion coefficients reflected only single-particle properties.

The incident light was at 5145 Å and was polarized either vertically (V) or horizontally (H) with respect to the scattering plane. The scattering light was studied as a function of angle and for the dynamic light scattering a polarizer was introduced to yield the HV scattering. The total intensity was studied without a polarizer in the scattered beam. The light scattering goniometer was a Brookhaven Instruments Model 240M. Angles as low as 10° could be routinely studied with this instrument. The scattered intensity for pure toluene accurately followed the expected $1/(\sin\theta)$ dependence of the scattering volume over the entire range. All measurements were carried out at 20 ± 0.2 °C. The absolute Rayleigh ratio for toluene under our conditions was measured to be 2.8×10^{-5} cm^{-1}. Excess intensities were then determined relative to the toluene solvent.

Dynamic light scattering was studied with a 96-channel Malvern correlator. The single-clipped intensity autocorrelation function was obtained. The relaxation function for the fluctuations is then obtained according to

$$C_k(t) = 1 + A\phi^2(t) \tag{9}$$

where A depends on the coherence area of the scattering, the sample time, and the clipping level. All these factors are known for our system and absolute values for $\phi^2(t)$ were obtained. A typical result is shown in Figure 2. The relaxation function was not a pure single-exponential decay, but the average decay rate could be reliably obtained by the method of cumulants.[12]

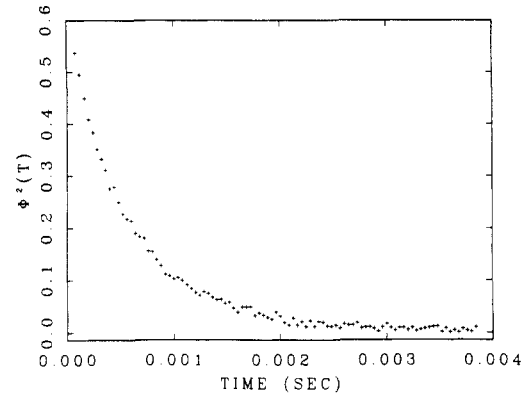

Figure 2. Typical light scattering relaxation function $\phi^2(t)$ observed for the depolarized (HV) intensity from solubilized polyacetylene in toluene at 20 °C. The scattering angle was 30°.

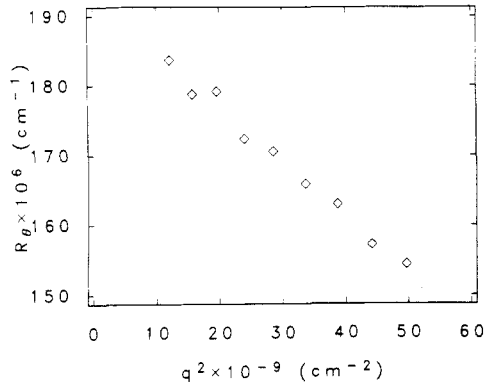

Figure 3. Excess Rayleigh ratio R_θ for solubilized polyacetylene in toluene plotted against q^2. The angular dependence leads to a characteristic length of 350 Å. This is a lower bound for the radius of gyration for the PA part of the particle.

4. Results and Discussion

The pure carrier polymer was studied first. In order to see the polymer more easily the polyisoprene was studied first in cyclohexane where the refractive increment was larger. The molecular weight was measured to be 1.8×10^5. The carrier polymer was too small to determine a radius of gyration directly from the angular dependence of the excess intensity. The self-diffusion coefficient of polyisoprene in cyclohexane was measured to be $D_0 = 1.4 \times 10^{-7}$ cm^2/s. The hydrodynamic radius was then calculated to be 160 Å. Although solvent quality does influence the hydrodynamic radius to some degree, it should not change very much. The dynamic light scattering of polyisoprene in toluene was also studied because the refractive increment is small but not actually zero. It required several hours to obtain a decent relaxation function. The hydrodynamic radius was observed to be the same as in cyclohexane. The diffusion coefficient differed only by the ratio of the viscosities of the two solvents.

Initial studies of the reaction mixture were carried out with vertically polarized incident light and no polarizer in the scattered beam. The excess intensity is converted to an absolute Rayleigh ratio and plotted against q^2 in Figure 3. From the linear dependence of the Rayleigh ratio on q^2 a characteristic length of 350 ± 70 Å was deduced. This is substantially larger than that for the carrier polymer,

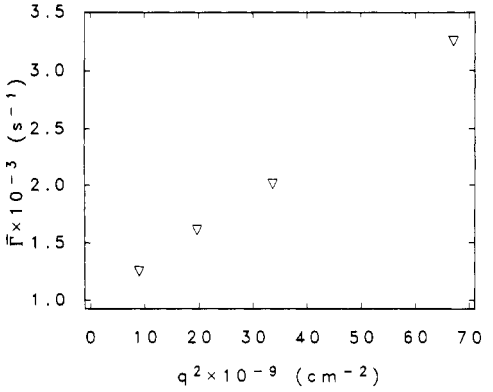

Figure 4. Average decay rate $\bar{\Gamma}$ for the depolarized (HV) Rayleigh scattering from solubilzed polyacetylene in toluene plotted against q^2. The slope yields the translational self-diffusion coefficient ($D_0 = 3.45 \times 10^{-8}$ cm^2/s) and the intercept is equal to 6 times the rotational diffusion coefficient ($\Theta = 153$ s^{-1}).

but as we will see below, it may not fully reflect the geometric size of the PA part of the particle.

Initial studies of the dynamic light scattering under the same conditions revealed a large change in the shape of the relaxation function with angle. At low q the long-time part of the decay changed as q^2, but the first cumulant became nearly independent of angle. This suggested that depolarized scattering was important. The VV relaxation function is a sum of the relaxation function due to the scalar part, which decays as D_0q^2, and the relaxation function due to the anisotropic part, which decays as $D_0q^2 + 6\Theta$. The first cumulant yields the average decay constant which is dominated by the 6Θ part, while the long-time decay is dominated by the D_0q^2 part. The HV relaxation function was easily measurable for the PA polymer. The large excess depolarized scattering is very unusual and suggests strongly that there is substantial orientation correlation between the PA subunits in the particle. The depolarized (HV) relaxation function did not change shape with angle and the second cumulant remained small. The average decay rate $\bar{\Gamma}$ is plotted against q^2 in Figure 4. The results behave as expected from eq 4. The translational self-diffusion coefficient is calculated to be 3.45×10^{-8} cm^2/s. The hydrodynamic radius of the particle is calculated to be 1050 ± 200 Å. This is very much larger than the carrier polymer and much larger than the characteristic length deduced from the angular dependence of the intensity. For a dense sphere the hydrodynamic radius is 50% larger than the radius of gyration, and the hydrodynamic radius is for the whole particle, including the carrier polymer. Even so, it must be concluded that 350 Å is only a persistence length for the correlation in orientation of the PA subunits in the particle. The rotational diffusion coefficient is calculated to be $\Theta = 153 \pm 20$ s^{-1}. The hydrodynamic volume is calculated to be 7.5×10^9 Å.[3] The radius of the equivalent sphere based on this volume is 1200 Å, which is within experimental error of the hydrodynamic radius. If we assume that the particle can be represented as an ellipsoid of revolution with major axis a and minor axis b, then the Perrin[9,10] equations can be used to estimate the axial ratio $\rho = b/a$. The present values for D_0 and Θ yield $a = 1800$ Å and $\rho = 0.4$. The oblate solution does not give a reasonable value for a. The limits of uncertainty on ρ are large (20%), but it is reasonable to conclude that the particles are prolate in shape with approximately a 1:2 axial ratio. In any case the average size of the particles giving rise to the light scattering is very much larger than any single graft copolymer molecule. This suggests that the molecules aggregate in solution to form a micellar particle with an average radius near 1050 Å. Within the aggregate there must be a high degree of orientation correlation between neighboring PA subunits.

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Dynamic Light Scattering of Polymer Solutions. 4. Semidilute Solutions of Polystyrenes and Their Binary Blends in Benzene

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ABSTRACT: Dynamic light scattering (DLS) measurements have been made on solutions of polystyrenes and their binary blends in benzene in the semidilute concentration range. The cooperative diffusion coefficient D_{coop} estimated from the gel mode has been shown to be independent of molecular weight M for homogeneous solutions as well as M of components for blends. The hydrodynamic screening length (or the blob size), ξ_H, has been found to be in proportion to the radius ξ_e of the tube formed by entanglements. The magnitude of ξ_e has been found to be about 5 times larger than ξ_H. The slow mode has been found for a solution of the binary blend of component polymers with $M = 42\,800$ and 775 000. Forced Rayleigh scattering measurements on a binary blend with about the same concentrations and molecular weights have shown that D_{slow} estimated from the slow mode observed by DLS does not represent the self-diffusion of the lower molecular weight component of the blend.

Introduction

Scaling theory based on the blob and the reptation models[1] has given a new guide for studying equilibrium as well as nonequilibrium properties of polymer solutions in the range of polymer concentration which is higher than the critical overlapping concentration c^*. According to the

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