Intersegmental Interaction and Critical Concentrations in PET–HFIP Solutions

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SYNOPSIS

Spectroscopic determinations of the concentrations associated with the onset of intermolecular interaction in solutions of poly(ethylene terephthalate) (PET) are described. The intersegment forces perturb the electronic spectra and induce ground-state aggregation. These phenomena become observable at different chain densities, reflecting the influence of concentration on the coil dimensions, as well as the dynamical nature of the interactions. An estimate of the equilibrium constant for PET dimer formation in hexafluoroisopropanol is reported.

INTRODUCTION

Polymer chain segments may interact either with units on the same chain or segments on other chains. In good solvents at very dilute concentrations, the segment density is discontinuous and nonuniform: neither interchain nor intrachain interactions are very probable because the segment density is low.[1] As the concentration of polymer increases, segment–segment interaction becomes more probable; however, polymer self-avoidance, resulting in a decreased radius of gyration, will promote intrachain contacts while interchain interactions remain low. At some concentration (denoted c^*), increasing the polymer content will result in significant coil overlap and interchain contacts; the segment density becomes continuous but still nonuniform. At a sufficiently high concentration (denoted c^+) solutions acquire a roughly uniform segment density. In such concentrated polymer solutions interchain interactions dominate, since polymer additional to the chain overlap concentration must necessarily pack into space already occupied by other chains. Because the rheological properties of polymer solutions depend critically on the nature and number of segment interactions, the determination of chain overlap concentrations and the occurrence of any polymer aggregation in solution has been the focus of experimental and theoretical investigations.[2-4]

In this report, two independent determinations, the concentration dependence of the red shift of poly(ethylene terephthalate) (PET) fluorescence and the formation of PET ground-state aggregates (dimers), have been used to identify transitions from dilute to semidilute to concentrated regimes in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) solutions. The experimentally obtained values of c^* for two molecular weights of PET are compared with those calculated from estimates of the chain coil size. The discrepancy between these determinations is discussed.

EXPERIMENTAL

Additive-free PET (amorphous pellets, intrinsic viscosity 0.94 dL/g, from Allied Signal Inc. and semicrystalline Cleartuf 5901, I.V. = 0.54 dL/g, from Goodyear Tire and Rubber Co.) was used as received. HFIP (99+%, 1,1,1,3,3,3-hexafluoro-2-propanol from Aldrich) was employed as the solvent. The HFIP exhibits no absorption above 225 nm, and no fluorescence emission over any of the excitation wavelengths utilized in this study. All concentrations expressed herein are based on the PET repeat unit ("monomer").

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Fluorescence spectra were taken with a Spex Fluorolog 212 spectrofluorimeter using a 450 W, high-pressure xenon lamp. Fluorescence measurements were made observing front face emission with slit widths constant at 0.35 mm. After a 30-min warm-up, lamp jitter was less than 5% and low frequency intensity fluctuations were negligible. Concentration effects on the PET excitation spectra were assessed by comparing the wavelengths at half-intensity from the lowest energy edge (LEHH) for each spectrum.

Concentrations were varied by addition of a measured weight of a concentrated PET in HFIP solution to one of lower concentration after the spectrum of the latter had been obtained. Solutions were allowed to equilibrate for 20 minutes. Longer equilibration times did not quantitatively affect results, consistent with the observations of others.[5] Samples were not routinely deaerated, since even the most concentrated solutions at the lowest temperatures showed negligible oxygen quenching, as a consequence of the very short fluorescence lifetimes (ca. 10^{-9} s) of both the monomer and dimer entities.[6]

RESULTS AND DISCUSSION

Measurements of the crossover from dilute to semidilute (c^*) concentration have been undertaken by a variety of methods. Correlation spectroscopy has been utilized to measure the concentration and temperature dependence of polystyrene diffusion in hexane.[2] A minimum in the diffusion constant occurs at a concentration identified with c^*. In another study, the radius of gyration of deuterated polystyrene in CS_2 was monitored as a function of concentration.[7] While a discontinuity in the slope was observed, the authors noted the c^* and its dependence on coil size cannot be determined accurately either by experiment or theory. Excimer fluorescence has also been used to probe chain overlap. The growth of polystyrene excimer emission in a good solvent (1,2-dichloroethane) was monitored as a function of concentration.[8] Discontinuities in the ratio of excimer intensity and monomer intensity as a function of polymer concentration identified not only the dilute to semidilute crossover (c^*), but also the semidilute to concentrated solution transition (c^+).

We have described the formation of ground-state aggregates (dimers), previously observed in PET films,[6,9-11] in solutions of PET in HFIP.[12] The formation of the aggregates is primarily a result of interchain contacts, while their dissociation is promoted by heating of the solutions. In these experiments, dimer emission was associated with polymer concentrations sufficient for chain overlap as calculated from the radius of gyration R_G.[13]

In Figure 1 are fluorescence excitation and emis-

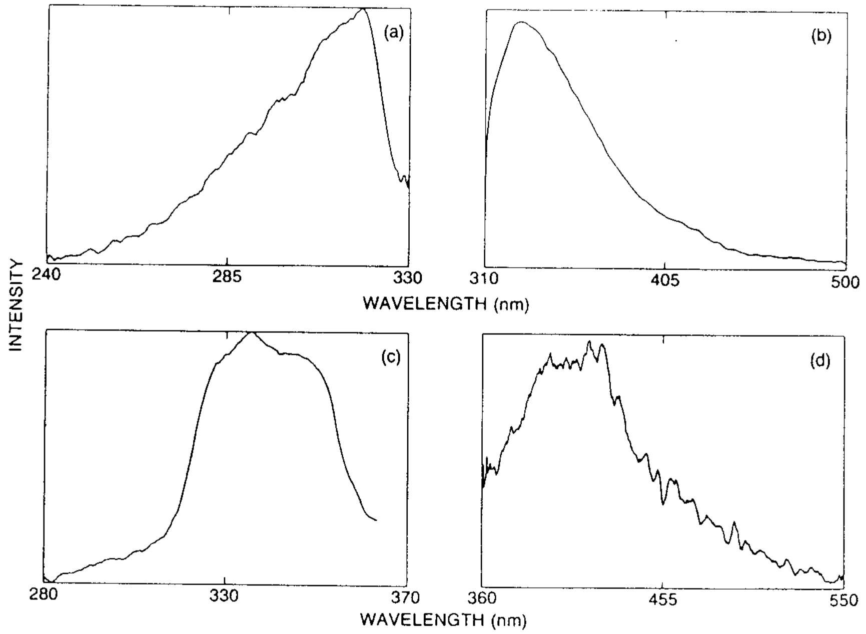

Figure 1. Excitation and emission spectra of 0.3 M PET in HFIP (a) monomer excitation λ_{emiss} = 340 nm; (b) monomer emission λ_{excit} = 300 nm; (c) dimer excitation λ_{emiss} = 390 nm; (d) dimer emission λ_{excit} = 340 nm.

sion spectra from the isolated PET lumophore (monomer) and from the dimer. The absorption that results in the dimer excitation appears as a tail to the main PET absorption, extending to ca. 390 nm. The exact location of the low-energy absorption of PET is not well defined owing to a concentration dependence of the absorption band. This concentration dependence is discernible in the absorption spectra, but is seen more clearly in measurements of the monomer fluorescence excitation spectrum.

As displayed in Figure 2, as the concentration of dissolved PET increases, the excitation spectrum shifts to longer wavelength. The concentration dependence of this red shift is depicted in Figure 3 for PET of two molecular weights. Note that for both molecular weights, at very low concentrations ($< 10^{-4}$ M in monomer) there is only a slight variation in the red shift of the PET excitation spectrum. At PET concentrations greater than 0.1 M, for both molecular weights, there is again only a modest dependence of the red shift on concentration. Between these two extremes, however, a strong dependence of the red shift of PET excitation of polymer concentration is observed. This marked concentration dependence of the wavelength of excitation is attained with the higher molecular weight PET at ca. 2×10^{-4} M, and at about 1×10^{-3} M for the lower molecular weight polymer.

These phenomena are a consequence of the excluded volume; the radius of gyration decreases due to repulsive interactions between polymer segments.

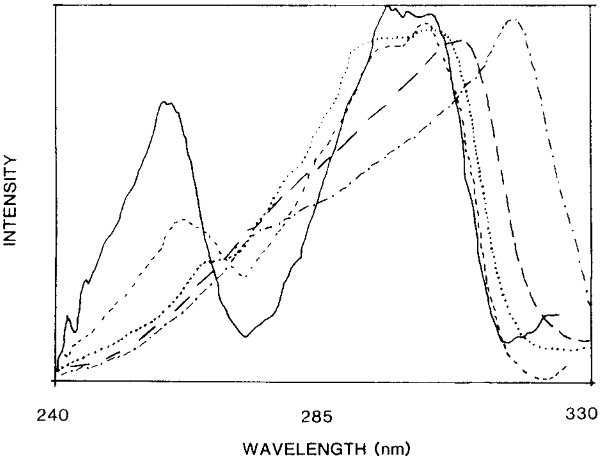

Figure 2. Fluorescence excitation spectra of PET (IV = 1.04 dL/g) in HFIP at various concentrations (— 2.5×10^{-5}M, --- 2×10^{-4}M, – – – 8×10^{-4}M, ····· 2.5×10^{-3}M, -·-·-· 9.2×10^{-2}M). The red shifting of the spectrum with concentration is less pronounced at higher concentrations, and ceases completely when theta conditions prevail.

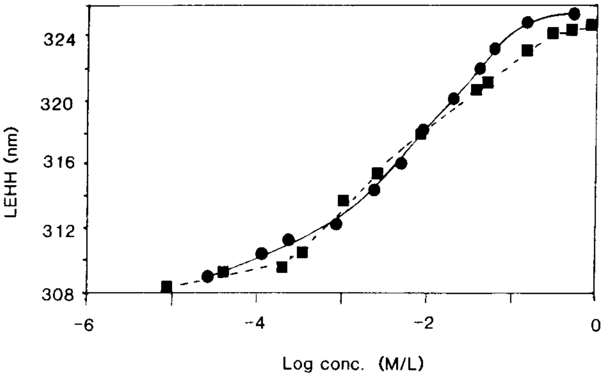

Figure 3. LEHH of PET (●●●● IV = .54, ■■■■ IV = .94) in HFIP vs. logarithmic concentration in units of mol/L by monomer. The error in the measured LEHH is about 5 Å.

As a chain begins to see more polymer and less solvent (but prior to interchain overlap), it contracts due to self-avoidance among chain segments.[7,8] Such a change in environment probably underlies the observed red shift of PET excitation. In corroboration, a red-shifting of PET fluorescence excitation similar to that in Figure 2 was induced by the addition of acetone or $CHCl_3$ to dilute solutions of PET in HFIP. These poorer solvents cause a contraction of the chain coil.

In the dilute solution regime, polymer chains act as individual units; their dimensions simply reflect the swelling power of the solvent. The present fluorescence measurements exhibit no evidence of a concentration regime in which the emitting terephthalate moieties behave independently of one another, although the interaction is not strong at concentrations below 10^{-4} M.

In the second concentration regime, a strong molecular weight dependence becomes apparent. This occurs at concentrations lower than those associated with the semidilute transition. It has been suggested that this corresponds to concentrations for which the solution volume has become fully occupied by nonoverlapping chains. The high occupancy promotes transient interchain contacts, although chain overlap per se may be negligible.[8,14,15] This occurs at a concentration of roughly 10^{-3} M in monomer in good solvents, although the particular concentration will be to some degree a function of the measuring technique (vide infra).

At a sufficiently high concentration, the red shift of the low energy absorption approaches that of neat, amorphous PET. This concentration c^+ is approximately 1 M for both molecular weights and is close to the c^+ reported for polystyrene.[8] An absence of any molecular weight dependence in the attainment of the concentrated solution regime was also seen in solutions of polystyrene in dichloroethane,[8] and has been theoretically justified on the basis of the screening principle.[16]

As mentioned, the existence of ground-state aggregates (dimers) in neat PET is well documented.[6,9–11] These dimers also have been observed in solutions of PET in HFIP.[12] Figure 4 shows the concentration dependence of PET (IV = 0.94) monomer and dimer emission spectra at room temperature. Also shown is the correction function applied to the integration of monomer emission intensities necessary because of the shifting of the absorption spectrum with PET concentration described previously. In Figure 4 it is seen that the integrated emission intensity from the monomeric lumophore is strongly and negatively correlated with the growth of dimer emission. The nonzero concentration intercept for dimer emission is evidence that interchain overlap is responsible for the formation of the dimers. The concentration at which dimer emission appears is thus directly related to c*, with a value of approximately 0.003 M PET deduced from the present results.

The discrepancy between this value for c* and those above inferred from the spectral red shifting arises from complicating factors within the experiments. As pointed out above, the sensitivity of a method to the relevant chain dynamics will affect the value determined for the critical concentrations. Fluorescence techniques, which depend on intermolecular complexes such as dimer or excimer/exciplex species, will give lower values of c* than unimolecular probes or rheological determinations. This is due to the ability of fluorophores in solution to radiatively[4] or nonradiatively[6] transfer their excitation to acceptors, which upon formation of a trapping complex (such as dimers or excimers), will radiate at the detection frequency.[17,18] This energy migration results in a higher probability that the exciting photon will find the species identifying the chain overlap concentration. In contrast to intermolecular complexes, unimolecular probes (such as the red shift of an electronic absorption) will be less likely at low concentration to sense a segment–segment contact since many sties cannot be sampled. Accordingly, unimolecular probes should provide higher determinations of c*, consistent with the present experiments.

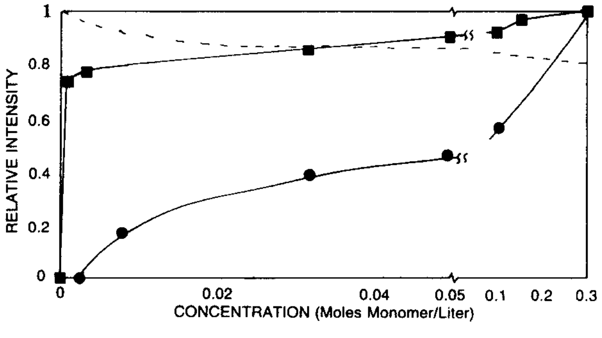

Figure 4. Concentration dependence of monomer (■■■■) and dimer (●●●●) integrated emission intensities. Values in each series are normalized to the solution of highest fluorescence intensity. Monomer spectra are corrected for the slight change in fluorescence excitation spectrum as a function of concentration in this range. The concentration-dependent correction factor is given by the dashed line.

Rheological properties generally reflect molecular events occurring on longer time scales, or the consequence of such events averaged over the observation time. Furthermore, the physical phenomena associated with rheological determinations of c* likely involve chain entanglements[19] (i.e., topological constraints to motion transverse to the chain), not simply the chain overlap detected herein. Rheological determinations should therefore indicate chain overlap at higher concentrations than spectroscopic probes of the microenvironment. It appears that the assignment of critical concentrations as markers of rheologically observed phenomena are perhaps misleading. The solution characteristics are more a reflection of the balance between segmental interactions and free-volume limitations.

Such considerations make quantitative discussion of Figure 4 difficult. It has been shown that PET is capable of exhibiting energy migration in films and solutions,[6,12] so that the intensities reported in Figure 4 are weighted by the probability of such migration. The complications incurred in steady-state fluorescence experiments when energy migration is possible are made apparent from a simple accounting of the sources of the fluorescent intensity for monomers and dimers. Ignoring constants associated with lamp intensity,[20,21] for the monomers

$$I_m = \epsilon_m c_m \varphi_m - 2/\pi^{1/2} \epsilon_m c_m \varphi_m c_d \exp\{-c_d^2\} \times (1 - 2/\pi \int_0^{cd} \exp\{-x^2\}\, dx) \quad (1)$$

and for the dimers

$$I_d = \epsilon_d c_d \varphi_d \quad (2)$$

where *I* represents the observed fluorescence intensity, ϵ is the absorptivity, φ is the quantum yield for fluorescence, and c_m and c_d are the respective monomer and dimer concentrations. Implicit herein is the assumption that, while the excitation of dimers without concomitant excitation of monomers can occur, thus resulting in a Beer's law type expression [eq. (2)], the overlap of PET emission with that of dimer absorption precludes the converse. Assuming that $c_d/(c_d + c_m)$ is less than 0.1 (an upper limit based on relative absorption measurements and fluorescence lifetimes), the ratio of dimer to monomer emission intensity is given by eq. (3) (ignoring numerical constants),

$$I_d/I_m \propto \epsilon_d c_d \varphi_d / \epsilon_m c_m \varphi_m (1 - c_d) \qquad (3)$$

From the equilibrium expression for the formation of dimers from monomers (assuming that dimers are the only complex formed), c_d can be replaced with Kc_m^2, (where K is the equilibrium constant) yielding

$$I_d/I_m \propto \epsilon_d c_d K[c_m] / \epsilon_m c_m (1 - Kc_m^2) \qquad (4)$$

It is seen that the ratio of dimer intensity to that of the monomer will depend on the concentration of monomer present (a known quantity) and the equilibrium constant (an unknown). The equilibrium constant for dimer formation may be concentration dependent, as might both the quantum yield for fluorescence and the molar absorptivity, since these are both related to the coil size, which in turn depends directly on polymer concentration. Despite these uncertainties, direct application of the model with only the value of K as an adjustable parameter can be made to the experimental data, provided $Kc_m^2 > 1$. From Figure 5, an apparent value of 10^4 is obtained for K. This is probably an overestimate, the error arising from the assumed constancy of the radius of gyration. Extending the model to consider trimer formation does not as accurately account for the data. In any case, given the uncertainties of the model, the experimental results can only be considered to be consistent with, but not substantiation of, the dimer model.

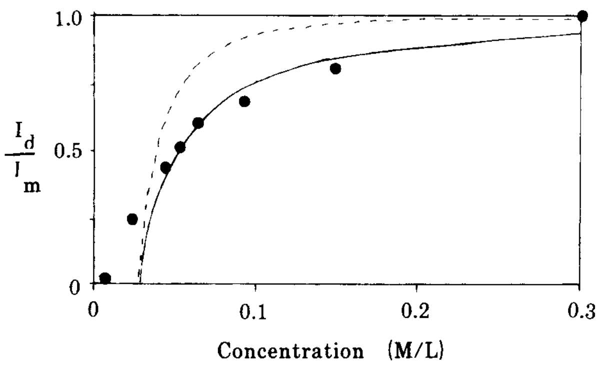

Figure 5. Experimentally determined ratio of dimer to monomer fluorescence emission (●●●) intensity compared with that predicted by a model for dimer formation (——) using K = 10^4 and trimer formation (- - -) using K = 10^6. The calculated intensities have been normalized to the value at the abscissa intercept, and the experimental intensities are normalized to the I_d/I_m at 0.3 M.

CONCLUSIONS

Experimental observations reveal the concentration dependence of PET intersegmental interactions. Different measures of critical concentrations are obtained from the two spectroscopic means employed herein. Ground-state aggregates, serving as traps for electronic energy transfer, are sensitive probes of chain overlap since the probability of their fluorescence emission is enhanced by the large number of sites sampled by each excitation. The observed red shift of PET absorption and fluorescence excitation spectra with increasing concentration is believed to be the result of stabilization of the PET ground electronic state (relative to the first excited state) with increasing concentration. Such mean-field couplings are sensitive to the changing radius of gyration and suggest the presence of two critical concentrations: first, a chain density at which the coil begins to contract due to intersegmental repulsion, and second, a concentration at which the macromolecule assumes theta dimensions, becoming invariant. Spectroscopic measurements of critical concentrations do not provide unique determinations, and must be interpreted with regard to their sensitivity to the polymer coil dimensions.

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