Ultraviolet Absorbance of Dilute and Semidilute Polymer Solutions

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ABSTRACT: Far-ultraviolet absorption spectra of poly(oxyethylene) in water and of poly(vinyl acetate) in acetonitrile have been obtained by using two spectrophotometers and cells of two different path lengths. In contradiction with previous reports, the crossover between dilute and semidilute solution behavior is not detected from absorbance changes. Apparent deviations from the Beer-Lambert law found under some conditions in the relevant concentration range are shown to be due to instrument artifacts.

Introduction

Polymer solutions exhibit different physical properties in the dilute concentration range, where, on the average, polymer chains are separated by large expanses of solvent, and in the so-called semidilute range, where chains are in sufficient concentration that intermolecular interactions cause long-range correlations to be screened out. In particular, dependences of properties on chain length that prevail in dilute solution are altered, or may even disappear, in the semidilute regime. A distinction between dilute and semidilute solution behavior has long been recognized[1,2] (though expressed in different terms); but during the past decade the school of theoreticians at the Collêge de France have aroused new interest in this area by applying the concepts of scaling theory.[3] The power law dependences they have derived are asymptotic relations for very long chains in good-solvent systems and differ in some ways from predictions of familiar mean-field treatments, such as the Flory-Huggins theory.[2]

We are concerned here with the chain-length dependence of the crossover concentration, denoted C^* (weight/volume), between dilute and semidilute regimes in polymer solutions, for which the scaling law is

$$C^* \sim \text{const} \times M^{-4/5} \qquad (1)$$

where M denotes the molecular weight of the polymer. Studies of the crossover phenomenon have been made by a number of experimental techniques, including osmometry,[4] neutron and light scattering,[4,5] viscometry,[6] sedimentation velocity,[7] and ultraviolet absorption spectroscopy,[8] and some data[7,8] have been interpreted as supportive of eq 1. Since in all but the last case there is a primary dependence of a measured property on chain length at fixed concentration in the dilute regime and a different dependence or none in the semidilute regime, these methods might be conjectured to afford relatively unambiguous means of assessing C^*. On the other hand, to the approximation of independent chromophores, light absorption is related only to the concentration of chromophores and not to molecular weight; hence detection of C^* by ultraviolet absorption spectroscopy would a priori be expected to depend on secondary effects and thus be problematical. In physical terms, the absorbance is presumably sensitive to local interactions of much shorter range than the characteristic screening distance at the crossover concentration.

These expectations notwithstanding, the absorption spectral data of Destor, Langevin, and Rondelez[8] for poly(oxyethylene) in water and poly(vinyl acetate) in acetonitrile appear to manifest clearly a crossover effect in good agreement with eq 1. However, their measurements, utilizing far-ultraviolet bands, are technically so difficult as to challenge the capabilities of the best instrumentation. Furthermore, there is the difficulty that the crossover does not represent a discontinuity in a physical property, but rather an intersection of two asymptotic dependences. For these reasons we have attempted to confirm the findings of Destor et al.[8] by absorption spectral measurements on the same systems, though not the same samples. Our failure to do so, as detailed in the following discussion, leads us to conclude that experimental artifacts, rather than the dilute-semidilute crossover, are reflected in their data. We have also obtained some data on polystyrene in chloroform, a system for which Destor et al.[8] found no evidence of a crossover from ultraviolet absorption.

Experimental Section

Poly(oxyethylene) (POE) samples with $M = 1 \times 10^5$, 3×10^5, and 6×10^5 were purchased from Aldrich Chemical Co. Methoxypoly(ethylene glycol), $M = 5000$, was obtained from Union Carbide Corp. Narrow-distribution polystryenes (PS), M(light scattering) = 5.10×10^4, 4.11×10^5 and 1.20×10^6, were obtained from Pressure Chemical Co. All these molecular weights were provided by the respective suppliers. For the PS samples they are results from detailed characterization.

Poly(vinyl acetate) (PVAc) fractions (designated 5-7-3, 5-7-1, 5-6-2, 5-5-2, and 5-3-1) from a series studied by Berry, Hobbs, and Long[9] were kindly provided by Professor G. C. Berry. We measured intrinsic viscosities of these polymers in acetonitrile at 30 °C, using a Cannon-Ubbelohde viscometer (size 25). Viscometric molecular weights, M_v, calculated by using the Mark-Houwink relation of Kalpagam and Rao[10] are, respectively, 5.48×10^5, 7.95×10^5, 1.14×10^6, 1.84×10^6, and 3.48×10^6. These results are in good agreement with the light scattering molecular weights reported by Berry et al.[9] for the last three samples. In addition, a PVAc fraction of lower molecular weight, $M_v = 6.50 \times 10^4$, was also examined. This polymer is designated 532-6 in a series prepared by Berry, Nakayasu, and Fox.[6]

All polymer samples were stored in a vacuum desiccator after pumping overnight. Stock solutions of each polymer were prepared by dissolving a measured weight of the material to make up the desired volume of solution and stirring for 24 h. Solutions of lower concentration were then prepared by volumetric dilution of the original solution. The water used as the solvent in all the POE studies was purified by passage through a Corning LD-5 water purifier equipped with organic removal and ultrahigh purity (ion exchange) columns followed by distillation under oxygen in an all-glass apparatus. Chloroform, the solvent in all PS measurements, was ACS certified grade from Fisher Scientific Co. It was purified on a silica gel column prior to use. Acetonitrile (UV grade) was purchased from Burdick and Jackson Laboratories and was used directly as the solvent in all PVAc experiments. This solvent was free of trace impurities, often present even in carefully purified material, that absorb at 210 nm, the wavelength of the PVAc absorption studied by us and by Destor et al.[8]

Two Perkin-Elmer spectrophotometers, Model 575 and Model 330, were used. Each instrument had been calibrated for linearity of response at 250 nm by using a series of six neutral-density filters. The instruments show less than ±0.5% deviation from linearity at absorbances up to 2 for Model 575 and up to 2.5 for Model 330.

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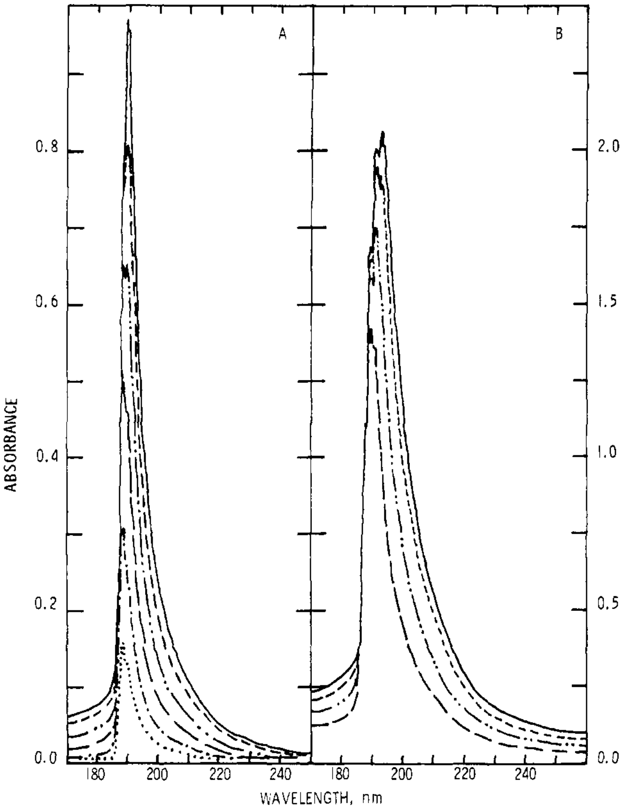

Figure 1. Far-ultraviolet absorption spectra of POE ($M = 1 \times 10^5$) in water obtained with the Perkin-Elmer Model 575 spectrophotometer and 10-mm cells at concentrations of (A) 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mg/mL and (B) 2.0, 3.0, 4.0, and 5.0 mg/mL.

Our experimental procedures were intended to be comparable to those of Destor et al., so far as their methods are disclosed.[8] Ultraviolet absorption spectra were recorded in the double-beam mode, using matched sets of Quarasil cells (Precision Cells, Inc.) of 1- and 10-mm path lengths. The solvent was always used as the reference. We did not attempt to purge the optical system of either spectrophotometer of air; hence oxygen absorption may contribute to the severe attenuation of the total signal that ultimately makes measurements impossible in the far ultraviolet.[11] For all three polymer + solvent systems, dependences of the spectra on molecular weight and concentration were determined. Nine or ten solutions were measured in each concentration series. Absorption spectra were recorded for each solution; however, with one exception, data used in the analysis were obtained from the digital readout of the spectrophotometer (by interrupting the scan at the desired wavelength).

Results

As Destor et al.[8] found a crossover effect in the POE and PVAc solutions, these systems are of primary interest.

Spectra for POE in water obtained with the Model 575 spectrophotometer and 10-mm cells are shown in Figure 1 for one of our polymers. Under these conditions we find for each of the four samples that the position of the first absorption band maximum, λ_{max}, at ca. 190 nm undergoes an apparent bathochromic shift and the bandwidth at half-height increases with increasing concentration. This and the apparent collapse of the spectrum on the low-wavelength side are suggestive of an instrument artifact associated with severe loss of signal at the short-wavelength limit of the spectrophotometer.

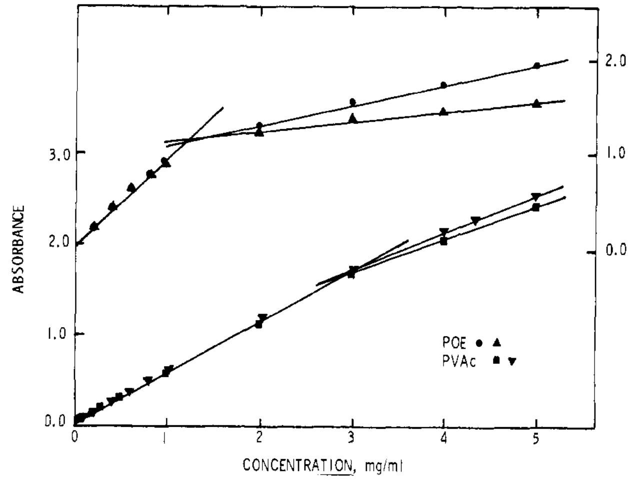

Figure 2. Concentration dependence of absorbance due to polymer as measured with 10-mm cells and the Model 575 spectrophotometer. Upper plot: POE in water measured at λ_{max} (●) and at fixed wavelength 190 nm (▲); from spectra in Figure 1. Lower plot: PVAc in acetonitrile at 210 nm for $M = 5.48 \times 10^5$ (■) and $M = 1.14 \times 10^6$ (▼).

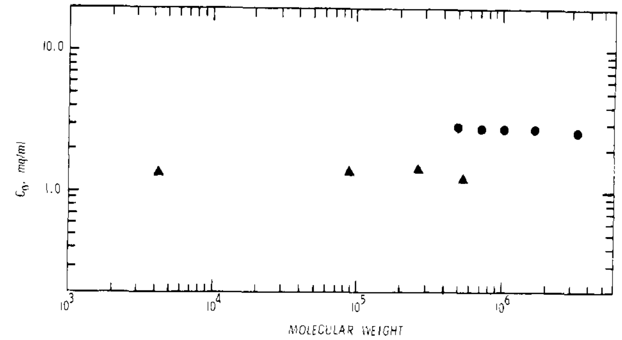

Figure 3. Apparent crossover concentration C_0 vs. molecular weight for POE (▲) in water (190 nm) and PVAc (●) in acetonitrile: data obtained with the Model 575 spectrophotometer and 10-mm cells.

From Figure 2, where a plot of POE absorbance at 190 nm vs. concentration from these spectra is shown, a linear relation can be seen at low concentration, as would be expected from the Beer–Lambert law; but above 2 mg/mL the data conform to a different linear relation. If the absorbances at λ_{max} rather than at 190 nm are plotted, a different linear fit is obtained at high concentration; but the two asymptotes still intersect at about the same point to define an apparent crossover concentration C_0. This behavior is found with all four POE samples.

Qualitatively the results observed at 190 nm are similar to those of Destor et al.[8] obtained at the same wavelength in that these investigators could fit their data with two straight lines and determine a C_0 from the intersection. However, in contradiction with Destor et al.,[8] we find (Figure 3) that C_0 does not depend on molecular weight. Although their C_0 values are similar to ours at low molecular weight, Destor et al.[8] found that

$$C_0 \propto M^{-0.75\pm0.10}$$

Observing their values of C_0 to correspond in order of magnitude to the condition for nonoverlapping chain domains to fill the solution volume, they then identified C_0 with C^* in eq 1.

Spectra obtained for two of our POE samples ($M = 1 \times 10^5$ and 6×10^5), still taken with the 10-mm cells but using the Model 330 spectrophotometer, again reveal two distinct absorbance ranges linear in concentration at 190 nm. However, the apparent deviation from Beer's law at high concentration is significantly less than that measured with the other photometer although C_0 has not changed markedly. Measurements on these two POE samples with 1-mm cells in both spectrophotometers show no deviation from Beer's law over the concentration range studied with

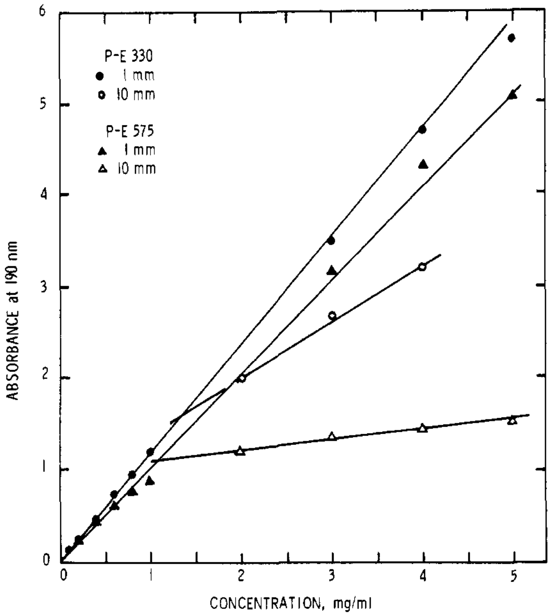

Figure 4. Comparison of absorbances of POE in water measured at 190 nm with two spectrophotometers. Absorbances for 1-mm cells have been multiplied by 10. On the scale of the plot, data points at $C < 1$ mg/mL for 10-mm cells coincide with the points shown for the 1-mm cells.

10-mm cells. These comparisons are shown in Figure 4 for one POE sample.

Finally, if POE spectra that show an apparent C_0 at 190 nm or at λ_{max} are analyzed at 210 nm,[11] there is no indication, within experimental uncertainty, of a crossover to semidilute behavior.[12]

Turning to spectral data on PVAc in acetonitrile obtained with 10-mm cells in the Model 575 apparatus, we find λ_{max} at 210 nm and a band shape invariant with concentration. As with POE, two linear concentration dependences of absorbance at λ_{max} can be used to fit the data on the five high-molecular-weight samples. In this case, C_0 is found to be near 3 mg/mL and the slopes of the linear asymptotes for the two concentration ranges are more alike than in the corresponding POE measurements: i.e., the deviations from Beer's law are markedly smaller. The data for two PVAc samples are plotted in Figure 2. It is evident that the absorbances are indistinguishable in the Beer's law region. The data plotted here for the linear absorbance range at high concentration represent the extreme of variations among the PVAc samples. Despite the apparent slight molecular weight dependence of absorbance beyond C_0, the value of C_0 is the same for all the samples (Figure 3).

For the low-molecular-weight PVAc ($M = 6.50 \times 10^4$) studied under the same conditions, no break in absorbance vs. concentration is seen up to 4 mg/mL.[13] The Beer's law slope is, however, the same as that found for the other PVAc samples.

When the Model 330 spectrophotometer is used with 10-mm cells, PVAc ($M = 6.50 \times 10^4$, 7.95×10^5, 1.14×10^6, and 1.84×10^6), in contrast to POE, shows no deviation from Beer's law up to concentrations of 5 mg/mL. With 1-mm cells, the PVAc data obtained with both spectrophotometers conform to Beer's law throughout the concentration range used in the other measurements.

Finally, we made spectral absorbance measurements at 260 nm on chloroform solutions of the three polystyrene samples, using 1-mm cells and both spectrophotometers. The observed concentration dependences of absorbance are indistinguishable. There are no departures from Beer's law, at least up to 8 mg/mL, where the absorbance is 1.7. Destor et al.[8] also failed to observe crossover behavior in this system, but their data differ from ours in showing a gradual curvature in the concentration dependence of the absorbance.

Discussion

Since the appearance and magnitude of deviations from Beer's law depend on the spectrophotometer used and the path length in the absorbance cell rather than on concentration per se, we are forced to conclude that the effects we observed must be instrument artifacts that arise because the spectral measurements are made in an energy region that taxes the detection limits of both spectrophotometers.

Our data imply the qualitative generalizations (a) that the Model 575 instrument shows the greater tendency to give spurious deviations from Beer's law and (b) that the effect increases with decreasing wavelength in both instruments.

From Figure 2 we note that the absorbance of POE at its apparent C_0 is 1.1 at 190 nm in a 10-mm cell. As the absorbance of the water alone is 0.35, an important portion of the total attenuation in the solutions is due to the solvent. More important, at 190 nm the total energy delivered to the detector photomultiplier of the Model 575 instrument through a 10-mm cell containing water alone is only about 2.8% of the value at 260 nm. At 210 nm the situation is more favorable, with the total energy transmitted about 71% of the value at 260 nm. It is consistent with this that the POE absorbance at 210 nm does not show deviations from Beer's law.[12] At the apparent crossover concentration for PVAc the 210-nm absorbance of the solution is 2.0 (the absorbance of acetonitrile is less than 5% of the total). Presumably, the still more favorable situation at 260 nm precludes any appearance of an apparent crossover in the PS solutions in the absorbance range we have studied.

There is a legitimate question as to whether light scattering from a macromolecular solution might be sufficiently great to contribute appreciably to the measured ultraviolet absorbance. Since the polymer turbidity (absorbance per unit path length due to scattering) is proportional to concentration in very dilute solutions, passes through a maximum in the vicinity of C^*, and then declines to a low level in the semidilute range, apparent deviations from Beer's law from this cause are in principle possible. However, since absorbances due to scattering and to true absorption are additive and both simply proportional to path length in the solution cell, the disappearance of the absorbance anomalies in our data when the path length is sufficiently reduced at fixed concentration demonstrates that light scattering cannot account for our results.

Since the POE samples have broad molecular weight distributions, any real crossover should be diffuse. Nevertheless, the fact that samples covering a 100-fold average molecular weight range give the same Beer's law dependence without deviation (when studied in the same spectrophotometer under conditions that eliminate the spurious crossover behavior) argues strongly against any manifestation of semidilute behavior in absorbance.

Similarly, the PVAc data also show a common Beer's law dependence at all concentrations when the suprious effects at high absorbance are eliminated. This counters the argument that some of the PVAc fractions (say $M \geq 7.95 \times 10^5$) might be of such high molecular weight that a true crossover could have disappeared toward the origin in plots like those in Figure 2. Had this occurred, the high molecular weight samples might appear to obey Beer's law but would give a smaller slope than the low molecular weight sample ($M = 6.5 \times 10^4$), which has undoubtedly been studied in its dilute concentration range.

Although the Varian Model 219 spectrophotometer that Destor et al.[8] used is roughly equivalent in its capabilities to the Perkin-Elmer Model 575 instrument, direct comparison of data would be difficult since the instruments operate on different principles. The Varian instrument is designed to automatically adjust slits to compensate for loss of intensity, which sacrifices spectral resolution. It can operate at a set resolution (fixed slits), but then sacrifices sensitivity. Both Perkin-Elmer instruments make scans at a fixed slit width to preserve resolution; and they compensate, in part, for the lower sensitivity by increasing the gain of the photomultiplier. Nonetheless, given the internal evidence afforded by our results with different cells and spectrophotometers, we propose that the apparent crossover seen by Destor et al.[8] is, like that we have obtained, an instrumental artifact despite its plausible molecular weight dependence. The lack of any real crossover in the concentration range where it should appear on the basis of simple physical reasoning, and where it has been detected in other properties, leads to the conclusion that ultraviolet absorption is not a useful method for detecting the onset of semidilute behavior in the systems considered here. For the reasons stated in the Introduction, we suspect that this insensitivity is a general one.

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(11) Effective exclusion of oxygen would require purging the entire optical system, as well as the sample compartment and the solution, with nitrogen. Only measurements below 200 nm might be affected by oxygen; however, since our POE samples (unlike most of those of Destor et al.[8]) contained no carbazole end groups, our ability to analyze data at wavelengths above 200 nm would not be impaired.

(12) The POE absorbances at 210 nm show considerable scatter since they were obtained directly from plots of spectra recorded with λ_{max} adjusted to full scale (see Figure 1).

(13) This experiment may not be strictly comparable with corresponding measurements on the other PVAc samples since it was made later, after a routine instrument servicing.

Raman Spectroscopic Study of the High-Pressure Phase of Polyethylene

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ABSTRACT: The Raman spectra of polyethylene at 5.1 kbar were obtained as a function of increasing temperature in the orthorhombic, intermediate, and melt phases. It was found that a plot of $r = I(1130)/I(1090)$, an order parameter related to the relative concentration of trans bonds, vs. temperature, T, was sigmoidal. The steepest change of r with T occurred in the intermediate phase. Comparison of r values in the intermediate phase with an approximate calibration curve and with values obtained from lipid membrane phase transition data indicates that the intermediate phase has significant but variable trans bond population, ranging from 62 to 68%. Analysis of the high-frequency C–H stretching region, which is indicative of changes in lateral order as well as changes in chain conformation, indicates that the intermediate phase has hexagonal symmetry, in agreement with X-ray data, and also reflects the changing trans bond ratio in this phase. Preliminary evidence on chain conformation in the melt as a function of increasing pressure points to preferential gauche bond formation at high pressures.

Introduction

The high-pressure phase of polyethylene (PE), discovered by Bassett and Turner[1] and Yasuniwa and Takemura,[2] occurs below its melting temperature at pressures above ~3 kbar. While the ordinary crystal structure of PE is orthorhombic, the structure of the intermediate phase was determined to be hexagonal by Piermarini et al.[3] The properties of this intermediate phase are important because the resultant crystalline morphology of PE is dependent upon whether or not this phase is traversed upon crystallization, either by cooling or by pressurization. When PE is crystallized below ~3 kbar, its morphology is lamellar. However, above this pressure, when the intermediate phase interposes between the crystal and the melt, the morphology commonly known as

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