Fluorescence Excitation Spectroscopy of Polystyrene Near the Critical Concentration c*

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ABSTRACT: The critical concentration c^* was measured using both fluorescence excitation spectroscopy and light scattering for four narrow molecular weight distribution samples of polystyrene (MW = 225,000–1,500,000) in bicyclo[4.4.0]decane (decahydronaphthalene, decalin) at 20 and 30°C. A discontinuity in the corrected intensity of a band in the excitation spectrum (assigned to the dimmer complex) as a function of concentration allowed determination of the critical concentration, c^*, from the excitation spectra. The c^* resulting from fluorescence and light scattering were identical within experimental error and were comparable to c^* values calculated from literature methods. Fluorescence excitation spectroscopy should be a convenient method for determining c^* for aromatic polymers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 360–364, 2007

Key words: polystyrene; phase diagrams; fluorescence; light scattering; solution properties

INTRODUCTION

Solutions of polymers have been of interest for many years.[1–3] Polymer solutions above the θ-temperature are generally divided into three temperature–concentration regions: dilute, semidilute, and concentrated. At low concentrations, dilute solutions are characterized by the essential lack of intermolecular polymer–polymer interactions. At higher concentrations, semidilute solutions are characterized by the presence of intermolecular polymer–polymer interactions. The boundary between dilute and semidilute solutions, known as the critical concentration or c^*, is the concentration threshold where polymer chains are close enough for intermolecular interactions to occur.[4–8] This concentration is related by theory to the polymer radius, increasing the utility of determinations of c^*.[5–7]

A significant body of work exists for studies of polymers employing fluorescence spectroscopy.[9–13] Polymeric excimers are known to form through both intermolecular and intramolecular interactions of chromophores. Hirayama[14] studied the intramolecular excimer fluorescence of diphenyl and triphenyl alkanes at very dilute concentrations (to minimize intermolecular excimer formation) and reported that these excimers can form only if the chromophores are separated by three carbons. As a corollary, Torkelson et al.[15] used dilute solutions of polystyrene to determine that intramolecular excimer formation by nonadjacent chromophores is not significant.

There have been studies of intermolecular excimer formation in polystyrene using fluorescence emission spectroscopy. Nishihara and Kaneko[16] demonstrated that increasing the concentration of polystyrene caused an increase in the ratio of excimer to monomer intensity (I_E/I_M) even for dilute concentrations. This contradicted an earlier study by Vala et al.[17] who reported little change in the I_E/I_M ratio of dilute solutions. Later, Roots and Nystrom[18] noted an upward curve in the I_E/I_M plot for polystyrene fluorescence. They concluded that this curvature was due to the transition between the dilute and semidilute concentration regions and hence was a measurement of the critical concentration or c^*. Torkelson et al.[19] then performed experiments similar to those of Roots and Nystrom[18] and found that the observed curvature of the I_E/I_M plot was due to self-absorbance by the polymer and not c^*. They then showed that the plots of I_E/I_M corrected for self-absorbance were linear up to very high concentrations.

We report the use of fluorescence excitation spectroscopy to observe intermolecular interactions and determine the critical concentration c^*. Four different molecular weights of polystyrene were studied in bicycle[4.4.0]decane (also known as decahydronaphthalene or decalin) at both 20 and 30°C. The temperature dependence reveals that higher temperatures cause c^* to decrease because of an increase in the polymer size (radius of gyration). As expected, increasing the molecular weight also causes c^* to decrease.

EXPERIMENTAL

Materials

Spectroscopic-grade decahydronaphthalene (cis–trans mixture) was used without further purification. All polymer samples were manufactured by Scientific Polymer Products, Inc of Ontario, NY. The polystyrene samples were narrow molecular weight distribution primary standards. The molecular weights and polydispersities were $M_w = 223,200$, $M_w/M_n = 1.11$; $M_w = 560,900$, $M_w/M_n = 1.04$; $M_w = 1015,000$, $M_w/M_n = 1.03$; and $M_w = 1571,000$, $M_w/M_n = 1.03$.

For each polymer studied, a stock solution of the highest concentration measured (approximately double the calculated value for c^* at 20°C based on the Mark-Houwink equation[5–7,20,21]) was prepared in a 50 mL volumetric flask, and aliquots of this solution were transferred using graduated pipettes into 10 mL volumetric flasks and diluted to the mark with solvent.

Fluorescence measurements

All fluorescence measurements were performed on a Jobin-Yvon Spex τ-2 (FL1T11) Spectrofluorimeter consisting of a 450 W ozone-free xenon lamp, a single grating excitation monochromator, a single grating emission monochromator, and a T-box sampling module. All spectra were measured using front-face sampling (15° from incident light) and collected on a room temperature Hamamatsu R928 red-sensitive photomultiplier tube with a low-energy cut-off of 930 nm. Slit widths were 0.5 mm. The fluorescence excitation spectra were scanned from 240 to 320 nm with the emission monochromator set to 332 nm. The fluorescence emission spectra were scanned from 265 to 400 nm with the excitation monochromator set to 250 nm. All spectra were corrected for detector response by Rhodamine B and were an average of two separate scans to reduce noise. Error in the fluorescence measurements was determined by running multiple scans at varying concentrations of each molecular weight and noting the largest variability. For polystyrene in decalin, the largest error measured for I_{291} was ±9000 cps ($< ±0.5\%$ at c^*) and for I_{291}/I_{314} was ±0.05 ($< ±1.7\%$ at c^*), regardless of molecular weight. These error values were used for the error bars in Figure 3). Cell temperatures were maintained using a constant temperature bath, which was circulated through the cell holder. The cells were allowed to equilibrate to temperature for at least 30 min and checked using a mercury thermometer before the measurements were taken. Far UV quartz (Spectrosil®) 1-cm path length cells with stoppers to prevent evaporation were used for all measurements.

Light scattering measurements

Light scattering data were measured on a Wyatt Technologies Dawn EOS (Enhanced Optical System) Light Scattering Detector (SN 249-E) equipped for scintillation vials. The output data was analyzed using Astra for Windows software version 4.73.04. Samples were transferred to scintillation vials via syringes and passed through 0.02 μm filters for solvents and 0.2 μm filters for solvent/polymer samples, and the first 1 mL passed through each filter was discarded. Sample temperature was maintained by an integrated Peltier Heater/Cooler controlled by a Watlow thermocontroller. Samples were allowed to equilibrate for 30 min before any measurements were taken. Data were obtained over 1 s intervals for a 2-min acquisition period thereby giving 120 data points. Spectroscopic-grade toluene was used as a calibration standard and a narrow molecular weight polystyrene standard ($M_w = 32,200$) in decalin was used as the normalization standard. The dn/dc value for polystyrene in decalin is 0.110 mL/g.[22] Data from the detectors at 23° and 28° were not included in the analysis because of excessive noise. All data were fitted to a Zimm model. Light scattering data were generated from each molecular weight at 0.05, 0.1, 0.25, 0.5, 0.75, and 1.0 g/L.

RESULTS

Typical fluorescence emission spectra for several concentrations of polystyrene ($\bar{M}_w = 223,000$ Da) in decalin are shown in Figure 1. To eliminate the self-absorbance effects observed by Torkelson et al.,[19] all
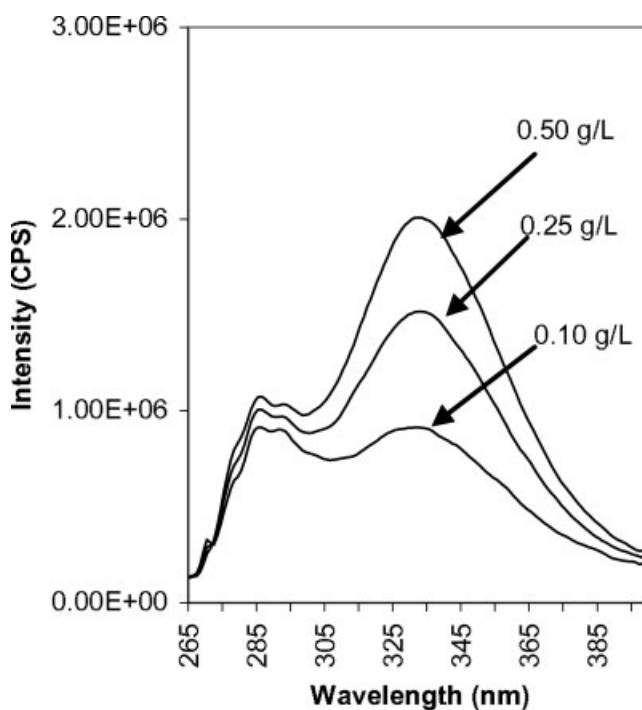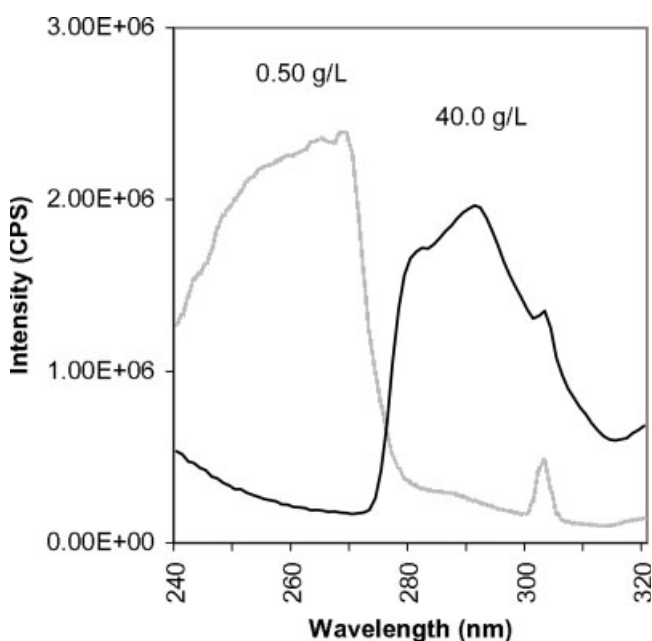

Figure 1 Fluorescence emission spectra of polystyrene ($\bar{M}_w = 223,200$) at three concentrations in decalin at 20°C (excitation at 250 nm). The band at 285 nm is the fluorescence due to polystyrene monomer, while the band at 332 nm is due to polystyrene excimer.

fluorescence readings were taken from the front face of the cell. These results are similar to the previously published spectra by Roots and Nystrom[18] and Torkelson et al.[19] The spectra show the maximum fluorescence intensity of polystyrene monomer at 285 nm and the maximum fluorescence intensity of polystyrene excimer at 332 nm. It is clear from these spectra that as the polymer concentration is increased, the excimer intensity grows relative to the monomer intensity. This is expected, since as the concentration is increased, the excited polymer chains are more likely to come into contact with other chains, enhancing the formation of excimers.

Typical fluorescence excitation spectra for polystyrene ($\bar{M}_w = 223,000$ Da) in decalin are shown in Figure 2. Spectra for the other samples are similar in appearance to Figure 2. The emission monochromator was set to the wavelength of the excimer λ_{max} (332 nm) so the corresponding excitation spectra measure excitation leading to excimer fluorescence. Excimers can be formed through a number of pathways as shown in Scheme 1: excitation of ground state dimers or "dimer complexes" form excimers directly, while excitation of isolated chromophores may be followed by intramolecular motion to form an intramolecular excimer, by diffusion to form an intermolecular excimer, or by energy migration to an excimer-forming site.[23–24]

Under certain conditions, aromatic compounds are known to form ground state dimers or "dimer complexes" with absorption and emission spectra that are
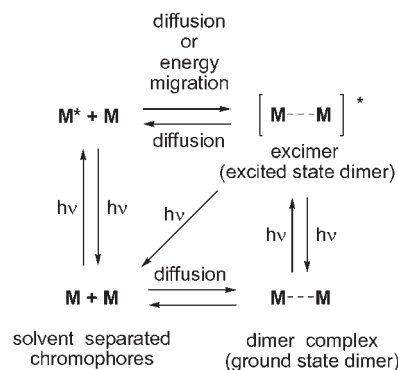
Scheme 1 Pathways for the formation and emission of excimers in aromatic polymers.

broadened and shifted to lower energy.[23–24] For the paracyclophanes, the formation of dimer complexes is enforced by covalent bonding, and these compounds are known to have shifted absorption bands between 280 and 320 nm which are absent in monomeric benzene derivatives.[23–24] We call such shifted absorptions from dimer complexes "complex bands" by analogy to the exciton bands observed in aromatic crystalline solids (i.e., anthracene) and in certain molecular aggregates.[23–24] Since complex bands occur when ground state dimer complexes (or higher-order complexes such as trimers or tetramers) are excited as a single entity, detection of complex absorption by excimer monitored fluorescence excitation spectroscopy should provide more direct information about contacts between chromophores in the ground state (and therefore polymer–polymer contacts) than measurement of excimer emission. The band at 291 nm (I_{291}, similar to paracyclophane absorbances) that dominates the excitation spectra of polystyrene at higher concentrations (Fig. 2) is attributed to complex absorption. This absorption could then be used as a marker for the critical concentration c^*, where such intermolecular contacts are expected to increase sharply.

The change in I_{291} as a function of concentration near c^* can be seen clearly when corrected for scattering. Rayleigh light scattering increases with concentration and particle size, so it is quite intense for polymer solutions near c^*.[25] Scattering was noted in all of the polystyrene fluorescence excitation spectra as an increase in the baseline. The excitation intensity at 314 nm was used as a reference wavelength for scattering in the excitation spectra. This wavelength was chosen because there is little fluorescence due to polystyrene absorption at that wavelength (Fig. 2), and therefore the increases in intensity are almost entirely due to scattering.

Figure 3 shows a plot of I_{291}/I_{314} versus concentration at 20 and 30°C for polystyrene ($\bar{M}_w = 223,000$ Da). As the concentration increases from zero, the corrected intensity increases, then plateaus, until the value for I_{291}/I_{314} becomes approximately constant. The

Figure 2 Fluorescence excitation spectra of polystyrene ($\bar{M}_w = 223,200$) at two concentrations in decalin at 20°C (excimer emission at 332 nm). Light line, 0.5 g/L; dark line, 40 g/L. The band at 291 nm in the 40 g/L spectrum is assigned to complex formation. The relatively sharp peak at 304 nm is from Raman scattering.
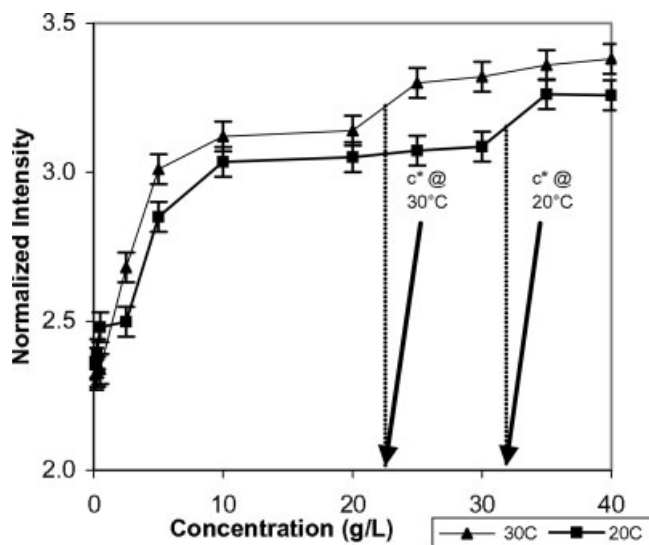
Figure 3 Corrected complex intensity versus polystyrene concentration for polystyrene ($\bar{M}_w = 223{,}200$) in decalin at 20 and 30°C. Data points are connected by lines for ease of interpretation. The critical concentration c^* is apparent between 30 and 35 g/L at 20°C and between 20 and 25 g/L at 30°C.

corrected intensity remains fairly constant until it makes a sudden increase between 30 and 35 g/L for the 20°C samples and between 20 and 25 g/L for the 30°C samples. This increase is assigned to the increase in intramolecular and intermolecular interactions, including dimer complexes, because of crowding of the polymer chains. This corresponds to the transition between the dilute and semidilute solution phases known as the critical concentration (c^*). The decrease in c^* with increased temperature is expected due to expansion of the polymer chains with increased thermal energy and greater polymer–solvent interactions.

Excitation spectra were evaluated for four molecular weights of polystyrene at 20 and 30°C and the results are collected in Tables I and II. The fluorescence c^* values were determined from the corrected complex intensity versus concentration graphs simi-

TABLE I
Critical Concentration (c^*) Values for Polystyrene in Decalin at 20°C

	c^* (g/L)		
PS MW	Calculated (18°C)[a]	Fluorescence[b]	Light scattering[c]
223,200	27.5	32.5 ± 2.5	28.0 ± 3.0
560,900	17.3	17.5 ± 2.5	22.0 ± 4.0
1,015,000	12.9	13.8 ± 1.2	13.8 ± 1.0
1,571,000	10.4	12.5 ± 0.5	13.1 ± 1.3

[a] Calculated using eq. (2) and data from ref. 22.
[b] Calculated from fluorescence excitation spectra as described in the text.
[c] Calculated from R_g derived from light scattering data using eq. (1).

TABLE II
Critical Concentration (c^*) Values for Polystyrene in Decalin at 30°C

	c^* (g/L)		
PS MW	Calculated[a]	Fluorescence[b]	Light scattering[c]
223,200	21	22.5 ± 2.5	25.0 ± 5.0
560,900	13	12.5 ± 2.5	11.3 ± 3.2
1,015,000	10	11.0 ± 1.0	12.0 ± 0.5
1,571,000	8.0	9.0 ± 1.0	9.5 ± 0.5

[a] Calculated using Mark-Houwink parameters K = 1.0 × 10⁻⁴ mL/g and a = 0.5, calculated from the fluorescence data.
[b] Calculated from fluorescence excitation spectra as described in the text.
[c] Calculated from R_g derived from light scattering data using eq. (1).

lar to Figure 3 We assign a value to c^* between the last point of the plateau where I_{291}/I_{314} is approximately constant and the first point where I_{291}/I_{314} has increased. For example, Figure 3 ($\bar{M}_w = 223{,}000$ Da) shows c^* between 30 and 35 g/L at 20°C and was therefore reported as 32.5 ± 2.5 g/L.

For comparison, values of c^* were also determined using light scattering data, a method that has been previously used for determining R_g, which can then be used to calculate c^*.[5–7,26] The light scattering values for c^* were calculated from the z-average radius of gyration using

$$c^* = \frac{\bar{M}_w}{(4/3)\pi R_g^3 N_A} \quad (1)$$

where $\bar{M}_w$ is the weight-averaged molecular weight of the polymer, R_g is its z-average radius of gyration, and N_A is Avogadro's number.[26] Light scattering studies were performed on several dilute concentrations of each molecular weight of each polymer, as detailed in the Experimental section. Data for each molecular weight of polystyrene in decalin were fitted to the Zimm model to generate the z-average radius of gyration (R_g). Values for c^* were calculated using eq. (1) from R_g data at 20 and 30°C and are presented in Tables I and II. The c^* values from light scattering and fluorescence generally agree within experimental error.

DISCUSSION

To test the validity of our results against the literature, the c^* values determined by fluorescence excitation spectroscopy and light scattering were compared to c^* values calculated by a published method.[20–22] The equation used to calculate c^* was based on the Mark-Houwink equation and is given by

$$c^* = \frac{1}{KM^a} = \frac{1}{[\eta]} \quad (2)$$

where M is the weight average molecular weight of the polymer ($\bar{M}_w$) and K and a are the Mark-Houwink constants for a given polymer/solvent system. For polystyrene in decalin at 18°C, $K = 77 \times 10^{-3}$ mL/g and $a = 0.50$.[22] This calculation is known to frequently underestimate the true value of c^*.[20–22]

Table I shows the comparison of c^* values for four different molecular weight polystyrene samples in decalin at 18–20°C. The c^* values derived from fluorescence are comparable to the c^* values calculated using eq. (2), with some of the calculated values slightly lower as expected. The fluorescence derived c^* values correlate well with the light scattering derived c^* values and the error in the fluorescence values is generally comparable to the error in the light scattering values.

A comparison of c^* values for the four different molecular weight polystyrene samples in decalin at 30°C using fluorescence and light scattering is shown in II. The fluorescence c^* values show good agreement with the light scattering values. The errors in the two different measurements are, on average, approximately equivalent. We did not find literature values for K and a for polystyrene in decalin at 30°C, however, the fluorescence or light scattering data can be used to calculate K and a by plotting logôc* versus logôM. Using the fluorescence data, such a plot gives a correlation coefficient > 0.95. The best fit returns values of $K = 1.0 \times 10^{-4}$ mL/g and $a = 0.5$. In accordance with scaling theories, a was constrained to be ≥0.5.[5–7] Since θ for polystyrene in decalin is 18°C,[22] it is not surprising that a is still near 0.5 at 30°C. This value of K is on the low side,[5–7] but varying the fluorescence data within the error ranges in Table II gave values of a between 0.4 and 0.6 and values of K between 3.2×10^{-5} and 6.8×10^{-4}, all with correlation coefficients above 0.95. To use fluorescence measurements to determine Mark-Houwink parameters with greater precision, one would need more and better determined values of c^*. However, the predicted c^* values from the best fit Mark-Houwink analysis are entered in Table II, and are generally within the experimental error of the fluorescence and light scattering results.

CONCLUSIONS

In this article, we have demonstrated a novel way of measuring the critical overlap concentration, c^*, of polystyrene using excimer-detected fluorescence excitation spectroscopy. This method was used successfully on four different molecular weights. These results have been compared against c^* values calculated using the Mark-Houwink equation and c^* values calculated by an accepted method (from R_g based on light scattering), and the results are in good agreement. Mark-

Houwink parameters were calculated from the fluorescence data at 30°C. Since the fluorescence method measures c^* directly, the relationship between c^* and R_g can then be used to approximate R_g. Fluorescence excitation spectroscopy allows for limits to be determined for c^* and R_g for aromatic polymers by a method which has easier sample preparation and uses more common laboratory instrumentation than either light scattering or osmometry.

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