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Phase transition pattern of 2,5-diphenyloxazole/γ-cyclodextrin (PPO/γ-CD) self-assembly aggregates

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Abstract

The molecule 2,5-diphenyloxazole (PPO) organizes into non-covalently bonded self-assembled aggregates of guest–host complexes with γ-cyclodextrin (γ-CD) in aqueous solutions. This structure is held together by weak interactions between the PPO and the γ-CD molecules. Therefore a small activation energy allows deterioration of these self-assembled aggregates. In this study, we report the effect of temperature and pH on this unique ensemble of aggregates. We report a phase transition pattern in which the structure disassembles from long to short (i.e. basic unit) aggregates. The relative fluorescence intensities of the excimer and monomer of PPO have been used to study this transition. Earlier investigations reported that these self-assembled aggregates were destroyed by an increase in temperature up to 80 °C. In this study, we examined the effect of temperature on this structure and found a phase transition pattern of the temperature-dependent structure. Both the intensity and polarization of the steady state fluorescence reveal similar values of the critical temperature at 46 ± 8 °C and 49 ± 7 °C for the monomer and excimer fluorescence respectively. In addition, earlier studies proposed that hydrogen bonding between the guest and host molecules may play an active role in stabilizing the linear beads. We examined this hypothesis by changing the pH to an acidic or basic medium. A change in the aggregates was observed at approximately pH 12, which is the pK_a value of γ-CD. For the pH range 10–13, a phase transition is centered at about pH 12.

Keywords: Phase transition patterns; PPO/γ-CD self-assembly aggregates; Guest–host complexes

1. Introduction

Extensive spectrophotometric studies of 2,5-diaryloxazoles have been conducted in the past, because these compounds possess better scintillation characteristics than other oxazoles [1]. One such compound is 2,5-diphenyloxazole (PPO), a well-known scintillator and laser dye. This compound forms excimer fluorescence in concentrated solutions [2–4]. The formation and degradation of these excimers have been investigated thoroughly [5–10]. The monomer fluorescence of PPO is present at shorter wavelengths (375 nm), whereas the excimer emission can be viewed at longer wavelengths (430 nm) as a less intense, broadened peak of emission [2,3,5,11,12]. In addition, fluorescence lifetime measurements have suggested longer lifetime values for the excimer (approximately 13.6 ns) and a much shorter lifetime (1.6 ns) for the monomer in organic solvents [12–15]. There are many factors, including the choice of solvent, concentration and temperature, which can affect the excimer fluorescence [2,11]. For aliphatic and alcohol solvents, an increase in viscosity can cause a decrease in dimerization. However, for aromatic solvents with similar viscosities, the dimers are less readily formed. In organic solvents, the monomer fluorescence of PPO has a quantum yield of unity [2]. Many factors, including solubility limitations and short lifetimes of the monomer, cause the excimer to have a much lower photon count.

Cyclodextrins (CDs) are cyclic oligosaccharides that can selectively incorporate guest molecules through size exclusion and weak interactions, such as hydrophobic interactions and van der Waals' forces. The inner cavity diameters of α-, β- and γ-CDs, which are 5.7, 7.8 and 9.5 Å respectively, allow the CDs to include selectively guest molecules based on size [16,17]. The CDs have the ability to perturb the photochemical and photophysical properties of the guest molecules, which allows them to be widely used in many different applications. In 1988, Agbaria and Gill [18] first introduced the idea of aqueous solutions of CDs with PPO arranged as extended linear beads. Since this work first appeared, many such studies have followed and support the formation of similar structures with CDs and a variety of guest molecules [19–25]. For example, Harada et al. [19] constructed tubular

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polymeric structures from a thread of several covalently linked α-CD molecules to form a self-assembly. These molecular tubes, previously called "molecular necklaces", are formed through a series of reactions that begin with the synthesis of polyrotaxanes formed by stringing the α-CD beads on a polyethylene glycol chain and then capping both ends with a bulky organic group [20–22]. Harada's work used only α-CD, but such self-assembly can also be achieved with β-CD [23]. Another study found that rigid molecular nanotube aggregates of β- and γ-CDs were formed through a non- covalent linkage with *trans*-1,6-diphenyl-1,3,5-hexatriene [24]. The nanotube aggregates contained about 20 β-CDs or 20–35 γ-CDs; however, no aggregates were observed with α-CD.

The formation of molecular tubes supports the idea of the formation of extended linear aggregates with PPO molecules. In the case of PPO, its solubility in water is increased on complexation with γ-CD, a common characteristic observed for inclusion complexes with CDs [16]. Complexing PPO with γ-CD will also increase, compared with free PPO, the quantum yield and lifetime of its excimer [18]. A turbid appearance of the PPO/γ-CD solution signals the formation of extended aggregates. Polarization and light scattering experiments by Agbaria and Gill [18] have confirmed that the aggregates consist of 60–500 PPO/γ-CD basic units. In Ref. [18], this aggregation was described as a 2 : 1 PPO/γ-CD complex made of single basic units. These basic units can aggregate, or self-assemble, at high CD concentrations and yield excimer fluorescence [18,25]. The partial inclusion of two PPO molecules in one CD cavity can only take place with β- or γ-CD due to their larger inner diameters [16]. However, aggregation of the basic units that yield excimer fluorescence occurs only with γ-CD. This complex involves a non-covalent interaction by which the aromatic groups on the PPO molecules are included in the hydrophobic cavity of γ-CD. Since the oxazole ring is hydrophilic, its heterocyclic groups will probably be exposed to water and possibly form hydrogen bonds with the hydroxyl groups located on the rim of the CD [18].

Steady state fluorescence and anisotropy are two indirect techniques that can be used to analyze the PPO/γ-CD complex. In this work, we report a thorough study of this complex by varying the physical and chemical conditions, i.e. variations in pH and temperature. Changes in the fluorescence intensity and anisotropy values are used to characterize the influences of pH and temperature on the complex. More specifically, the variation of temperature produces a sigmoidal dependence of the fluorescence intensity and polarization which is typical of a phase transition phenomenon.

2. Experimental details

A Photon Technology International (PTI) luminescence spectrophotometer (LS-100) was used to obtain the steady state fluorescence and polarization spectra. The excitation wavelength for PPO was 313 nm and the emission was monitored from 350 to 550 nm. Anisotropy measurements were acquired with Glan-Thomson polarizers in the excitation and emission paths. All measurements were performed in a 1 cm quartz cell at ambient room temperature. A thermostatically controlled cell housing was used to heat the sample holder gradually for the temperature studies.

PPO (99%) was purchased from Aldrich (Milwaukee, WI) and was used as received. The γ-CD was a gift from G.A. Reed of American Maize Products (Hammond, IN). A stock solution of 1.0×10^{-3} M PPO was prepared in ethanol. Aqueous solutions of the inclusion complexes were prepared by adding 1.0 ml of 1.0×10^{-3} M of PPO into culture test tubes. The solvent was then evaporated under a stream of nitrogen gas. A 4.0 ml volume of an aqueous solution of 1.0×10^{-2} M γ-CD was added to each tube to bring the final concentration to 2.5×10^{-4} M PPO. The samples were sonicated for 15 min and allowed to equilibrate for at least 2 h, but were usually left to incubate overnight. After incubation, the samples were very turbid with a small amount of white precipitate on the bottom of the test tubes.

For the pH studies, the PPO/γ-CD aqueous solution was prepared according to the method described above. The stock solution was filtered with coarse filter paper (20 mm, Fisher, Pittsburgh, PA) to remove the precipitate. No acid or base was added to the normal solutions. Normal samples were prepared by adding 1.0 ml aliquots of the PPO/γ-CD solution and diluting with water to give a total volume of 3.0 ml. Stock solutions of 4.0 M sodium hydroxide (Fisher, Fair Lawn, NJ) and 1.0 M hydrochloric acid (EM Science, Gibbstown, NJ) were prepared in deionized water. Appropriate volumes of hydrochloric acid or sodium hydroxide stock solutions were added to PPO/γ-CD to obtain various pH values. The acid or base was added to 1.0 ml of the complex to bring the final volumes to 3.0 ml.

3. Results and discussion

3.1. Effect of increasing temperature

When an ethanolic solution of PPO is excited at 313 nm, the monomer ($\lambda_{em(max)}=375$ nm) and excimer ($\lambda_{em(max)}=430$ nm) can be observed simultaneously at room temperature [2,3,5,11,12]. The excimer emission was determined by the difference between the dilute PPO solution and the concentrated solution. The concentrated ethanolic solution was measured using front-face emission. The same maxima occurred, within an error of 5 nm, for the PPO/γ-CD complex [18,25]. Similar excimer emission values suggest that PPO molecules can align in the CD cavity as they would in a homogeneous solution.

Steady state fluorescence anisotropy (polarization) was used to determine the degree of rotation of the PPO/γ-CD complex. Polarization in emission can be described by the anisotropy r

$$r = (I_{VV} - GI_{VH}) / (I_{VV} + 2GI_{VH}) \quad (1)$$

where I_{VV} and I_{VH} are the observed intensities of emission when the excitation polarizer has a vertical orientation and the emission polarizer has a vertical (parallel) or horizontal (perpendicular) orientation. The G factor is defined as

$$G = I_{HV}/I_{HH} \quad (2)$$

where I_{HV} and I_{HH} are the intensities that are oriented horizontal to the excitation polarizer and perpendicular to the vertical and horizontal emission polarizers. By applying the Perrin–Weber equation [26,27], the anisotropy can be related to the rotational correlation time ϕ of the fluorophore

$$r_0/r = 1 + \tau/\phi \quad (3)$$

where r_0 is the anisotropy of the fluorophore in a frozen state in which it cannot undergo rotational diffusion and τ is the fluorescence lifetime. It is assumed that rotational diffusion is the only process by which anisotropy is lost. In addition, the rotational correlation time of the fluorophore is related to the volume of the rotating unit V by

$$\phi = V\eta/RT \quad (4)$$

where η is the viscosity of the medium, T is the absolute temperature and R is the ideal gas constant. When the fluorescence lifetime and viscosity remain constant, an increase in the anisotropy suggests an increase in the size of the complex.

Fig. 1(a) shows the spectra of the emission intensities (monomer and excimer) as a function of temperature. We chose to monitor the monomer emission at 375 nm and the excimer emission at 450 nm to reduce the contributions from each component to the other. A spectral fit of the total emission spectrum to the monomer and excimer emissions suggests that the contributions of the monomer at 450 nm and the excimer at 375 nm are negligible. Therefore the intensities of the monomer and excimer fluorescence were taken directly from the total spectrum without further attempts to fit the spectrum for two components.

Fig. 1(b) displays the intensities of the monomer and excimer emission maxima as a function of temperature. The spectra taken in this figure are the average of several spectra, including those in Fig. 1(a). In these experiments, the emission intensity is the sum of I_{VV} and $2I_{VH}$ taken from the anisotropy studies. The intensity of the excimer becomes less prominent, while that of the monomer is enhanced, as the temperature is increased from 24 to 75 °C. High monomer and low excimer intensities at higher temperatures (above 55 °C) suggest a partial or complete disassembling of the aggregates. The complex slowly reforms into an extended aggregate once the temperature is decreased below 45 °C. A phase transition gives the temperature range in which the excimer emission shifts to monomer, or vice versa. A critical temperature can be obtained from the inflection points of the monomer and excimer phase transitions. The center inflection point was taken as the intensities centered around the average

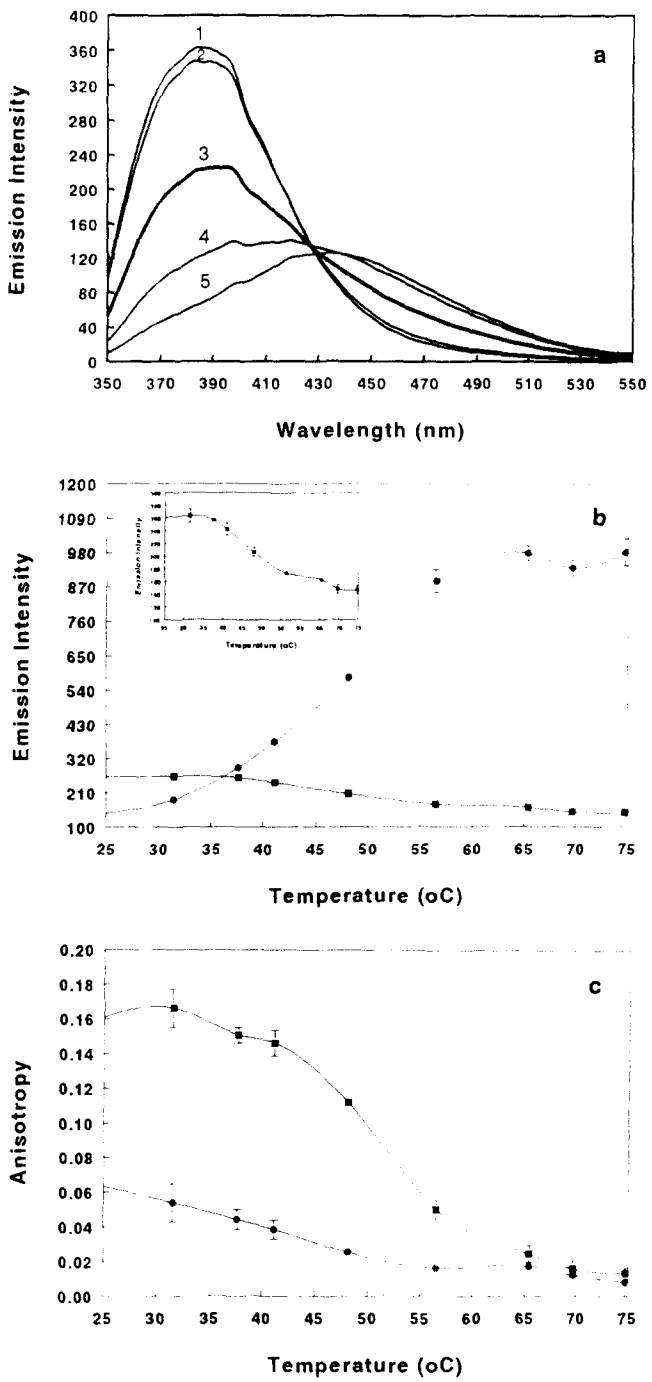

Fig. 1. Steady state fluorescence spectrum and plot of the PPO/γ-CD complex. (a) Spectra of the sum of the intensities at (1) 75 °C, (2) 65 °C, (3) 48 °C, (4) 38 °C and (5) 24 °C. (b) Plot of the sum of the fluorescence emission intensity vs. temperature of the monomer at 375 nm (●) and excimer at 450 nm (■). The inset shows the expanded excimer dependence on temperature. (c) Fluorescence anisotropy vs. temperature of the monomer at 375 nm (●) and excimer at 450 nm (■).

value, together with the lowest and highest intensities of the sigmoidal curve. An estimation of the transition temperature can be obtained in a manner similar to calculating the equivalence point in a titration curve since the two curves are similar in shape. These transition temperatures were estimated to be 46 ± 8 °C and 49 ± 7 °C for the monomer and

excimer fluorescence respectively. It should be noted that these temperatures are well below the melting point of PPO (72–74 °C). A broad phase transition suggests that the system is heterogeneous. This inhomogeneity is likely to be caused by variations in the relative orientations assumed by the asymmetric PPO molecules when included in the large CD cavity. Symmetric compounds, such as 2,5-diphenylfuran (PPF) and 2,5-diphenyl-1,3,4-oxadiazole (PPD), which can form similar aggregates, are expected to exhibit a narrower transition. However, even these compounds cannot eliminate completely the heterogeneity of the system, due to different relative orientations of the pairs of molecules that bridge between two CD molecules. It should be noted that fluctuations in the fluorescence intensity occur at temperatures close to the melting point of PPO. The slight decrease in the intensity around 70 °C (Fig. 1(b)) could also be due to artifacts.

A plot of the anisotropy as a function of the temperature of the monomer and excimer emission (Fig. 1(c)) illustrates the transition temperature, and shows the degree of rotation of the aggregates. The largest rotation occurs at temperatures greater than 60 °C. At this temperature, the monomer emission is most abundant and individual PPO/γ-CD complexes can rotate faster. From this plot, the transition temperatures are estimated to be 43 ± 9 °C for the monomer and 46 ± 8 °C for the excimer. Differences between the transition temperatures estimated by the fluorescence intensities and anisotropy values are within experimental error. These small differences can also be due to extrinsic factors that might affect fluorescence depolarization [27], such as changes in the viscosity of water at different temperatures.

3.2. Effect of varying pH

Hydrogen bonding can potentially play a crucial role in the formation of the self-assembled aggregates; therefore fluorescence studies were performed at various pH values. The fluorescence emission spectra of normal, acidic and basic pH solutions of the PPO/γ-CD complex are presented in Fig. 2(a). When no acid or base is added to the stock solution, the measured pH is 5.4. We refer to this as the normal solution. The normal solution exhibits a broad fluorescence band composed of the PPO excimer emission at 430 nm with a small monomeric shoulder at 375 nm. Interestingly, the fluorescence emission at low pH is not significantly altered relative to the normal sample. The acidic sample (pH 0.4) exhibits a slightly higher excimer fluorescence at a shorter wavelength than the normal solution. The blue shift could be caused by an improper alignment of the PPO molecules in the CD cavity. Since the pK_a value of PPO is 0.84 [28], PPO is predominantly in the protonated form at pH 0.4. Protonation of PPO should weaken hydrogen bonding and, consequently, a disassembling of the aggregates is possible. As a result, the fluorescence intensity of the monomer should increase, while that of the excimer should decrease at a shorter wavelength (424 nm). In addition, CDs may be susceptible to acid hydrolysis, especially under extreme conditions of high temperature and low pH values [29]. However, our data suggest that the aggregates are not disrupted in acidic conditions. Although we used a low pH, hydrolysis of CDs was not significant on the time scale of our measurements performed at ambient temperature.

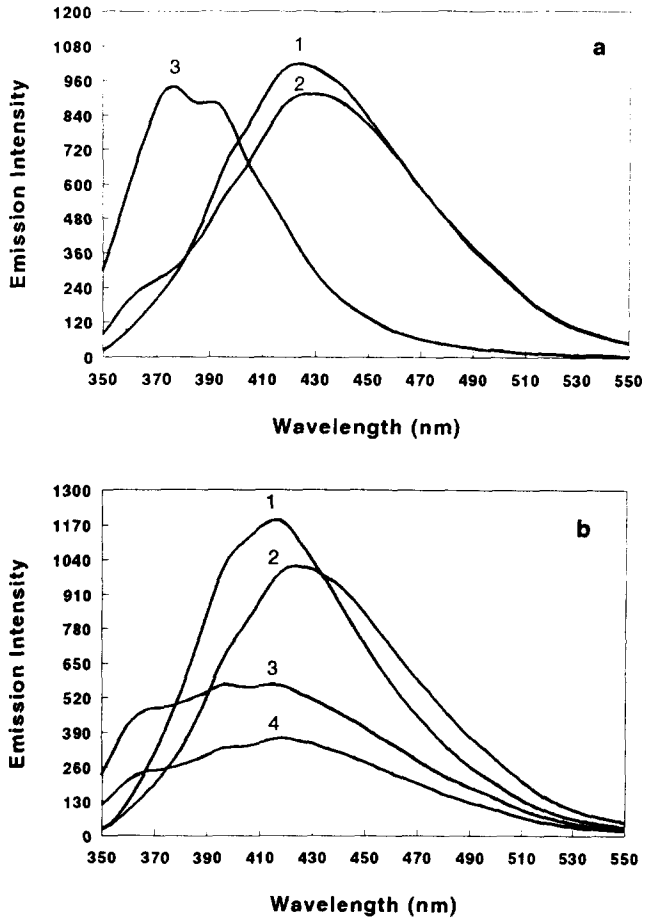

Fig. 2. (a) Steady state fluorescence spectra of (1) acidic (pH 0.4), (2) normal (pH 5.4) and (3) basic (pH 13.2) media of the PPO/γ-CD complex. (b) Further investigation of the acidic media after (1) and before (2) heating, and after separating the precipitate (3) from the supernatant (4) after centrifugation.

Aggregate formation is apparently unaffected by acid. In contrast, the complex at pH 13.2 has a dramatically different fluorescence emission spectrum. The intensity of the monomer emission of the basic solution is enhanced, while the excimer intensity is greatly diminished. A loss in turbidity of the basic sample accompanies this change in the fluorescence spectrum. Therefore changes caused by exposure of PPO in aqueous solutions of γ-CD to a strong base were investigated further. To eliminate ionic strength contributions, samples of the complex were prepared in sodium chloride with the same ionic strength as the basic sample. The fluorescence emission spectrum of the sample with sodium chloride is identical to that of the normal sample. Thus the variation caused by the addition of base to the complex is not simply an effect of the ionic strength of the solution.

For the temperature studies, the samples were not filtered but the precipitate was not used, i.e. only the supernatant was

used for the measurements. To determine the reproducibility of the results, samples from different stock solutions were compared. An error of 3% was found for the fluorescence intensity and a standard deviation of 0.008 was determined for the anisotropy measurements. Any uncomplexed PPO suspended in the aqueous solution of γ-CD will slightly enhance the monomer emission and excimer formation at high concentrations. However, it should be noted that the fluorescence intensity of the filtered samples exhibited a noticeable decrease, but the position and shape of the fluorescence bands were unaltered. Both methods yielded a filtrate or supernatant that was turbid at normal or low pH and room temperature. However, filtering with a 0.45 μm filter paper decreased the amount of turbidity and greatly enhanced the monomer fluorescence. For the anisotropy measurements, it also increased the vibrational structure of the monomer and excimer bands. To investigate the reproducibility of the results further, the acidic solution was used in Fig. 2(b). After centrifugation, the supernatant was analyzed separately from the precipitate. A small volume of water, 1 ml, was added to the precipitate before measuring its emission. Centrifugation resulted in a decrease in the excimer intensity and an increase in monomer formation. Although there was a difference between the absolute intensities of the supernatant and precipitate, the vibrational structure of the fluorescence bands was unchanged. No further studies were performed to quantify the precipitate before and after centrifugation. Filtering the aqueous solution after heating above 85 °C produced an 8 nm blue shift. Heating the sample destroyed the aggregate and increased monomer formation. Once cooled, the PPO/γ-CD complex reformed at a slower rate and hysteresis occurred. Thus the heated sample has a larger maximum intensity and a greater contribution of monomer fluorescence.

The interaction of the base with the complex was also studied by preparing a series of samples at various basic pH values. The fluorescence spectra, at pH values ranging between 10.12 and 13.00, are recorded in Fig. 3(a). The degree of monomer emission intensity is enhanced and the excimer emission intensity is reduced as the base concentration gradually increases. It should be noted that the effect of pH is not significant below about pH 10. Thus, in a less basic medium, the spectra will not follow the trend observed in Fig. 3(a). From titration with sodium hydroxide, it is shown that a decrease in protons causes a shift to shorter wavelengths, i.e. monomer formation. Therefore it is necessary for the environment of the PPO/γ-CD complex to be less basic than pH 10 to observe strong excimer emission. One possible explanation for this phenomenon is that the protons in acidic media are essential for hydrogen bonding between the PPO heteroatoms and the outer hydroxyl groups of γ-CD. The most interesting chemistry of azole compounds arises from their basic properties, since they may undergo protonation or hydrogen bonding in acidic media [30]. Another possible explanation for the lack of excimers in basic media is that

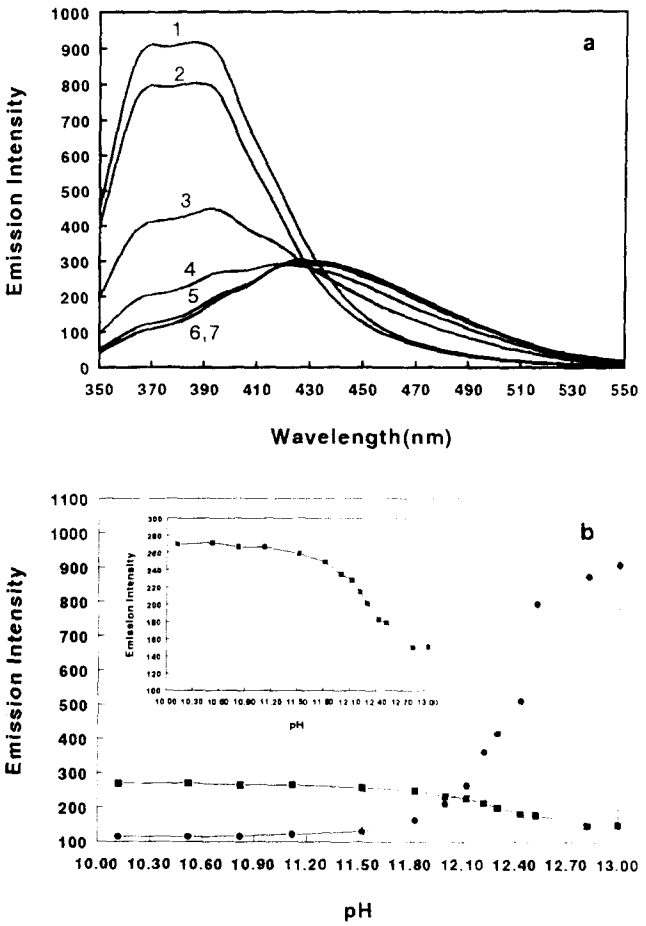

Fig. 3. (a) Fluorescence spectrum of the PPO/γ-CD complex at various basic pH values: (1) 13.00, (2) 12.52, (3) 12.30, (4) 12.00, (5) 11.52, (6) 10.82 and (7) 10.12. (b) Plot of the emission intensity as a function of pH at 375 nm (●) and 450 nm (■) (inset).

electrostatic repulsion from charged species forces the complex apart at high pH values.

The emission spectra of the PPO/γ-CD complex are plotted as a function of pH in Fig. 3(b). From the inflection points of the curves, a transition phase is detected as the pH of the PPO/γ-CD complex is increased. The titration is plotted at basic values between pH 10.12 and 13.00. Two distinct phases are apparent after plotting the monomer and excimer emission intensities. For the monomer, there is a transition phase at pH 12.4 ± 0.5 (i.e. 0.08 mmol of added NaOH). A transition of the excimer emission occurs at pH 12.2 ± 0.2 (i.e. 0.05 mmol of added NaOH). It is known that γ-CD is not susceptible to base hydrolysis at higher pH values and temperature, and that the oxazole ring is stable with increasing basicity [1,29]. However, the pK_a value of the secondary hydroxyl groups of γ-CD is 12 [29,31]. Thus the endpoint of the titration may reflect a simple deprotonation of the γ-CDs that causes separation of the extended aggregates due to electrostatic repulsion.

The anisotropy values of the normal and acidic samples from 350 to 550 nm are similar, as are their fluorescence emission spectra. The anisotropy values in the wavelength

range of the PPO monomer emission are relatively low (approximately 0.1). At least three possible monomer populations can be counted. These are: (1) the free PPO molecules, (2) single units of the PPO/γ-CD complex and (3) monomers in the linear aggregate. The measured anisotropy is the average of the anisotropies of these monomer populations. In contrast, the excimer emission is primarily due to pairs of PPO molecules in the extended aggregate. Thus, at longer wavelengths corresponding to excimer emission, the anisotropy values of the normal and acidic samples approach 0.26 and 0.22 respectively. This suggests that these species are more hindered than the species that emit at shorter wavelengths. Similarly, the excimer emission may represent a variety of aggregate sizes. In normal, acidic and basic media the complex exhibits similar bands at 450 nm. However, the sample at pH 10 has a slightly lower anisotropy value (0.19). The pH 13.2 sample, on the other hand, has a constant anisotropy of 0.02, suggesting that the molecules have a high degree of rotational freedom.

4. Conclusions

Our data suggest that pH and temperature contribute to increased monomer emission of PPO in the PPO/γ-CD complex. In a basic medium, above pH 12.0, the complex begins to shift from excimer to monomer emission. Increasing the temperature above 40 °C causes a similar trend. Above pH 13 and at 64 °C, the excimer is decreased to very low intensities. After complexation, our data suggest that the extended linear aggregates of PPO/γ-CD will disassemble when exposed to extremes of pH and temperature. The large, broad phase transition patterns for the pH and temperature studies suggest that several different orientations may occur inside the CD cavity, producing a heterogeneous system. Further studies, including time-resolved fluorescence and light scattering, are crucial in order to understand this system better.

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References

[1] R. Lakham and B. Terani, in A.R. Katritzki and A.J. Boulton (eds.), *Advances in Heterocyclic Chemistry*, Vol. 17, Academic Press, New York, 1974.
[2] I.B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 2nd edn., 1971.
[3] I.B. Berlman, *J. Chem. Phys., 34* (1961) 1083.
[4] J.B. Birks and L.G. Christophoru, *Proc. R. Soc. London, Ser. A, 277* (1964) 571.
[5] T. Förster and K. Kasper, *Z. Elektrochem., 59* (1955) 976.
[6] B. Stevens, *Nature, 192* (1961) 725.
[7] J.B. Birks, *Nature, 214* (1967) 1187.
[8] D.J.S. Birch, A.D. Dutch, R.E. Imhof, B. Nadolski and I. Soutar, *J. Photochem., 38* (1987) 239.
[9] D.J.S. Birch, A. Dutch, R.E. Imhof, K. Davidson and I. Soutar, in C.E. Hoyle and J.M. Torkelson (eds.), *Photophysics of Polymers*, Am. Chem. Soc. Symp. Ser. 358, American Chemical Society, Washington DC, 1987.
[10] D.J.S. Birch, A.S. Holmes, R.E. Imhof and J. Cooper, *J. Chem. Phys. Lett., 148* (1988) 435.
[11] J.B. Birks, D.J. Dyson and I.H. Munro, *Proc. R. Soc. London, Ser. A, 275* (1963) 575.
[12] W.R. Ware, D. Watt and J.D. Holmes, *J. Am. Chem. Soc., 96* (1974) 7853.
[13] D.J.S. Birch, R.E. Imhof and A. Dutch, *J. Lumin., 31* (1984) 703.
[14] Y. Yguerabide and M. Burton, *J. Chem. Phys., 37* (1962) 1757.
[15] D.L. Horrocks, *J. Chem. Phys., 51* (1969) 5443.
[16] J. Szejtli, *Cyclodextrins and their Inclusion Complexes*, Akademiai Kiado, Budapest, 1982.
[17] K. Kano, I. Takenoshita and T. Ogawa, *Chem. Lett.*, (1982) 321.
[18] R.A. Agbaria and D. Gill, *J. Phys. Chem., 92* (1988) 1052.
[19] A. Harada, J. Li and M. Kamachi, *Nature, 364* (1993) 516.
[20] A. Harada, J. Li and M. Kamachi, *Nature, 356* (1992) 325.
[21] G. Wenz and B. Keller, *Angew. Chem. Int. Ed. Engl., 31* (1992) 197.
[22] H.W. Gibson and H. Marand, *Adv. Mater., 5* (1993) 11.
[23] M.J. Pregel, L. Jullen and J.M. Lehn, *Angew. Chem. Int. Ed. Engl., 31* (1992) 1637.
[24] G. Li and L.B. McGown, *Science, 264* (1994) 249.
[25] R.A. Agbaria and D. Gill, *J. Photochem. Photobiol. A: Chem., 78* (1994) 161.
[26] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum, New York, 1983.
[27] G. Weber, in D.M. Hercules (ed.), *Fluorescence and Phosphorescence Analysis*, Wiley, New York, 1966.
[28] O.P. Shvaika, N.G. Korzhenevskaya and L.P. Snagoshchenko, *Khim. Geterotsikl. Soedin., 2* (1985) 193.
[29] S. Li and W.C. Purdy, *Chem. Rev., 92* (1992) 1457.
[30] M. Meot-Ner, J.F. Liebman and J.E. Del Bene, *J. Org. Chem., 51* (1986) 1105.
[31] A. Ueno, I. Suzuki and T. Osa, *J. Chem. Soc., Chem. Commun.*, (1988) 1373.