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Fluorescence and Viscometry Studies of Poly(4-hydroxystyrene) in Solution

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ABSTRACT: Fluorescence and viscosity of dilute solution of poly(4-hydroxystyrene) (PHS) were measured in methanol in the temperature range 5 to 55°C. The fluorescence spectrum of PHS showed two emission bands at around 308 nm and 356 nm, corresponding to the monomer and the excimer bands, respectively. From the temperature-dependent fluorescence measurements, a plot of the excimer to monomer intensity ratio I_d/I_m *versus* temperature was obtained, which shows double lines with positive slopes crossing at *ca.* 35°C. From temperature-dependent viscosity measurements, a plot of the limiting viscosity number $[\eta]$ *versus* temperature was obtained, which shows double lines with negative slopes crossing at *ca.* 40°C, above which the slope was decreased. These results indicate that there is stronger solvation of solvent molecules to polymer coil at temperatures below *ca.* 35—40°C, arising from hydrogen bond formation between PHS and methanol molecules.

KEY WORDS Poly(4-hydroxystyrene) / 4-Ethylphenol / Excimer / Fluorescence / Polymer Conformation / Polymer Solution / Temperature Dependence / Viscosity /

Many vinyl polymers with aromatic chromophores exhibit intramolecular excimer fluorescence in solution.[1] Excimers are excited-state complexes formed by a couple of chromophores placed face to face at a short distance. The formation of an excimer is due to association of two aromatic groups separated by three carbon atoms along the chain, one of which has been electronically excited.[2] It is characteristic for excimer fluorescence to appear in a considerably lower energy region than monomer fluorescence and to have no mirror image relation to the absorption spectrum. The intramolecular excimer formation for vinyl polymers is governed by both the conformation and configuration of the chains.

Excimer formation has been observed in polystyrene[3-5] and its derivatives such as poly(α-methylstyrene),[6,7] and poly(4-methylstyrene),[8] but not in such analogous polymers as poly(4-chlorostyrene) and poly(4-bromostyrene).[9] Jiang *et al.*[9] showed that the fluorescence spectrum of poly(4-hydroxystyrene) (PHS) has a vibrational structure and cannot be attributed to the formation of excimer. They insist that the presence of bulky hydroxyl substituents in PHS does not allow parallel arrangement of aromatic rings along with the polymer chain, which is a necessary condition for the excimer formation. However, when Figure 3 in ref 9 is examined, their interpretation does not seem consistent with the view that the monomer fluorescence spectrum is the single mirror image of the absorption spectrum. The fluorescence spectrum in the figure shows the anomalous fluorescence emission band at the longer wavelength than that where the fluorescence emission band corresponding to the mirror image of the absorption spectrum appears. The lower energy band of this fluorescence spectrum

may be attributed to the fluorescence of the intramolecular excimer.

The purpose of the present work is to clarify more the fluorescence spectra of PHS in solution and to obtain information on the behavior of polymer chain in solution using fluorescence and viscometry methods. In general, the ratio of the emission intensities of excimer and monomer depends on intrinsic and extrinsic characteristics of the system, for example, solvent, temperature, polymer tacticity, and molecular weight etc.[10] They were studied here in the temperature range from 5 to 55°C.

EXPERIMENTAL

Materials

PHS fractions with molecular weights of 48000 and 551000 were obtained by complete hydrolysis of poly(4-acetoxystyrene) (PAS), whose polymerization and fractionation were carried out with almost the same procedure as described in the previous paper.[11] Hydrolysis was carried out in the following manner. PAS was dissolved in dioxane, and subsequently aqueous 0.8 mol l^{-1} sodium hydroxide solution was added with stirring at room temperature. The air in the reaction vessel was substituted with a nitrogen atmosphere. The resulting mixture was added slowly with stirring into a large excess of dilute aqueous hydrochloric acid. The recovered polymer was washed with water until no chloride ion was detectable, and then dried in a vacuum oven to constant weight. Molecular weight was determined by intrinsic viscosity measurements using the appropriate Mark–Houwink–Sakurada equation.[12]

Methanol of specific quality for fluorescence measurement and 4-ethylphenol were purchased from Nacalai Tesque Inc. 4-Ethylphenol was purified according to the standard procedures.

Fluorescence Measurements

Absorption spectra were measured with a Jasco spectrophotometer UVIDEC 670 at 25 ± 0.1°C. The concentrations of solutions for PHS ($M_w = 48000$) and 4-ethylphenol were 4.26×10^{-4} mol l^{-1} (chromophore unit) and 3.96×10^{-4} mol l^{-1}, respectively. Fluorescence spectra were measured with a Jasco fluorescence spectro-fluorometer FP-770. Fluorescence measurements were conducted by the excitation of 279 nm with an emission slit width of 10 nm and an excitation slit width of 20 nm. The same conditions were used for all measurements. The concentrations of solutions for PHS ($M_w = 48000$) and 4-ethylphenol were 3.8×10^{-5} mol l^{-1} (chromophore unit) and 1.23×10^{-4} mol l^{-1}, respectively. Temperature deviation in the measuring cell was maintained within ± 0.1°C at all temperature ranging from 5 to 55°C.

Viscosity Measurements

Viscosity measurements of PHS ($M_w = 551000$) solutions were carried out using an Ubbelohde suspension-type capillary viscometer in a water bath controlled within ± 0.01°C at several temperatures. Both the shear rate and kinetic energy correction were negligible. The limiting viscosity number, $[\eta]$, was determined by the Huggins plot and Fuoss–Mead plot.

RESULTS AND DISCUSSION

Figure 1 shows the absorption and fluorescence spectra of PHS in methanol at 25°C. For the purpose of comparison, the absorption and fluorescence spectra of the corresponding monomer chromophore, 4-ethylphenol, were measured in methanol at 25°C and shown in Figure 2. The absorption spectrum of PHS was very similar to that of 4-ethylphenol, and the fluorescence spectrum of PHS contained two main bands, a simple mirror image of the absorption band appearing at about 308 nm and a broad, structureless one at about 356 nm shifted toward longer wavelengths.

The remarkable similarity between the ab-

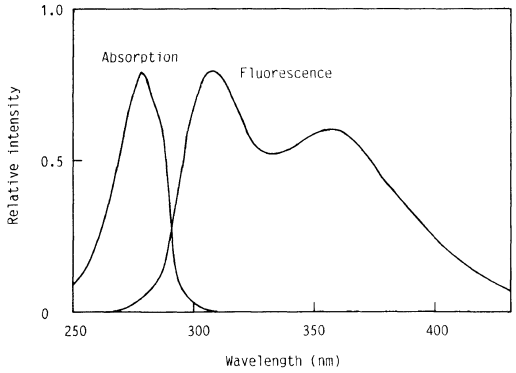

Figure 1. Absorption and fluorescence spectra of PHS in methanol at 25°C.

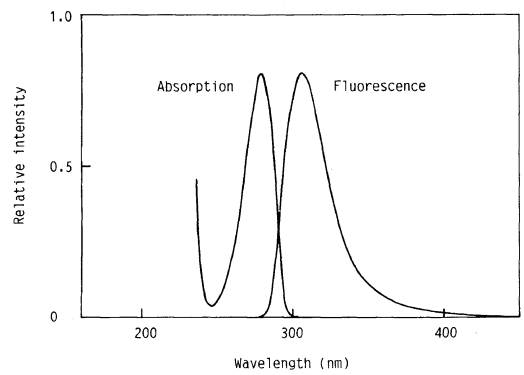

Figure 2. Absorption and fluorescence spectra of 4-ethylphenol in methanol at 25°C.

sorption spectra of the PHS and 4-ethylphenol leads to the conclusion that there are very weak interactions between polymer substituent chromophores in the ground state. The chromophores act independently of one another in absorbing the incident radiation.

If substituent chromophores radiatively return to the ground state after excitation by absorption of light in a manner independent of the conformation of the surrounding chromophores and if it is this emission that is responsible for the fluorescence of the polymer, one would be able to expect the fluorescence spectrum of the polymer to be similar to that of 4-ethylphenol. The actual fluorescence spectra of 4-ethylphenol and PHS are, however,

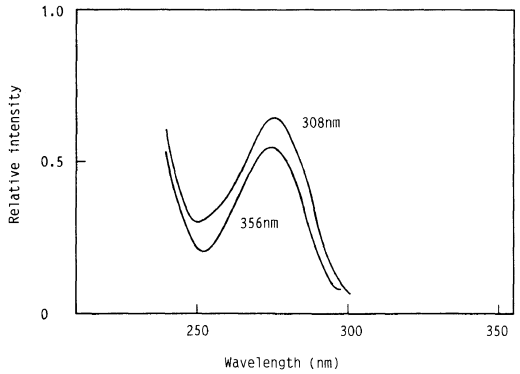

Figure 3. Excitation spectra of PHS obtained at fluorescence wavelengths of 308 nm and 356 nm.

very different. Therefore, some characteristic changes in conformation in the polymer chain should occur after absorption and before emission of light.

If the emission obserbed at about 356 nm for PHS is due to impurities, these impurities should reveal the absorption spectra in the wavelength region of about 330 to 400 nm where the absorption band corresponding to the mirror image of the fluorescence emission band should appear. However, no absorption was detectable in these regions even when the concentration of the polymer was increased. The possibility of emission at about 356 nm by decomposition products produced by the ultraviolet radiation may also be eliminated, since continuous exposure of the polymer samples to the excitation light produced no change in fluorescence emission.

Generally the intensity of the anomalous emission increases with concentration at the expense of normal emission intensity. In this investigation, increasing polymer concentration produced no notable changes in the ratio of emission intensity at 308 nm to emission intensity at 356 nm.

Figure 3 shows the fluorescence excitation spectra of PHS in methanol at 25°C. The excitation spectra of PHS at the fluorescence wavelength 308 nm and 356 nm exhibited the identical spectral patterns. This means that the

fluorescence at about 356 nm is not caused by any impurity.[13] The fluorescence spectrum of PHS was measured in methanol at −196°C. The excimer emission has no appreciable intensity and only monomer fluorescence is observed. This may be due to a lack of excimer forming sites geometrically suitable for excimer formation in low temperature rigid glass.[14]

From these experimental results, it is concluded that the emission obserbed at about 356 nm originates from some intra-chain interaction. The higher energy band must be assigned to the fluorescence of the monomer phenol group and the lower energy one must be attributed to the fluorescence of the intramolecular excimer.

Temperature-dependent fluorescence measurements are particularly interesting in that, through steady-state experiments, they yield information on conformational change of a coil. Figure 4 shows the temperature-dependent fluorescence spectrum of PHS in methanol. As the temperature is raised, the intensities of the monomer and excimer decrease. However, the intensity of the monomer band decreases more with increasing temperature than that of the excimer band. In addition, the excimer band shifts progressively to a longer wavelength as a function of temperature.

The intensities of monomer fluorescence (I_m) and excimer one (I_d) in arbitrary units are given in Figure 5 as a function of temperature, where I_m and I_d are the intensities of the monomer peak and that of excimer peak, respectively. The intensities of monomer band decrease linearly in the range of 5 to 55°C, while the plot of those of excimer band show two different linear lines crossing at *ca.* 35°C. This indicates that excimer dissociation does not lead to an excited monomer. The intensities of excimer emission band decrease slightly with an increase in temperature, and decrease more greatly above *ca.* 35°C.

Hoyle *et al.*[15] reported that the excimer to monomer intensity ratio (I_d/I_m) increases with decrease in the solubility parameter and the limiting viscosity number of the solution. Sivadasan *et al.*[16] reported that the extent of intramolecular excimer formation (given by the parameter I_d/I_m) provides a measure of the statistical conformation of the polymer chain. A large value of I_d/I_m suggests polymer chain contraction whereas a small value of I_d/I_m

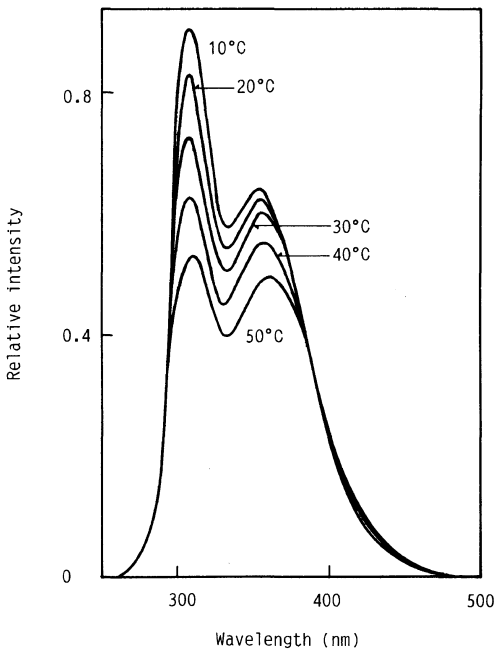

Figure 4. Fluorescence spectra of PHS in methanol at several temperatures.

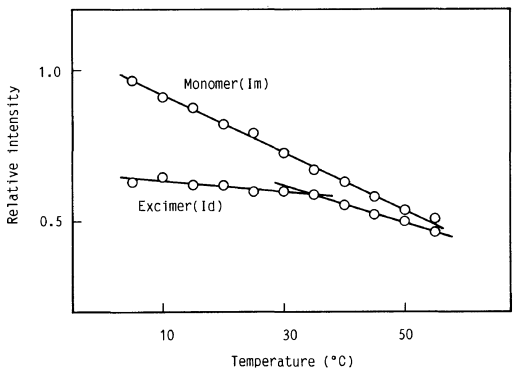

Figure 5. Temperature dependence of fluorescence intensity of excimer (I_d) and monomer (I_m) bands for PHS in methanol.

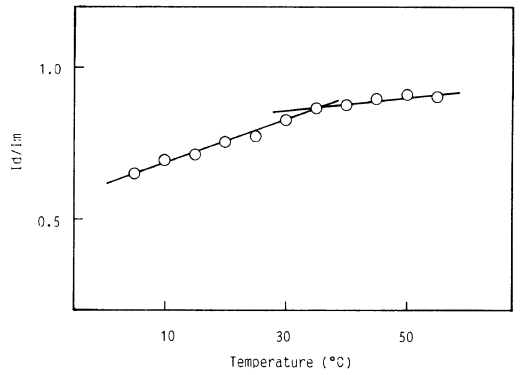

Figure 6. Temperature dependence of the ratio of excimer to monomer fluorescence intensity of PHS in methanol.

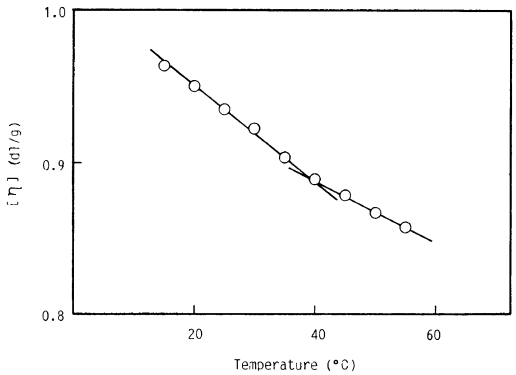

Figure 7. Temperature dependence of $[\eta]$ for PHS in methanol.

suggests polymer expansion.

Figure 6 shows the effect of temperature on the I_d/I_m ratio for PHS in methanol. Plots of I_d/I_m show double lines with positive slopes. The different linear lines cross at *ca.* 35°C, above which the slope is small. The increase in I_d/I_m might be attributed to the polymer chain contraction producing a compact structure. Consequently, it may be concluded that the change in polymer conformation occurs at *ca.* 35°C.

To investigate conformational changes of PHS, the temperature dependence of the limiting viscosity number $[\eta]$ in methanol was studied. The effect of temperature on $[\eta]$ is displayed in Figure 7. Plots of $[\eta]$ show double lines with negative slopes crossing at *ca.* 40°C, above which the slope is observed to be small. Decrease in $[\eta]$ with increasing temperature can be attributed to the formation of a more compact structure of PHS.

The partial molar entropy of dilution of solvent ΔS_1 can be calculated using the following relationship

$$\Delta S_1 = R\psi_1/v_2^2$$

where R is the gas constant, ψ_1 the entropy parameter and v_2 the volume fraction of polymer. The ψ_1 can be evaluated from the slope of $[\eta]$ *versus* temperature. The temperature coefficient of $[\eta]$ is negative in this study and thus ψ_1 must be negative. This indicates that the energetic interaction is exothermic in PHS–methanol system. The magnitude of decrease in $[\eta]$ with increasing temperature is related to the extent of solvation of solvent molecules to polymer coil. Therefore, it is concluded that there is a stronger solvation of solvent molecules to polymer coils at temperatures below *ca.* 40°C.

There are several reports on the effects of hydrogen bonds on the conformation of PHS in a solid and solution. Nakamura *et al.*[17] showed that the glass transition temperature, T_g, of poly(4-hydroxy-*co*-4-acetoxystyrene) increases with the increase of the composition of 4-hydroxystyrene, and decrease considerably with the addition of small amount of water. They explained these results by hydrogen bonds in this copolymer.

In our previous report,[18] it was also reported that the contribution of solubility parameter δ_h arising from hydrogen bond formation to the total value of the solubility parameter δ_2 of PHS is considerably larger than that of the other vinyl polymers. This large δ_h for PHS represents great ability of intramolecular hydrogen bond formation. We reported[12] that the Flory–Huggins entropy and enthalpy parameter for dilution of PHS in various

solvents are all negative, and absolute values are considerably large. These results indicate that there exist strong thermodynamic interactions in solution of PHS arising from hydrogen bond formation between polymer and solvent molecules.

All these results show that the hydrogen bond formation plays a very important role for PHS in both a solid and solution. Then it may be presumed that the interaction between hydroxyl groups in PHS and methanol owing to hydrogen bonds is weakened by increasing temperature and may be broken near temperatures of 35—40°C.

CONCLUSIONS

The fluorescence spectrum of PHS shows two emission bands at about 308 nm and 356 nm. The former corresponds to a mirror image of the absorption spectrum of 4-ethylphenol and assigned to be the monomer emission band. The structureless fluorescence band at about 356 nm, which shifted about 4400 cm^{-1} towards longer wavelength from 308 nm, was assigned to be the excimer emission band. From the temperature-dependent fluorescence and viscosity measurements, plots of I_d/I_m *versus* temperature and those of $[\eta]$ *versus* temperature were obtained, which show two lines intercepting at a point which has been ascribed to a transition temperature. It seems reasonable to assume that intermolecular hydrogen bonds between hydroxyl groups of PHS and methanol may be broken at the transition temperature.

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