Fluorescence Studies of Polystyrene in Different Solvents

[1]M. S. KHAN*, [1]W. KHAN , [2]S. A. KHAN AND [3]Y. IQBAL
[1]National Centre of Excellence in Physical Chemistry
University of Peshawar, Peshawar 25120, Pakistan
[2]PCSIR Laboratories, Jamrud Road, Peshawar , Pakistan.
[3]Chemistry Department, University of Peshawar, Pakistan

Summary: This investigation was done to have a systematic study of the Fluorescence of Polystyrene polymer with respect to concentration and solvent. A wide range of concentration was selected for Fluorescence studies and four different solvents i.e 1,2- Dichloroethane, Cyclopentane, n-Butylacetate and Cyclohexane were employed for this work. The Fluorescence peak at 335 nm was selected to be due to excimer emission while the peak at 283 (or 286) nm was selected to be due to monomer emission, and the excimer and monomer intensities were measured at these wavelengths for all the solvents under investigation. The R values (i.e. I_E/I_M ratio) were found for all the solutions and were found to increase with concentration. This increase is thought to be due to several effects including intermolecular excimer formation, remote adjacent intramolecular excimer formation, coil contraction and so on. The R values remarkably depend upon nature of the solvent. The Fluorescence emission intensity ratio (I_E/I_M) is in the order of n-Butylacetate <1,2-Dichloroethane <Cyclohexane < Cyclopentane. R is shown to be higher in poor solvent while it is low in good solvent.

Introduction

Fluorescence techniques have long been employed widely for the study of biological macromolecules[1] but intensive studies of their application to the investigation of synthetic polymers have been reported only in recent years[2-3].

Polystyrene was one of the first polymers to be studied by fluorescence techniques [4-5]. An early concentration study was done by Vala [6], who found that the ratio of excimer to monomer fluorescence intensity, I_E / I_M, was insensitive to small changes of concentration in a very dilute solution. Excimer formation in polymer - solvents systems may result from both intra - and intermolecular interactions depending on the concentration of the polymer solution [7].Torkelson and others [8] carried out the fluorescence and absorbance study of polystyrene in solution over a wide range of concentration for several molecular weights and solvents. The ratio of excimer to monomer fluorescence intensities, I_E / I_M were determined. Roots and Nystrom [9] reported the concentration dependence of the fluorescence of three molecular weight of polystyrene and found that the curve representing I_E/I_M showed an apparent upward curative at C [η] $\approx$ 1 for all molecular weights.

Nishihara and Kaneko [10] did an extensive study of polystyrene in six solvents. Contrary to Vala [6] they showed that I_E/I_M increased linearly with concentration even at concentrations approaching infinite dilution.

Clearly, there is little agreement among the various studies of the concentration dependence of polystyrene fluorescence. A possible contribution to this lack of agreement is that at high polymer concentration the effect of self-absorption of monomer fluorescence by the sample may become significant. As obvious from the above work that there is discrepancy among various workers and so there is room for further work on the concentration dependence of fluorescence of polystyrene. Therefore we started systematic study on the role of concentration and solvents on polystyrene fluorescence.

Results and Discussion

Intensities of Excimer emission (I_E) and monomer emission (I_M) were determined for each solution, and their ratio was calculated. The intensities of excimer emission (I_E) and monomer emission (I_M) and their ratio (I_E/I_M) are presented in Table 1-4 for all the solvents studied.

Table-1: Fluorescence intensities of excimer and monomer emissions and their ratio for polystyrene in 1,2 - dichloroethane.

Conc. (g/dl)	I_E (335)	I_M (283)	I_E / I_M
0.02	29.0758	28.0268	1.0374
0.04	33.0035	19.5978	1.6840
0.06	30.3975	14.4147	2.1087
0.08	26.7300	10.4586	2.5557
0.10	21.5293	7.6461	2.8157

*To whom all correspondence should be addressed.

Table-2: Fluorescence intensities of excimer and monomer emissions and their ratio for polystyrene in cyclopentane.

Conc. (g/dl)	I_E (335)	I_M (283)	I_E / I_M
0.02	73.8250	5.0850	14.5181
0.04	51.2263	3.5548	14.4104
0.06	40.1044	2.4891	16.1120
0.08	29.5240	1.8965	15.5676
0.10	20.4487	1.1208	18.2447

Table-3: Fluorescence intensities of excimer and monomer emissions and their ratio for polystyrene in n-Butyl acetate.

Conc. (g/dl)	I_E (335)	I_M (283)	I_E / I_M
0.02	16.4897	18.7214	0.8807
0.04	18.7680	16.8102	1.1164
0.06	18.6601	14.2006	1.3140
0.08	15.1048	11.1740	1.3517
0.10	13.4108	9.3164	1.4394

Table-4: Fluorescence intensities of excimer and monomer emissions and their ratiofor polystyrene in cyclohexane.

Conc. (g/dl)	I_E (335)	I_M (283)	I_E / I_M
0.02	34.5264	13.9671	2.4719
0.04	39.4253	11.5902	3.4016
0.06	36.2963	8.5884	4.2262
0.08	31.0204	6.5234	4.7552
0.10	25.6609	4.6195	5.5549

Effect of Concentration of Excimer Fluorescence Emission:

The fluorescence study of polystyrene in solution has been reported over a wide range of concentration. In figure (1-4) we present the recorded fluorescence spectra of 1×10^5 M.Wt Polystyrene in different solvents at different concentrations in a 1 cm-cell. From comparison with model dibenzyl compounds and in agreement with the results of Vala [6] and similarly the results of Ishii et al [11] we conclude that the polystyrene fluorescence peak at the 335 nm is due to excimer emission while the peak at the 283 and 286 nm is due to monomer emission.

The ratio R $(\lambda_E/\lambda_E) = I_E(\lambda_E)/I_M (\lambda_M)$ was calculated and , is shown in Table-1 for polystyrene in 1,2, dichloroethane. These data are in agreement with similarly uncorrected results of Roots and Nystrom [9]. Similarly we studied polystyrene in all other solvents which are mentioned in experimental section. In Table 1-4 the values of R are shown for 1×105 M.Wt polystyrene in different solvents. It can be seen from the tables that R values increase with concentration. These are in agreement with that of Torkelon [8]. The major contribution to the variation in R with Polymer concentration and Polymer molecular weight is attributable to absorption of the monomer fluorescence both by the polymer itself and by different levels of absorbing impurities in the sample preparation.

The R (I_E/I_M) value increases slowly and smoothly from lower to higher concentrations.

In any case, this apparent increase in R with polymer concentration is independent of molecular weight and shows no obvious indication of the onset of intermolecular polymer overlap. Several effects could contribute to a residual increase in R. these include contributions from intermolecular excimer formation due to coil contraction as the polystyrene concentration increases. For intermolecular excimer formation to occur, two chromophores form different polymer molecules must come into a nearly coplanar sandwich –like structure with separation less than ~ 3.7 A° [12-13] In a semidilute solution, the average distance between interpolymer contacts,ξ is believed to depend on $C^{3/4}$ in a good solvent [14-16] so that the number of binary contacts in a unit volume is then proportional to $C^{9/4}$.If the change in R were due solely to intermolecular excimers then, ΔR (i.e. $\Delta R =$ R-1.00), the increment in the number of intermolecular excimers formed per monomer unit, should be proportional to the product $mC^{9/4}$. $C^{-1} = C^{5/4}$ However, upon using this prediction with our results, one sees that ΔR is not proportional to $C^{5/4}$ for polystyrene in 1,2 dichloroethane. At 0.02 g/dL, $\Delta R = 0.0374$ and $C^{5/4} = 0.0075$. Thus the value of ΔR is not proportional to $C^{5/4}$. So other effects must contribute to the residual increase in R. The phenomenon of chain contraction with increasing polymer concentration is well documented [14,17,18], and this contraction may contribute to an increase in remote excimer formation with increasing concentration. However, other work has shown that remote excimer formation is insigni-ficant even in polystyrene chains that are near precipitation [19-20], accordingly it is unlikely that remote excimer formation is an important contributor to the increase in R. The decrease in coil dimensions may also affect vicinal excimer formation through changes in local conformation. This could increase R by facilitating the diffusions formation of excimer.

Solvent Effect on Excimer Fluorescence Emission

The excimer and monomer intensities ratio (I_E/I_M) of polystyrene solution has remarkable dependence on the nature of solvent used. The I_E/I_M value of polystyrene in different solvents are give in Table 1-4 while the fluorescence spectra are given in Figures 1-4. The shape of the fluorescence spectra is
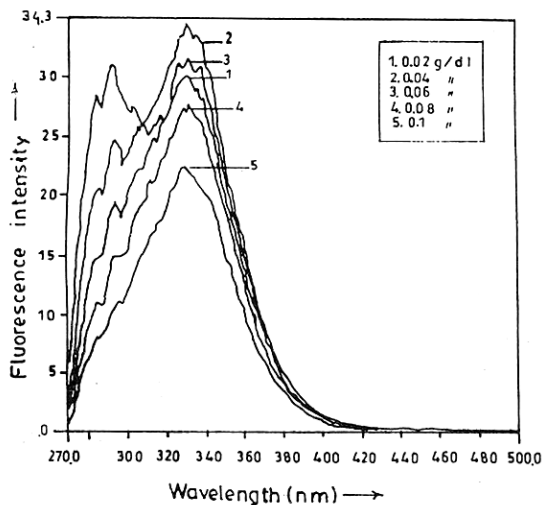
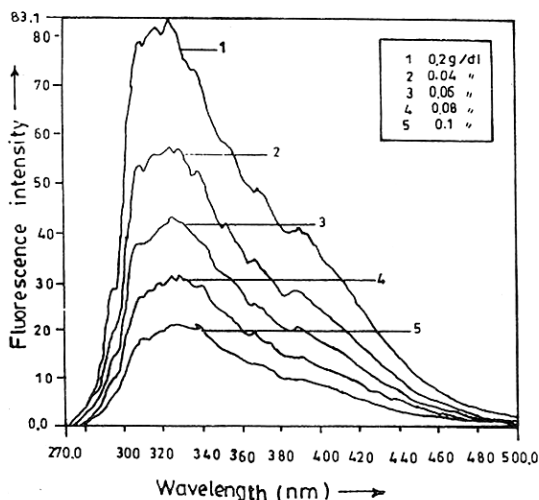Fig. 1: Fluorescence emission spectra for Polystyrene solutions in 1,2-dichloroethane.

Fig. 2: Fluorescence emission spectra for Polystyrene solution in cyclopentane.
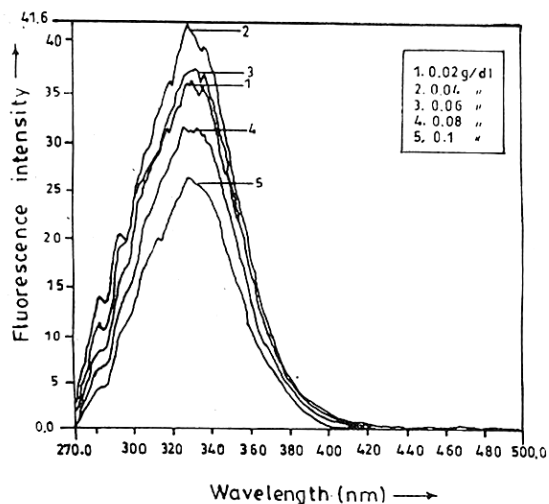

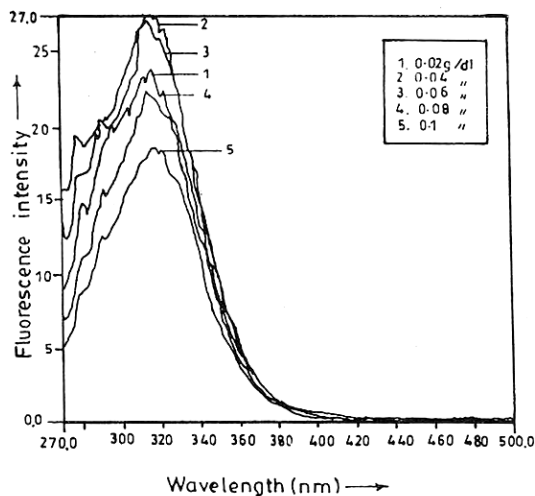Fig. 3: Fluorescence emission spectra for Polystyrene solutions in cyclohexane.

Fig. 4: Fluorescence emission spectra for Polystyrene solutions.

the same in all the solvents whether it is good or poor. Studies on alternating copolymer, head to head polystyrene etc indicates that the excimer formation is dominated by nearest neighbor interactions. Furthermore kinetic studies based upon nearest neighbor interaction in polymers having pendant phenyl groups also implies that long-range interactions are unimportant in determining the number of excimer forming. Our results agree very well with these conclusions and we observed similar spectra in all the solvents. The excimer formation, as measured by the ratio I_E/I_M has a dynamic component that is sensitive to chain mobility and solvent viscosity (no. in addition, this ratio has configurational component [21-23]

Factors that increase the mean separation of Excimer forming groups lead to a decrease in I_E/I_M. Conversely factors that compress the polymer dimension resulting in a smaller mean separation lead to an increase in I_E/I_M. In this way I_E/I_M should be sensitive to the quality of the solvent in which the polymer is dissolved. It is clear from these tables that the fluorescence intensities ratio is in the order of n-butyl acetate < 1,2 dichloroethance < cyclohexane< cyclopentane. As cyclopentane is poor solvent while n-butyl acetate is good solvent for polystyrene, so, the value of R are higher in poor solvent while it is lower in good solvents. As the solvent quality is reduced the polymer coil contracts, so that the tighter coiling of a long chain around itself in the poorer solvents might cause non adjacent, (i.e., remote) chromophores to come into close coplanar contact, thus facilitating excimer formation. The ratio of fluorescence intensities, I_E/I_M, varied sensationally with a change in solvent. One effect is due to solvent viscosity to the ratio I_E/I_M increases with chain length in poor solvents for polystyrene, but remains constant in good solvents. So the solvent viscosity is also playing its role in this case.

Experimental

The polystyrene used in this work was obtained from BDH Chemicals Ltd. England. The solvents which are used in this work are, 1,2 dichloroethane, n-Butylacetate cyclopentane, cycloherane.

For fluorescence study of polystyrene (M.W= 100,000 approximately) a series of solutions with concentration ranging from 0.02 g/dl to 0.1 g/dl were prepared in four different solvents i.e in 1,2 - Dichloroethene, cyclohexane, cyclopentane and n-Butyl acetate. Then the fluorescence spectra of these solutions were recorded at Perkin Elmer Luminescence Spectrometer LS 50 B (interfaced with PC), using 260 nm as a Excitation wavelength. All the spectra were recorded at room temperature. Excimer and Monomer intensities I_E/I_M were determined from the spectra.

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