UV Absorbance Studies of Dilute Polystyrene Solutions in Different Solvents

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Summary: This study was carried out to have a systematic knowledge of the polystyrene absorbance (M.Wt: 100000) with respect to temperature, concentrations and solvent. A wide range of concentration was selected for these studies and four different solvents i.e.; 1,2-dichloroethane, ethylacetate, carbontetrachoride and cyclohexane were employed for this work. The absorption spectra of polystyrene were measured in these four solvents at different temperatures of 10° C, 20° C, 30° C, 40° C, 50° C and 60° C. The effect of concentration, temperature and solvent was determined.

Introduction

Different physical properties are exhibited by the polymer solutions in dilute and so-called semi-dilute concentration range. In dilute concentration range, the polymer chains are separated on the average by large expanses of solvents and in semi-dilute range chains are in sufficient concentration that interactions screen out the long-range correlation. The chain properties are different in both kinds of solutions. Number of experimental techniques including osmometery [1] neutron and light scattering [1 -3] viscometrey [4], sedimentation velocity [5-8] and UV absorbance spectroscopy [9] have been employed to check the difference and change in properties from dilute to semidilute regions. Absorption method is an important method and to the approximation of independent chromophores, light absorption will be related to the concentration of the chromophores in dilute region and not on molecular weight. Absorption studies on Polymer solution have been done by many workers [9]. Polystyrene is one of the most widely used thermoplastic polymer, mostly employed as an insulator, as a buoyancy medium and in packaging [6]. Various studies on Polystyrene absorption have been reported. Destor *et al.*, [9] made absorption measurements of Polystyrene in chloroform along-with Poly (oxyethylene) in water and Ploy (vinyl acetate) in acetonitrile. For Polystyrene they found absorbance Vs concentration curve to be linear at low concentration but progressively curved for higher concentrations and explained it to be due to changes in polarizability of the medium with increasing polymer concentration. The replacement of a solvent molecule by a monomer alters the polarity and consequently the absorption frequency and molar absorptivity. Lee, Waddell and Casassa [11] have repeated these measurements and found that absorption of polystyrene to be linear unto 8 g/L of concentration and said that the data of Destor *et al.*, was affected by instrumental artifacts. Torkelson *et al* [12] reported the polystyrene absorbance in a wide range of concentration in order to check any curvature and to get crossover or critical concentration C* where dilute region and semidilute regions of concentration cross each other. They worked in 1,2 dichloroethane & cyclohexane and only at two temperatures.

As temperature and solvent plays an important role in absorption by any chromophore, and all the previous studies were done in only one or two solvents and at single or two temperatures, so this a factor that we feel has not been properly treated in all previous work. There is a need to have a systematic study of polystyrene absorption to confirm or deny the presence of any curvature or crossover concentration. We have done a systematic study of Polystyrene absorbance over a wide range of temperature i.e. 10° C to 60° C and in four different solvents namely 1,2-dichloroethane, ethyl acetate, carbon tetrachloride and cyclohexane. The results of absorbance with respect to these parameters are given and their implications are discussed.

Results and Discussion

The absorption spectra of polystyrene solutions are shown in Figs; 1, 2, 3 & 4 in different

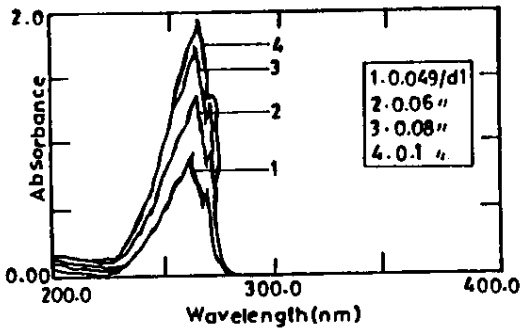

Fig. 1: Absorption spectra of Polystyrene in 1,2-dichloroethane at six temperatures (10°C, 20°C, 30°C, 40°C, 50°C, 60°C).

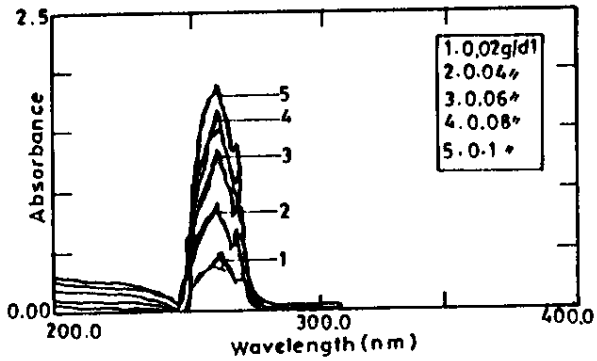

Fig. 2: Absorption spectra of Polystyrene in ethyl acetate at six temperatures (10°C, 20°C, 30°C, 40°C, 50°C, 60°C).

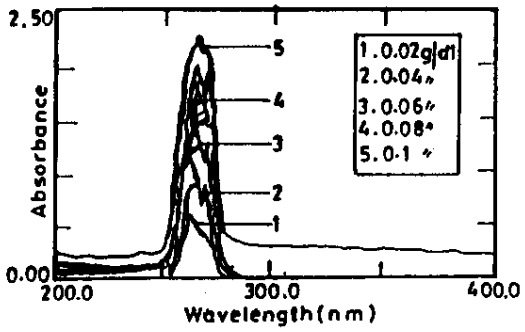

Fig. 3: Absorption spectra of Polystyrene in carbon teterachloride at six temperatures (10°C, 20°C, 30°C, 40°C, 50°C, 60°C).

solvents. The maximum absorption in all solvents and at almost all temperatures is at 260 nm so this was chosen and plots of absorbance Vs concentration

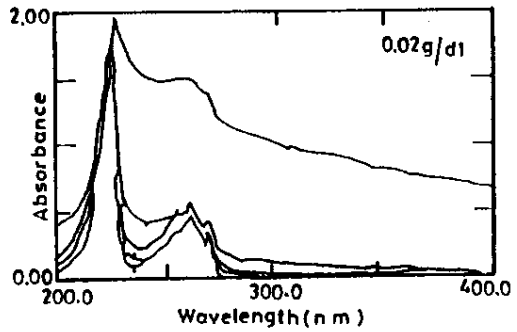

Fig. 4: Absorption spectra of Polystyrene in cyclohexane at four temperatures (30°C, 40°C, 50°C, 60°C).

were drawn to get idea of its behavior. These plots are shown in Figs: 5, 6, 7 & 8 for various solvents. It can be seen from these plots that absorbance depends on concentration linearly and there was no curvature found in this concentration range studied. This is in agreement to Torkelson et al [12] and Lee et al [11] but in contrary to Destor et al [9]. Solvents were varied in order to see whether any onset of overlap or change in behavior appears or not, but in all four solvents there is no indication of any obvious onset of curvature. The curvature is indicative of polymer overlap showing shifting of properties and also change from dilute to semidilute region.

The C* values i.e. $C^* = 1/[\eta]$ is indicative of the crossover concentration between dilute and semidilute regions in polymer solutions, were calculated from viscosity measurements and its values are given in Table 1.

Table: 1 Values of Intrinsic Viscosity and C^* of Polystyrene in 1-2 Dichloroethane at Different Temperatures.

Temp.°C	Intrinsic Viscosity[η],dl/g	Critical concentration, C*=1/[η],g/L
25	0.47118	21.22
30	0.44795	22.32
40	0.46780	21.38
50	0.44097	22.68
60	0.44662	22.39

The average value of C* found in this manner is 21.223 g/L similar to the value 23.9 g/L of Torkelson et al [12] for the same molecular weight at similar temperature of 25°C. This C^* values indicates that the overlap concentration of polymer molecules will be at a concentration above 21.223 g/L. As in our case, the concentration of the solutions is lower

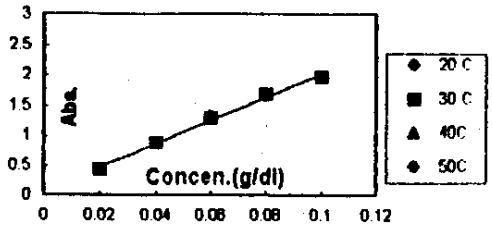

Fig. 5: Polystyrene in 1,2 Dichloroethane at 261 nm.

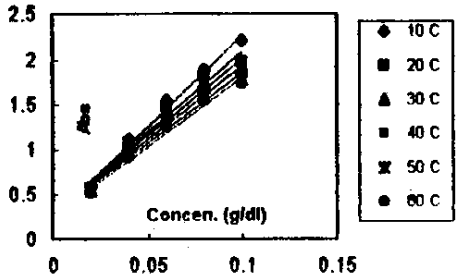

Fig. 6: Polystyrene in CCl_4 at 262 nm.

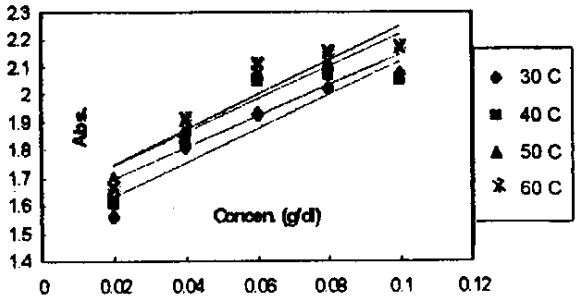

Fig. 7: Polystyrene in Cyclohexane at 223 nm.

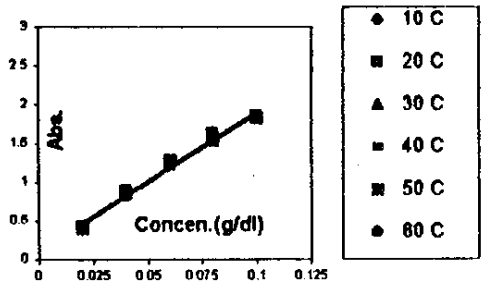

Fig. 8: Polystyrene in Ethyl acetate at 262 nm

than this suggested overlap concentration, so the result obtained by the absorption studies are confirmed here also and it shows that there is no overlap concentration present. In other words the self-absorption effect will be minimum in this range.

Temperature Effect

We have tried to find out the effect of temperature on the absorption spectrum of polystyrene. It was seen from the absorption values that there is no or little change as for as the absorption is concerned. The $\lambda_{max.}$ appears at the same position in all the temperatures, while there is some change in the intensity of the absorbance values which decreases with the temperature rise. This means that the temperature increase suppresses the absorbing species concentration. Furthermore, it is also possible that with increase in temperature the volume increases which in a way produces dilution effect and hence absorption decreases. All solvents except cyclohexane show this behavior. Cyclohexane shows somewhat irregular behavior.

Experimental

Polystyrene samples with Mw=$1x10^5$ was purchased from BDH chemicals Ltd. Poole England. Spectroscopic quality 1,2 dichloroethane (Merck, England), cyclohexane (BDH, England), ethyl acetate (BDH, England) and carbon tetrachloride (BDH, England) were used without any purification.

A series of solutions with concentration ranging from 0.02 g/dl to 0.1g/dl were prepared by weighing polystyrene into 25 ml volumetric flasks and diluting with solvents. Sufficient time (more than 24 h) was allowed for solutions.

All absorption measurements were made with a UV-160A UV-Visible recording spectrophotometer of Shimadzu, Japan. Stray light was sufficiently low over the required wavelength 200-400 nm. to permit reliable measurements of absorbance. These spectra were recorded at different temperatures from 10°C to 60°C with 10°C intervals and all the solvents mentioned above.

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