Effect of Solvents on the Photophysical Properties of the Polystyrene Solutions

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ABSTRACT:

The aim of this work was to investigate the photophysical behavior of polystyrene solutions under the effect of different solvents at different concentrations .Testband at 262 nm. There was no effect of solvents and concentration on the position of the maximum absorption wavelength. The data show that a strong dependence between absorbance intensity and concentration. Polystyrene in chloroform, cyclohexane and dichloromethane showed fluorescence monomer emission at 296nm. Excimer emissions were recorded for polystyrene in chloroform, cyclohexane, dichloromethane and tetrahydrofuran at 307nm, 325nm, 327nm and 330nm respectively. Solvents have effect on the fluorescence quantum yield magnitude, where highest value of it had been recorded in cyclohexane (55%)

Keywords: Polystyrene; absorption; fluorescence spectroscopy; excimer emission

INTRODUCTION

Polystyrene (PS) or Poly (1-phenylethylene) regards the group of thermoplastics that also includes polyethylene, polypropylene, and polyvinyl chloride. When the electromagnetic radiation hit the chromophore one or more electrons can be promoted to a higher energy level (excited energy state). After absorbing the photons energy, an electronic transition occurs and the chromophore undergoes an electric dipole transition and the absorbed energy of the photon becomes part of the energy of the excited state molecule[1]. The absorption process is followed by several deactivation processes by losing their excess energy within a very short period through a variety of deactivation processes, and back to the ground state. The deactivation physical processes are divided into two groups, the first is Radiative transitions, these processes involves the emission of electromagnetic radiation as the excited molecule relaxes to the ground state like (Fluorescence and phosphorescence), and the second is radiationless transitions, these processes do not involve the emission of electromagnetic radiation. The quantum yield or quantum efficiency is measurement of the probability of a molecule to fluorescence or phosphorescence. The quantum yield for fluorescence and phosphorescence is the ratio of the number of molecules that luminescent to the total number of excited molecules. For highly fluoresce molecules, the quantum efficiency approaches to one, while molecules that do not fluoresce have quantum efficiencies that approach to zero [2]. The difference between frequency or wavelength of the emitted and absorbed light is called the Stokes shift. Stokes shift is affected by a variety of factors, some of these factors are intrinsic to the fluorophore, and some are due to interactions of the fluorophore with its environment. One of the main factors that effect on the magnitude of Stokes shift is the solvent polarity. If the fluorophore has a larger dipole moment in the excited state (which is usually the case, especially for polar fluorophores), the solvent will rearrange to stabilize the greater charge separation. The solvent rearrangement effect depends on solvent properties, with more polar

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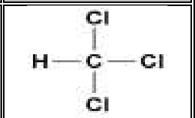
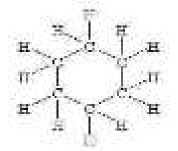
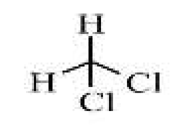
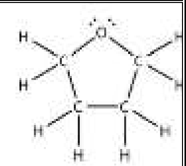
solvents exhibiting greater wavelength shift [3-5]. Stokes shift increases with increasing solvent polarity.

Experimental Part:

Solvents and Materials:

In this work pure laboratory polystyrene made in (HiMedia) company (India) had been used. Also four solvents had been used which they are chloroform, cyclohexane, dichloromethane and tetrahydrofuran. The chloroform and tetrahydrofuran (THF) are made by the French company (Scharlau) with purity of 99% and 99.8% respectively, the cyclohexane was manufactured in the Germany company (Merck) with purity of 99.9% and finally the dichloromethane (DCM) was made by the United Kingdom company (Gainland Chemical Company GCC) with purity of 99.8%. These solvents have been selected in order to study the effect of polarity and the dielectric constant on the absorption and emission spectrum of pure polystyrene solutions. Some physical properties of the solvent are shown in Table (1). Note that the absorption spectrum of these solvents does not overlap with the absorption spectrum of the samples that used in this work.

Table (1) some physical properties and molecular structure of the solvents.

Solvents	Polarity index	Dielectric constant	$\lambda_{max.(nm)}$ Absorption	Reflactive index	Molecular structure
Chloroform	4.1not polar	4.8	240	1.445	
Cyclohexane	0.2not polar	2.02	200	1.426	
Dichloromethane(DCM)	3.1polar aprotic	9.1	230	1.424	
Tetrahydrofuran(THF)	4polar aprotic	7.5	220	1.407	

Devices and Tests:

In this study, all absorption tests were done using ultraviolet-visible single beam spectrophotometer device made by Lasany Company, model (LI-295). Fluorescence tests were done using ultraviolet-visible single beam fluorometer device made by the Japanese company Shimadzu (RF-5301PC). At first the average molecular weight of PS was calculated by viscosity method which it equal to 1.159×10^{5} g/mol. Five concentrations of PS in each solvent were prepared, which they are (1×10^{-6} [M], 3×10^{-6} [M], 5×10^{-6} [M], 7×10^{-6} [M] and 1×10^{-5} [M]).

Results and Discussion:

Fig.1 shows the absorption spectrum of polystyrene using different solvents and The results show that the maximum absorption wavelength for polystyrene is at 262 nm, it is clear that the solvents have no effect on the absorption peak position of polystyrene. . Examination of fig. 1 shows that increasing concentration the peak at 262 nm increases in intensity, this is due to the linear relationship between absorbance and concentration in Beer-Lambert law, the increasing of the solution concentration means increasing of solved molecules, absorbance occurs when a molecule of solute is struck by a photon and absorbing the photon, by having more molecules confined in the same amount of volume; the chance a molecule is struck by a photon increases which leads to increasing of the total absorbance. . Figure (2) shows that the absorbance intensity increases with increasing the concentration of polystyrene solutions in all solvents, this is due to the linear relationship between absorbance and concentration according to Beer-Lambert law**.** From the figure, the absorbance intensity of polystyrene in chloroform is the highest among the others due to the difference in higher solubility and least degree of aggregation of the monomers [6].

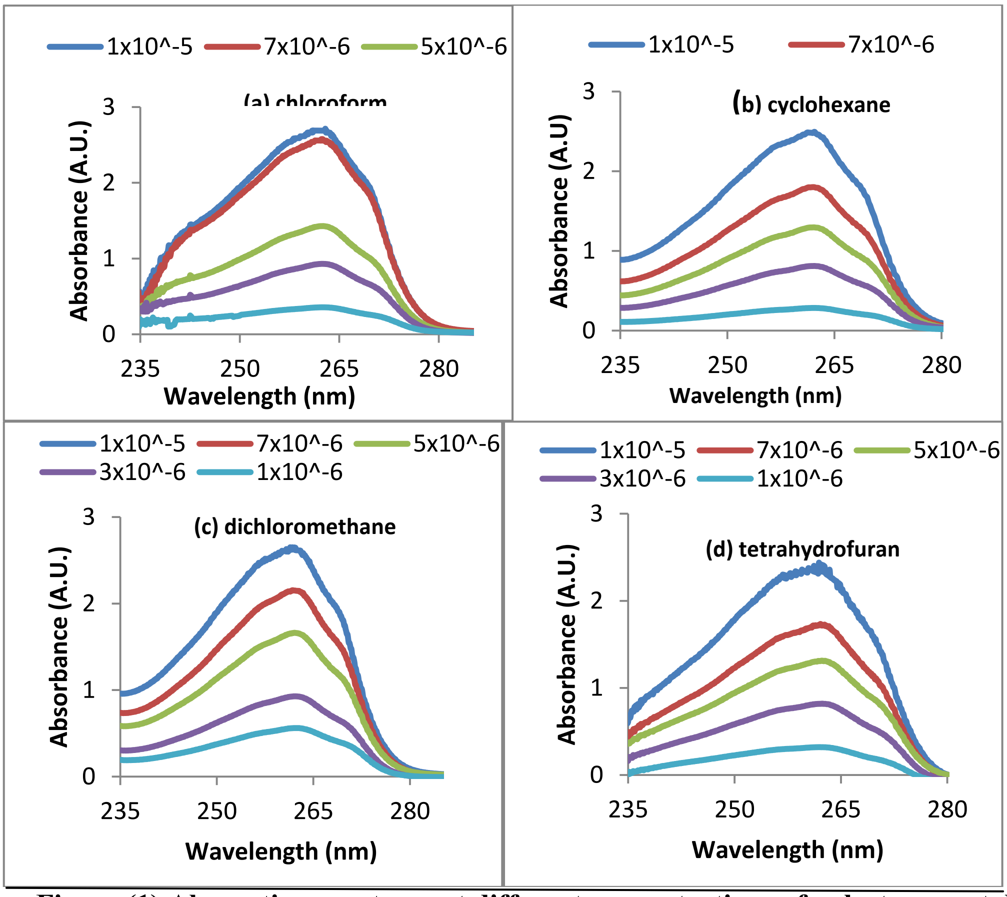
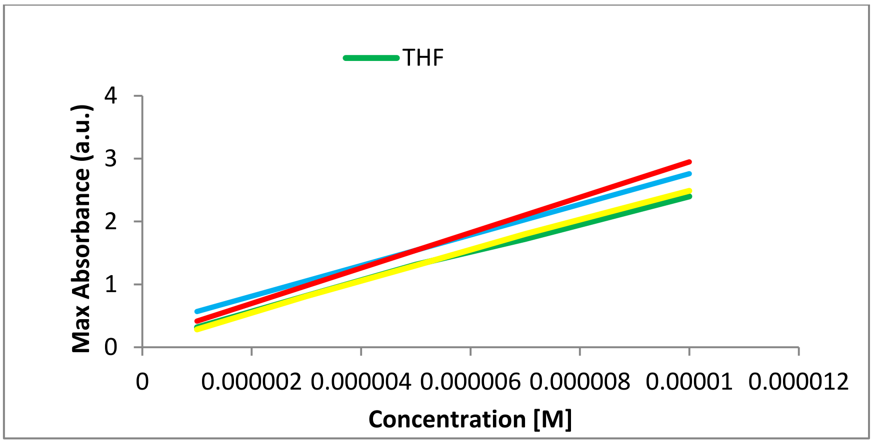


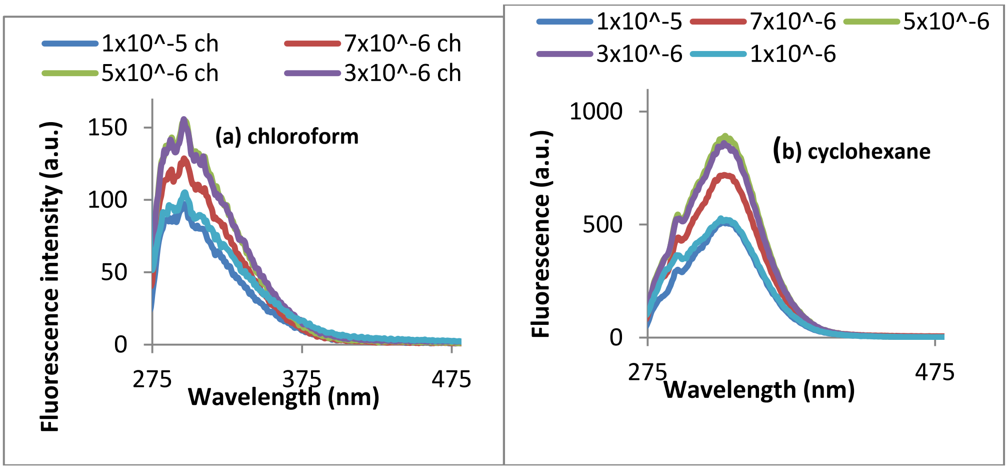
Figure (1) Absorption spectrum at different concentrations of polystyrene at different solvents

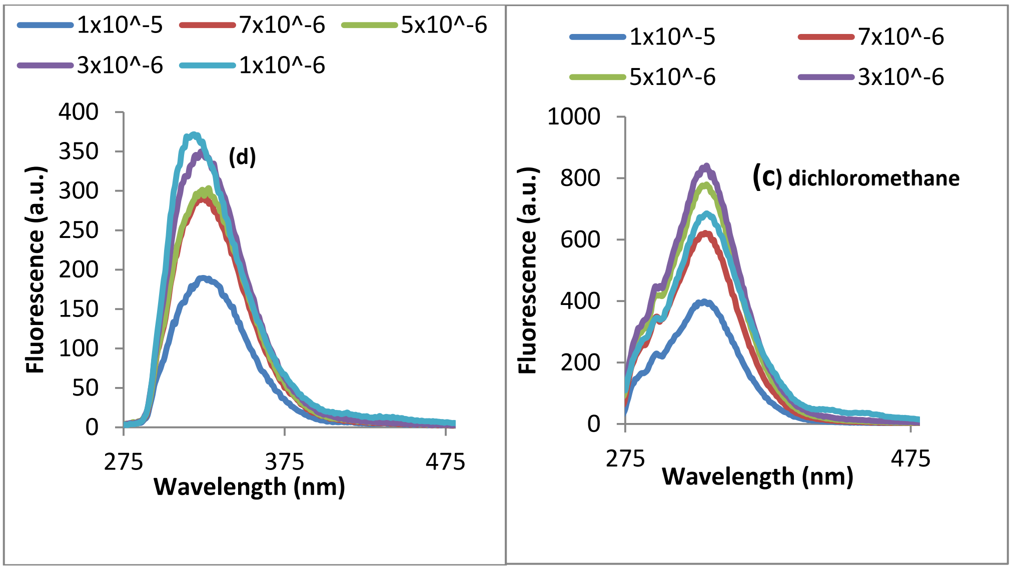


Figure(2) relationship between concentration and max. absorbance for polystyrene in different solvents

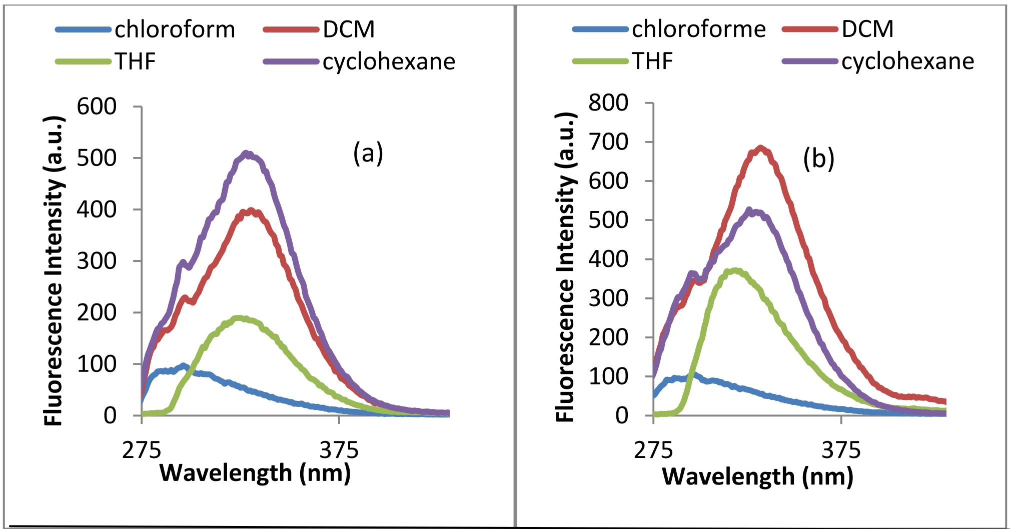
Fig.3 shows polystyrene fluorescence results in different solvents at different concentrations at room temperature. The monomer fluorescence peak position of polystyrene in chloroform,cyclohexane and dichloromethane are shown at 296 nm while polystyrene in tetrahydrofuran could not show showing monomer fluorescence peak. Excimer fluorescence peak position of polystyrene in tetrahydrofuran, cyclohexane and dichloromethane is shown at 325 nm, 327 nm and 330 nm respectively.

There are a red shift in the fluorescence peak position of polystyrene in dichloromethane and tetrahydrofuran due to solvent relaxation while the red shift of polystyrene peak in cyclohexane is because of the viscosity of cyclohexane which is higher than those of other solvents, which leads to increasing of the vibrational collisions and losing of amount of the absorbed energy. The intensity Excimer emission of polystyrene in tetrahydrofuran increases with decreasing of concentration linearly, while, the fluorescence intensity of polystyrene in cyclohexane and dichloromethane shows the same behavior as tetrahydrofuran at the high concentrations, and an opposite behavior can be observed at low concentrations. It is notable that the fluorescence intensity of polystyrene is different in magnitude as the used solvent changed, where the polystyrene shows Excimer emission in cyclohexane, dichloromethane and tetrahydrofurane and shows monomer emission in cyclohexane, dichloromethane and chloroform, as shown in fig.4. These results are compatible with those reached by others [7-12].





Figure(3) Fluorescence of polystyrene at excitation wavelength of 262 nm at different solvents



Figure(4) polystyrene fluorescence spectrum in different solvent at (a) 1X10^{-6} [M] and (b) 1X10^{-6} [M].

The quantum yield of polystyrene solutions was calculated by reference method, this method involved the using of stander material as a reference, which it's the quantum yield known. In this work Rodhamine B was used as reference, the quantum yield of Rodhamine B is equal to 0.65. Table 2 shows the quantum yield of polystyrene in different solvents at different concentrations. Polystyrene in cyclohexane has the higher quantum yield, while polystyrene in chloroform has the lowest quantum yield.

Table (2)The quantum yield of polystyrene in different solvents at different concentrations.

Concentration [M]	dichloromethane	chloroform	tetrahydrofurane	cyclohexane
7X10^{-6}	0.17	0.03	0.1	0.23
5X10^{-6}	0.27	0.06	0.13	0.38
3X10^{-6}	0.38	0.07	0.18	0.45
1X10^{-6}	0.37	0.09	0.2	0.55

DISCUSSION

The study showed that the polystyrene absorption peak at different solvents is not affected by the solvent polarity, while it affects the absorption intensities at 262nm. We found an effect of solvents on fluorescence emission spectrum for polystyrene, where the polymer in chloroform, cyclohexane and dichloromethane show monomer emission at wavelength 296nm, while in tetrahydrofurane solvent did not show monomer emission. Also polystyrene in chloroform tetrahydrofurane cyclohexane and dichloromethane shows excimer emission at wavelengths 307,325,327 and 330nm respectively. Polystyrene in cyclohexane shows higher fluorescence intensity, while it has lowest fluorescence intensity in chloroform.

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