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Modification of Spectral Properties of Polystyrene / Diethyl phthalate in Different Solutions

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Abstract:

The influence of Diethyl phthalate (DEP) on the optical characteristics of polystyrene solutions in the range between 200 to 400 nm at solvents of different polarities; chloroform, cyclohexane, dichloromethane, and tetrahydrofuran have been recorded. The experimental results showed that the behavior of the photophysical processes of polymer solutions depends on the nature of its environment. The intensity of the absorption and fluorescence spectra depends on the interactions between solvent-solute molecules. The experimental results indicate that the maximum most absorbance bands occur around 262 nm, which depends on the concentration of the quencher. The results did not determine any change in the positions of the most absorption bands. Fluorescence spectra of the polystyrene were measured in chloroform, cyclohexane, dichloromethane, and tetrahydrofuran diluted solutions at room temperature. Fluorescence emission spectra were characterized by one broad main band centered at 295 nm in chloroform and 305 nm in tetrahydrofuran and the emission intensity is dramatically reduced due to strong fluorescence quenching. In cyclohexane and dichloromethane fluorescence spectra of PS/DEP have two bands monomer and excimer emissions at 295 and 328 nm respectively. The presence of DEP quenches the fluorescence and excimer. The excimer emission is more intense. The results showed that the use of different solvents caused a change in the behavior of the fluorescence emission.

Keywords: Polystyrene, Diethylphthalate, absorption, fluorescence emission, Fluorescence quenching, excimer emission.

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تعديل الخصائص الطيفية لـ البوليسترين / ثنائي إيثيل الفثالات في محاليل مختلفة

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الخلاصة

في هذا البحث سجلنا تأثير الملدن ثنائي إيثيل الفثالات على الخصائص الطيفية لمحاليل البوليسترين في نطاق يتراوح بين 200 إلى 400 نانومتر في مذيبات مختلفة القطبية :- كلوروفورم ، سيكلو هكسان ، ثنائي كلورو ميثان تتراهريدوروفوران. أظهرت النتائج التجريبية أن سلوك العمليات الضوئية لمحاليل البوليمر يعتمد على طبيعة الظروف المحيطة بالبولمر . تشير النتائج ، أن حزم الامتصاص القصوى حوالي 262 نانومتر تعتمد على تركيز الملدن (المخمد) . بالإضافة إلى ذلك ، لاحظنا أن أطياف الامتصاص لا تعاني من

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أيأزاحة في موقعه. تم قياس أطياف انبعاث الفلورة للبوليسترين في محاليل الكلوروفورم ، السيكلو هكسان ،
داي كلورو ميثان و تيتراهيدروفوران المخففة في درجة حرارة الغرفة. تميزت أطياف الابعاث بنطاق رئيسي
واسع واحد متمركز عند 295 نانومتر في الكلوروفورم و 305 نانومتر في رباعي هيدروفوران .
انخفظت كثافة الانبعاث بشكل كبير بسبب إخماد الفلورة القوي. في مذيب سيكلو هكسان وثنائي كلورو ميثان
اطياف الفلورة لديها اثنين من نطاقات انبعاث المونومر وانبعاثات الاكسايمر في 295 و 328 نانومتر
على التوالي . وجود الملدن DEP يخمد. انبعاث الفلورة والاكسايمر الاعلى شدة. وأظهرت النتائج أن
استخدام المذيبات المختلفة تسبب في تغيير في سلوك انبعاث الفلورة

1. Introduction

Electronically excited molecules lose their energy in different ways; radiative emission from the first excited state is identical to normal fluorescence and non-radiative transitions appear during many mechanisms. Internal conversion(IC) which cause the molecule to return to the vibration levels with lower energy (energy dissipates in the form of heat). Intersystem crossing (ISC) the molecule shift to the triplet excited state $3M^*$. [1-3]. The energy of the excited molecule may transfer to a neighboring molecule (quencher molecule). Generally, energy transfer takes place through to the following equations [4].

$$A^* + Q \rightarrow A + Q + heat \qquad (1)$$
$$or \qquad A^* + Q \rightarrow A + Q^* \qquad (2)$$

Quenching processes occur by electron transfer or energy transfer. In each case, the energy of the excited state is deactivated due to the presence of the quencher [5]. The quenching of fluorescence emission happens by dynamic or static quenching. The first process obtains from interactive collisions between fluorophore and quencher through the lifetime of the excited molecule. This method is determined throughout the transfer of energy from the molecule among the excited state to a different molecule within the ground state. This method is the collision between two molecules the donor molecule and the acceptor, that depends on the temperature and viscosity [6-10].

The quantum efficiency of the fluorescence emission φ_F^o within the absence of a quencher is given by [11, 12]:

$$\varphi_F^o = \frac{k_f}{k_f + k_{ic} + k_{isc}} \qquad (3)$$

Where k_f, k_{ic}, and k_{isc} are the rate constants for fluorescence, internal conversion, and intersystem crossing respectively. The quantum efficiency of the fluorescence emission φ_F in the presence of quencher [Q] is given by:

$$\varphi_F = \frac{k_F}{k_f + k_{ic} + k_{isc} + k_q[Q]} \qquad (4)$$

Where k_q represents the quenching rate constant of the quencher. The ratio of equations 3 and 4 is:

$$\frac{\varphi_F^o}{\varphi_F} = \frac{t_o}{t} = \frac{I_O}{I} = 1 + k_q t_o[Q] \qquad (5)$$

since $k_q = \frac{k_{sv}}{t_o}$

$$\frac{\varphi_F^o}{\varphi_F} = = 1 + k_{sv}[Q] \qquad (6)$$

Where, I_O is the intensity of sathe mple without quencher, t_o fluorescence lifetime, K_{sv} is the Stern-Volmer constant for quenching and $[Q]$ is the molar concentration for a quencher. The parameter ($\frac{\varphi_F^o}{\varphi_F}$ -1) increases linearly with [Q], in this situation the k_q can be obtained by the (initial) slope of a linear Stern.

In this paper, we concentrate on describing the absorption and fluorescence spectra of polystyrene solutions by addition of different molecular concentrations of the quencher Diethyl phthalate (DEP) with different solvents at room temperature.

2. Experimental

Polystyrene has been supplied from (HiMedia) company. All samples were examined using solvents chloroform, cyclohexane, dichloromethane and tetrahydrofuran. The chloroform and tetrahydrofuran we got by the Scharlau company with 99 and 99.8% purity respectively, cyclohexane solvent was produced from Merck company with 99.9% purity, dichloromethane (DCM) by GC

Company from the United Kingdom with 99.8% purity. These solvents were chosen as a result of they have absorption bands far away from the absorption bands of the samples. All absorption spectra were carried out at room temperature using UV-Vis 160 spectrophotometer (Shimadzu, Japan). Emission spectra were recorded on Shimadzu RF-5301PC Shimadzu Fluorescence Spectrophotometer. In this research, we used the viscosity method to calculate the average molecular weight of polystyrene which is equal to 1.159×105 g/mol. The stock solution of polymer was prepared by dissolving 0.144 gm of polystyrene in 25 ml of solvent to get a solution with concentration 5×10-6 M.

We prepared a series of solutions containing a constant concentration of polymer 5×10^{-6} M and with concentrations of DEP quencher ranging from5×10^{-5} M, 7×10^{-5} M,   1×10^{-4} M, 3×10^{-4} M to 5×10^{-4} M.

3. Results and Discussion

In this paper, we concentrate on describing the absorption and fluorescence spectra of polystyrene solutions by addition of different molecular concentrations of the quencher Diethyl phthalate (DEP) with different solvents at room temperature. Figure-1 illustrated absorption spectra of PS with different solutions of DEP (5×10^{-5} M, 7×10^{-5} M, 1×10^{-4} M, 3×10^{-4} M 5×10^{-4} M) in Chloroform. It causes the appearance of a strong absorption band at 262 nm and the absorption intensity increases when the concentration of the quencher is increased. All the absorption bands occur due to $\pi - \pi^*$ transitions.
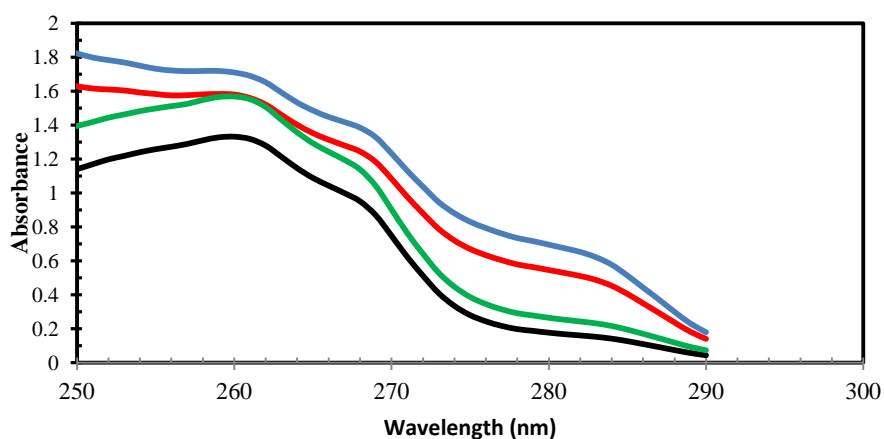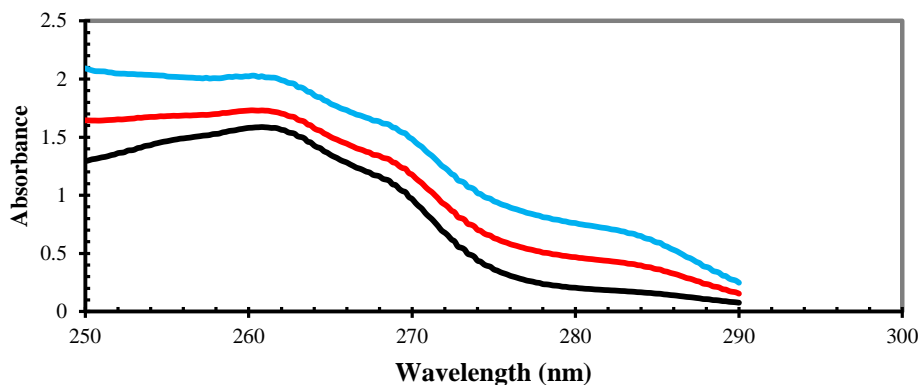

Figure 1-The absorption spectrum of polystyrene at different concentrations of DEP (1) 5×10^{-4} M, (2) 3×10^{-4} M, (3) 5×10^{-5} M, (4) 1×10^{-4} M in Chloroform

Figure-2 also indicated absorption spectra of polystyrene in Cyclohexane using same concentrations which were mentioned in the preceding paragraph. The characteristic of the absorption bands is weak broad symmetrical absorption bands, structureless even at low concentration.
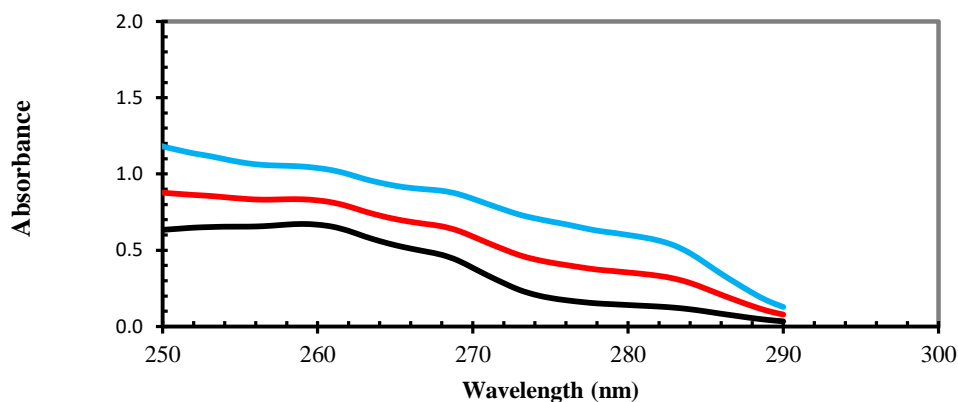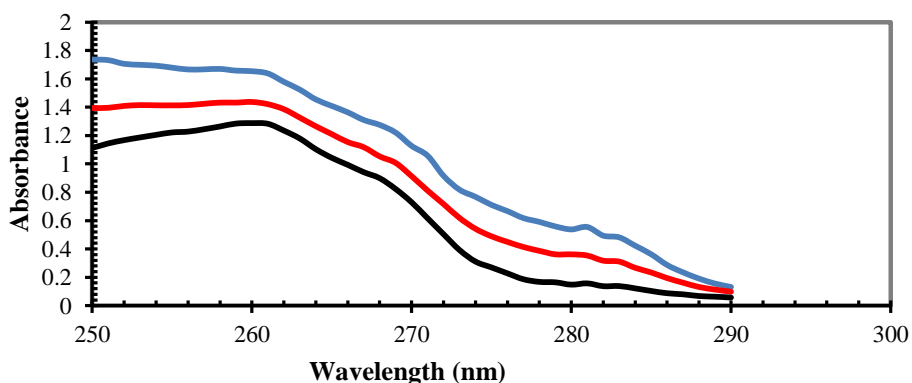

Figure 2-The absorption spectrum of polystyrene at different concentrations of DEP (1) 5×10^{-4} M, (2) 3×10^{-4} M, 1×10^{-4} M in Cyclohexane

Figures-(3, 4) represent the absorption spectra in dichloromethane and tetrahydrofuran, which are approximately symmetrical in shape, varying in the intensity of the maximum absorption package at wavelength 262 nm. It is found that the intensities and the behavior of the absorption curves are usually modified [14].


Figure 3-The absorption spectrum of polystyrene at different concentrations of DEP (1) 5×10^{-4} M, (2) 3×10^{-4} M, (3) 1×10^{-4} M in Dichloromethane


Figure 4-The absorption spectrum of polystyrene at different concentrations of DEP (1) 5×10^{-4} M, (2) 3×10^{-4} M, (3) 1×10^{-4} M in Tetrahydrofuran

In another meaning, the maximum band absorption is found to be highly dependent on solvent and quencher concentration. Figure-5 represents the fluorescence emission spectra of the polymer in the chloroform solution, in the absence of a quencher a monomer emission was observed at a 295 nm. The significant spectral broadening in the emission spectra as well as a dramatic reduction in the efficiency of emission spectra indicative of the strength of the effect of the quenching.
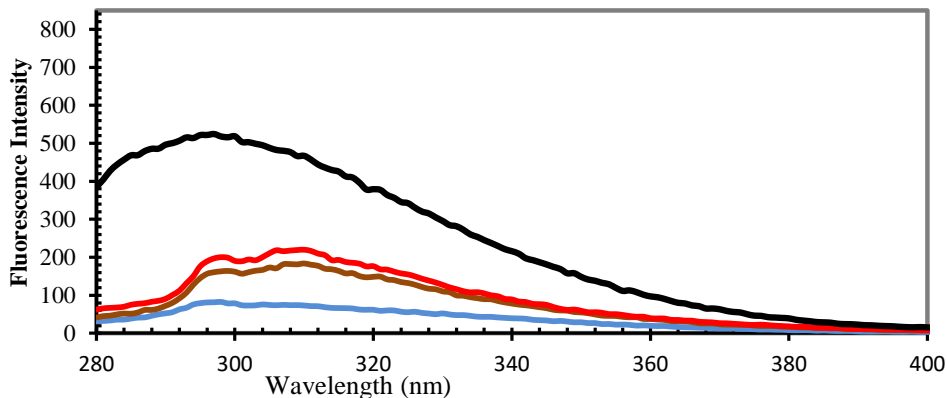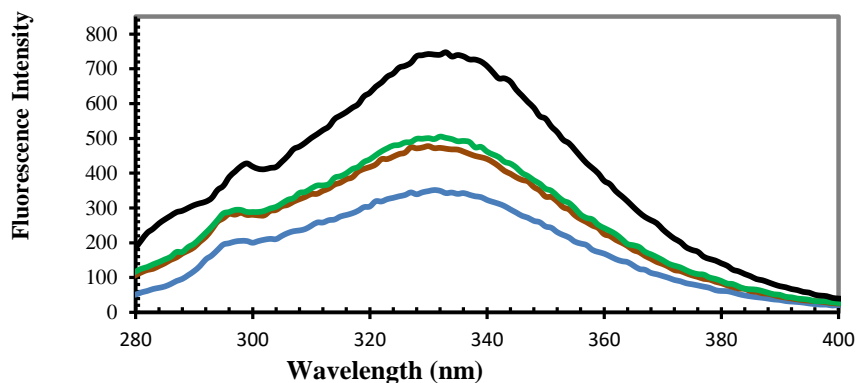

Figure 5-Fluorescence of polystyrene at different concentrations of DEP (1) 0M, (2) $7X10^{-5}$M, (3) $3X10^{-4}$M, (4) $5X10^{-4}$M in Chloroform

It was shown during this work that in Cyclohexane and Dichloromethane the monomer and excimer emission are determined at 295 and 328 nm respectively. The experimental results in Figures- (6, 7) indicated that the most intensity of the monomer and excimer of vinyl-ring polymer solutions were clearly affected with the concentration of the quencher and the nature of the solvent.
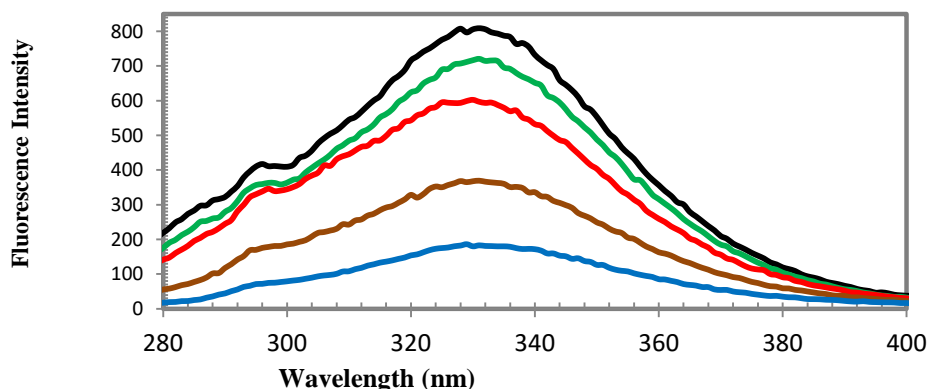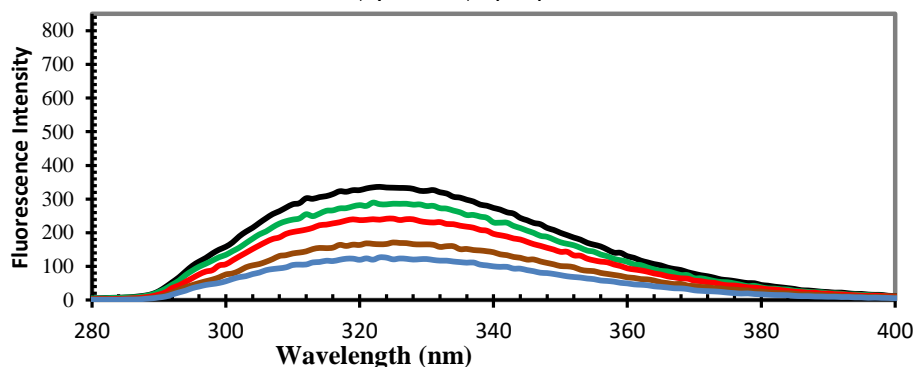

Figure 6-Fluorescence of polystyrene at different concentrations of DEP; (1)0M, (2)5X10^{-5}M,((3)7X10^{-5}M, (4)3X10^{-4}M, (5)5X10^{-4} M in Cyclohexane

Figure 7-Fluorescence of polystyrene at different concentrations of DEP;(1)0M,(2)5X10^{-5}M, (3)3X10^{-4}M,(4)5X10^{-4} M in Dichloromethan.

The effect of solvent on the emission spectra was due to on the refractive indexes. The excimer appearance has been determined by the interaction between an excited molecule and the adjacent molecule in the same chain. Hirayama was examined the excimer formation in styrene polymer solutions at room temperature [15]. Figure-8 represents the fluorescence emission spectra in tetrahyrofuran with series DEP concentrations. The spectrum is characterized by one a broad band centered at 305 nm (excimer emission). The intensity of these bands depends on the quencher concentration because of nonradiative decay pathways [16].

Figure 8-Fluorescence of polystyrene at different concentrations of DEP;(1)0M, (2)5X10^{-5}M, (3)7X10^{-5}M, (4)3X10^{-4}M,(5)5X10^{-4} M in Tetrahydrofuran

Previous relevant research has indicated that fluorescence quenching can occur by different mechanisms such as excited-state reactions, resonance energy transfer (RET), intersystem crossing, ground-state complex formation and collisional quenching [12,17]. The influence of solvent molecules on the fluorescence characteristic is certainly one of the most complex issues in fluorescence measurement. Eventually, every excited state molecule shows some dependence of its quantum yield on the chemical structure of the surrounding solvent.

This observation is to some extent due to fluorescence quenching by the solvent [18]. This quenching is due to the prompt of non-radiative transitions by changing in the energy level of the ground state, singlet excited state as well as the triplet state [19].

In this work, the decreasing in the fluorescence intensity occurs by collisional quenching. Through this process, the excited state of the molecule is returned to the ground state throughout a close encounter with the quencher. The dynamic quenching agent provides a nonradiative route for loss of the excited state energy [12, 20].

4. Conclusion

In this paper, we have displayed an experimental study to describe the photophysical processes of polystyrene -Diethyl phthalate solutions. Absorption and emission spectra of PS-DEP are recorded in solvents of various polarities. The Results demonstrated that the intensity of the absorption band occurs at 262 mn increases with increasing DEP concentrations.

We observed two emission bands at 295 and 328 nm, which belong to the monomer and excimer respectively. The emission spectrum of the polymer with various concentrations of Diethyl phthalate contains one broad emission band, the excimer at 325 nm, whose intensity decreases by increasing the concentration of the quencher.

Emission Spectra of the Polystyrene with the quencher in the cyclohexane and in Dichloromethane have two emission bands, the first around 295 nm attributed to monomer emission while the second band at 328 nm to excimer emission, because of a dimer formed between chromophores on a similar polymer chain [21]. The fluorophore molecule is quenched by the interaction with the surrounding solvent molecules or by the nonradiative process (internal conversion) in which the excitation energy is converted into heat. The fluorescence quenching becomes concentration-dependent due to the collisional quenching between a singlet excited state of fluorophore and quencher molecule [22].

Acknowledgment

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