Temperature Variation Effect on Behavior of Block Copolymer of 2- Isopropenylnaphthalene and Methacrylic Acid in Ethanol

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دراسة تأثير تباين درجات الحرارة في سلوك بلوك كوبوليمر المتألف من ٢- ايزوبروبينايل نفثالين وحامض الميثاكريليك المذاب في الايثانول جواد كاظم عبيس - قسم الكيمياء / كلية العلوم / جامعة واسط

ملخص البحث

تم في هذا البحث دراسة أطياف الفلورة (الانبعاث) لمحلول مخفف من بلوك كوبوليمر المتألف من ٢- ايزوبروبينايل نفثالين وحامض الميثاكريليك المذاب في الايثانول المطلق في عدة درجات حرارة تحصمت من ٩.٥ الى ٤٥ م٥ اظهرت اطياف الفلورة (الانبعاث) حزمتي انبعاث الأولى عند الطول الموجي ٣٤٢ نانوميتر و الثانية عند ٣٨٧ نانوميتر وهما يعودان لمونمر النفثالين والاكسايمر على التوالى .

أظهرت هذه الدراسة تغيير أطياف الفلورة (الانبعاث) مع تغيير درجة الحرارة ، وعند رسم قيم نسبة مقابل درجة الحرارة اظهر الرسم ان هناك IE/IM)شدة حزمة الاكسايمر الى شدة حزمة المونمر (تزداد بشكل IE/IM)خطين بميل موجب يتقاطعان عند درجة الحرارة ٢٥ مه . كذلك يبين الرسم أن (بسيط عند رفع درجة الحرارة من ٩.٥ - ٢٥ مه ثم تحدث زيادة حادة بين ٢٥-٥٠ مه . وتبدأ الزيادة عند درجة حرارة ٣٥ مه هذه النتائج تدلل على التغير في وضعية البوليمر من الوضعية الملفوفة الى الوضعية المفتوحة تحدث فوق ٢٥ مه وبالتحديد عند ٥٣ مه.

Abstract

Fluorescence dilute solution of blockcopolymer of 2spectra of and methacrylic acid (2- IPN – MA) in ethanol Isopropenylnaphthalene have been measured in temperature range of $9.5 - 50^{\circ}C$. The fluorescence spectra show two emission bands at 342 nm and 387nm corresponding to monomer and excimer bands, respectively. From temperature dependent fluorescence measurements a plot of excimer to monomer intensity ratio (I_E/I_M) versus temperature was obtained, which shows that (I_E/I_M) value increases linearly in the temperature range of 9.5- $25\,^\circ C$ and sharp increasing at a bout $~35\,^\circ C$,then I_E/I_M increases smoothly above 35°C. These results Indicate that the conformational change of the

polymer chain from contraction form to expansion form takes place at about 35°C.

Introduction

Photophysical processes such as fluorescence, excimer emission and energy transfer have been widely used to study polymer properties such as interactions, conformation, solvation, aggregation, ... etc.

Excimer is an excited state complex formed by a couple of aromatic rings placed in a fully – eclipsed, parallel sandwich arrangement . The formation of excimer is due to the association of two aromatic groups one of which has electronically excited. $^{(1)}$

When excimer is formed between two chromophores in solution, it is called an intermolecular excimer ⁽²⁾; When it is formed between two chromphores attached to the same molecule it is called intramolecular excimer. ⁽³⁾

It is characteristic for excimer fluorescence to appear in a considerably lower energy region than monomer fluorescence and has no mirror image relation to the absorption spectrum .

The intramolecular excimer for polymer is governed by both the conformation and configuration of the chains .Excimer formation has been observed in polystyrene⁽⁴⁻⁶⁾ and its derivatives such as poly (α -methtystyrene)^(7,8) and poly (4- methylstyrene)⁽⁹⁾. Also, intramolecular excimer is noticed in poly (1- vinylnaphthalene)⁽¹⁰⁻¹²⁾ and poly (2-vinylnaphthalene)⁽¹³⁾.

Guillete et. al.^(14,15) have used excimer emission to study conformational changes of poly (1- naphthylmethacrylate)and poly-(2- naphthylmethacrylate) in different solvents .

Excimer emission was used as a valuable tool to elucidate the state of intra and intermolecular aggregation of aromatic groups in liquid crystalline polymers.⁽¹⁶⁻¹⁸⁾

C. David and Co-workers ⁽¹⁹⁾ have investigated temperature effect on polyvinylnaphthalene and polyacenaphthylene fluorescence.

Shozo Himuro ⁽²⁰⁾ noticed excimer emission in poly (4-hydroxystyren) and used this emission to investigate the solvation of the polymer at several temperatures.

The purpose of the present work is to investigate the effect of temperature variation on florescence spectra of blockcopolymer of 2-Isopropenylnaphthalene and methacrylic acid in ethanol to obtain

information about the behavior of polymer chain in solution . Florescence spectra were studied here in the temperature range of $9.5-50^{\circ}$ C.

Experimental

I-Materials

1-block copolymer of 2- isopropenylnaphthalene and methacrylic acid (2-IPN-MA) with molecular weight of 10338 was already synthesized and purified according to general procedure⁽²¹⁾.

2-Ethanol of special quality for fluorescence measurements with purity > 99.99% was purchased by Flucka company .

II – **Instruments**

Fluorescence spectra were measured with a Jasco spectrofluorometer FP-770 .Fluorescence measurements were carried out with excitation wavelength of 280 nm with an excitation slit width of 3nm and emission wavelength of 300nm .

Spectrofluorometer was connected to a water bath (Lauda , Germany) Digital thermometer type (Jenway PWA1, UK) was used to measure the temperature . The temperature controlled within $\pm 0.1^{\circ}$ C during the measurements . The concentration of the polymer solution was 0.008g/dI.

Results and Discussion :-

Figure 1 shows the fluorescence spectrum of the block copolymer of (2 - IPN-MA) in ethanol . The spectrum contains two emission bands , one appearing at about 342 nm which belongs to monomer naphthalene group and abroad structureless one at about 387 nm shifted towards longer wavelength at room temperature , which is attributed to intramolecular excimer emission ⁽⁴⁾. These results are in good agreement with previous measurements ⁽²²⁾.







Temperature - dependent fluorescence measurements are particularly interesting in that , through steady state experiments ,they yield information on conformational change of a coil form of the polymer . Figure 2 apparently show the temperature- dependent fluorescence spectra of block copolymer of 2- Isopropenylnaphthalene and methacrylic acid (2-IPN-MA) in ethanol . As the temperature is raised , the intensities of the monomer and excimer decrease . However , the intensity of the monomer band decrease more with increasing temperature than that of the excimer band .



Figure 2: Fluorescence spectra of block copolymer of 2 -IPN-MA in ethanol at several temperatures

The intensities of monomer fluorescence (I_M) and excimer one (I_E) in arbitrary units are given in figure 3 as a function of temperature , where I_M and I_E are the intensities of the monomer peak and that of the excimer peak , respectively . the intensities of monomer band decrease linearly in the range of 9.5 - 25°C , then a slight decrease in I_M at the temperature rang of 25 - 50°C , while the plot of those of excimer band



show different linear lines crossing at ca $.25^{\circ}$ C. The intensities of excimer emission band decrease in the temperature range of $9.5-25^{\circ}$ C and decrease smoothly above 35° C. This indicates that excimer formation extent above 35° C leads to decrease an excited monomer.

Holye et al.⁽²³⁾reported that the excimer to monomer Intensity ratio (I_E / I_M) change with the change of solubility parameter . Sivadasan et al⁽²⁴⁾ reported that the extent of intramolecular excimer formation given by the parameter (I_E/I_M) provides a measure of the statistical conformation of the polymer chain. In our previous work⁽²⁵⁾, it was reported that a large value of I_E/I_M was due to polymer expansion ,whereas a small value of I_E/I_M was attributed to polymer chain contraction . However , Figure 4 shows the effect of temperature on the I_E/I_M ratio for block copolymer of (2-IPN- MA) in ethanol . One can observe that I_E/I_M increase slightly as the temperature is increased until the temperature 25°C , there is abrupt increasing in I_E/I_M From these results, it may be concluded that the change in conformation of block copolymer of (2-IPN-MA) takes place above 25°C , exactly at 35°C.



The change in conformation can be attributed to molecular interactions between ethanol molecules and the polymer chain, which will be strongly above 25°C. The molecular interactions caused uncoil the polymer chain from rather compact coil form to expansion form ,which facile 2-IPN movements leading to form parallel, sandwich-like arrangements, the necessary condition to form excimer. ⁽³⁾

The abrupt increase in I_E/I_M might be attributed to more expansion on polymer coil producing an unfolded structure which is favorite structure for excimer formation⁽³⁾.Consequently ,it may be concluded that the charge in polymer conformation occurs at ca_35°C.

All these arguments show that temperature plays a very important role in block copolymer of (2-IPN-MA) behavior in solution.

Conclusions :-

The fluorescence spectrum of block copolymer of (2- IPN- MA) two emission bands at about 342nm assigned to monomer shows naphthalene group and structure less, red shifted band at about 387nm, assigned to be excimer emission . From temperature dependent fluorescence ,plots of I_E/I_M versus temperature were obtained, which show that I_E/I_M increases abruptly at a point which has been ascribed a transition temperature . It is reasonable to to assume that conformational change of the polymer chain occurs at the transition temperature .

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