Study of Molecular Interactions of Water- Soluble Polymer at Several Temperatures in Solution

Jawad Kadhim Abaies*

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Abstract:

Molecular interactions between 2-isopropenylnaphthalene-methacrylic acid (IPNMA) block copolymer(as a model for water- soluble polymer) and methanol at several temperatures were studied using fluorescence techniques , Fluorescence spectrum for (IPNMA) exhibits two emission bands at around 342 nm and 387 nm corresponding to the monomer and the excimer bands , respectively .The fluorescence spectra of dilute solution of (IPNMA) in methanol were recorded in temperature range of 8- 45˚C . Plot of the excimer to monomer intensity ratio I_e/I_m versus temperature was obtained, which shows double lines with positive slopes crossing at 25˚C , the increasing of slope value above this temperature is small which indicates that there is stronger solvation of methanol molecules to polymer coil at temperature below 25˚ C arising from hydrogen bond formation between the polymer and the solvent .

Key words :(fluorescence spectroscopy , excimer , molecular interaction , polymer conformation, temperature- dependence).

Introduction:

Water-soluble polymers are added to many commercial products, such as paints , inks , cosmetics , food - stuff ,and water born coatings[1]. In recent years. interest in these polymers has been rejuventated , as a consequence of the growing concerns about the safety of more traditional organic-based fluids . They also can be used as analogous in understanding the behavior of biological macromolecules. Amphilic copolymers which contain hydrophobic and hydrophilic segments in the same molecule , in particular , are effective in this role[2].

Fluorescence spectroscopy (especially excimer fluorescence) has been found to be a versatile techniques for investigations of the polymer properties . Many polymers with aromatic chromophores exhibit intra molecular excimer fluorescence . Excimer is excited - state complex formed by a couple of aromatic rings placed face to face at a short distance . The formation of excimer is due to association of two aromatic groups one of which has electronically excited[3].It is characteristic for excimer fluorescence to appear in a considerably lower energy region then monomer fluorescence .

In last two decades , many researches have been carried out for investigation this kind of polymers . Using excimer fluorescence.

Strauss and vesnaver [4] used fluorescence teqnique to investigate microenvironment and conformational transitions of copolymer of maleic anhydride and akyl vinylether . Morawetz and co-

*Department of Chemistry, College of science, University of Wassit

workers[5,6] have reported kinetics of the cooperative complex formation and dissociation of poly (Acrylic acid) and poly(ethylenc oxide). They have also studied the conformational transitions of poly (methacrylic acid) after change of its degree of ionization .

Turro and Okubo[7] have investigated excimer formation in poly(styrenesulfonate). Watanabe and Matsuda [8] have studied properties of polystyrene-poly(methylmethacrylate) graft copolymer. Turro et.al[9] studied intramolecular interactions of some water-soluble polymers.

Excimer formation of 1-pyrenemethanol on polystyrene latex particles and aqueous phase was reported[10]. Guillete and Nowakowska[11] have investigated isomerization of provitamin D_3 by polymers containing pendant naphthalene group .

Gorochovceva and Makuska[12]synthesized and studied viscosity and solubility of chitosan-o-poly(ethylene glycol) graft copolymers in aqueous solutions at several PH .

Group of workers[13] have investigated the antimicrobial effect of a triglucsan /copolymer dentifrice on microorganisms from dental plaque , saliva and the tongue then compared the results with fluoride dentifrice.

Fusco et.al[14] reported that polymer (ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)(PEO-PPO-PEO) tri-block copolymers have amphilic characterstics and show thermoreversible gelation around body temperature and, therefore , are particularly suitable for biomedical applications such as drug delivery , and gene therapy.

The main purpose of present work is to investigate the fluorescence spectra of 2 - Isopropenylnaphthalene - methacrylic acid block copolymer (as a model for water-soluble polymer) in methanol at several temperatures to report information on the solvation , interactions and conformational transitions of polymer chain in solution . The ratio of the emission intensities of excimer and monomer depend on intrinsic and extrinsic characteristics of the system , for example , solvent ,temperature … etc[15]. They were studied here in the temperature range of 8-45˚C.

Materials and Methods:

1 – Materials:

I. 2-Isopropenylnaphthalene-methacrylic acid block copolymer (IPNMA) with molecular weight of 10338 was already synthesized and purified according to general procedure [16] .

II. Methanol of special quality for fluorescence measurements with purity >99.99% was purchased by Flucka company .

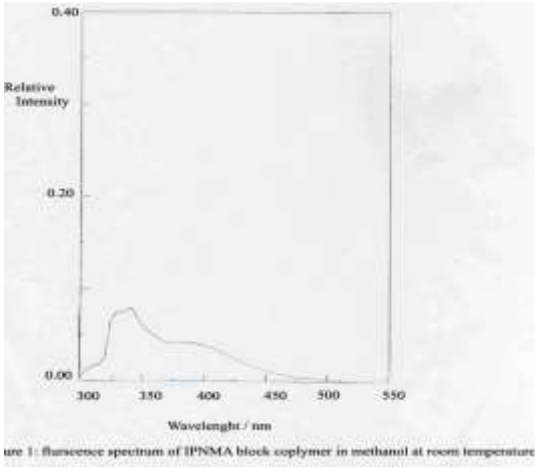
2 – Instruments

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 ± 0.1˚ C during the measurements . The concentration of the polymer solution was 0.002 g/25ml.

Results and Discussion:

Figure (1) shows fluorescence spectrum of 2-Isopropenylnaphthalene and methacrylic acid block copolymer of (IPNMA) in methanol .The fluorescence spectrum of the polymer contain two bands at a bout 342nm belong to monomer naphthalene group , and a broad , structure less , red- shifted one at 387nm .This structure less band resembles the emission band observed in previous works,[3,17] therefore this attributed to excimer emission .It was found that the excimer band independent on polymer concentration ;thus it originate from an intramolecular excimer ,[18,19].



ure 1 : fluorescence spectrum of IPNMA block coplymer in methanol at room temperature

Temperature dependent fluorescence measurements are particularly interesting , they yield information on solvation, behavior and conformational transitions of the polymer chain coil .

Figure (2) shows fluorescence spectra of block copolymer (IPNMA) in methanol. As the temperature is raised, the intensities of the monomer and excimer decrease . However , the intensity of the monomer band decreases more with increasing temperature than that of excimer band .

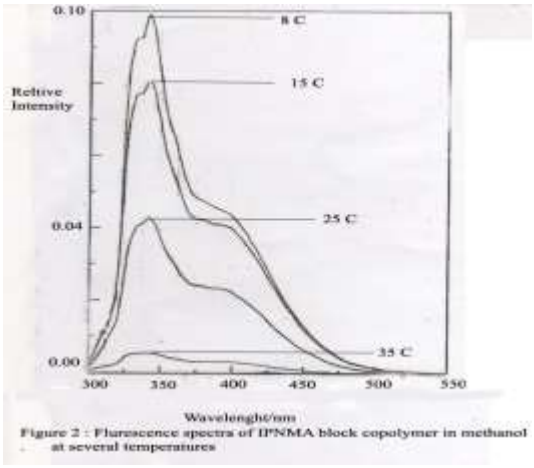


Figure 2 : Fluorescence spectra of IPNMA block copolymer in methanol at several temperatures

The intensities of monomer band (I_m) and excimer one (I_e) in arbitrary units are given in Figure (3) as a function of temperature. The intensities of monomer band

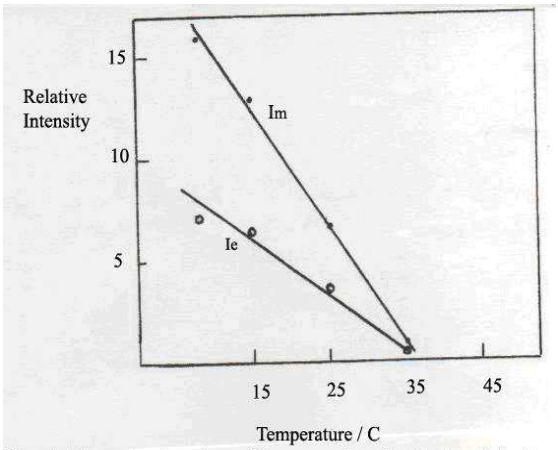


Figure 3 : Temperature dependence of fluorescence intensity of excimer (Ie) and monomer (Im) bands for IPNMA block copolymer in methanol

decrease linearly in the rang of 8-45˚C , while the plot of those of excimer band Show two different linear lines crossing at 25˚C. This indicates that excimer formation lead to decrease an excited monomer.

Sivadsan et.al[20] 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 .A large value of I_e/I_m suggests polymer chain expansion whereas a small value of I_e/I_m suggests polymer chain contraction . However , plotting of I_e/I_m ratio as a function of temperature given in

Figure 4,which show double lines cross at ca.25˚C, a above which the slope is

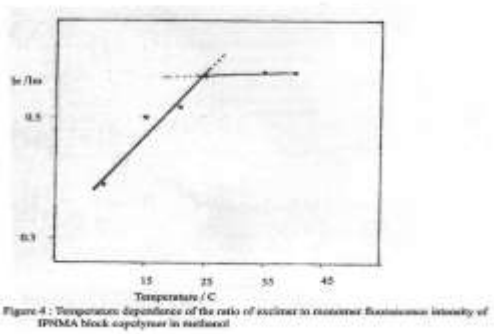


Figure 4 : Temperature dependence of the ratio of excimer to monomer fluorescence intensity of IPNMA block copolymer in methanol

small. The magnitude of increase in I_e/I_m with increasing temperature is related to the extent of solvation of solvent molecules to polymer coil . The increase in I_e /I_m might be attributed to polymer chain expansion form ,which Facile of parallel arrangement (sandwich like) configuration between neighboring naphthalene groups , which necessary condition to form excimer[3]. Consequently ,it may be presume that the change in polymer conformation occurs at 25˚C .Therefore its concluded that there is stronger salvation of methanol molecules to polymer coils at temperature 25˚C arising from the molecular interaction especially , the hydrogen bonding between the solvent molecules and the polymer at about 25˚C. Thus it may be presumed that the interaction as hydrogen bonds between carboxyl groups in the polymer and methanol are weakened and may be broken by increasing temperature above 25˚C .

Conclusions:

The fluorescence spectrum of (IPNMA) block copolymer exhibits two emission bands at about 342nm and 387nm which are assigned to monomer naphthalene and excimer , respectively . From the temperature-dependent fluorescence spectra measurements , plots of I_e/ I_m versus temperature were obtained , which show two lines intercepting at a point ascribed to a transition temperature . It reasonable to assume that intramolecular hydrogen bonds between carboxyl groups of the polymer and methanol may be broken at the transition temperature.

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دراسة التآثرات الجزيئية لبوليمر ذو قابلية الذوبان في الماء على مدى عدة درجات حرارية في المحلول

جواد كاظم عبيس*

*قسم الكيمياء – كلية العلوم – جامعة واسط

الخلاصة:

تمت دراسة التاثرات الجزيئية بين 2-ايزوبروبينايل نفثالين –حامض الميثاكريليك بلوك كوبوليمر والميثانول على مدى عدة درجات حرارية باستخدام تقنية الفلورة (الانبعاث) . اظهر طيف الفلورة لمحلول مخفف للبوليمر في الميثانول وجود حزمتي انبعاث عند الطول الموجي 342 نانوميتر و 387 نانوميتر يعودان الى مونومر النفثالين والاكسايمر على التوالي . تم قياس اطياف الفلورة لمحلول البوليمر على مدى عدة درجات حرارية من 8-45 م˚ وعند رسم نسبة شدة حزمة الانبعاث للاكسايمر الى شدة حزمة الانبعاث للمونومر (I_e/I_m) كدالة لدرجة الحرارة ظهر وجود خطين بميل موجب يتقاطعان عند 25 م °، فوق هذه الدرجة تكون الزيادة في الميل جدا قليلة هذا يعني وجود اذابة قوية للبوليمر من قبل جزيئات الميثانول عند درجة حرارة اقل من 25م ° تعزى هذه الاذابة الى التاثرات القوية وعلى الخصوص الاصرة الهيدروجينية بين جزيئات الميثانول والبوليمر حيث تكون على اشدها تحت 25م˚ .