Temperature Effect on Excimer / Polymer Fluorescence of Some Para-Substituted Polystyrene In Solid Films and In Solution

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Abstract

The fluorescence spectra of poly (para-methoxystyrene), poly(para-ethoxystyrene), poly (para-methoxyphenylstyrene) and poly (para-methoxy-o-methylstylene) were studied in solid films and in dichloromethane solution. Both poly (para-methoxystyrene) and poly (para-ethoxystyrene) gave an excimer fluorescence in solid films and in solutions, where poly (para-methoxyphenylstylene) and poly (para-methoxy-ω-methylstylene) gave only a monomer fluorescence in both phases. An increase in temperature of the solid films of these four polymers caused a decrease in the intensity of both monomer and excimer emissions. The activation energies for intermolecular excimer formation were calculated.

Introduction

The formation of excimer structures from polymers containing aromatic chromophores has stimulated the study of complex photophysical processes in macromolecules. Polystyrene and some para-substituted polystyrene were found to form excimer emission in solid films and solution. Varying the molecular weight of polystyrene resulted in changes of the intensity of excimer to monomer fluorescence emission

Harrah(7) has reported an observation of the temperature influence on polymer and excimer emissions in both fluid and rigid solutions of poly (2-vinyl naphthalene). He showed that, in fluid solutions, chain conformational changes

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dominated the excimer formation and the dissociation processes. But in rigid solutions, the increase in excimer emission was attributed to the low activation energy of excimer conformations.

In this paper, the effect of increase of temperature on the excimer and polymer emissions in solid film was reported.

The activation energies of these polymers were calculated and compared with the activation energies of other polymers.

Experimental

Polymer preparations:

Poly (para-methoxystyrene) (PPMS), poly (para-ethoxy-styrene) (PPES) and poly (para-methoxyphenylstylene) (PMPMS), were prepared by thermal free radical polymerization at 80°C of the purified monomers\(^6\).

PMS, PES and PMPS monomers were obtained from Koch Light Lab. Ltd. These monomers were purified by drying with CaH\(_2\) for 24 hours, and then distilled under vacuum. Para-methoxy-\(\alpha\)-methylstyrene (PM\(\alpha\)MS) was prepared earlier and was used without further purification\(^5\).

Polymerization of the dried monomers was carried out in an evacuated, sealed glass ampoule for a period of 3 days at 80°C with 0.1% weight of AIBN (azo bis-isobutoxinitrile) that added as an initiator. The resulting polymer was freed of residual monomer by precipitation in methanol from dichloromethane solution.

Solvent Purification:

Dichloromethane was obtained from (BDH) company and was purified by washing in turn with 5.0 M H\(_2\)SO\(_4\) solution, distilled water, aqueous (1.0 M) NaOH solution and distilled water. The purified dichloromethane was left in contact with NaOH pellets and calcium chloride overnight in order to eliminate any residual water. It was then refluxed for 24 hours over freshly ground calcium hydride, followed by fractional distillation. The fraction boiling at 40°C was collected, and then was stored over a sodium wire.

Tetrahydrofuran was obtained from (BDH) company and was purified by refluxing with sodium hydroxide pellets for 24 hours and then fractionally distilled.
over freshly ground CaH₂, then refluxed for 24 hours followed by fractional distillation at 66.5°C into a container containing fresh a sodium wire⁵.

Acetonitrile was obtained from (Aldrich) company and was dried over CaH₂ for 24 hours, refluxed over phosphorous (V) oxide for a further 24 hours, followed by fractional distillation. The middle fraction (b.p. 81.5°C) was collected. The purification method used for dichloromethane was also used for the purification of benzene, (obtained from (BDH) company).

Fluorescence measurements and sample preparations:

Fluorescence spectra were recorded on a Perkin-Elmer MPF-43(USA) automatic recording fluorescence spectrophotometer, fitted with a high sensitivity multi range Perkin-Elmer Model 56 recorder with a fast pen response and self-balancing. The instrument was fitted with a 150W Osram Xenon lamp. Fluorescence measurements were conducted at an excitation frequency range of (310-280) nm, with an emission and excitation width of 4 nm. Conditions were the same for all measurements. The concentration of all polymer solutions was 5x10⁻⁴ mol dm⁻³.

Films were cast from purified dichloromethane solutions on quartz plates at room temperature. All films were dried by pumping under vacuum for six hours in order to eliminate any residual solvent, and were mounted between two plates to eliminate positional wandering during temperature variation.

Results and Discussion

The fluorescence spectra for (PPMS), (PPES), (PPM ~ MS) and (PMMPS) in dichloromethane solution and in solid films are shown in (Fig. 1). For (PPMS) and (PPES) spectra (I, II) in dichloromethane solution, each spectrum consists of two bands, one is assigned to the polymer emission band and the other is the excimer emission band. The main reason for the observation of a weak band of the excimer emission in solution was attributed to the deactivation of excimer conformation by solvent molecules, and also to the relative low molecular weight of the polymer⁵. It has been proved that the ratio (Fₚ/Fₑ) (monomer emission to excimer emission ratio) is dependent on molecular weight of the polymer⁶.

The decrease in polymer emission in solid films compared to that in dichloromethane solution for both (PPMS) and (PPES), (III, IV) appears to be attributed to the absence of solvent molecules in one side and to the low activation energy for the excimer formation in favorable sites.
Further that as one would expect, the chain conformations in solid films of these two polymers do not attain collision deactivation by the presence of solvent molecules. These observations are close to what has been observed in vinyl polymers(n).

For poly(pare-methoxyphenylstylene) and poly(para-methoxy-α-methylstyrene) emission spectra (V, VI), only polymer emission is observed in both solid films and dichloromethane solution. This may arise either from a small barrier to excimer formation for favorable sites, or to the partial thermal relaxation of the chain segments which are more loosely bonded in the solvent medium.

Fig.1.

Corrected emission spectra at 298K, I-(PPTMS), II-(PPES) at 5x10^-4 M in Dichloromethane solution. III-(PPTMS), VI-(PPES), V-(PPTMS) and IV-(PPMABS) films cast at 298K and at exciting wavelength (200-319)nm.
1- Temperature effect in solid films

It was observed that the increase in temperature of the films of these four polymers caused a decrease in the intensity of both monomer and excimer emissions over a temperature range of (295-378 K). It has been observed that upon cooling the heated films, the emission intensity of both monomer and excimer emissions did not show any considerable increase, indicating the presence of thermal degradation in these polymers.

The significant experimental parameter for examining excimer formation and its stability towards the change in temperature, is the ratio log \( \frac{F_E}{F_M} = R \), (the excimer intensity \( F_E \) to the monomer intensity \( F_M \) ratio). The changes in this ratio with respect to changes in temperature for (PPMS) and (PPES) films are plotted in (Fig.2), as log \( \frac{F_E}{F_M} \) was plotted versus \( \frac{1}{T} \). Two temperature regions were distinguished, the first was observed between room temperature and the glass transition temperature (\( T_g \)). The second is between (\( T_g \)) and 383K. The decrease in the ratio \( R \) is due to the electronic dissociation of the excited complex at fixed site distribution. This temperature dependence is similar to that observed for poly (4-vinyl naphthalene)\(^{(7)}\).

In (Fig.2), at about 360± 5K for (PPMS) and 356± 5K for (PPES), the data began to deviate from the initial destabilization and then followed by a rather rapid increase in the ratio \( R \). These two points were found to be close to the (\( T_g \)) values for the above two polymers. Also, these (\( T_g \)) values are in good agreement with what we have obtained from the mechanical transition temperature measurements by (HPLC) for (PPMS) and (PPES) which yielded 365 K and 370 K respectively.

Similar behavior was also obtained by Frank\(^{(8,9)}\), in his study to see the temperature effect on poly(2-vinyl naphthalene)-polystyrene films. In that study a (\( T_g \)) value was obtained from a heating curve and another from a cooling curve and found to be similar. Although these obtained (\( T_g \)) values are arbitrary, they are useful for comparing the fluorescence values with that obtained from mechanical results, as in table (1).
Table (1): Comparison of Fluorescence and Mechanical Results

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Fluorescence</th>
<th>Mechanical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_e K$</td>
<td>$M_n$</td>
</tr>
<tr>
<td>Poly (P-methoxystyrene)</td>
<td>360 ± 5</td>
<td>9000</td>
</tr>
<tr>
<td>Poly (P-ethoxystyrene)</td>
<td>356 ± 5</td>
<td>23500</td>
</tr>
<tr>
<td>Poly (P-methoxyphenylstyrene)</td>
<td>−</td>
<td>10000</td>
</tr>
<tr>
<td>Poly (P-methoxy-α-methylstyrene)</td>
<td>−</td>
<td>24000</td>
</tr>
</tbody>
</table>
2- Activation energy for excimer formation

As described the experimental, solid films were cast from dichloromethane solvent. The polymer solution is allowed to evaporate at room temperature, then the resulting cast films will have a thermal distribution of chain conformations which is characteristic of that temperature. If we assume that the activation energy of the excimer site conformation with respect to the ground state conformation is, $\Delta E$. Then $\Delta E$ may be obtained from the following expression$^{(10)}$:

$$\log \frac{F_{M'}}{F_M} = \frac{\Delta E}{2.3RT}$$

where $F_M$ and $F_{M'}$ are excimer emissions at temperature at which the film was cast, and other higher temperatures respectively. A plot of $\log \frac{F_M}{F_{M'}}$ versus $\frac{1}{T}$ for (PPMS), and (PPES) is shown in (Fig. 3).
From the slopes of these plots, the following activation energies are calculated and shown in table (2):

**Table (2): Comparison of Activation energies for excimer formation**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Activation Energy (KJ / mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (P-methoxystyrene)</td>
<td>16.72 ± 0.05</td>
</tr>
<tr>
<td>Poly (P-ethoxystyrene)</td>
<td>17.55 ± 0.05</td>
</tr>
<tr>
<td>Polystyrene(11)</td>
<td>5.852</td>
</tr>
<tr>
<td>1,3 di (2-naphthyl propane)(11)</td>
<td>18.81</td>
</tr>
<tr>
<td>Poly (methyl methacrylate)(12)</td>
<td>18.0</td>
</tr>
</tbody>
</table>

It is possible that the lower value of activation energy of (PPMS) compared to that for (PPES) indicates a more favorable conformation available to adjacent chromophores on the chain, but more likely it reflects singlet migration through the chromophores of a given chain to a favorable conformation for excimer formation.

From the obtained data on the thermal effect on cast films of (PPMS) and (PPES), it was noticed that there is a gradual decrease in emission intensities of both excimer and polymer chromophores. Normally, thermal quenching of excimer emission results in the production of either excited polymer chromophore, dissociation to two ground state chromophores or a thermal digrandation of the polymer chains(9, 12, 13, 14). We notice no increase in either polymer emission or excimer emission upon cooling the heated films, which may indicates a possible thermal digradation in the polymer chains. Frank(9) concluded in his studies on poly(2-vinylnaphthalene) and polystyrene, that excimer dissociation does not lead to excited polymer chromophore. Similarily Danq(12) et al postulated that thermal digradation of poly(methylmethacrylate) produces anhydride from ester group of the polymer. Also, Prasad(14) concluded that all polymers are chemically digradable by the influence of heat. According to these facts, and to the obtained data, it can be concluded that although no chemical analysis was made on solid films durig heating, but our data show that a chemical degradation has occurred upon heating the solid films of (PPMS) and (PPES).

**Conclusion**

In temperature effect on intensity of polymer emission to excimer emission ratio, this ratio comes to minimum value of temperature close to the \( T_b \) value for
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both (PPMS) and (PPES) and correlate very well with the \( (T_g) \) values that obtained from (HPLC) technique. This fluorescence technique, may be used as a probe for \( (T_g) \) measurement for polymer that gives excimer emission in solid films.

The thermally activated quenching of the excimer fluorescence of (PPMS) and (PPES) does not involve deactivating process to yielded two polymer conformations or excited polymer conformation, indicating a possible thermal degradation as a result of the chemical oxidation \(^{13,14}\) in the polymer chains.

التأثير الحراري لفلورورة بعض ميلمرات البولستيرين

خلاد الغانى

ملخص

تمك تقياسات انبعاث الفلورورة (Fluorescence) في بوليمر (4- ميثوكسي ستايرين)، بوليمر (4- أثوكسي ستايرين)، بوليمر (4- مثيل ستايرين) في الأفلام الصلبة وفي محلول ثنائي كلوريد الميثان. أعطت أطياف الانبعاث إلى بوليمر (4- ميثوكسي ستايرين) بوليمر (4- أثوكسي ستايرين) انبعاث آخر هو انبعاث الأكسايمر (Excimer emission) في الأفلام الصلبة وفي محلول ثنائي كلوريد الميثان، في حيث لم يعطى هذا النوع من الانبعاث في حالة البوليمرات الأخرى. كما وجد أن رفع درجة حرارة الأفلام الصلبة لهذه البوليمرات يؤدي إلى انخفاض تدريجي في شدة كلا من انبعاث الفلورورة وانبعاث الأكسايمر الناتج من هذه البوليمرات. وقد تم حساب طاقة تنشيط تكون الأكسايمر من هذه الأطياف.

References:


