ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 4023–4031

polymer

www.elsevier.com/locate/polymer

Fluorescence response from anthracene labeled polystyrene to study its thermal transitions

S.G. Turrión, D. Olmos, N. Ekizoglou, J. González-Benito*

Departamento de Ciencia e Ingeniería de Materiales e Ingeniería Química, Universidad Carlos III de Madrid, Avda. Universidad, 30, 28911 Leganés, Madrid, Spain

Received 3 May 2004; received in revised form 19 January 2005; accepted 16 March 2005

Abstract

In this work, thermal transitions of polystyrene, PS, were studied as a function of molecular weight (M_w) and thermal history using the fluorescence response of anthracene chemically bonded to the polymer chain ends. For each PS sample the fluorescence spectra of the anthracene were collected as a function of temperature in cycles of heating and cooling. Two photophysical parameters were selected in order to study thermal transitions of the PS samples: (i) the first moment of the fluorescence band, $\langle \nu \rangle$; and (ii) the integrated fluorescence intensity, I. In every case, a sharp change in the photophysical parameter was observed at a certain temperature that was assigned to the α relaxation temperature and which was clearly different depending on the PS molecular weight and the thermal history. In fact, the relaxation temperature increased with M_w during a heating scan, decreased with M_w during a cooling scan and was clearly lower in the cooling scans. These results were interpreted in terms of a reorientation of the anthryl groups to the surface of the polymer.

Keywords: Anthracene; Fluorescence; Poly(styrene)

1. Introduction

Although there are several theories to explain the glass transition phenomenon, those based on the concept of the free volume, kinetic aspects and the thermodynamic are the most accepted. However, it is still needed new experimental data, which give a different perspective to focus the problem in such a way that could be deeply understood, at least, when a thermal relaxation at the surface of the polymers is concerned. For instance, in order to reach the knowledge necessary to create polymer films with tailored gradients of glass transition temperatures from the bulk of the polymer to its surface, it would be interesting to answer, among others, the following questions: Are all the monomeric units randomly distributed in the whole polymer sample? Is there any dependence with the molecular weight? What is the effect of the thermal history?

It is well known that the glass transition temperature of an amorphous polymer depends, among others, on the thermal history and the molecular weight. The first effect is observed, for instance, when the glass transition temperature determined upon a cooling experiment differs from that obtained during a heating experiment. The second effect corresponds to an increase of the glass transition temperature with the molecular weight of the polymer independently if the study was done upon cooling or upon heating. One of the simplest expressions describing this behavior, the Flory–Fox equation, is based on the free volume theories [1]:

$$T_g = T_g^\infty - \frac{C}{\bar{M}_n} \qquad (1)$$

where T_g and T_g^∞ are the glass transition temperatures of a polymer with a number-average molecular weight, $\bar{M}_n$, and a polymer with an infinite molecular weight, respectively; while C is a constant.

However, when samples of low molecular weight are concerned, there are deviations and the data can be better fitted with a modification of the Eq. (1) as proposed by

---

* Corresponding author. Tel.: +34 1 624 88 70; fax: +34 1 624 94 30.
E-mail address: javid@ing.uc3m.es (J. González-Benito).

0032-3861/$ - see front matter
doi:10.1016/j.polymer.2005.03.056

Unberreiter and Kanig for polystyrene [2]:

$$\frac{1}{T_g} = \frac{1}{T_g^\infty} + \frac{A}{\bar{M}_n} \tag{2}$$

where A is a constant.

These molecular weight dependences have been studied by methods that average the analytical response from the whole system. However, there is additionally the necessity of having that information, at a molecular scale, from specific sites, since there are several factors that should be also taken into consideration, for instance, surface area to volume ratio [3,4], substrate effects and sample thickness. Examples of the later effects have been showed in recent works, for instance, J. L. Keddie et al. showed that thin PS films have a decrease in glass transition temperature, which depends on the film thickness [5,6], J. H. van Zanten et al. [7] and C. J. Ellison et al. [8] found using X-ray reflectivity and the pyrene fluorescence emission, respectively, that the T_g of poly(2-vinylpiridine) films supported on silica substrates increased relative to the bulk, being that increment higher the thinner was the film. On the other hand, Forrest et al. showed a dramatic reduction of T_g in polystyrene films with a decrease in the film thickness below 70 nm [9] and reveled a significant molecular weight dependence of that T_g reduction when the molecular weight is high enough [10]. Although these experimental results have led to the development of models which qualitatively explain them [11–14] there are not yet enough evidences to support them.

An interesting attempt has been based on the study of the embedding of noble metal nanoclusters into the surface of monodisperse polystyrenes as a probe for the glass transition determination in a region near the surface [15]. An onset embedding temperature, T^*, was defined which characterizes the beginning of the embedding process and it was found that $T_g(\text{bulk}) - T^*$ increases with molecular weight. The observed molecular weight dependence was explained in terms of intrinsic models for a surface region with enhanced chain mobility [15].

The use of scanning force microscopy is being also a way of studying surface molecular motions of polymers particularly PS films [16,17]. For instance, the temperature-dependent lateral force microscopy was applied to the examination of surface relaxation processes for monodisperse PS films [18]. It was shown that the co-operativity at the surface was intensively reduced in comparison with its interior bulk region being suggested that the thermal molecular motion at the PS surface is activated by not only the surface localization of chain ends groups but also the reduced co-operativity.

The use of fluorescence to detect thermal transitions is taking a great interest due to the possibility of locating fluorescent molecules at specific sites and being able to get information from there [19–21].

A fluorescent group (fluorophore) is always affected by its immediate surroundings. Its fluorescence response can be clearly perturbed if there is any physico–chemical change in the site, where the fluorophore is immersed (rigidity, polarity, …) [22,23]. Due to this, changes in the free volume of a polymer matrix (for instance when a glass transition is taking place) in which the fluorophore is located should modify the number and type of interactions between the polymer and the fluorophore and, therefore, changes in the fluorescence response of it should occur [24–26].

J. M. Torkelson et al. [21] and M. Talhavini et al. [27,28] have used the fluorescence intensity from probes and labels to study temperature induced polymer relaxation processes. In those studies plots of the fluorescence intensity vs. temperature exhibited slope changes that were interpreted as co-operative influence of the polymer chain motions on the photophysical properties of the excited states of the chromophore used. However, these fluorescence methods does not eliminate the effect of intensity variations arising from external factors such as, lamp intensity, optical alignment, probe location and excitation area. Furthermore, in most of the samples the slope changes are so weak that are not easily distinguishable. Due to this, other methods were tried as the use of intensity ratios although they do not seem to be very sensitive [28].

In other works, the variation of the energy of the fluorescence emission with the temperature was used to determine thermal transitions as the T_g [20,23,29,30].

R. Albalá et al. [20] used the fluorescence response from dansyl moiety chemically attached to the surface of silica particles to obtain the thermal transitions associated to the interphase formed between silica fillers and an epoxy matrix in a composite. In this work [20], a new parameter, based on the first moment of the fluorescence band, $\langle \nu \rangle$, was used for this kind of determination

$$\langle \nu \rangle = \frac{\sum I_F(\nu_F)\nu_F}{\sum I_F(\nu_F)} \tag{3}$$

where $I_F(\nu_F)$ is the fluorescence intensity at a specific wavenumber, ν_F. The first moment of the fluorescence band can be easily calculated with a standard error of about $\pm 2\ \text{cm}^{-1}$ and was demonstrated to be very useful to monitor polymerization processes, where important changes in the free volume are taking place [31].

In this work, thermal transitions of polystyrene, PS, is proposed to be studied as a function of molecular weight (M_w) and thermal history using steady state fluorescence of anthracene chemically bonded to the polymer chain ends. Fluorescence spectra of anthracene for each PS sample will be collected as a function of temperature in cycles of heating and cooling at 0.5 °C/min.

Two photophysical parameters will be selected in order to study thermal transitions in the PS samples: (i) the first moment of the fluorescence band, $\langle \nu \rangle$ and (ii) the integrated fluorescence intensity, I. Furthermore, classical DSC experiments will be performed and their results will be compared with those obtained by fluorescence.

2. Experimental part

2.1. Materials

Polystyrenes end capped with anthracene, PS's, were synthesized using the following chemicals supplied by Aldrich Co.: styrene as the main monomer, 9-vinylanthracene to end-capping the polymer chains and *sec*-butyl lithium as the anionic initiator. Calcium hydride (CaH_2), methanol, cyclohexane, benzene (used along the process for preparing the polyestyrenes) and tetrahydrofurane (THF, used as the solvent for the SEC characterization), were also purchased from Aldrich Co.

2.2. Sample preparation

As a control sample, a film of PS doped with free anthracene (fluorescent probe), PS-control, was prepared from a THF solution by solvent casting. The PS had a molecular weight of 1.3×10^4 g/mol and a polydispersity of $\Gamma(M_w/M_n)=1.85$.

PS of three different molecular weights (5.14×10^3, 1.98×10^4, 1.12×10^5 g/mol, named as: PS-5K, PS-20K and PS-110K, respectively) and polydispersities, $\Gamma(M_w/M_n)$, 1.1, 1.07 and 1.04, respectively, were synthesized by anionic polymerization with high vacuum techniques according to literature [32]. The initial concentration of styrene monomer in benzene was 10% (w/w) independently of the sample to be prepared while the amount of *sec*-butyl lithium initiator varied as a function of the molecular weight to be obtained. Subsequently, the living polymer samples (carbanions) were labeled with the fluorescence anthracene moiety by an end-capping reaction (addition reaction) in benzene for 24 h. As received 9-vinylanthracene (without further purification) in a 5% over the stoichiometric amount necessary for reacting with all the active PS chain ends was used. The reaction was quenched with degassed methanol and after that, the labeled polystyrenes were isolated by means of a double precipitation into an excess of methanol and vacuum dried. TLC experiments showed no free anthracene moiety in the labeled polymer samples.

2.3. Size exclusion chromatography (SEC)

Shimazu SEC equipment with refractive index detection relative to PS standards was used to determine the molecular weight of the PS samples and their distributions.

2.4. Differential scanning calorimetry (DSC)

DSC dynamic scans from 5 to 200 °C at 10 °C/min in a nitrogen atmosphere were performed using a Mettler Toledo 12E differential scanning calorimeter. Pure indium was used as a standard for calorimetric calibration. Runs were carried out using an empty aluminum cell as the reference. The analysis of the thermograms allowed obtaining the glass transition temperature, T_g, from the inflexion point of the DSC traces.

2.5. UV–vis absorption spectroscopy

A spectrometer UV–vis Perkin Elmer Lambda 14 was used to estimate the concentration of the anthracene in the four polymeric samples prepared.

2.6. Steady state fluorescence

All the fluorescence spectra were performed with a fluorimeter Perkin Elmer LS-50B. The fluorescence emission spectra of the doped polystyrenes at room temperature were recorded at several wavelengths of excitation using a front face accessory. The excitation and emission slits were set with a band pass of 5 and 10 nm, respectively, while the scan rate used was 60 nm/min. Furthermore, the fluorescence spectra of anthracene for each PS sample were collected as a function of temperature in two cycles of heating and cooling, going the first cycle at 20 and 10 °C/min for the heating and cooling, respectively, and the second one at 0.5 °C/min in both scans. The scanned temperature ranges were (35–150) °C for the PS-control, PS-5K and PS-20K samples and (20–170) °C for the PS-110K sample. The second cycle was chosen in order to ensure the same thermal history in all samples. These experiments were carried out with the fluorimeter coupled to a DSC (Perkin Elmer DSC7) with an optical fiber cable to both excite and collect the fluorescence of the sample placed into the oven of the DSC. The excitation and emission slits were set with a band pass of 4 and 5 nm, respectively. Every spectrum was recorded between 380 and 600 nm setting the excitation wavelength at 365 nm and the scan rate at 120 nm/min.

3. Results and discussion

3.1. Characterization of the samples

0.01 g of each doped polystyrene sample: PS-Control, PS-5K, PS-20K and PS-110K were dissolved in 25 ml of THF to prepare the solutions for estimating the concentration of anthracene. The concentration of anthracene in the PS-control sample was calculated from the UV absorption spectra taking the molar excitation co-efficient of antrhacene in cyclohexane ($\varepsilon=9700\ \mathrm{L\ mol^{-1}\ cm^{-1}}$ at 356.25 nm) [33]. The estimated concentration of anthracene in the PS-control was 5×10^{-3} mol/kg. On the other hand, the concentrations of anthryl groups in the end capped polystyrene samples were calculated from the UV absorption spectra assuming that their molar excitation coefficients are the same as that of the 9-methylanthracene in cyclohexane ($\varepsilon = 10295\ \mathrm{L\ mol^{-1}\ cm^{-1}}$ at 366 nm) [33]. The estimated concentrations of anthracene were 2.7×10^{-4} mol/kg for the PS-5K sample, 2.1×10^{-4} mol/kg for the PS-20K sample and 1.0×10^{-3} mol/kg for the PS-110K sample. The results obtained in terms of concentration of anthracene for the labeled PS suggest that the end capping reaction was not quantitative which may be due to the very slow rate of addition of these kinds of reactions in pure benzene [34]. Furthermore, the concentrations obtained may be considered contradictory since, one would expect a higher concentration of anthracene for the lowest molecular weight polystyrene. However, it has been demonstrated that in similar polystyrene end capping reactions in the same solvent there is an inefficient crossover if the molecular weight is low or relatively low [35].

In Fig. 1 the fluorescence emission spectra (at room temperature before the thermal treatments) at several excitation wavelengths of the labeled polystyrenes PS-5K, PS-20K and PS-110K are presented. The independence of the emission spectra on the excitation wavelengths suggests that there is only one kind of anthracene in terms of being localized in only one specific site. However, the spectra obtained greatly differ from those arising from anthracene in solution [36,37]. The typical vibrational structure of the anthryl groups does not appear well resolved when they are bonded to the chain end of the polystyrenes (Fig. 1). The spectra of the samples PS-5K and PS-20K show a maximum at 415 nm and two shoulders at 395 and 437 nm, respectively. On the other hand, the spectra of the sample PS-110K shows a maximum at 428 nm and two shoulders at 410 and 455 nm, respectively, that reflect a great change respect to the spectra of anthracene in solution. This apparent shift of the vibronic bands respect to those obtained for the samples PS-5K and PS-20K might be due to an important change in their contribution to the total fluorescence. As can be seen in Fig. 1, the 0,0 emission band (395 nm) is very weak and, even though, in the case of PS-110K can not be observed not even as a shoulder, indicating that the trivial radiative energy transfer [38,39] (auto absorption phenomenon) seems to be very important. This phenomenon is more clearly reflected by the intensity ratio at the wavelengths of 395 and 416 nm, I_{395}/I_{416}: 0.48 for PS-5K; 0.45 for PS-20K and 0.32 for PS-110K. This result is completely in accordance with that expected with a high concentration of anthryl groups in the three polymers, at least locally. According to the order in concentration: PS-5K $\approx$ PS-20K $<$ PS-110K, it would be expected the same order in terms of the effectiveness for the radiative energy transfer, as it was obtained.

3.2. Measurement of thermal relaxations

In Fig. 2 is represented the fluorescence spectra for the three PS samples at different temperatures obtained during a second cycle of heating–cooling at 0.5 °C/min. These spectra are similar to those obtained without any thermal treatment although the contribution of the higher energy range to the total fluorescence spectra seems to be reduced. This result suggests that the thermal treatment (first cycle of heating–cooling) may induce a molecular reorganization with an increase of the local concentration of anthryl groups, which would enhance the trivial radiative energy transfer (re-absorption of emitted photons). Besides, in Fig. 2 it is

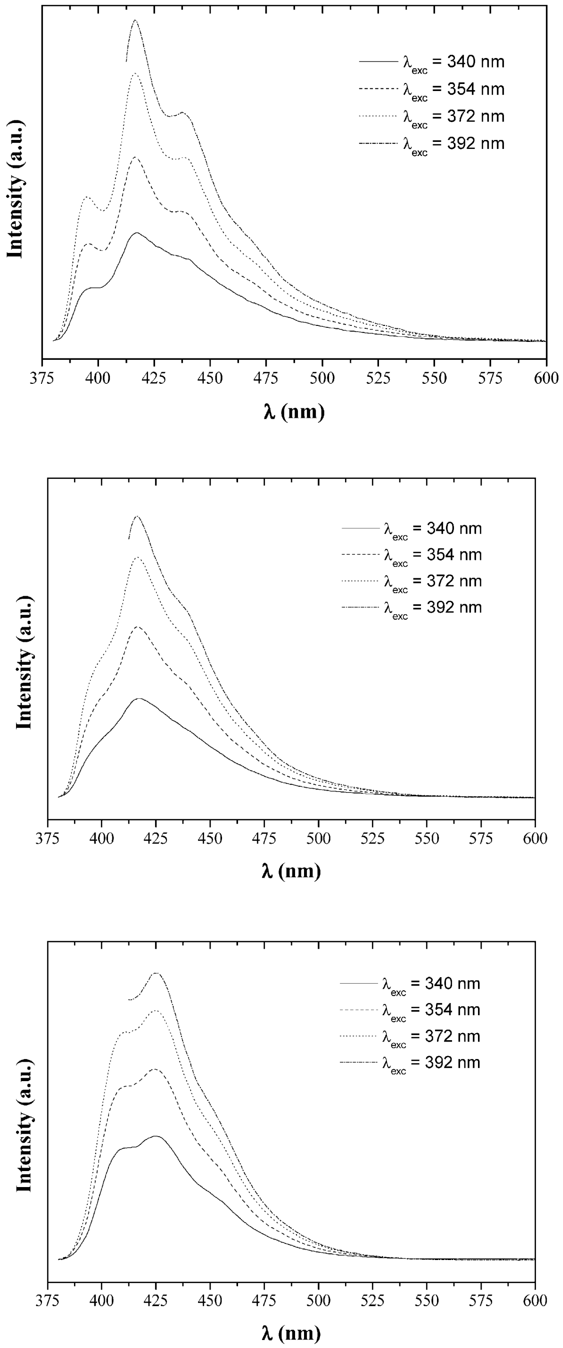

Fig. 1. Fluorescence emission spectra at room temperature of the labeled polystyrenes at several wavelengths of excitation. Top (PS-5K), middle (PS-20K) and bottom (PS-110K).

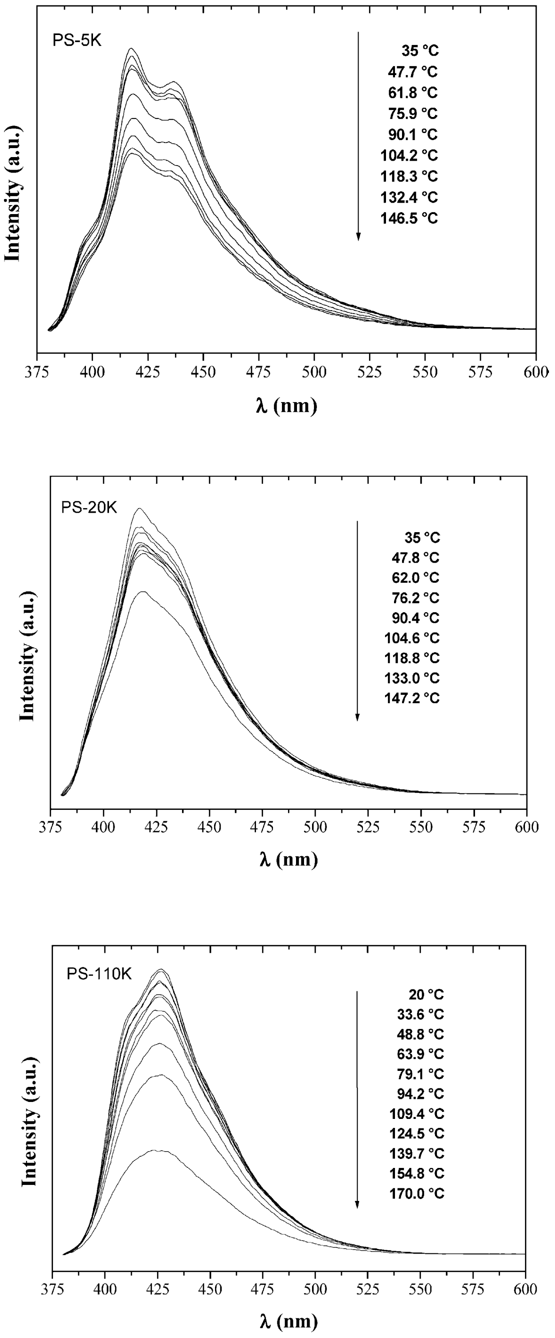

Fig. 2. Fluorescence spectra ($\lambda_{exc} = 365$ nm) of the three PS samples at different temperatures obtained throughout the second cycle of heating–cooling at a rate of 0.5 °C/min. Top (PS-5K), middle (PS-20K) and bottom (PS-110K).

observed that the global intensity decreases when the temperature increases. This observation can be interpreted in terms of an increase in the non-radiative deactivation processes represented by an enhancement of the non-radiative rate constant, k_{nr}.

In Fig. 3 are represented, for every sample of anthracene labeled PS, the value of the fluorescence intensity, integrated over the wavenumber, as a function of temperature for the second cycle of heating and cooling at 0.5 °C/min. As usual, the ordinate shows arbitrary units for the fluorescence intensity, since the values of this parameter cannot be taken as absolute ones to compare different experiments. However, the intensity variation in the experiments of the labeled polystyrenes ranges between 26 and 54%. In both scans, heating and cooling, it can be observed a relatively typical behavior in polymers [20,38]. There is a sharp change in the fluorescence intensity at a certain temperature that usually is attributed to a polymer relaxation temperature, for instance a T_g. In fact, in the heating scan, the values obtained of the temperatures at the onset of the sharp change in the fluorescence intensity for the three polystyrenes under study, T_I^H, are similar to the glass transition temperature obtained from the inflexion point in the DSC traces, T_{DSC}, (Table 1) showing the same tendency with the molecular weight. The onsets of the sharp changes, T_I, are defined as the temperatures for which there is a deviation from the initial fitted straight line of more than 1% respect to the total intensity variation. This initial straight line arises from the best fit taking as many points as possible before the inflexion point. Furthermore, after the relatively sharp change in the fluorescence intensity the slope of the curves decreases at a certain temperature for PS-5K and PS-20K samples.

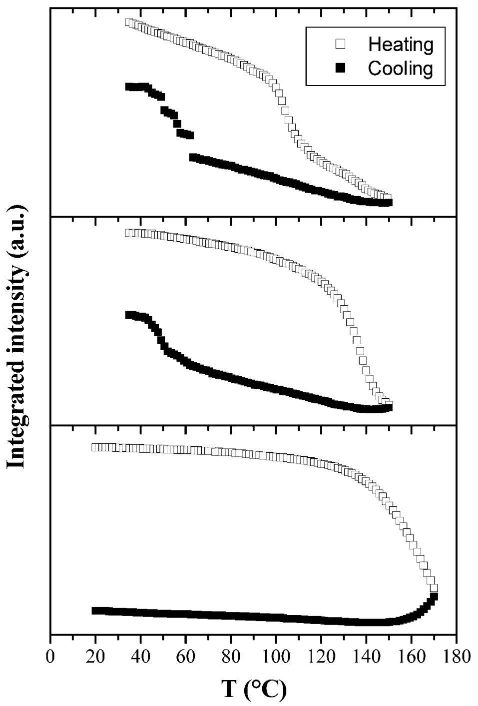

Fig. 3. Fluorescence intensity integrated over the wavenumber as a function of temperature for the second cycle of heating and cooling at 0.5 °C/min. Top (PS-5K), middle (PS-20K) and bottom (PS-110K).

These phenomena of fluorescence can be understood considering the equation for the fluorescence quantum yield,

Table 1
Relaxation temperatures for the polystyrenes under study obtained by DSC and fluorescence (see text)

Sample	T_{DSC} (°C)	T_I^{H} (°C)	T_I^{C} (°C)	$T_{\langle\nu\rangle}^{\mathrm{H}}$ (°C)	$T_{\langle\nu\rangle}^{\mathrm{C}}$ (°C)
PS-5K	91.1	92 ± 2	62 ± 1	83 ± 3	63 ± 1
PS-20K	100.4	100 ± 4	60 ± 2	99 ± 3	61 ± 1
PS-110K	105.0	110 ± 5	<20	121 ± 4	<20

ϕ_{F}, and/or the fluorescence intensity, I:

$$\phi_{\mathrm{F}} = \frac{k_{\mathrm{F}}}{k_{\mathrm{F}} + k_{\mathrm{nr}} + k_{\mathrm{RET}}} = \frac{k_{\mathrm{F}}^0 n^2}{k_{\mathrm{F}}^0 n^2 + k_{\mathrm{nr}} + k_{\mathrm{RET}}} \propto I \text{ (Fluorescence intensity)} \qquad (4)$$

where k_{F}, k_{nr} and k_{RET} are the fluorescence, non-radiative and radiative energy transfer constant rates, respectively, k_{F}^0 is a constant independent of temperature and n is the refraction index. k_{F} only depends on temperature through the refraction index [37]. The dependence on temperature of k_{nr} is unknown but it is usually assumed an Arrhenius-like behavior [39], therefore:

$$k_{\mathrm{nr}} = A\mathrm{e}^{-E_{\mathrm{a}}/RT} \qquad (5)$$

where A is a pre-exponential constant, T the absolute temperature, R the gas general constant and E_{a} the activation energy for the non-radiative deactivation of the fluorescence. In the low temperature range it can be assumed that only k_{F} and k_{RET} account for the fluorescence intensity. On the other hand, in the high temperature limit when the motions of the polymer chains are enough, a balance between two opposite effects should be taken into account: (i) the deactivation of the fluorescence by non-radiative processes (k_{nr} increases) and (ii) an important increase of the free volume which, on average, would reduce the local concentration of anthryl groups decreasing, therefore, the radiative energy transfer (k_{RET} decreases). The results observed in the Fig. 3 suggest that, at a certain temperature, there is an important increase of the non-radiative processes which is translated into a sharp decrease of the fluorescence intensity. On the other hand, when the temperature is high enough, the reduction of the radiative energy transfer contribution is so important as to partially compensate the effect of the non-radiative processes decreasing, therefore, the slope of the plot intensity vs. temperature.

If it is assumed that k_{RET} is temperature non-dependent in the temperature range in which there is a sharp change in the fluorescence intensity, the data of the Fig. 3 could be fitted by means of a non-linear method using as a fitting function the Eq. (4). From the best fit, the activation energy, E_{a}, can be obtained as a fitting parameter.

The values of E_{a} obtained after the best fits were: E_{a}(PS-5K) $= 82\pm20$ kJ/mol, E_{a}(PS-20K) $= 105\pm13$ kJ/mol, E_{a}(PS-110K) $= 114\pm6$ kJ/mol. In spite of the errors associated to the fit, these results seem to reflect that E_{a} increases when the molecular weigh of the PS increases, suggesting that the activation energy for the non-radiative deactivation of the fluorescence is related with the activation energy associated to the relaxation of the polymer. It is interesting to point out that although these apparent activation energies were quite smaller than those reported for both the bulk [40] and the surface [18] associated to the PS's α relaxation, they have the same order of magnitude.

Two more observations can be done from Fig. 3 and Table 1, where the values obtained of the temperatures at the onset of the sharp change in the fluorescence intensity for the three polystyrenes under study in both the heating and cooling scans, T_I^{H} and T_I^{C}, are shown: (i) the existence of a kind of hysteresis, since the sharp change in the fluorescence intensity occurs at a considerable lower temperature upon cooling (solid symbols in Fig. 3), and (ii) the higher the molecular weight the higher the difference between T_I^{H} and T_I^{C} (Table 1).

A possible explanation for these observations may be the consideration of a reorganization of the anthryl groups to the surface of the polymer. The phenomenon of hysteresis, the first observation, may be explained as follows: during the heating scan it is only possible an effective deactivation of the fluorescence when the co-operative motion of the PS chain units is so important as to generate enough free volume. This free volume might facilitate the effective collisions between the excited anthryl groups and their immediate surroundings. On the other hand, during the cooling scan, the deactivation of the fluorescence finishes when the anthryl groups stop moving. If it is considered the tendency of the polymer chain ends to move to the surface, since they should have higher freedom of movement, it is expected that they will be the last ones to stop when the cooling of the sample is taking place. This results would confirm the specificity of the information (at a molecular scale) given by the fluorescence emission from fluorescent labels which will be complementary to the information given by techniques as DSC from the whole system.

The polymers under study have the anthryl groups bonded to the chain ends and, therefore, they will stop moving at lower temperatures than that needed for the disappearance of the co-operative motions of the chain units which are ascribed to the polymer relaxation. Therefore, during the cooling scan the deactivation of the fluorescence should take place at lower temperature than in the case of a heating scan, being in accordance with the results obtained.

Taking into account the last explanation for the hysteresis phenomenon, the increase in the difference between T_I^{H} and T_I^{C} as the molecular weight increases might be due to differences in the concentration of the anthryl groups at the surface of the polymers. In fact, the whole concentration of anthryl groups in the PS's under study increases the higher the molecular weight is. In addition to this, in the case of a PS with larger molecular weight, the probability for the chains ends to be located near the surface region should be higher if the surface free energy of the end groups is small enough to allow them to segregate to the surface [18]. Taking into account the low polarity associated to the anthryl end groups; one can assume a very small surface free energy for them, yielding, therefore, a tendency to greatly increase its concentration locally at the surface of the polymer. On the other hand, this would not be true for a shorter chain because the chain would suffer too large loss in entropy on account of its smaller internal freedom if the most chain ends are localized at the surface [18].

Taking into account the bad resolution of the vibrational structure of the fluorescence spectra obtained at different temperatures, instead of the intensity band ratios to follow the variation of the radiative energy transfer as a function of temperature, the use of the first moment of the emission band is suggested (Eq. (3)). Since, the first moment of the emission band is an average of the fluorescence in terms of wavenumbers, an increase of the bands in the region of high energy when the temperature increases will be translated into an increase of the first moment value, which can be determined very accurately [31].

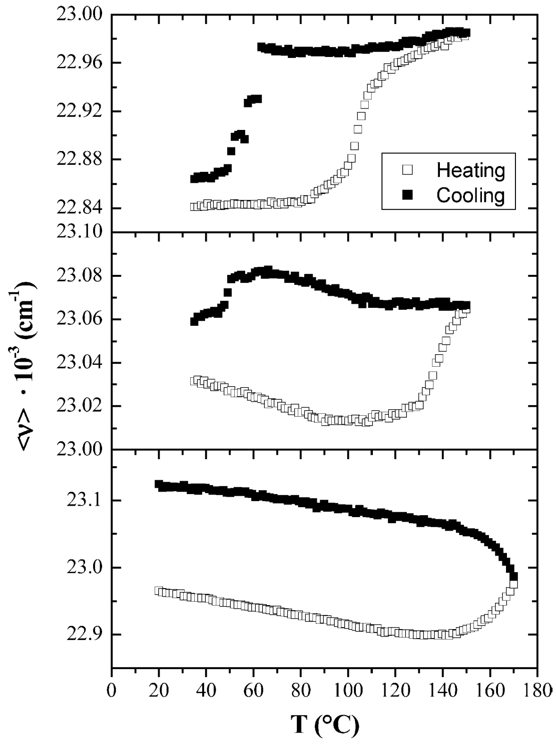

Fig. 4. First moment of the fluorescence band, $\langle\nu\rangle$, as a function of temperature for the second cycle of heating and cooling. Top (PS-5K), middle (PS-20K) and bottom (PS-110K).

In Fig. 4 is represented, for the three labeled polymers under study, the value of the first moment of the fluorescence band, $\langle\nu\rangle$, as a function of temperature for the second cycle of heating and cooling. During the heating scan, for the PS-5K sample it is observed that the $\langle\nu\rangle$ is nearly constant at lower temperatures than 81 °C while sharply increases with temperature at higher temperatures. For the PS-20K and PS-110K samples it is observed during the heating scan that the $\langle\nu\rangle$ decreases at lower temperatures than 93 and 120 °C, respectively, while at higher temperatures the first moment sharply increases with temperature as in the case of the polymer PS-5K. During the cooling scans it was obtained a kind of hysteresis (Fig. 4) as in the case of the evolution of the integrated fluorescence intensity with the temperature (Fig. 3).

In Table 1 are grouped the values obtained for the temperatures at the onset of the sharp change in the first moment (it was taken the same criterion than that for the fluorescence intensity) for the three labeled polystyrenes under study in both, the heating and cooling scans, $T^{\mathrm{H}}_{\langle\nu\rangle}$ and $T^{\mathrm{C}}_{\langle\nu\rangle}$, respectively. It can be seen that the values of $T^{\mathrm{H}}_{\langle\nu\rangle}$ are very close to the T_g obtained by DSC, therefore, it seems that the sharp change in the first moment may be due to an α relaxation phenomenon.

Again, these observations (Fig. 4) may be explained in terms of a variation in the radiative energy transfer when the temperature changes. When the temperature increases two effects may affect the fluorescence from the anthryl groups (fluorophores) bonded to the polymer chains: (i) the thermal activation of the fluorophores and (ii) the continuous enhancement of the free volume in the system. The first effect should decrease the value of the first moment because of an increase of the population of the upper vibrational levels [20]. On the other hand, the second effect should increase the value of the first moment if there is a decrease on the effectiveness of the radiative energy transfer (there is an increase of the more energetic vibrational bands in the fluorescence spectra). In fact, on average, the fluorphores should be more separated on increasing the temperature because of the free volume enhancement. Therefore, a balance between these two effects should be taken into account.

Assuming this balance it is possible to explain the two regions observed in the plots on Fig. 4. In the first region, before the polymer relaxation (low temperature in the heating scans and high temperatures in the cooling scans), the thermal activation is more important while in the second region, the thermal relaxation is taking place since, there is a sharp change in the free volume of the system.

Furthermore, it is interesting to highlight that the slope throughout the first region increases as the molecular weight of the polymer increases (during the heating scan: 0.1 for PS-5K, −0.3 for PS-20K and −0.6 for PS-110K). This result seems to be due to a more pronounced increase of the free volume with temperature the smaller the polymer chain is.

Additionally, in the case of the first moment analysis, the existence of a kind of hysteresis and the increase of the difference between T_I^{H} and T_I^{C} as the molecular weight of the PS increases (Table 1) might be explained again considering the reorientation of the anthryl groups to the surface of the polymer but now in terms of the effectiveness of radiative energy transfer.

During the heating scan it is only possible an important decrease of the radiative energy transfer when the co-operative motion of the PS chain units is so important as to generate enough free volume to greatly compensate the thermal activation effect. On the other hand, during the cooling scan, the effectiveness of the radiative energy transfer is recovered when the anthryl groups stop moving. Again one can consider the tendency of the polymer chain ends to migrate to the surface. Therefore, during the cooling scan the recovering of the most effective radiative energy transfer should take place at lower temperature than in the case of a heating scan, being in accordance with the results obtained. Besides, the increase in the difference between $T_{\langle\nu\rangle}^{\mathrm{H}}$ and $T_{\langle\nu\rangle}^{\mathrm{C}}$ as the molecular weight increases might be due to a higher concentration of the anthryl groups at the surface of the polymer and it may be explained as it was done in the case of the integrated fluorescence intensity.

Furthermore, there is another observation. Although the profile is the same, the spectra at room temperature before and after the second cycle of heating–cooling are slightly different: (i) the whole intensity decreases and (ii) the first moment of the emission band increases (Figs. 3 and 4). These observations may be explained considering small variations in the sample disposition respect to the excitation beam. In fact, those differences were lower in the third cycle and higher in the first cycle and, therefore, they do not seem to be due to structural changes of the polymers.

Finally, as a result of a control experiment, in Fig. 5 is shown for the PS-control sample the fluorescence integrated intensity (top) and $\langle\nu\rangle$ (bottom) as a function of temperature for the second cycle of heating and cooling at 0.5 °C/min. During the heating scan a typical photophysical behavior of fluorescent probes in polymers is observed which only would reflect the interaction between the fluorophore and its immediate surroundings [20,38]. For the integrated fluorescence intensity (Fig. 5, top) it can be observed a sharp change at a certain temperature (100 °C) that may be attributed again to a polymer relaxation temperature, for instance, the T_g. Furthermore, for this sample the slope of the curve does not decrease along the sharp change as happened for PS-5K and PS-20K samples. This result suggests that there are not changes in the effectiveness of the autoabsorption phenomenon. On the other hand, the first moment of the emission band continuously decrease when the temperature increase (Fig. 5, bottom), showing a slope reduction around 100 °C. Similar behavior was found from the fluorescence of dansyl moiety in epoxy/silica composites [20] being assigned to a relaxation of the polymer which might be the glass transition.

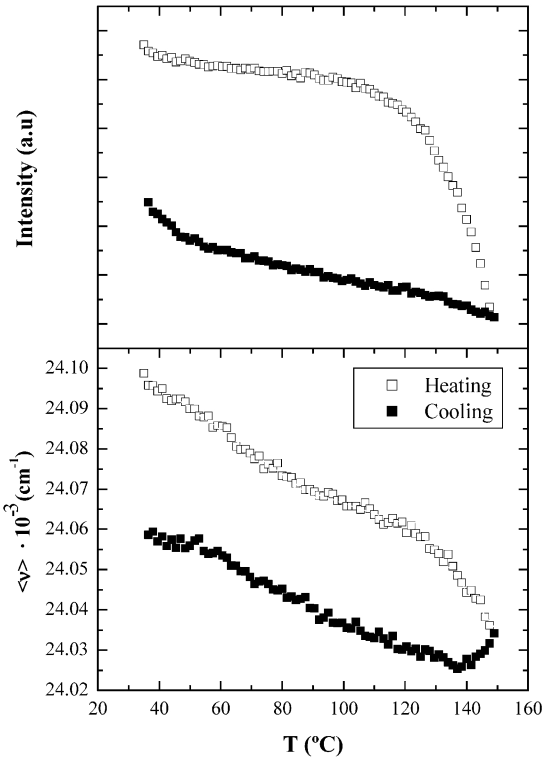

Fig. 5. Fluorescence integrated intensity (top) and $\langle\nu\rangle$ (bottom) as a function of temperature for the second cycle of heating and cooling at 0.5 °C/min. PS-control sample.

In the case of the cooling scan the maximum variation of I and $\langle\nu\rangle$ is so small (less than 10% and 30 cm^{-1} respectively) that only a continuous increase in both parameters can be inferred when the temperature decreases. Actually, the profiles for the photophysical parameters in both, the heating and cooling scans, seems to be the same, suggesting, therefore, that there is not hysteresis behavior when the anthracene chromofore is freely immersed in the polymer as a fluorescent probe. Besides, if the hysteresis observed in the case of labeled polystyrenes were not dependent of the character of the fluorophore (free or attached) one would expect to observe a sharp change of the photophysical parameters between 63 and 53 °C for the PS-control sample attending to its molecular weight, however, it was not observed. This result suggests that free anthracene cannot give information from the surface of the polymer. In the case of considering migration of free anthracene, after reaching the surface it would sublimate loosing the possible information from there which is in accordance with the results obtained.

4. Conclusions

In this work, thermal transitions of polystyrene, PS, were studied as a function of the molecular weight (M_w) and the thermal history using steady state fluorescence of anthracene chemically bonded to the polymer chain ends. The independence of the emission spectra of the attached anthryl groups on the excitation wavelengths suggested that there is only one kind of anthracene in terms of being localized in only one specific site. Furthermore, the analysis of the fluorescence spectra of the labeled PS showed an important contribution of trivial radiative energy transfer which was dependent of the PS sample due to differences in the local concentration of the antryl groups.

On the other hand, using the fluorescence response of the anthracene bonded to the polymer chain ends it was possible to determine the T_g of three polystyrenes with different molecular weights. These T_g values depended on the thermal history, being lower when a cooling scan was been carried out and obtaining a kind of hysteresis in the heating–cooling cycles. Furthermore, the width of the hysteresis increased the higher the molecular weight was. These results were interpreted considering a reorientation of the anthryl groups to the surface of the polymer with a higher tendency for this phenomenon the higher the molecular weight was.

Acknowledgements

Authors gratefully acknowledge to Fibrodont (MAT2001-0677-P3) project for financial support.

References

[1] Fox TC, Flory PJ. J Appl Phys 1950;21:581.
[2] Unberreiter K, Kanig G. J Colloid Sci 1952;7:569.
[3] Ding J, Xue G, Dai Q, Cheng R. Polymer 1993;34:3325.
[4] Xue G, Lu Y, Shi G, Dai Q. Polymer 1994;35:892.
[5] Keddie JL, Jones RAL, Cory RA. Faraday Discuss 1994;98:219.
[6] Keddie JL, Jones RAL, Cory RA. Europhys Lett 1994;27:59.
[7] Van Zanten JH, Wallace WE, Wu WL. Phys Rev E 1996;53:R2053.
[8] Ellison CJ, Kim SD, Hall DB, Torkelson JM. Eur Phys J E 2002;8:155.
[9] Forrest JA, Dalnoki-Veress K, Stevens J, Dutcher JR. Phys Rev Lett 1996;77:2002.
[10] Forrest JA, Dalnoki-Veress K, Dutcher JR. Phys Rev E 1998;58:6109.
[11] Ngai KL, Rizos AK, Plazek DJ. J. Non-Cryst Solids 1998;235–237:435.
[12] De Gennes PG. Eur Phys J E 2000;2:201.
[13] Dalnoki-Veress K, Forrest JA, De Gennes PG, Dutcher JR. J Phys IV 2000;10:221.
[14] Forrest JA, Mattsson J. Phys Rev E 2000;61:R53.
[15] Erichsen J, Kanzow J, Schürmann U, Dolgner K, Günther-Schade K, Strunskus T, et al. Macromolecules 2004;37:1831.
[16] Satomi N, Takahara A, Kajiyama T. Macromolecules 1999;32:4474.
[17] Kajiyama T, Tanaka K, Satomi N, Takahara A. Macromolecules 1998;31:5150.
[18] Tanaka K, Takahara A, Kajiyama T. Macromolecules 2000;33:7588.
[19] Lenhart JL, Van Zanten JW, Dunkers JP, Parnas RS. Macromolecules 2001;34:2225.
[20] Albalá R, Olmos D, Aznar AJ, González-Benito J. J Colloid Interface Sci 2004;277:71.
[21] Ellison CJ, Torkelson JM. J Polym Sci: Part B Polym Phys 2002;40:2745.
[22] Lakowicz JR. Principles of fluorescence spectroscopy. New York: Kluwer Academic; 1999.
[23] Loufty RO. Macromolecules 1981;14:270.
[24] Hofstraat JW, Veurink J, Gebben B, Verheij HJ, Verhoeven JW. J Fluoresc 1998;8:335.
[25] Murakami HM, Kushida T. J Lumin 1997;72-74:961.
[26] Martins TD, Yamaki SB, Prado EA, Atvars TDZ. J Photochem Photobiol 2003;156:91.
[27] Talhavini M, Atvars TDZ, Cui C, Weiss RG. Polymer 1996;37:4365.
[28] Talhavini M, Atvars TDZ, Schurr O, Weiss RG. Polymer 1998;39:3221.
[29] Eisenbach CD, Fisher K. Polym Prepr 1988;29:501.
[30] Ficht K, Fischer K, Hoff H, Eisenbach CD. Makromol Chem Rapid Commún 1993;14:515.
[31] Mikes F, González-Benito J, Serrano B, Bravo J, Baselga J. Polymer 2002;43:4331.
[32] Hadiichristidis N, Latrou H, Pispas S, Pitsikalis M. J Polym Sci: Part A Polym Chem 2000;38:3211.
[33] Berlman IB. Handbook of fluorescence spectra of aromatic molecules. New York: Academic Press; 1971.
[34] Quirk RP, Schock LE. Macromolecules 1991;24:1237.
[35] Quirk RP, Lee B. Macromol Chem Phys 2003;204:1719.
[36] Gilbert A, Baggott J. Essentials of molecular photochemistry. Boca Raton: CRC Press; 1991, p. 169.
[37] Birks JB. Photophysics of aromatics molecules. New York: Wiley; 1970.
[38] Dorado AP. Movilidad de nudos en una red, Doctoral Thesis, F. CC. Químicas U.N.E.D., Madrid; 1995, p. 138.
[39] Turro NJ. Modern molecular photochemistry. USA: U.S.B.; 1991 [Chapter 6].
[40] Santangelo PG, Roland CM. Macromolecules 1998;31:4581.