Temperature Perturbation to Intrinsic Fluorescence of Phenyl Multimers in Glassy Polystyrene

Shing Wong

Polymer engineer, 32 York Street West, Ontario N0B 1S0. Email: swongph7@yahoo.ca

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Abstract

The newly discovered fluorescence in polystyrene is used as a probe to understand the phenyl motions in glassy polystyrene fine particles when temperature increases from room temperature to 62°C. The large changes in fluorescence profiles (intensities and shapes) suggest profound phenyl motions and reorientations under 62°C. When excite a single phenyl ring ($\lambda_{\text{ex}} = 260$ nm), proposed phenyl dimers ($\lambda_{\text{ex}} = 277$ nm and 296 nm), and proposed tetramers ($\lambda_{\text{ex}} = 360$ nm and 380 nm), the heating has negative effects on the fluorescence intensities of all emissions, while the heating exhibits positive effects on the fluorescence emissions when excite proposed trimers ($\lambda_{\text{ex}} = 325$ nm and 340 nm). This implies that the phenyl motions and reorientations under 62°C in the studied time frame are in the direction of favoring the formations of proposed phenyl trimers, at the cost of proposed phenyl dimers and tetramers. With continuous heating under 62 °C, the emissions at $\lambda_{\text{ex}} = 277$ nm showed different responses to the heat in its shorter wavelength region (350-367 nm) from its longer wavelength regions (374-426 nm), which is believed to be caused by the larger and increasing contributions of emissions from excited trimers ($\lambda_{\text{ex}}=340$ nm) to the emissions at its longer wavelength side, through either indirect excitation of phenyl trimers by energy transfer or formation of excited trimers from some excited dimers, or both.

Keywords: polystyrene particles; phenyl multimers, phenyl motions; fluorescence; temperature; glassy state.

1. Introduction

As an important part of materials science and widely used in industrial, polymers display various macroscopic characteristics and features that are fundamentally controlled by the chain motions and dynamics due to the abundance of the internal degrees of freedom of polymer chains [1-6]. It is important to understand the molecular motions in a polymer chain for better material design. Especially, understanding the chain motions in a polymer in its glassy state is one of the unsolved

mysteries of materials science and has attached much experimental and theoretical interest.

Recently new structured fluorescence emissions were reported in longer wavelengths (360-460 nm) than polystyrene excimer emission in polystyrene fine particles [7], cast film [7], and solutions [8]. The emissions and excitations were also assigned to different phenyl multimers based on the energy transfer diagram and previous studies [9]. In this work, the newly-discovered fluorescence in polystyrene fine particles is used to probe molecular motions, particularly the phenyl motions, in its glassy state (62°C).

2. Materials and methods

The molecular weights and polydispersities of polystyrene were $M_w = 223,000$ and $M_w/M_n = 1.06$, respectively. Methanol and tetrahydrofuran (THF) in spectroscopic-grade were used without further purification. The polystyrene fine particles were prepared on a piece of quart plate following the method described in [7]. In order to minimize the effect of solvent evaporation on the fluorescence of the prepared polystyrene fine particles [7], the deposited polystyrene particles were allowed to dry in a vacuum intensively until the fluorescence intensity remains stable. The sample cell of the fluorescence spectrometer was preheated to 62 °C, and then the polystyrene sample was put into the sample cell for measurements. The fluorescence of polystyrene particles was monitored over a 30 hrs time period. The temperature of the sample cell was maintained at 62 °C through entire process of measurements.

Fluorescence spectra were recorded with a Jobin-Yvon SPEX F212 using the front-face mode at 62°. The slit widths were set to 1.0 nm for all measurements. To reduce noise, each reported spectrum was an average of two to three separate scans, moreover, some plotted spectra were reasonably smoothed.

3. Results and discussion

Fig. 1 presents the time dependence of fluorescence emissions of polystyrene fine particles at 62 °C at

different excitation energies. The excitation energies correspond to the peaks shown in the excitation spectra in Fig. 2 of [7]: 277nm, 296nm, 325 nm, 340 nm, 360 nm, 380 nm and excitation energy of a single phenyl at 260 nm. The time dependence of fluorescence emissions at $\lambda_{\text{ex}}=260$ nm is shown in both the left and the right columns for comparison. It should be noted that polystyrene particles required a certain time (estimated 0.5 hr) to reach the destination temperature 62°C when the sample stored in room temperature was put in 62 °C sample cell, and the polystyrene particles before reaching 62 °C were in different temperatures between room temperature (~25°C) and 62°C. The polystyrene particles measured under zero heating time should be considered to be at room temperature 25°C.

At $\lambda_{\text{ex}}=260$, 277 and 296 nm, the emission profiles show the strongest peaks at 367 nm at room temperature (0 hr heating), but their relative intensities of the major emissions changed differently with heating. At $\lambda_{\text{ex}}=260$ nm, all the strong emissions between 350-385 nm decrease, and the intensities of the peaks located at 367 nm, 374 nm and 385 nm became very similar after 30 hrs' heating at 62°C. The emission peaks located at 374 nm and 385 nm became dominant in the case of $\lambda_{\text{ex}}=277$ nm, while the strongest peak remains at 367 nm at $\lambda_{\text{ex}}=296$ nm. Different from the cases at $\lambda_{\text{ex}}=260$, 277 and 296 nm, the emissions at $\lambda_{\text{ex}}=325$ and 340 nm exhibited large intensity increase in the first two hrs of heating. After 2 hrs's heating, the emissions showed much slow increase and then a slight decrease in their intensities. Similar to the cases at $\lambda_{\text{ex}}=260$, 277 and 296 nm, the fluorescence intensities of emissions at $\lambda_{\text{ex}}=360$ and 380 nm decrease with heating. However the decrease was only very obvious in the first two hours of heating, which is different from the cases at $\lambda_{\text{ex}}=260$, 277 and 296 nm.

When excite a sing phenyl group at $\lambda_{\text{ex}}=260$ nm, there are two possible paths leading to the emissions at longer wavelength than the excimer emission at 325 nm: 1) the energy transfer from the emissions of single phenyl group and excimers; 2) forming the excited multimers by interacting of an excited single phenyl with surrounding phenyl groups. In either path, it requires large density of phenyl aggregations (aggregations of phenyl groups in proper geometry and distance) to produce strong emissions. The decrease in fluorescence at $\lambda_{\text{ex}}=260$ nm with heating suggests that the temperature increasing from 25 °C to 62 °C can reduce the density of these phenyl aggregations with emitted fluorescence at longer wavelengths (either directly or indirectly). Polystyrene is in a glassy state at both 25 °C and 62 °C, and molecular motions in the glassy state are largely restricted to vibrations and short-

range rotational motions. It was reported that the most prevalent motion in glassy polystyrene is restricted phenyl rotation with a sizable average jump angle [10]. The high-frequency ring flips in combination with high frequency main-chain rotational reorientation occur at a small fraction of sites within some of the polystyrenes [10]. Based on this previous study, I propose that the thermal energy gained from temperature increase can promote these phenyl rotations and reorientation to relieve local steric constraints imposed by the hydrophobic interactions during polystyrene reprecipitation and fast solvent removal. These motions can either conquer the molecular interactions that hold the fluororous phenyl multimers together to dissociate multimers into free phenyl rings, or facilitate the formations of only one or two preferred multimers at the cost of other multimers. In both cases, some energy transfer paths are cut, which results in weaker emissions. The same observations are found for the fluorescence emissions at excitation energies of $\lambda_{\text{ex}}=(277\text{ nm and }296\text{ nm})$, and $\lambda_{\text{ex}}=(360\text{ nm and }380\text{ nm})$ which correspond to the excitations of proposed phenyl dimers and tetramers, respectively [9].

However at $\lambda_{\text{ex}}=325$ nm and 340 nm, two excitation energies corresponding to proposed excitations of phenyl trimers [9], the intensities of fluorescence emissions increase greatly in the first 2 hours' heating. This suggests that the increased thermal energy can facilitate the formations of the proposed phenyl trimers. This is an interesting phenomenon. It is not sure whether these new phenyl trimers are formed from the existed phenyl dimers or tetramers, or three free phenyl groups, but it seems that the phenyl trimers are more thermal stable than the phenyl dimers and tetramers within the studied time frame and temperature.

With increasing heating time, the emissions at $\lambda_{\text{ex}}=277$ nm shows much less decrease in intensity in the range of 374-394 nm than the range of 350-367nm, but this is not observed for the emissions at $\lambda_{\text{ex}}=260$ and 296 nm. Considering the positive effects of heating on the emissions (374-394 nm) at $\lambda_{\text{ex}}=325$ nm and 340 nm, this might indicate that energy transfer path(s) involving the indirect excitation of phenyl trimers contributes much more to the overall energy transfers occurred at $\lambda_{\text{ex}}=277$ nm than at $\lambda_{\text{ex}}=260$ nm and 296 nm. The heating can facilitate the formation of phenyl trimers and increase the emissions in the energy range of 374-394 nm, which can compensate for the intensity loss in the emissions of 374-394 nm at $\lambda_{\text{ex}}=277$ nm from other emission paths.

The intensity variations of major fluorescence emissions as pointed by arrows in **Fig.1** (f 325, f 350 and so on) with heating time at 62 °C are plotted in **Fig. 2**.

Fig. 1. The time dependence of fluorescence at different excitation energies with heating at 62°C. The Fluorescence intensities are divided by the same number.

Fig. 2. The variations of fluorescence at different excitation energies over heating time at 62°C. Different symbols are used for fluorescence at different excitation energies (see the legend of plot **f 404 nm** for a complete list of symbols). f 325 nm means the fluorescence emission at 325 nm, and so on. These fluorescence are indicated by arrows in **Fig. 1**. The Fluorescence intensities are divided by the same number.

plot, different symbols correspond to the same fluorescence at different excitation energies (see the legend of the plot of Fluorescence at 404 nm.). One should keep in mind that most of these emissions are overlapped and hard to deconvolute, thus the intensity of one emission peak has the contributions from others, especially the emissions with closer wavelengths. Although the intensities of these emissions are only approximations, their change over time can still provide some insight into the fluorescence changes due to

phenyl motions in polystyrene.

All the fluorescence emissions show strongest intensity with the excitation energy at 260 nm (λ_{ex} = 260 nm, grey squares). This suggests that the excitation of the single phenyl groups in polystyrene particles leads to the most efficient and strongest fluorescence, regardless of which multimers the emissions emit from.

At excitation energies λ_{ex} = 260, 277 and 296 nm, the excimer emissions (f 325 nm) shows different inten-

sities and their intensities decrease with increasing heating time. The rates of decrease become slightly flatter with increasing excitation energies. The fluorescence at 350 nm (f 350) and 357 nm (f 357) also shows similar intensity decreases as f 325, but different from f 325 nm, both f 350 and f 357 have almost the same intensities at the two different excitation energies 277 nm and 296 nm during the course of heating, as indicated by the overlapping of triangles ($\lambda_{\text{ex}} = 277$ nm) and grey circles ($\lambda_{\text{ex}} = 296$ nm) in the figures of f 350 and f 357. This suggests that under the excitation energies of 277 nm and 296 nm, both f 350 and f 357 are emitted from the same excited dimers and from the same energy transfer paths, if there are any. However, for the emissions with longer wavelengths, they show increasing differences in their heating responses at two excitation energies at 277 and 296 nm. The f 367 shows slight intensity differences at $\lambda_{\text{ex}} = 277$ and 296 nm, but all the other fluorescence (f 374 - f 426) shows much bigger differences in their heating responds at $\lambda_{\text{ex}} = 277$ and 296 nm. Not only are their intensities quite different at $\lambda_{\text{ex}} = 277$ and 296 nm, but also their changes over heating time have different trends. The f 374 - f 426 all decrease with heating time at $\lambda_{\text{ex}} = 296$ nm, but they tend to increase slightly first and then decrease at $\lambda_{\text{ex}} = 277$ nm. This suggests the excitation of 277 nm and 296 nm have different contributions to the emissions at longer wavelengths 374 nm-426 nm during the course of heating, but the same contributions to the emissions at 350 nm and 357 nm, and very similar contributions to the emission at 367 nm.

The heating have negative effects on the fluorescence intensities of most emissions, and the only positive effects are found on the emissions resulting from the excitation at 325 nm and 340 nm, as indicated by the curves in green circles (325 nm) and red circles (340 nm), respectively, in **Fig. 2**. This positive effect is most profound on the emissions at 384 nm and 394 nm, especially the emission at 394 nm which the fluorescence intensities are raised to the same level (the highest level) as the excitation at 260 nm after a certain heating time. It is interesting to observe that the heating can raise the fluorescence intensities of each emission of f 385, f 404 and f 426 at $\lambda_{\text{ex}} = 340$ to the same intensity as those at $\lambda_{\text{ex}} = 277$, as indicated by the overlapping of triangles ($\lambda_{\text{ex}} = 277$ nm) and red circles ($\lambda_{\text{ex}} = 340$ nm) appeared after a period of relative longer heating time. This suggests that the excitation at 277 nm can either facilitate the formation of excited trimers. This confirms the above conclusion that with heating, the emissions from excited trimers has bigger or complete contributions to the emissions in longer wavelengths at the excitation of 277 nm (excited dimers), through either indirect excitation of phenyl trimers by energy transfer

or formation of excited trimers from some excited dimers, or both.

4. Summary

To probe the phenyl motions in glassy polystyrene, the polystyrene fine particles after intensive vacuum drying to remove solvent were investigated regarding their fluorescent responses to heating at 62 °C. In glassy polystyrene fine particles under either room temperature or 62 °C, it was found that the excitation of the single phenyl groups ($\lambda_{\text{ex}} = 260$ nm) in polystyrene particles leads to the most efficient and strongest fluorescence, regardless of which multimers the emissions emit from. Compared with the fluorescence emissions at room temperature (~25°C), most emissions showed decreased intensities with heating at 62 °C, with the exception of the emissions from the excitations at 325 nm and 340 nm (proposed phenyl trimers [9]). This implies that there are profound phenyl motions and reorientations occurred in polystyrene fine particles when heat under 62 °C. It can be also concluded that the thermal energy gain from temperature increase can facilitate the formations of proposed phenyl trimers by phenyl motions and reorientations in the studied time period, at the cost of proposed phenyl dimers and tetramers. With continuous heating under 62 °C, the emissions at $\lambda_{\text{ex}} = 277$ nm showed different responses to the heat in shorter wavelengths (f 350- f 367) than at longer wavelengths (f 374- f 426), which is believed to be caused by the larger and increasing contributions to the emission at longer wavelengths from excited trimers, through either indirect excitation of phenyl trimers by energy transfer or formation of excited trimers from some excited dimers, or both. This can also explain the observation that after a period of relative longer heating time, when excite at $\lambda_{\text{ex}} = 340$ nm, the fluorescence intensities of each emission at longer wavelengths among 385nm, 404 nm and 426 nm were all increased to the same level as the emissions at $\lambda_{\text{ex}} = 277$. In conclusion, this work demonstrates that we can use the rich intrinsic fluorescence in polystyrene as a probe for its chain motions without the extrinsic fluorescence labels.

The fluorescence fluctuations with heating at 62 °C is only reported for the 30 hrs' heating period here, although the fluorescence was monitored in longer period. It was found that fluorescence intensities ultimately decreased for all the emissions at all the selected excitation energies when the polystyrene particles were heated long enough. At the same time, the baselines of the fluorescence spectra were also shifted down. This suggests that there might be some other contributes rather than molecule motions attributed for such changes occurred in long heating time.

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