Sensitive and reliable detection of glass transition of polymers by fluorescent probes based on AIE luminogens†

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The glass transition of polymers is an immensely-used yet less-understood phenomenon concerning the dynamics of polymer chains in bulk or in confined surroundings, which dictates directly their performances in engineering sectors. Monitoring of the glass transitions or dynamics of polymers is hampered by the lack of facile yet robust methodologies. Herein, we developed a sensitive, reliable and straightforward approach for the detection of glass transitions of polymers using fluorescent probes based on aggregation induced emission (AIE) luminogens. Fluorescence emission of polymers doped with AIE luminogens, including tetraphenylethene (TPE) or its derivatives, showed a sensitive response to the glass transitions of polymers. The sensitivity of fluorescence to glass transition could be optimized by increasing TPE loading. Fluorescence intensity of TPE-doped polymers dropped as much as 25 fold with increasing temperature in the investigated range. The temperature dependence of the fluorescence intensity gave rise to the straightforward determination of the glass transitions of the polymers. Moreover, it is worth mentioning that simply mixing AIE luminogens with polymers, rather than covalently labeling, is possible due to the AIE characteristics of the probes. This significantly facilitated measurements. Given the significant advantages of AIE luminogens as probes, including high and tunable sensitivity, immunity to aggregation, facile operation and simple data processing, fluorescence techniques based on AIE luminogens offer new access for the investigation of the glass dynamics of polymer chains in confined spaces.

Introduction

The glass transition is a reversible transition between the brittle, glassy state and soft rubbery state in amorphous polymers, which is accompanied by significant variations in the mechanical properties, viscosity, thermal-expansion coefficient, and specific heat.1,2 For instance, the elastic modulus of a polymer drops by several orders of magnitude when it is converted from the glass state into the rubbery state by raising the temperature.3 The glass transition temperature \( T_g \) of a polymer, at which glass transition takes place, dictates directly its service temperature. For example, plastics must be used at temperatures below \( T_g \), whereas rubbers are used at temperatures above \( T_g \). Determining \( T_g \) of polymers, particularly the onset temperature of glass transition, is extremely crucial for their applications in engineering sectors. Moreover, investigating glass transitions or dynamics of polymer chains is essential for fundamentally understanding the performances of polymers, particularly at interfaces or surfaces with applications in adhesion, solar cells, and drug release.1,2

A number of techniques have been used to determine glass transitions of polymers, including dilatometry, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). Dilatometry measures the volume change of a polymer during glass transition. Dilatometry is simple and facile, but suffers from poor accuracy.4 DMA, mainly used for engineering materials, determines glass transition by testing viscoelastic properties of polymeric materials. DMA requires massive samples (a few grams).5 Compared with the aforementioned methods, DSC has been immensely used due to the relatively
small amount of sample needed (a few milligrams) and ease of operation.5,7 However, some technical issues prevent thermal-based DSC from providing an accurate and a reliable determination of the $T_g$ of polymers, including baseline drift and fluctuation (ESI†). Moreover, DSC measurements give a temperature range at which glass transition occurs. Different definitions of glass transition temperature make numeric results of $T_g$ very different from each other (ESI†).

With the rapid extension of applications of polymers in emerging fields, including lithography, solar cells and selective membranes, new requirements must be met to determine the glass transitions of polymers for special applications. For instance, to determine $T_g$ of polymers confined in limited spaces such as of polymer films the approaches mentioned above fail to work and new methods with high sensitivity must be developed, because only a small amount of materials is available for measurements.8–13 Fluorescence techniques are emerging as a promising approach for investigating glass transitions due to their high sensitivity.14–22 The determination of $T_g$ by fluorescence was pioneered by Torkelson.23–26 Pyrene (Scheme 1) was used as a fluorescent probe to label polymers. The variation of fluorescence emission of pyrene-labeled polymers during glass transition of the polymers allowed the determination of $T_g$ of the polymers. Although this technique is applicable to polymer films, the transition is ambiguous and plausible probably due to weak fluorescence.23 Even worse is that fluorescence intensity cannot be enhanced by increasing the concentration of probes, which leads to the aggregation of the probes and consequent aggregation-caused quenching (ACQ) of fluorescence. This results in the limited sensitivity of fluorescence to glass transitions of polymers. Moreover, covalently labeling of pyrene into polymers involved fussy synthetic procedures, and it was not applicable to existing polymers. All these limitations restrict further applications of the fluorescent probes.

In contrast to ACQ probes, aggregation-induced-emission (AIE) luminogens emit intense light in the solid state based on the mechanism of restriction of intramolecular motions (RIM).27,28 The aggregation or vitrification of AIE luminogens activates the RIM process, which consequently results in strong fluorescence emission, either in the aggregated state or monomer state.29,30 Taking the advantage of AIE luminogens, the fluorescence intensity of polymers doped with AIE dyes can be efficiently enhanced by increasing probe loading without the need to avoid the aggregation of the probes. This promises enhanced sensitivity of fluorescence to glass transitions of polymers. Herein, we report the sensitive and reliable detection of glass transitions of polymers using fluorescent probes based on AIE luminogens. A class of typical AIE luminogens, including tetrphenylethene (TPE), ethyl 4-(1,2,2-triphenylvinyl)benzoate (TPE-C2) (Scheme 1) and 2-(tetraphenylethoxy)ethanol (TPE-C2OH) were utilized as fluorescent probes to dope the polymers. Taking advantage of the high quantum yield and AIE characteristics of TPEs, all the issues encountered by the methods mentioned above, such as poor accuracy, large amounts of samples needed, and poor sensitivity, can be addressed. Glass transitions of polymers can be detected in a sensitive, reliable and straightforward manner. Given significant advances in the synthesis of AIE dyes in recent years,31–34 fluorescence techniques based on AIE luminogens as probes offer new opportunities for fundamentally understanding the glass transitions or dynamics of polymer chains in confined surroundings.

Results and discussion

Amorphous polystyrene (PS) with narrow molecular weight distribution was selected as a model polymer. TPE was utilized as the fluorescence probe due to its AIE characteristics, high quantum yield and ease of synthesis.31,32 TPE-doped polystyrene (PS/TPE) emitted intense blue light upon UV radiation (365 nm) (Fig. 1). X-ray diffractometry (XRD) was used to characterize the dispersion of probes in the polymer matrix. No diffraction peaks from TPE were detected for PS/TPE, suggesting that TPE was uniformly dispersed in the PS matrix without the formation of large aggregates probably due to resemblance in chemical constitutions and good miscibility between PS and TPE.

The glass transitions of pristine PS and PS/TPE were determined using differential scanning calorimetry (DSC) (Fig. S1,
Glass transition of PS took place in a temperature range of 78 °C–98 °C, centered at 89.5 °C \( (T_g) \). Doping PS with a small amount of TPE did not noticeably affect the glass transition of the polymer matrix.

Fluorescence spectra of PS/TPE at various temperatures are presented in Fig. 2. PS/TPE emitted strong blue light (470 nm) at room temperature. With rising temperature, the intensity of fluorescence decreased. Plots of fluorescence intensity at 470 nm against temperature showed that the fluorescence intensity dropped linearly and drastically with increasing temperature. The straight line leveled off when temperature approached 80 °C. Thereafter, fluorescence intensity decreased slightly with further increase in the temperature. The transition temperature was determined to be 80 °C in the temperature range determined using DSC (78 °C–98 °C), which is close to the onset temperature (78 °C). A possible reason is that in the glassy state, TPE molecules are embedded in rigid polymer matrices. The intramolecular motions (i.e. rotation, vibration, torsion, and bending) of phenyl rings of TPE are restricted to some extent. The energy of the excited state is annihilated through radiation decay, and thus TPE emits efficiently. When the polymers are in the rubbery state, intramolecular motions of TPE are activated due to the movement of polymer segments and significantly increased free volume in the polymer matrices. The intramolecular motions consume the energy of the excited state. This leads to the weak fluorescence emission of TPE in the rubbery state of the polymers.27,28

Moreover, it was interesting that the fluorescence intensity of PS/TPE decreased more drastically at low temperature, indicating that the fluorescence of PS/TPE is more sensitive to thermal expansion below \( T_g \) than to segmental movements above \( T_g \). This is rational because the size of the phenyl rings of TPE is a few angstroms (<3 Å) (Scheme S1, ESI†). To restrict the motions (i.e. rotation, vibration, torsion, and bending, and so on) of the phenyl rings of TPE, they have to be compacted into a small space of a few angstroms (<3 Å). In other words, a subtle change in the free volume of the polymer matrix has significant effect on the intramolecular motions of TPE. This leads to an evident decrease in fluorescence intensity at temperatures below \( T_g \). When the temperature reaches \( T_g \), the mobility of the polymer segments is significantly enhanced. The restriction on intramolecular motions of TPE molecules further decreases due to the drastically increased free volume, resulting in further decreased fluorescence intensity.

We checked the reproducibility of fluorescence spectra of the PS/TPE at various temperatures. Fluorescence spectra of PS/TPE switching between 40 °C (<\( T_g \)) and 110 °C (>\( T_g \)) are presented in Fig. 3. The fluorescence spectra of PS/TPE at 40 °C showed a distinct emission peak at 470 nm, whereas the emission was considerably weaker at 110 °C. The fluorescence emission was capable of reversibly switching by repeatedly altering temperature between 40 °C and 110 °C. This revealed that PS/TPE was stable for repeated thermal treatments.

Improving sensitivity of the fluorescence to glass transition is possible. We investigated the effect of TPE loading on the fluorescence of PS/TPE, as shown in Fig. 4. Compared with PS doped with 0.1 wt% TPE, PS doped with 1.0 wt% TPE showed a more distinct glass transition (Fig. 4A). The fluorescence intensity dropped as much as 25 fold (from 5.8 to 0.23), which is considerably larger than that for 0.1 wt% TPE (10 fold, from 4.2 to 0.4, Fig. 2). Interestingly, the glass transition temperature was still determined to be 80 °C. This demonstrated that it was possible to improve the sensitivity of the fluorescence to the glass transition by simply increasing the probe loading.

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**Fig. 2** (A) Fluorescence spectra of PS doped with 0.1 wt% TPE at various temperatures and (B) fluorescence intensity at wavelength of 470 nm as a function of temperature normalized to 110 °C. Excitation: 350 nm.

**Fig. 3** (A) Fluorescence spectra of PS doped with 0.1 wt% TPE at 40 °C and 110 °C and (B) fluorescence intensity (470 nm) at 40 °C and 110 °C. Excitation: 350 nm.

**Fig. 4** Fluorescence intensity at 470 nm of PS doped with 1.0 wt% TPE (A) and 0.05 wt% TPE (B) as a function of temperature. Excitation: 350 nm.
without affecting the numeric results of \( T_g \). This is inaccessible to ACQ probes such as pyrene, where increasing the concentration of probes leads to the formation of excimers or aggregates and consequent fluorescence quenching.\(^35\)–\(^37\) For AIE luminogens such as TPE, aggregation favors emission, and thus allows the enhancing of fluorescence intensity by increasing AIE luminogen loading. This promises enhanced sensitivity of fluorescence to glass transitions of polymers. Monitoring glass transitions of polymers at low TPE loading is also feasible. We detected the glass transition of PS at the low a TPE loading of 0.05 wt%. Glass transition was again recognized at 80 °C. This reveals that \( T_g \) can be reliably obtained regardless of the amount of TPE loading used, which is crucial for practical measurements.

TPE can be readily modified to adapt polymers with various constitutions and polarities. Taking another model polymer, poly(methyl methacrylate) (PMMA), as an example, a TPE derivative with a polar tail (TPE-C2, Scheme 1B) was synthesized for improved miscibility between PMMA and the probes. Fluorescence spectra of PMMA doped with 0.1 wt% TPE-C2 (PMMA/TPE-C2) at various temperatures are shown in Fig. 5. PMMA/TPE-C2 emitted intense blue light (476 nm) at room temperature. Fluorescence intensity at 476 nm decreased linearly and drastically with rising temperature. The straight line bent downwards when temperature reached 103 °C. DSC results of PMMA showed that glass transition of PMMA occurred in a temperature range of 100 °C–119 °C, centered at 110 °C (Fig. S2, ESI†). The transition temperature determined using TPE-C2 as a fluorescent probe (103 °C) was close to the onset temperature of glass transition determined using DSC.

TPE derivatives (TPE-C2 and TPE-C2OH) were also used to dope PS. Fluorescence spectra of PS doped with TPE-C2 and TPE-C2OH are shown in Fig. 6 and 7, respectively. The transition temperature was determined to be 80 °C, which is identical to the value using TPE as a fluorescent probe. This illustrated that TPE based AIE luminogens are universal fluorescent probes for monitoring the glass transitions of polymers. Significant advances in the synthesis of AIE dyes in recent years enrich fluorescent probes used for monitoring glass transitions of polymers.\(^31\),\(^32\)

Torkelson and coworkers obtained the fluorescence spectra of pyrene-labeled PS at various temperatures.\(^23\)–\(^26\) They used the temperature dependence of the ratio of the intensity of the third peak (386 nm) to the intensity of the first peak (375 nm) \((I_3/I_1)\) of the fluorescence spectra to determine the \( T_g \) of PS, as shown in Fig. 8. Compared with pyrene, TPE as a probe possesses overwhelming advantages: (1) the fluorescence intensity of TPE-doped polymers changes abruptly during the glass transition, revealing that the fluorescence of TPE-doped polymers is considerably more sensitive to the glass transition of poly-

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**Fig. 5** (A) Fluorescence spectra of PMMA doped with 0.1 wt% TPE-C2 at various temperatures and (B) fluorescence intensity at wavelength of 476 nm as a function of temperature normalized to 110 °C. Excitation: 350 nm.

**Fig. 6** (A) Fluorescence spectra of PS doped with 0.1 wt% TPE-C2OH at various temperatures and (B) fluorescence intensity at wavelength of 476 nm as a function of temperature normalized to 110 °C. Excitation: 350 nm.

**Fig. 7** (A) Fluorescence spectra of PS doped with 0.1 wt% TPE-C2 at various temperatures and (B) fluorescence intensity at wavelength of 476 nm as a function of temperature normalized to 110 °C. Excitation: 350 nm.

**Fig. 8** (A) Fluorescence spectra of pyrene-labeled PS at various temperatures and (B) the ratio of intensities at the third and first peaks as a function of temperature. Reprinted with permission from ref. 23.
mers. For example, fluorescence intensity varied as much as 25 fold (from 5.8 to 0.23) for TPE-doped PS in the temperature range investigated (Fig. 4A), whereas it varied by 1.3 fold for pyrene-labeled PS (intensity of maximal peak varied from 1.0 to 0.8 in Fig. 8A). (2) The sensitivity of fluorescence of TPE-doped PS to glass transition can be optimized by increasing TPE loading. Taking the advantage of the AIE characteristics, the fluorescence intensity of TPE-doped PS can be efficiently enhanced by increasing the loading of TPE without avoiding aggregation of TPE. This is impossible for pyrene, which is a typical ACQ dye. (3) Immune to the aggregation of probes, it is not necessary to follow complicated synthesis procedures for labelling the polymers with probes to avoid the aggregation of probes. Simply mixing the polymers with TPEs promises sensitive and reliable detection of the glass transitions of the polymers. This significantly facilitates measurements. Moreover, TPE presents a single emission peak, which is considerably simpler than the emission spectrum of pyrene. The temperature dependence of fluorescence spectra of TPE-doped polymers gives rise to straightforward determination of $T_g$ without fussy calculation. In addition, TPE can be easily synthesized in high yields, and starting materials are cheap and easy to get. With all these advantages, TPE and its derivatives are excellent candidates for fluorescence probes for detecting the glass transitions or dynamics of polymer chains.

Conclusions

In summary, we developed a sensitive, reliable and straightforward approach for the detection of glass transitions of polymers using fluorescent probes based on AIE luminogens. Fluorescence emission of polymers doped with tetraphenylethene (TPE) or its derivatives showed a sensitive response to glass transitions of polymers. The sensitivity of fluorescence to glass transition can be optimized by increasing TPE loading. The fluorescent intensity of TPE-doped polystyrene decreased as much as 25 fold with increasing temperature in the range investigated. Such temperature dependence of the fluorescence intensity allowed for the straightforward determination of the glass transitions of the polymers. With significant advantages of using AIE luminogens as probes, including high and tunable sensitivity, immunity to aggregation, facile operation and data processing, and ease of synthesis, fluorescence techniques based on TPEs offer new opportunities for monitoring the glass transition or dynamics of polymer chains in a confined space.

Experimental

Materials

Tetraphenylethene (TPE) and its derivatives (TPE-C2 and TPE-C2OH) were synthesized according to protocols in the literature. Benzophenone, 4-hydroxybenzophenone, pyridine, n-butyl lithium and 4-bromobenzophenone were purchased from Sigma (China) without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. Polystyrene (PS) with narrow polydispersity ($M_w = 10.2 \text{ kg mol}^{-1}$, PDI = 1.09) was purchased from Aladdin Industrial Inc. Polymethyl methacrylate) (PMMA) with narrow polydispersity ($M_w = 105 \text{ kg mol}^{-1}$, PDI = 1.09) was purchased from Polymer Source Inc.

Characterization

Fluorescence spectra were recorded using a steady state spectrometer (Edinburgh Instrument Ltd, FLSP920) equipped with a temperature control system (Oxford instruments). To eliminate the interference of heating rates on the glass transition determination, heating rate was fixed at 1 °C min$^{-1}$ for all specimens. Fluorescence spectra were scanned every 1 min. X-ray diffraction (XRD) measurements were performed using an XRD diffractometer (D-MAX 2200 VPC) equipped with Ni-filtered Cu Kα radiation, having a wavelength of 0.154 nm. The diffractometer was scanned in the 2θ range from 1.5° to 50°, and the scanning rate used was 1.2° min$^{-1}$. DSC measurement was carried out using a Perkin-Elmer DSC-7 Instrument under a nitrogen atmosphere. Temperature was calibrated with indium prior to the test. Heating rate was set at 1 °C min$^{-1}$.

Preparation of polymers doped with AIE dyes

50 mg polymer and the prescribed amount of AIE dyes were dissolved in 10 mL freshly-distilled THF with stirring to yield a homogeneous solution. The resulting solution was cast onto clean quartz wafers. Polymer films with the thickness of 100 μm were obtained after the evaporation of solvent. The polymer films were annealed at 120 °C for 12 h in vacuum.

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Notes and references
