

The Location-influenced Fluorescence of AIEgens in the Microphase-separated Structures

Zhi Ya-Fang, Li Chao, Song Ze-Hua, Yang Zhong-Jia, Ma Hong-Wei, Gao Long-Cheng

Cite this article as:

Zhi Ya-Fang, Li Chao, Song Ze-Hua, Yang Zhong-Jia, Ma Hong-Wei, Gao Long-Cheng. The Location-influenced Fluorescence of AIEgens in the Microphase-separated Structures[J]. *Chinese J. Polym. Sci.*, 2019, 37(11): 1060-1064. doi: 10.1007/s10118-019-2333-x

View online: <https://doi.org/10.1007/s10118-019-2333-x>

Articles you may be interested in

MICROPHASE SEPARATED STRUCTURES AND PROPERTIES OF PDMS-MDI-PEG COPOLYMER SURFACE

Chinese J. Polym. Sci. 2009, 27(3): 327

pH-responsive AIE-active Polyethylene-based Block Copolymers

Chinese J. Polym. Sci. 2019, 37(9): 930 <https://doi.org/10.1007/s10118-019-2330-0>

Block Copolymer Colloidal Particles with Unique Structures through Three-dimensional Confined Assembly and Disassembly

Chinese J. Polym. Sci. 2019, 37(8): 744 <https://doi.org/10.1007/s10118-019-2294-0>

嵌段共聚物调控纳米粒子自组装的研究进展

Block Copolymer Controlled Nanoparticle Self-assembly

高分子学报. 2016(8): 1030 <https://doi.org/10.11777/j.issn1000-3304.2016.16082>

嵌段共聚物PVCH-b-PE-b-PVCH的多重结晶行为

MULTIPLE CRYSTALLIZATION BEHAVIOR OF BLOCK COPOLYMER PVCH-b-PE-b-PVCH

高分子学报. 2011(3): 313 <https://doi.org/10.3724/SP.J.1105.2011.10076>

调控氢键作用力在多组分嵌段共聚物共混体系中的自组装结构

Hydrogen Bonding Interactions Mediated Self-assembly Structures of Multicomponent Block Copolymer Mixtures

高分子学报. 2018(8): 1016 <https://doi.org/10.11777/j.issn1000-3304.2018.18020>

The Location-influenced Fluorescence of AIEgens in the Microphase-separated Structures

Ya-Fang Zhi^a, Chao Li^a, Ze-Hua Song^a, Zhong-Jia Yang^{a*}, Hong-Wei Ma^{b*}, and Long-Cheng Gao^{a*}

^a Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry, Beihang University, Beijing 100191, China

^b Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China



Electronic Supplementary Information

Abstract The fluorescent probe techniques have been widely applied. When the fluorescence probes are selectively located in nanostructures, the fluorescence properties are highly influenced by the environment. Here, we systematically studied the location-influenced fluorescence of AIEgens in the microphase-separated structures. The AIEgen tetraphenylethene (TPE) was doped into polystyrene-*b*-polyisoprene (PS-*b*-PI). TPE was selectively located in the PS nanodomains. The TPE fluorescence was affected by the structural relaxation of PS when investigated in a wide range of temperatures, including the glass transition and secondary transition. When TPE groups were selectively located in the PI nanodomains, the fluorescence was affected by the glass transitions of PI and PS blocks. Amphiphilic TPE derivative was located at the interface of the assembly. The fluorescence emission was influenced by the main transition and secondary transition of PS blocks, as well as the main transition of PI blocks. These results would give new understanding of the interrelation between fluorescence probes and the nanostructures.

Keywords AIE; Block copolymer; Secondary relaxation

Citation: Zhi, Y. F.; Li, C.; Song, Z. H.; Yang, Z. J.; Ma, H. W.; Gao, L. C. The location-influenced fluorescence of AIEgens in the microphase-separated structures. *Chinese J. Polym. Sci.* 2019, 37, 1060–1064.

INTRODUCTION

Fluorescence imaging techniques have been widely used for direct observation in polymer systems, especially the multi-component polymeric systems, such as copolymers, polymer blends, nanocomposites, *etc.* Fluorescence-based techniques have the advantages of fast response, low cost, and high contrast, and they are powerful tools to study the phase morphology in various blends.^[1–4] The typical blends form domains with a size of tens of microns, which makes the fluorescence microscopy a suitable technique for direct observation after doping AIEgens. Lu and coworkers designed fluorescent surfactants to image macrodispersion of inorganic fillers in organic-inorganic composites, which show some advantages over traditional electron microscope approaches.^[5–7] Peng and coworkers reported stereogenic amphiphiles with AIE fluorescence to directly observe the initial step of their self-assembly processes in selective solvents, with a higher sensitivity compared to the transmittance measurement.^[8] In these works, the fluorescence probes have been carefully selected so as to be more preferentially located in one phase,

or at the interfaces.^[2,3] Thus, the target profiles are isolated from the background.

There are systems with much smaller domain dimensions. For example, in the block copolymers (BCP) assembly, microphase separation structures are formed with feature size of tens of nanometers, instead of macroscopic phase separation in the micron scale. When fluorescent probes are introduced, they would not be uniformly dispersed. Instead, the spatial location fluctuates as a result of the selective solubility in nanodomains. As the domain dimensions are far below the resolution limit set by the diffraction of light, direct observation by traditional fluorescent techniques becomes impossible. The selective location of the probes is not noticed to be a question. The influences of probe location on the fluorescence properties are always neglected. Herein, we researched a model system to discover the location influences on the fluorescence properties. We chose a common BCP polystyrene-polyisoprene (PS-PI) and fluorescent probes with different structures based on tetraphenylethene (TPE), an excellent fluorescent probe candidate for its features of immunity to aggregation-caused fluorescence quenching, high fluorescence intensity, and easy synthesis.^[9–12] The fluorescence properties are tuned by controlling the rotation mode of benzene ring from free rotation to restricted intramolecular rotations (RIR). When doped with TPE, the polymer segment motions will interfere with the TPE intramolecular motions.

* Corresponding authors: E-mail yangzj@buaa.edu.cn (Z.J.Y.)

E-mail mahw@dlut.edu.cn (H.W.M.)

E-mail lcgao@buaa.edu.cn (L.C.G.)

Received June 14, 2019; Accepted August 7, 2019; Published online September 12, 2019

For example, the rheological behaviors vary abruptly before and after glass transition. The variations can be monitored by the fluorescence probe. We used the sample as the model to detect how the locations of AIEgens could affect the fluorescence.

EXPERIMENTAL

General Considerations

Tetraphenylethene (TPE) and TPE derivatives, 1-(hexyloxy)-4-(1,2,2-triphenylvinyl)-benzene (TPE-OC6) and 2-(4-(1,2,2-triphenylvinyl)phenoxy)ethanol (TPE-OH), were purchased from AIEgen Biotech Co., Ltd. and used without any purification. Chlorodimethylsilane (Alfa Aesar, 96%), Karstedt catalyst (Alfa Aesar), and triethylamine (Alfa Aesar, 99%) were used as received. PS homopolymer was polymerized in our lab by radical polymerization ($M_n = 2.6 \times 10^4$, PDI = 1.21). PS-PI BCP was synthesized by living anionic polymerization ($M_n = 2.2 \times 10^4$, PDI = 1.34).

Preparation of AIEgens-doped Polymers

Taking TPE@PS as an example, 1.0 g of PS and 0.01 g of TPE (0.03 mmol) were dissolved into 10 mL of dichloromethane and then thoroughly stirred. The solvent was volatilized in the air at room temperature and kept in a vacuum oven at 60 °C for 12 h.

Preparation of AIEgen-grafted BCP

As shown in Scheme S1 (in the electronic supplementary information, ESI), 0.7 g of PS-PI was dissolved in 10 mL of THF. 20 μ L of chlorodimethylsilane (1.85×10^{-4} mol) and catalytic amount of Karstedt catalyst were injected into the solution. After the reaction mixture was stirred at room temperature, 0.05 mL of triethylamine (3.6×10^{-4} mol) and 0.145 g of TPE-OH (3.7×10^{-4} mol) were added. The reaction was allowed to proceed at room temperature for 2 days. After that, the white powder product was obtained by participation in methanol for 3 times. The TPE graft content was about 0.05% by weight (from the $^1\text{H-NMR}$ analysis).

Characterization

$^1\text{H-NMR}$ measurements were carried out on a Bruker AV-400 spectrometer. The molecular weight of the polymers was determined by gel permeation chromatography (Waters 2410 instrument equipped with a Waters 2410 refractive index detector), with THF as the elution solvent at a flow rate of 1.0 mL/min. Fluorescence spectra were obtained from Nanolog infrared fluorescence spectrometer. The applied model was Nanolog FL3-2iHR. The sample films (~0.8 mm) were put in the holder equipped with a heating stage. The excitation wavelength was 365 nm. The fluorescence spectra were collected at elevated temperature every 10 °C. Differential scanning calorimetry was carried out by a Q100 instrument. In the process of recording DSC curves, the temperature rose to 200 °C under nitrogen atmosphere with a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Fluorescence of TPE in PS Nanophase

The PS-PI block copolymer was synthesized with PI volume

fraction of 0.48 (Figs. S1 and S2 in ESI). It forms lamellar structure, which can be seen from the small angle X-ray scattering pattern (Fig. S3 in ESI). From the DSC curve (Fig. S4 in ESI), we can see two glass transition temperatures (T_g). The lower one (about -60 °C) corresponds to the PI blocks, while the higher one (about 75 °C) is related with the PS blocks. We doped a small amount of TPE (0.5% by weight) into the BCP. Fig. 1(a) shows the fluorescence spectra of TPE@PS-PI at various temperatures. TPE@PS-PI emits strong blue light (about 460 nm). The fluorescence intensity decreases with the increase of temperature. The normalized fluorescence intensity as a function of temperature is plotted in Fig. 1(b). We can see only one transition at 75 °C corresponding to T_g of the PS blocks, and no influence from T_g of the PI blocks can be seen. The reason is that TPE molecules are selectively embedded in the PS microphase because of the similar polarity to PS. The fluorescence emission of TPE is mainly affected by the PS blocks. At low temperature, the intramolecular motions in TPE, including vibration, rotation, bending, and torsion, are restricted in the PS matrix. Thus, TPE emits efficiently because the excited state energy is annihilated through radiation decay. As temperature increases, the intramolecular motions are activated by the PS segments movement, which consumes the excited state energy and thus weakens the fluorescence emission. These results are in accordance with the results obtained by Tang and coworkers.^[13] Although the PI blocks are connected with the PS blocks, T_g of PI is much lower than that of PS. When PI undergoes the glass transition, there is little influence on the PS segments movements.

Besides, we can see wavelength transitions as temperature increases, as shown in Fig. 1(c). At around 0 °C below T_g of PS, the emission appears to red-shift. Such emission red-shift is also observed in the homopolymer PS (Figs. S6–S8 in ESI). This transition with temperature is attributed to the onset of β -relaxation process, which is assigned to the motions of small segments of the PS chains. Although the diffusion motions and structural changes of PS become highly restricted at temperatures below T_g , relatively fast relaxation of the vibration is inspired. TPE molecules adjust themselves to take twisted conformations before β -relaxation transition. And after the β -relaxation transition, the system provides more space for the intramolecular motions, resulting in the emission red-shift.^[14] The β -relaxation process of many polymers has been studied by dynamic mechanical,^[15,16] NMR,^[17,18] dielectric spectroscopy,^[19] and other techniques. For the first of time, we used the AIEgens to visualize the secondary relaxation. The fluorescence technique is a convenient, powerful tool for the observation of the secondary relaxation.

TPE can detect the main transition and the secondary transition of PS blocks due to the selective location in the PS nanostructures. However, if the probe molecule is selectively located in the PI phase, the fluorescence differs.

Fluorescence of TPE in PI Nanophase

Considering the poor solubility of TPE in PI, TPE was chemically linked to the PI main chains (see Scheme S1 in ESI). The weight content of TPE is around 0.05% (see Fig. S8 in

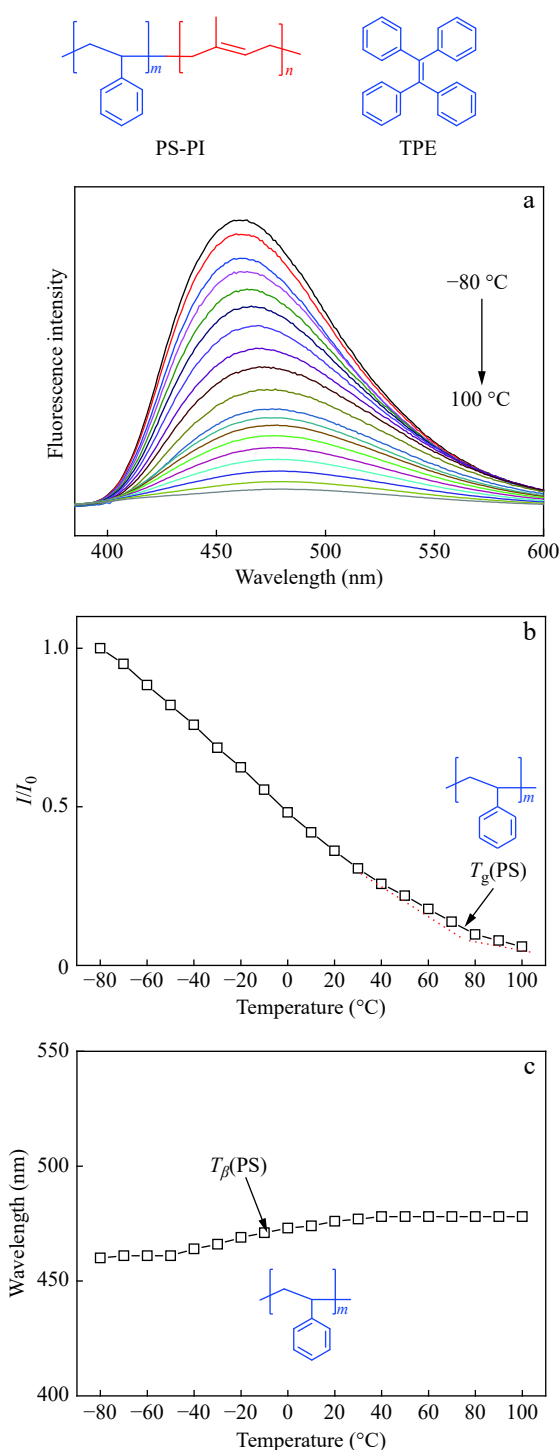


Fig. 1 Fluorescence properties of TPE@PS-PI. (a) Fluorescence spectra at different temperatures; Plots of (b) relative fluorescence intensity (I/I_0) and (c) emission wavelength versus temperature, showing the main transition (T_g) and secondary transition (T_β) of PS blocks

ESI). By this method, TPE has to be selectively located in the PI nanostructures rather than the PS phase. Fig. 2(a) shows the fluorescence spectra at various temperatures. We can see the fluorescent intensity drops as temperature increases. Fig. 2(b) shows the plots of intensity as a function of temperature. The fluorescence intensity decreases as the temperature in-

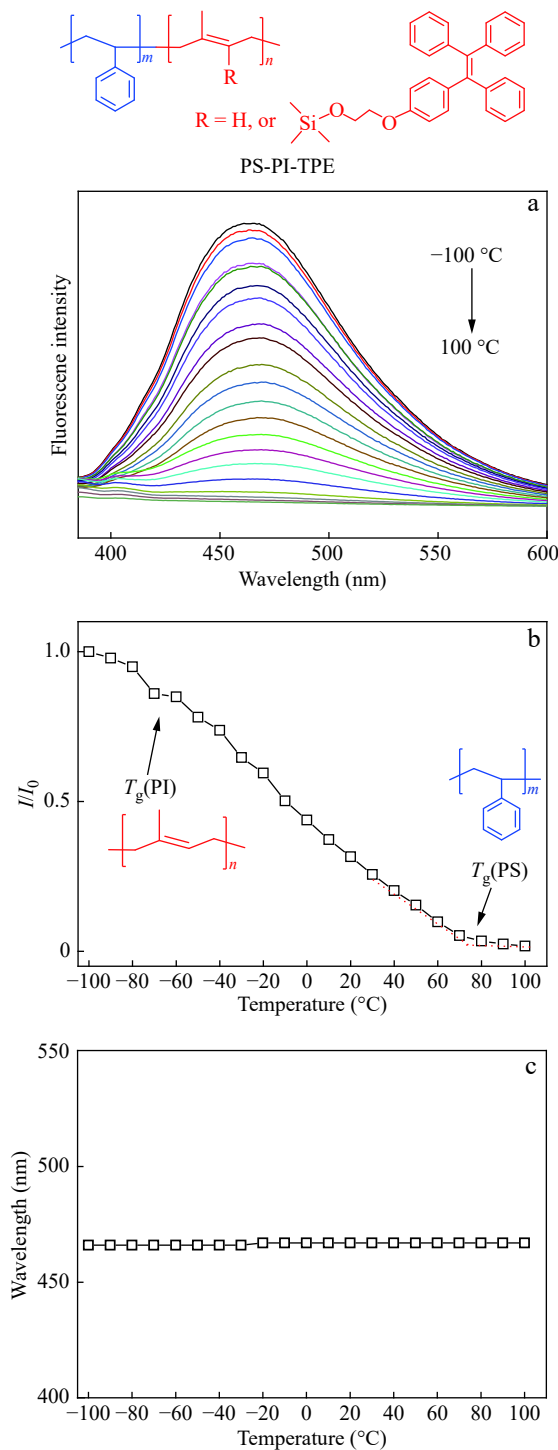


Fig. 2 Fluorescence properties of PS-PI-TPE. (a) Fluorescence spectra at different temperatures; Plots of (b) relative fluorescence intensity (I/I_0) and (c) emission wavelength versus temperature, showing the main transition (T_g) of both PS and PI blocks

creases, similar to those of TPE@PS-PI. The main difference is that two dramatic transitions at around -60 and 75 °C are observed, corresponding to T_g of PI and PS blocks, respectively, in agreement with the value above. Even though TPE is selectively located in the PI nanodomains, the PS segment movement actuates the motions of PI segments, and sequentially induces the intramolecular motions of TPE. It is

the covalent bond between the two blocks that plays key roles.^[20] From the T_g observation, we can see that the PS main relaxation can actuate the motions of PI segments above T_g (PS). However, the PS secondary relaxation cannot. From Fig. 2(c), we can see that the emission wavelength remains the same over the whole temperature range, different from the red-shift in the TPE@PS-PI system.

Fluorescence of TPE at the PS/PI Interface

Because TPE locations in the nanostructures of BCP are different, the fluorescence properties are markedly different. In the doped system, TPE is selectively dissolved in the PS nanodomains. Both the secondary transition and glass transition of PS influence the intramolecular motions of TPE, inducing the fluorescence wavelength transition in the β -relaxation process of PS and fluorescence intensity transition over glass transition of PS. In the grafted system, TPE is selectively located in the PI nanodomains. The intramolecular motions of TPE are not only activated by the PI segment movements, but also by the PS segment movements through the connection between the two blocks. The glass transitions of both PI and PS influence the intramolecular motions of TPE. On the intensity-temperature curve, two transitions can be observed. However, the β -relaxation process of PS has little influence on the fluorescence, because the influence of local movements cannot be delivered across the interface.

In order to verify the location-influenced fluorescence properties, we doped the copolymer with an amphiphilic TPE derivative (TPE-C6) with a long alkyl tail (Fig. 3). The phenyl rings are miscible with the PS nanodomains, while the alkyl chains are miscible with the PI nanodomains. Thus, the TPE-C6 probes would be located at the interface layer of the nanostructure, where TPE-C6 could contact with both PS and PI chains. Fig. 3(a) shows the fluorescence spectra at various temperatures. We can see the fluorescent intensity drops as temperature increases. Fig. 3(b) shows the plots of intensity as a function of temperature. The fluorescence intensity decreases as the temperature increases, similar to those of TPE@PS-PI. Different from that of TPE@PS-*b*-PI, two transitions at around -60 and 75 °C are observed, corresponding to the T_g of PI and PS blocks, respectively. Meanwhile, as shown in Fig. 3(c), wavelength transition takes place as temperature increases. At around 0 °C, a dramatic transition is seen, corresponding to the β -relaxation of PS. From these results, we can see that the locations of the probes have great influence on the fluorescence emission.

CONCLUSIONS

In conclusion, the location of AIEgens in the PS-PI assembly has great influence on the fluorescence properties. When the probe is selectively located in the higher- T_g PS nanodomains, the fluorescence emission is influenced by both the main transition and the secondary transition of PS blocks. The segments movements of PI have little influence on the fluorescence. When the probe is selectively located in the lower- T_g PI nanodomains, the main transitions of both PS and PI blocks show influences on the fluorescence intensity. However, the secondary transition of PS blocks has no influence

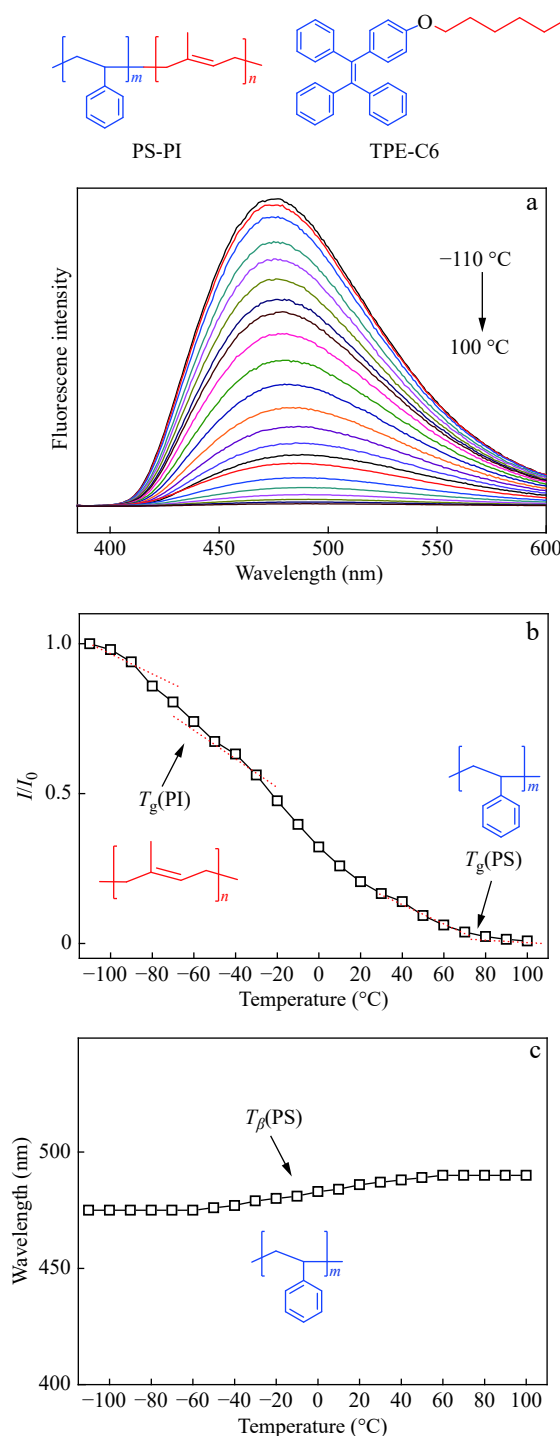


Fig. 3 Fluorescence properties of TPE-C6@PS-PI. (a) Fluorescence spectra at different temperatures; Plots of (b) relative fluorescence intensity (I/I_0) and (c) emission wavelength versus temperature, showing the main transition (T_g) and the secondary transition (T_{β}) of PS, as well as the main transition (T_g) of PI

on the fluorescence. When the amphiphilic probe is used, it is located at the interface of the assembly. The fluorescence emission is influenced by the main transition and the secondary transition of PS blocks, as well as the main transition of PI blocks. These results advance the understanding of the interrelation between fluorescence probes and nanostructures.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2333-x>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21875009 and 51703006) and the Fundamental Research Funds for the Central Universities.

REFERENCES

- Han, T.; Gui, C.; Lam, J. W. Y.; Jiang, M.; Xie, N.; Kwok, R. T. K.; Tang, B. Z. High-contrast visualization and differentiation of microphase separation in polymer blends by fluorescent AIE probes. *Macromolecules* **2017**, *50*, 5807–5815.
- Liang, G.; Wu, J.; Gao, H.; Wu, Q.; Lu, J.; Zhu, F.; Tang, B. Z. General platform for remarkably thermoresponsive fluorescent polymers with memory function. *ACS Macro Lett.* **2016**, *5*, 909–914.
- Wu, J. L.; Zhang, C.; Qin, W.; Quan, D. P.; Ge, M. L.; Liang, G. D. Thermoresponsive fluorescent semi-crystalline polymers decorated with aggregation induced emission luminogens. *Chinese J. Polym. Sci.* **2019**, *37*, 394–400.
- Liang, G.; Ren, F.; Gao, H.; Wu, Q.; Zhu, F.; Tang, B. Z. Continuously-tunable fluorescent polypeptides through a polymer-assisted assembly strategy. *Polym. Chem.* **2016**, *7*, 5181–5187.
- Guan, W.; Wang, S.; Lu, C.; Tang, B. Z. Fluorescence microscopy as an alternative to electron microscopy for microscale dispersion evaluation of organic-inorganic composites. *Nat. Commun.* **2016**, *7*, 11811.
- Feng, Z.; Zhong, J.; Guan, W.; Tian, R.; Lu, C.; Ding, C. Three-dimensional direct visualization of silica dispersion in polymer-based composites. *Analyst* **2018**, *143*, 2090–2095.
- Tian, R.; Zhong, J.; Lu, C.; Duan, X. Hydroxyl-triggered fluorescence for location of inorganic materials in polymer-matrix composites. *Chem. Sci.* **2018**, *9*, 218–222.
- Peng, H. Q.; Liu, B.; Wei, P.; Zhang, P.; Zhang, H.; Zhang, J.; Li, K.; Li, Y.; Cheng, Y.; Lam, J. W. Y.; Zhang, W.; Lee, C. S.; Tang, B. Z. Visualizing the initial step of self-assembly and the phase transition by stereogenic amphiphiles with aggregation-induced emission. *ACS Nano* **2019**, *13*, 839–846.
- Hong, Y.; Lam, J. W.; Tang, B. Z. Aggregation-induced emission. *Chem. Soc. Rev.* **2011**, *40*, 5361–5388.
- Mei, J.; Leung, N. L.; Kwok, R. T.; Lam, J. W.; Tang, B. Z. Aggregation-induced emission: Together we shine, united we soar! *Chem. Rev.* **2015**, *115*, 11718–11940.
- Luo, J.; Xie, Z.; Lam, J. W.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. *Chem. Commun.* **2001**, 1740–1741.
- Liu, Y.; Deng, C.; Tang, L.; Qin, A.; Hu, R.; Sun, J. Z.; Tang, B. Z. Specific detection of D-glucose by a tetraphenylethene-based fluorescent sensor. *J. Am. Chem. Soc.* **2010**, *133*, 660–663.
- Bao, S.; Wu, Q.; Qin, W.; Yu, Q.; Wang, J.; Liang, G.; Tang, B. Z. Sensitive and reliable detection of glass transition of polymers by fluorescent probes based on AIE luminogens. *Polym. Chem.* **2015**, *6*, 3537–3542.
- Dong, Y.; Lam, J. W. Y.; Qin, A.; Sun, J.; Liu, J.; Li, Z.; Sun, J.; Sung, H. H. Y.; Williams, I. D.; Kwok, H. S.; Tang, B. Z. Aggregation-induced and crystallization-enhanced emissions of 1,2-diphenyl-3,4-bis(diphenylmethylene)-1-cyclobutene. *Chem. Commun.* **2007**, 3255–3257.
- Cervený, S.; Ghilarducci, A.; Salva, H.; Marzocca, A. J. Glass-transition and secondary relaxation in SBR-1502 from dynamic mechanical data. *Polymer* **2000**, *41*, 2227–2230.
- Fakhraai, Z.; Forrest, J. A. Measuring the surface dynamics of glassy polymers. *Science* **2008**, *319*, 600–604.
- Schmidt-Rohr, K.; Kulik, A. S.; Beckham, H. W.; Ohlemacher, A.; Pawelzik, U.; Boeffel, C.; Spiess, H. W. Molecular nature of the β relaxation in poly(methyl methacrylate) investigated by multidimensional NMR. *Macromolecules* **1994**, *27*, 4733–4745.
- Kulik, A. S.; Beckham, H. W.; Schmidt-Rohr, K.; Radloff, D.; Pawelzik, U.; Boeffel, C.; Spiess, H. W. Coupling of α and β processes in poly(ethyl methacrylate) investigated by multidimensional NMR. *Macromolecules* **1994**, *27*, 4746–4754.
- Garwe, F.; Schönhals, A.; Lockwenz, H.; Beiner, M.; Schröter, K.; Donth, E. Influence of cooperative α dynamics on local β relaxation during the development of the dynamic glass transition in poly(*n*-alkyl methacrylate)s. *Macromolecules* **1996**, *29*, 247–253.
- Song, Z.; Lv, X.; Gao, L.; Jiang, L. Dramatic differences in the fluorescence of AIEgen-doped micro- and macrophase separated systems. *J. Mater. Chem. C* **2018**, *6*, 171–177.