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pH-responsive AIE-active Polyethylene-based Block Copolymers

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Electronic Supplementary Information

Abstract A novel synthetic strategy towards pH-responsive aggregation-induced emission (AIE)-active tetraphenylethene (TPE)-functionalized polyethylene-based block copolymers is presented. Tris(3-(4-(1,2,2-triphenylvinyl)phenoxy)propyl)borane was used to initiate the polyhomologation of dimethylsulfoxonium methylide to afford well-defined α -TPE- ω -OH linear polyethylenes (PE). The terminal hydroxyl groups were transformed to atom transfer radical polymerization (ATRP) initiating sites by esterification with α -bromoisobutyryl bromide, followed by polymerization of *tert*-butyl acrylate (*t*BA) to provide TPE-PE-*b*-PtBA block copolymers. After hydrolysis of the *t*Bu group to COOH group, the corresponding pH-responsive TPE-PE-*b*-PAA block copolymers were obtained. All synthesized block copolymers revealed AIE behavior either in solution or bulk. Due to the pH-responsivity of PAA chains, the aggregation state at different pH and consequently the fluorescence intensity changed. Also, the synthesized block copolymers exhibited ion-specificity fluorescence properties.

Keywords Polyhomologation; ATRP; Polyethylene-*b*-poly(acrylic acid); AIE; pH-responsivity; Ion-specificity

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INTRODUCTION

Conventional luminescent materials have attracted remarkable research attention due to their potential applications in electronic devices, chemosensor, and biomedical areas.^[1–4] In 2001, Tang's group reported, for the first time, luminogens with aggregation-induced emission (AIE) phenomenon.^[5] Compared to the conventional aggregation-caused quenching (ACQ) materials,^[6] the new luminescent materials can emit fluorescence (FL) in aggregation state.^[7–9] Since then, AIEgens have been introduced into polymers to afford AIE-active materials with improved properties such as processability, thermal stability, and structural diversity.^[10,11]

On the other hand, polymers with stimuli-responsive behavior are very important in drug delivery, sensor, and nanodevice sectors.^[12–15] Among them, thermoresponsive^[16] and pH-responsive^[17] polymers have attracted most of the attention. Other stimuli such as light, ultrasound, and electron transfer are also employed.^[18] However, detection and monitoring of the responses under stimuli at micro- or nanoscale is still an enormous challenge.^[19,20] To overcome this problem, fluorogens, such as AIE-active groups, could be incorporated into the stimuli-responsive polymers. As a consequence, the resultant stimuli-responsive AIE polymers would show emission in addition to their response to external

stimuli. For example, our group recently reported the synthesis of an AIE-active core crosslinked miktoarm star copolymer with many polyethylene (PE) and poly(methacrylic acid) (PAA) arms.^[21] The FL intensity of the copolymer increased with the decrease of temperature, exhibiting a temperature-responsive emission. Also, the FL intensity changed at different pH values.

Polyhomologation, recently developed by Shea *et al.*,^[22–24] is a powerful tool for the synthesis of well-defined linear polymethylene (equivalent to polyethylene, PE)-based materials.^[25–37] In our previous work, we have reported novel PE-based AIE-active block copolymers PE-*b*-PtBA synthesized by combining polyhomologation and ATRP.^[38] These block copolymers showed aggregation-induced emission (AIE) behavior either in solution or in bulk. In this study, we explore the AIE behavior of the corresponding amphiphilic block copolymers PE-*b*-PAA, after hydrolysis of the *t*Bu groups, at different pH and cations.

EXPERIMENTAL

Materials

4-Hydroxybenzophenone (98%), benzophenone (98%), zinc powder, titanium tetrachloride (TiCl₄, $\geq 98\%$), potassium carbonate (anhydrous, $\geq 99\%$), allyl bromide (99%), copper(I) bromide (CuBr, 99.999%), borane dimethylsulfide complex solution (1.0 mol·L⁻¹ in THF), α -bromoisobutyryl bromide (98%), trimethylamine *N*-oxide dihydrate (TAO·2H₂O, $\geq 99\%$), and trifluoroacetic acid (TFA, 99%) were

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purchased from Aldrich and used as received. Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) and *tert*-butyl acrylate ($\geq 99\%$) were distilled over calcium hydride (CaH_2) before use. Tetrahydrofuran (THF) and toluene were refluxed over sodium/benzophenone and distilled under a nitrogen atmosphere just before use. Dimethylsulfoxonium methylide was prepared according to Corey's method followed by switching the solvent from THF to toluene.^[39,40]

Measurements

The high-temperature gel permeation chromatography (HT-GPC) measurements were carried out on an Agilent PL-GPC 220 instrument equipped with one Plgel 10 μm MIXED-B column and a differential refractive index (DRI) detector. 1,2,4-Trichlorobenzene (TCB) was used as the eluent at a flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$ at 150°C . The system was calibrated with PS standards. ^1H - and ^{13}C -NMR spectra were recorded with a Bruker AVANCE III-400, 500, or 600 spectrometer. Transmittance measurements were performed on a Thermo Evolution 600 UV-Vis spectrophotometer in quartz cuvettes of 10 mm path length at a wavelength of 500 nm at room temperature. Photoluminescence spectra were recorded on a Thermo Lumina fluorescence spectrometer equipped with an external water circulator for the thermostatted cell holder. Dynamic light scattering (DLS) measurements were carried out with a Malvern Zetasizer Nano ZS device equipped with a TurboCorr correlator. The light source was a 30 mW He-Ne laser emitting vertically polarized light of 632.8 nm wavelength.

Synthesis of Block Copolymers TPE-PE-*b*-PtBA (Scheme 1)

TPE-PE-Br was synthesized as in our previous report.^[38] In a typical procedure for the synthesis of TPE-PE₈₂-*b*-PtBA₂₉, copper(I) bromide (CuBr, 14 mg, 0.1 mmol), TPE-PE₈₂-Br (160 mg, 0.06 mmol), *tert*-butyl acrylate (3.38 g, 26.4 mmol), and toluene (8 mL) were placed into a 25 mL Schlenk flask. The mixture was degassed by three freeze-pump-thaw (FTP) cycles, and then PMDETA (34 mg, 0.20 mmol) was added, followed by another freeze-pump-thaw cycle. The solution was immediately immersed into an oil bath set at 100°C to start the polymerization under stirring. After 24 h, the poly-

merization was stopped by cooling in a liquid nitrogen bath. The cloudy solution was heated to clear and poured into cold methanol (100 mL) with stirring. The white solid was filtered, dried under vacuum, and characterized by ^1H -NMR and GPC.

Synthesis of Block Copolymers TPE-PE-*b*-PAA (Scheme 1)

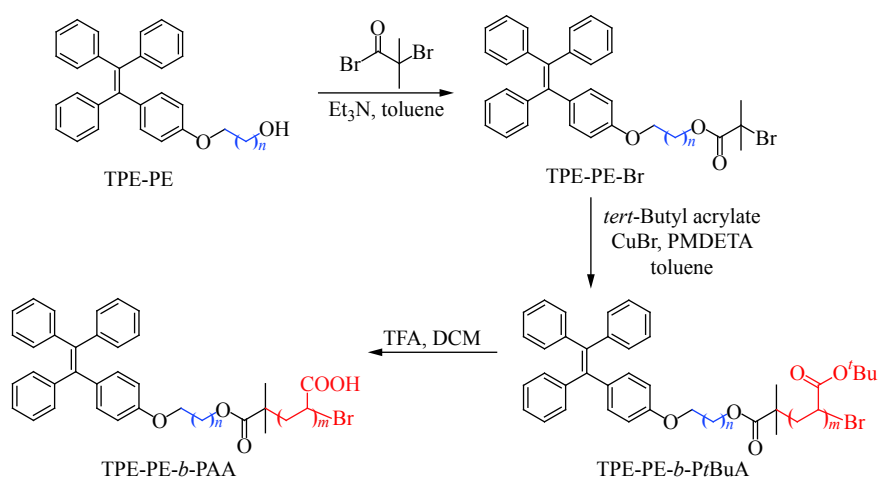
In a typical procedure for the synthesis of TPE-PE₈₂-*b*-PAA₂₉, TFA (2.0 mL, 29.0 mmol), TPE-PE₈₂-*b*-PtBA₂₉ (325 mg, 0.05 mmol), and DCM (5 mL) were placed into a 25 mL Schlenk flask. The mixture was stirred for 24 h at room temperature. Then, the solution was poured into cold methanol (100 mL) with stirring. The white solid was filtered, dried under vacuum, and characterized by FTIR.

RESULTS AND DISCUSSION

Synthesis and Characterization of TPE-PE-*b*-PAA

As illustrated in Scheme 1, a series of block copolymers TPE-PE-*b*-PtBA were synthesized from the same TPE-PE.^[38] The hydroxyl group of TPE-PE was modified with 2-bromoisobutyryl bromide to give the ATRP macroinitiator TPE-PE-Br. Then, TPE-PE-Br was employed to initiate the ATRP polymerization of *tert*-butyl acrylate affording the corresponding block copolymers TPE-PE-*b*-PtBA. As shown in Table 1, three different block copolymers with different DP (x) of *tert*-butyl acrylate were synthesized from the same macroinitiator TPE-PE₈₂-Br. These three copolymers were further treated with TFA to generate the amphiphilic block copolymers TPE-PE-*b*-PAA by removing the *tert*-butyl group. All polymers were characterized by ^1H -NMR, HT-GPC, or FTIR, and the molecular characteristics are shown in Table 1. The molecular weights were determined by ^1H -NMR end-group analysis and the polydispersity index ($\bar{D}$) (M_w/M_n) = 1.23–1.37 by high-temperature gel permeation chromatography (HT-GPC) with polystyrene standards.

As shown in Fig. 1, an obvious shift for the elution peak of TPE-PE₈₂-*b*-PtBA _{x} to the higher molecular weight side, as compared to the precursor TPE-PE₈₂-Br, can be observed. The ^1H -NMR spectra of TPE-PE-*b*-PtBA show both signals assigned to PE and PtBA blocks as well as those to TPE



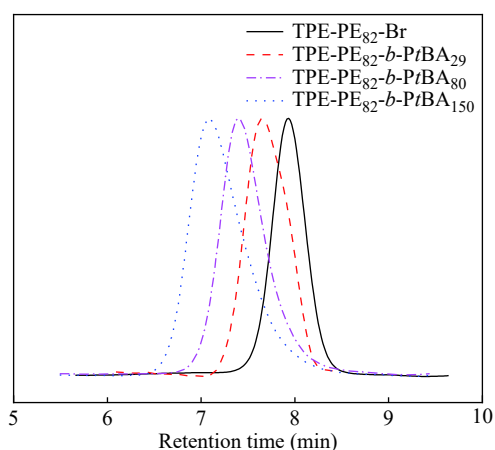
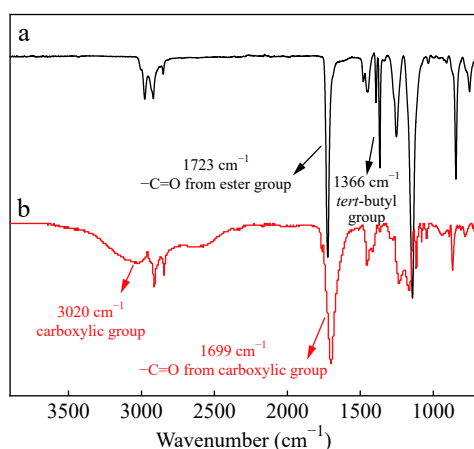
Scheme 1 Synthesis of TPE-PE-*b*-PAA block copolymers

Table 1 Molecular characteristics of TPE-PE₈₂ homopolymer as well as TPE-PE₈₂-*b*-PtBA_x and TPE-PE₈₂-*b*-PAA_x block copolymers

Entry	Sample	$M_{n,NMR}^a$	$M_{n,GPC}^b$	$M_{n,theor}^c$	DP ^a		$\bar{D}^b$
					PE	coblock	
1	TPE-PE ₈₂	2700	6300	—	82	—	1.07
2	TPE-PE ₈₂ - <i>b</i> -PtBA ₂₉	6500	9500	—	82	29	1.23
3	TPE-PE ₈₂ - <i>b</i> -PtBA ₈₀	13000	21400	—	82	80	1.32
4	TPE-PE ₈₂ - <i>b</i> -PtBA ₁₅₀	22000	41800	—	82	150	1.37
5 ^d	TPE-PE ₈₂ - <i>b</i> -PAA ₂₉	—	—	4900	82	29	—
6 ^d	TPE-PE ₈₂ - <i>b</i> -PAA ₈₀	—	—	8500	82	80	—
7 ^d	TPE-PE ₈₂ - <i>b</i> -PAA ₁₅₀	—	—	1400	82	150	—

^a $M_{n,NMR}$ and DP were calculated from ¹H-NMR spectra (600 MHz, C₂D₂Cl₄, 90 °C); ^b $\bar{D}$ (M_w/M_n) and $M_{n,GPC}$, determined by HT-GPC (1,2,4-trichlorobenzene, 150 °C, PS standards); ^c $M_{n,theor}$ of TPE-PE-*b*-PAA was calculated from $M_{n,NMR}$ of TPE-PE-*b*-PtBA; ^d Non soluble in normal NMR and GPC solvents. $M_{n,NMR}(TPE-PE) = (DP_{PE} + 1) \times 28 + MW_{TPE} + MW_{OH}$; $M_{n,NMR}(coblock\ polymer) = (DP_{coblock}) \times MW_{monomer\ of\ coblock} + M_{n,NMR}(TPE-PE)$; $M_{n,theor}(TPE-PE-*b*-PAA) = M_{n,NMR}(TPE-PE-*b*-PtBA) - (DP_{coblock}) \times 56$.

group (Fig. S1, in electronic supplementary information, ESI). For copolymers TPE-PE₈₂-*b*-PAA_x, ¹H-NMR and HT-GPC cannot be used because of their poor solubility. FTIR was thus used to monitor the hydrolysis of *tert*-butyl group to COOH. As shown in Fig. 2, a broad characteristic absorbance of carboxylic acid groups is present around 3020 cm⁻¹, while the characteristic absorbance of *tert*-butyl group at 1366 cm⁻¹ disappears. The characteristic absorbance of the carbonyl group also shifts from 1723 cm⁻¹ to 1699 cm⁻¹. All these changes indicate successful hydrolysis.

**Fig. 1** HT-GPC (TCB at 150 °C) traces of TPE-PE-*b*-PtBAs**Fig. 2** FTIR spectra of (a) TPE-PE₈₂-*b*-PtBA₁₅₀ and (b) TPE-PE₈₂-*b*-PAA₁₅₀

Aggregation-induced Emission

The emission characteristics of TPE-PE-*b*-PAA solutions were then investigated. TPE-PE₈₂-*b*-PAA₂₉ was dissolved in DMF at 100 °C; both of the two blocks were soluble in DMF at this temperature. After complete dissolution of the polymer, different amounts of cold toluene (non-solvent) were added into the DMF solution. The AIE study/results at a polymer concentration of 0.2 g·L⁻¹ are shown in Fig. 3(a). Obviously, the addition of toluene into the DMF solution induced molecular aggregation and gradually enhanced its photoluminescence (PL) intensities. At 90 vol% toluene fraction, the highest intensity was observed, which could be attributed to the highest degree of aggregation of TPE groups in the nanoparticles. For the other two block copolymers, similar results were observed (Fig. S2, in ESI).

The aggregation was then confirmed by dynamic light scattering (DLS) measurements, which suggested that the hydrodynamic diameter (D_h) of TPE-PE₈₂-*b*-PAA₂₉ nanoparticles (Fig. 3b, blue) increased with increasing the toluene fraction. D_h value was 93 nm for 30 vol% toluene addition, 96 nm for 70 vol% toluene addition, 138 nm for 80 vol% toluene addition, and 318 nm for 90 vol% toluene addition. The PL intensities at 483 nm (peak) of TPE-PE₈₂-*b*-PAA_x are summarized in Fig. 3(b) (red). Compared with TPE-PE₈₂-*b*-PAA₈₀ and TPE-PE₈₂-*b*-PAA₁₅₀, TPE-PE₈₂-*b*-PAA₂₉ has the highest PL intensity because of the highest TPE content. From Fig. 3(c), it is clear that the yellow color of its powder under room light turns to a strong greenish blue under UV irradiation.

pH Responsivity

Fluorescence properties of the block copolymers in buffer mixtures (Britton-Robinson buffer solutions, pH ranging from 1 to 13, see details in ESI) were then investigated (Fig. 4a). With an increase in pH from 5.0 to 13.0, the PL intensity decreased gradually (Fig. 4b). Since pK_a of PAA is 4.28, when pH increased from 5 to 13, the PAA chains changed from completely uncharged to a charged state, accompanied by a change of chain conformation from a contracted to an extended state as well as by an increased hydrophilicity of polymer chains. As a consequence, the degree of aggregation decreases due to the increased hydrophilicity of carboxyl groups, which leads to a decrease in PL intensity. With a decrease of pH from 5.0 to 1.0, the PL intensity of the solutions also decreased gradually (Fig. 4b). At pH < 4.2, the

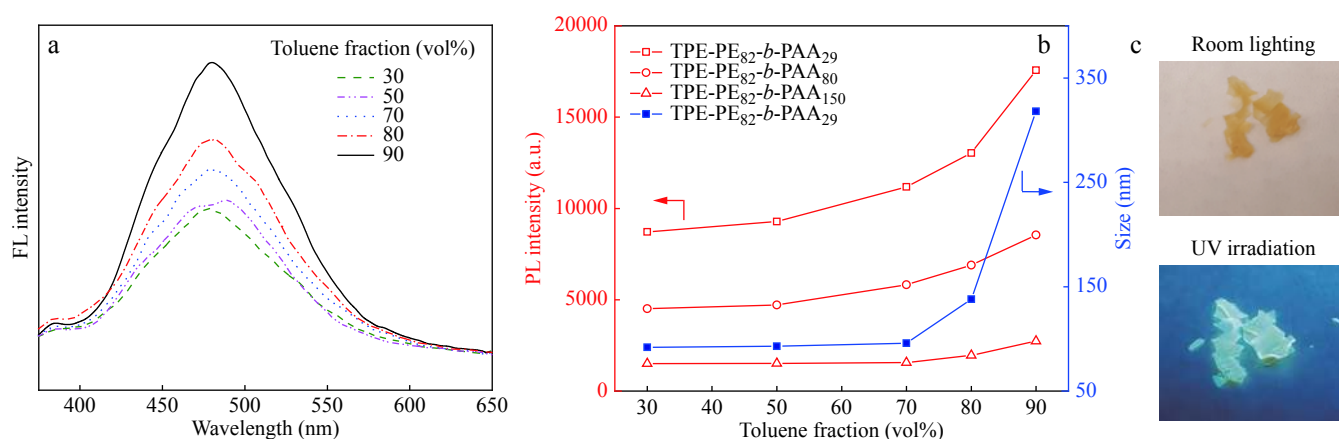


Fig. 3 (a) Photoluminescence (PL) spectra of TPE-PE₈₂-b-PAA₂₉ in DMF/toluene mixtures with different toluene fractions at a concentration of 0.2 g·L⁻¹; (b) Red: plot of peak intensity at 483 nm versus toluene fraction in the DMF/toluene mixture; Blue: hydrodynamic diameter of TPE-PE₈₂-b-PAA₂₉ in DMF/toluene mixtures versus toluene fraction; (c) Images of solid powder of TPE-PE₈₂-b-PAA₂₉ taken under room light and under 365 nm UV irradiation

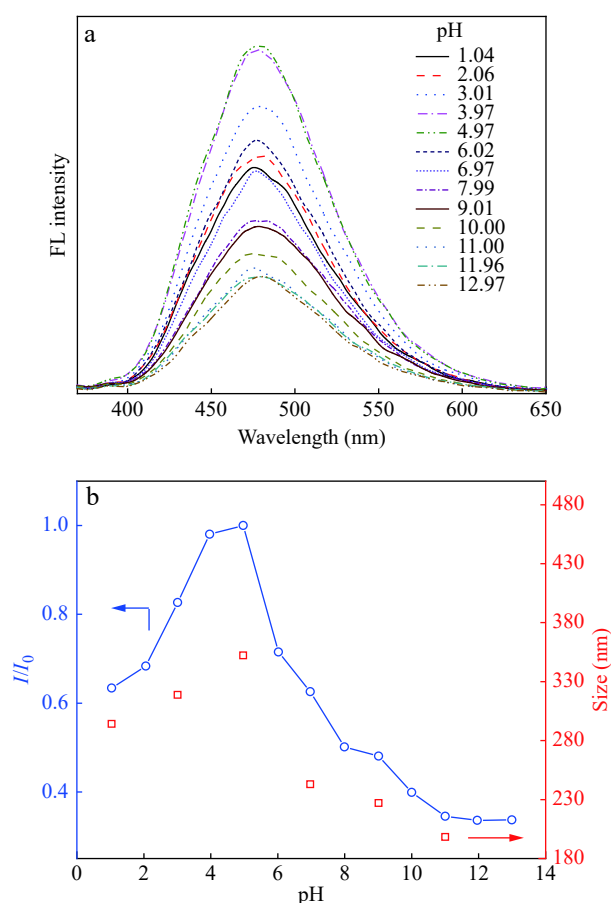


Fig. 4 (a) Photoluminescence (PL) spectra of TPE-PE₈₂-b-PAA₂₉ in buffer solution with different pH values at a concentration of 0.1 g·L⁻¹; (b) Blue: plot of I/I_0 at versus pH value (I_0 is PL intensity at pH 4.97); Red: hydrodynamic diameter of TPE-PE₈₂-b-PAA₂₉ in buffer solution versus pH value

PAA chains were protonated. The decreasing pH made the hydrophilicity of carboxyl groups (—COOH) be further decreased, and the PAA chains more contracted and less aggregated.^[21] As a result, the PL intensity decreased gradually. Furthermore, DLS measurements were used to detect the

average hydrodynamic diameter (D_h) of nanoparticles for the different polymer/buffer mixtures (Fig. 4b); the results show a same tendency in the plot of size versus pH value. In a recent paper, the pH-responsive properties of 4-arm PAA stars with one TPE molecule in the core showed a different tendency in the plot of PL intensity versus pH.^[41] We can conclude that the existence of PE chains plays a key role in the responsive properties and further work is in progress.

Ion Specificity

The influence of different cations on the fluorescence property of TPE-PE-*b*-PAA was also investigated by using different buffer solutions with various cations (Li⁺, Na⁺, K⁺, Cs⁺) at pH 2.0, 6.0, and 8.0 (Fig. 5). At pH 2.0, PAA was uncharged, and interactions between cations and PAA chains were dominated by nonelectrostatic cation adsorption. A bigger cation would exhibit stronger adsorption on the PAA chain due to the larger polarizability. The adsorption of cations made the PAA chains be charged again and transformed the contracted PAA chains to extended, which is in favor of the aggregation so that PL intensity is increasing. Meanwhile, the adsorption of cations on the chain surface led to electrostatic repulsions, resulting in an increase of the space between TPE molecules separated by water. This would make FL intensity to be decreased.^[42] The FL intensity of the polymer solution with different cations was influenced by these two factors. Since the size and polarizability of cations increased from Li⁺ to Cs⁺, the adsorption on PAA chains would increase from Li⁺ to Cs⁺. As a consequence, the FL intensity of polymer solution increased following the order of Li⁺ < Na⁺ < K⁺. In the case of the biggest and most polarizable Cs⁺, the FL intensity decreased since the second factor (electrostatic repulsions) is dominant (Fig. 5a). At pH 6.0, the PAA chains were partially charged. The adsorption between cations and uncharged PAA chains still strongly influenced the aggregation of the polymers, so that the fluorescence intensity kept the same tendency (Fig. 5b). When pH was increased to 8.0, PAA chains were fully charged. At this pH, the interactions between cations and PAA chains were dominated by counterion condensation. Fig. 5(c) shows

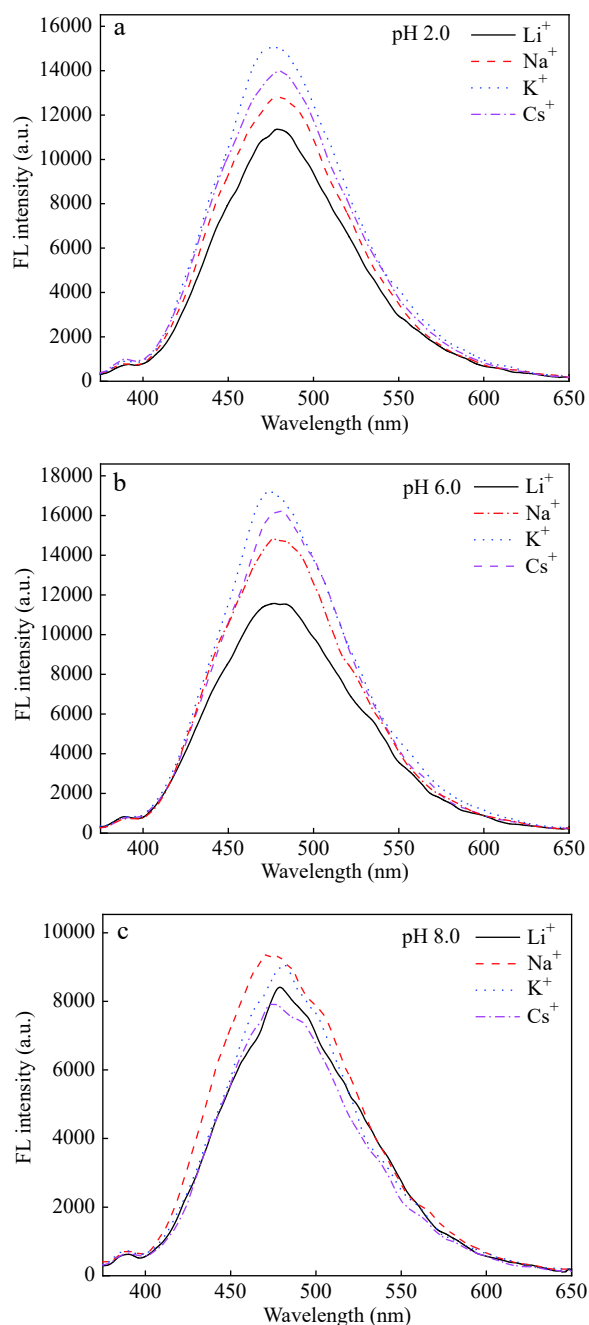


Fig. 5 Photoluminescence (PL) spectra of TPE-PE₈₂-b-PAA₈₀ in buffer solutions with different cations at (a) pH 2.0, (b) pH 6.0, and (c) pH 8.0 (at a concentration of 0.1 g·L⁻¹)

that the ion specificity of fluorescence intensity for the block copolymer at pH 8.0 is not as obvious as that at pH 2.0 and 6.0. At pH 8.0, the hydrophilicity and solubility of the polymer chains were higher than those that at pH 2.0, which led to lower fluorescence intensity. So, the change of fluorescence intensity induced by ion specificity might be less remarkable compared to that induced by hydrophilicity, but the difference can still be observed from Fig. 5(c).

CONCLUSIONS

In summary, a series of TPE-functionalized PE-based amphi-

philic block copolymers were synthesized by using polyhomologation (PE block) and ATRP (PtBA block), followed by hydrolysis of PtBA block. The synthesized block copolymers exhibited AIE characteristics either in solution or bulk. In addition, due to the pH responsivity of PAA chain, the block copolymers exhibited changes in fluorescence intensity at different pH because of different aggregation states of the TPE moieties. Moreover, our investigation indicates that the block copolymer had ion-specific fluorescence properties. This research opens new horizons toward the potential application of PE-based polymer in AIE-active and pH-responsive materials.

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/s10118-019-2330-0>.

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