Tetraphenylethene-Functionalized Polyethylene-based Polymers with Aggregation-Induced Emission

Yu Jiang, Nikos Hadjichristidis*

Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia

ABSTRACT: A novel synthetic strategy toward a series of tetraphenylethene (TPE)-functionalized polyethylene-based homo/copolymers is presented. Tris(3-(4-(1,2,2-triphenylvinyl)phenoxy)propyl)borane, synthesized by hydroboration of (2-(4-(allyloxy)phenyl)ethene-1,1,2-triyl)tribenzene with BH_3 , was used to initiate the polyhomologation of dimethylsulfoxonium methylide to afford well-defined TPE-terminated linear polyethylene (PE). Combining this efficient strategy with ring-opening polymerization (ROP) or atom transfer radical copolymerization (ATRP) TPE-functionalized PE-based block copolymers have been synthesized. All synthesized polymers showed **aggregation-induced emission (AIE)**-behavior either in solution or in bulk. Self-assembly of the PE-based block copolymer in DMF resulted in strong emission due to the AIE effect of the aggregated TPE-PM core, the fluorescence intensity of the solution is directly related to the composition of block copolymers and the size of the micelle. The response of the AIE-operative fluorescence behavior toward the concentration of the block copolymer solutions has also been used to locate the CMC value of the block copolymers. The non-emissive dilute solutions of block copolymers became fluorescent when increasing concentrations above CMC.

INTRODUCTION

Luminescent materials have attracted considerable attention in past decades due to their promising applications in electronic devices, chemosensors and biomedical areas.¹⁻⁴ However, the conventional organic luminogens only emit high fluorescence in dilute solution while undergoing complete quenching in aggregation state. This aggregation-caused quenching (ACQ) effect limits their application in real-world.⁵ In 2001, Tang's group first reported one particular silole molecule which has exactly opposite phenomenon of ACQ emitting strongly in aggregation state.⁶ This interesting phenomenon was coined by Tang aggregation-induced emission (AIE). Since then, several organic AIE molecules have been developed and applied in bioimaging, OLED, chemosensing, stimuli-responsive system and so on.⁷⁻¹¹ Depending on the development of AIE small molecules, AIE-active polymers have also been synthesized and investigated. The combination of polymers with the AIE small molecules have many advantages comparing to the small molecules, such as processability, good thermal stability and structural diversity.¹²⁻¹⁴ By introducing the AIE-gens into the polymer structures, the resulted AIE-active materials possess the polymer properties as well as the AIE characteristics and thus expand the application scope of AIE materials.

Recently, polymer micelle behavior¹⁵ has been a fascinating area and received considerable research attention, in particular of amphiphilic block copolymers,¹⁶ due to potential applications in drug delivery¹⁷ and catalysis.¹⁸ AIE-active amphiphilic block copolymers, which could self-assemble into micelles, have also been developed and applied in fluorescent probes area.¹⁹⁻²¹ For example, Zhu and co-workers synthesized PNIPAM-based AIE fluorophores-contained block copolymers. These dual-responsive polymers self-assembled into reversible micelles with AIE-active turn-on fluorescence. Zhu's report provided a novel approach to interpret the influence of

minor pH or temperature changes in cells.²² To our knowledge, AIE-active polyethylene-based block copolymers have never been reported. Since PE is a crystalline polymer, polyethylene-based block copolymers in general, since they can undergo crystallization-driven self-assembly (CDSA), is an interesting topic in recent years.²³⁻²⁶ Unique characteristics are added by crystallizable polymer micelles, such as strong solidification, “living growth” and complex structures.²⁷⁻³⁰ In the present work, we incorporate AIE-gens into polyethylene-based block copolymers to form AIE-active micelles, with the expectation to expand the potential applications of AIE materials.

Polyhomologation, recently developed by Shea et al³¹⁻³⁴, is a powerful tool for the synthesis of well-defined linear polymethylene (equivalent to polyethylene, PE)-based materials. The mechanism involves the formation of an ate complex between a ylide (monomer) and an organoborane (initiator), followed by insertion of $-\text{CH}_2-$ moiety into the three alkyl branches of borane with simultaneous release of dimethyl sulfoxide and regeneration of the alkyl borane species ready for the next cycle, affording a borane-link 3-arm star PE. A hydroxyl-terminated linear PE (PE-OH) is then obtained by oxidation/hydrolysis of the 3-arm star PE. A series of PE-based architectures are synthesized by combining this efficient C1 polymerization with other polymerizations.³⁵⁻⁵⁰ Herein, we wish to report the synthesis of AIE-active PE by using an AIE gens-contained initiator for polyhomologation. Different block copolymers were constructed by ATRP and ROP by using PE-based macroinitiators.

EXPERIMENTAL SECTION

Materials. 4-Hydroxybenzophenone (98%), benzophenone (98%), zinc powder, titanium tetrachloride (TiCl_4 , $\geq 98\%$), potassium carbonate (anhydrous, $\geq 99\%$), allyl bromide (99%), copper(I) bromide (CuBr , 99.999%), borane dimethylsulfide complex solution (1.0 M in THF),

^tBu-P₂ (2.0 M in THF), α -bromoisobutyryl bromide (98%), trimethylamine *N*-oxide dihydrate (TAO 2H₂O, $\geq$ 99%) were purchased from Aldrich and used as received. Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), ϵ -caprolactone (CL, $\geq$ 99%), styrene ($\geq$ 99%), and *tert*-butyl acrylate ($\geq$ 99%) were distilled over calcium hydride (CaH₂) 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 the Corey's method followed by switching the solvent from THF to toluene.⁵¹⁻⁵²

Measurements. The high-temperature gel permeation chromatography (HT-GPC) measurements were carried out with the Agilent PL-GPC 220 instrument equipped with one Plgel 10 μ m MIXED-B column and a differential refractive index (DRI) detector. 1,2,4-Trichlorobenzene (TCB) was used as eluent at a flow rate of 1.0 mL/min at 150 °C. The system was calibrated with PS standards. The ¹H and ¹³C 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 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 (4-(allyloxy)phenyl)(phenyl)methanone (Scheme 1). To a solution of 4-Hydroxybenzophenone (8.0 g, 40 mmol) in dry acetone (50 mL), dry K₂CO₃ (14.0 g, 48 mmol) and allyl bromide (5.81 g, 48 mmol) were added, and the mixture was stirred overnight, then filtered, and the solid was washed with acetone. The combined filtrate was evaporated, and the

solvent was removed to give the crude (4-(allyloxy)phenyl)(phenyl)methanone which was used without purification.

Synthesis of (2-(4-(allyloxy)phenyl)ethene-1,1,2-triyl)tribenzene (TPE-alkene, Scheme 1).

Zn powder (3.9 g, 60.0 mmol), benzophenone (2.73 g, 15.0 mmol) and (4-(allyloxy)phenyl)(phenyl)methanone (2.96 g, 15.0 mmol) were placed into a 250 mL two-necked flask equipped with a condenser. The flask was evacuated under vacuum and flushed with argon three times, followed by addition of anhydrous THF (80 mL). Then the mixture was cooled to -78 °C and TiCl_4 (3.3 mL, 30.0 mmol) was added dropwise. The mixture was slowly warmed to room temperature, stirred for 30 min, and then refluxed overnight. After cooling down to room temperature, the reaction was quenched by 10% aqueous K_2CO_3 solution, and after vigorous stirring for 5 min, the dispersed insoluble material was removed by vacuum filtration using a Celite pad. The organic phase was separated and the aqueous layer was extracted three times with diethyl ether (60 mL $\times$ 3). The combined organic fractions were washed with brine and dried over MgSO_4 . The solvent was removed to give the (2-(4-(allyloxy)phenyl)ethene-1,1,2-triyl)tribenzene (TPE-alkene).

Synthesis of tetraphenylethene-polyethylene (TPE-PE, Scheme 1). In a typical procedure for the synthesis of TPE-PE₄₁, 0.1 mL (0.5 mmol) of a THF solution of $\text{BH}_3 \cdot \text{Me}_2\text{S}$ (5.0 M) was added over 5 min to a toluene solution (4.9 mL, 0.70 g, 1.8 mmol) of (2-(4-(allyloxy)phenyl)ethene-1,1,2-triyl)tribenzene at 0 °C. The reaction was allowed to reach room temperature over 2 h. The final concentration of the initiator solution in toluene was 0.1 M.

3.0 mL of the initiator solution (0.1 M, 0.30 mmol) was added to a dimethylsulfoxonium methylide solution (110 mL, 0.8 M, 88.0 mmol) at 65 °C. After consumption of methylide, 0.20 g of TAO was added to the solution. Then, the solution was stirred for 2 h at 90 °C and precipitated

in methanol. The white solid was filtered, dried under vacuum and characterized by ^1H NMR and GPC (1.13 g, $M_{n,\text{NMR}} = 1.5 \times 10^3$, $\text{Đ} = 1.08$).

Synthesis of block copolymer TPE-PE-*b*-PCL (Scheme 2). $^t\text{Bu-P}_2$ (0.10 mL, 2 M, 0.2 mmol) was added to the solution of TPE-PE₉₇-OH (0.12 g, 0.04 mmol) in toluene (2.0 mL), then caprolactone (0.29 g, 2.5 mmol) was added to the mixture. The resulted solution was stirred in a preheated oil bath at 90 °C for 14 h. Then the reaction was quenched by adding CH₃COOH/MeOH (10 vol%) and cooled to room temperature. The mixture was precipitated in methanol. The white solid was filtered, dried under vacuum and characterized by ^1H NMR and GPC (TPE-PE₉₇-*b*-PCL₂₃, 0.21 g, $M_{n,\text{NMR}} = 5.7 \times 10^3$, $\text{Đ} = 1.21$).

Synthesis of macroinitiator TPE-PE-Br (Scheme 2). In a typical procedure for the synthesis of TPE-PE₈₂-Br, TPE-PE₈₂ (0.55 g, 0.20 mmol of OH) and toluene (20 mL) were placed into a 50 mL Schlenk flask and the mixture was kept under vigorous stirring at 90 °C under Ar. Pyridine (0.32 mL, 4.0 mmol) and 2-bromoisobutyryl bromide (0.92 g, 4.0 mmol) were added dropwise. After stirring for 12 h, the reaction mixture was cooled to room temperature and poured into 300 mL of acidic methanol (containing 20 mL of 1 M aqueous HCl). The solid was filtered, washed successively with methanol (2×20 mL), 1 M aqueous HCl (2×10 mL), and methanol (2×20 mL), and dried at 50 °C for 3 h in vacuum to give an off-white solid (TPE-PE₈₂-Br, 0.50 g, $M_{n,\text{NMR}} = 2.8 \times 10^3$, $\text{Đ} = 1.07$).

Synthesis of block copolymer TPE-PE-*b*-PS (Scheme 2). Copper(I) bromide (CuBr, 7 mg, 0.05 mmol), TPE-PE₄₁-Br (50 mg, 0.03 mmol), styrene (0.69 g, 6.6 mmol) and toluene (4 mL) was placed into a 25 mL Schlenk flask. The mixture was degassed by three freeze-pump-thaw (FTP) cycles and then pentamethyldiethylenetriamine (PMDETA, 17 mg, 0.10 mmol) was added and then the mixture was subjected to 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 polymerization 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 (TPE-PE₄₁-*b*-PS₃₈, 150 mg, $M_{n,\text{NMR}} = 5.6 \times 10^3$, $\text{Đ} = 1.10$).

Synthesis of block copolymer TPE-PE-*b*-PtBA (Scheme 2). In a typical procedure for the synthesis of TPE-PE₈₂-*b*-PtBA₂₉, copper(I) bromide (CuBr, 7 mg, 0.05 mmol), TPE-PE₈₂-Br (80 mg, 0.03 mmol), *tert*-butyl acrylate (1.69 g, 13.2 mmol) and toluene (4 mL) was placed into a 25 mL Schlenk flask.. The mixture was degassed by three freeze-pump-thaw (FTP) cycles and then pentamethyldiethylenetriamine (PMDETA, 17 mg, 0.10 mmol) was added and then the mixture was subjected to 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 polymerization 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 (TPE-PE₈₂-*b*-PtBA₂₉, 170 mg, $M_{n,\text{NMR}} = 6.5 \times 10^3$, $\text{Đ} = 1.23$)

Scheme 1. Synthesis of tetraphenylethylene-terminated polyethylene (TPE-PE)

RESULTS AND DISCUSSION

Synthesis and Characterization of PE-based AIE Polymers. As illustrated in Scheme 1, (2(4-allyloxy)phenyl)(phenyl)methanone was synthesized from 4-hydroxybenzophenone in the first step, followed by the McMurry coupling reaction to afford the alkene-functionalized tetraphenylethylene (TPE-alkene). The chemical structure of TPE-alkene was confirmed by ^1H NMR and ^{13}C NMR (Figure S1). TPE-alkene was reacted with BH_3 to afford the initiator of the subsequent polyhomologation (Scheme 1). A series of well-defined TPE-terminated polyethylenes (TPE-PEs) with different molecular weight were synthesized. The molecular characteristics of TPE-PEs are given in Table 1. **The molecular weight was determined by ^1H NMR end-group analysis and calculated according to the formula (Table 1).** The polydispersity index ($\text{Đ} = M_w/M_n$) was determined by high-temperature gel permeation chromatography (HT-GPC) with polystyrene standards ($\text{Đ} = 1.07\text{-}1.14$). All GPC traces are monomodal with narrow molecular weight distributions (Figure 1). All polymers were characterized by ^1H NMR, as an example the ^1H NMR spectrum of polymer TPE-PE₄₁ is shown in Figure 2b. Comparison to that of the corresponding TPE-alkene (Figure 2a), reveals that the resonance signals (a), (b) and (c) belonging to allyl group disappeared and new signal (f') between 1.20-1.40 ppm belonging to the PE chain appeared, thus proving the success of polymerization. The signals (d') at δ 6.70, 6.95 and 7.15 ppm with an integration ratio of 15:2:2, assigned to protons of TPE, indicate that the TPE group remained intact during the polyhomologation.

Figure 1. HT-GPC (TCB at 150 °C) traces of TPE-PEs.

Table 1. Molecular characteristics of TPE active PE-based polymers

Entry	Sample	$M_{n, \text{NMR}}^a$	$M_{n, \text{GPC}}^b$	DP^a		$\bar{D}^b$
				PE	coblock	
1	TPE-PE ₄₁	1500	3500	41	-	1.08
2	TPE-PE ₈₂	2700	6300	82	-	1.07
3	TPE-PE ₉₇	3100	7700	97	-	1.14
4	TPE-PE ₁₆₇	5100	12100	167	-	1.10
5	TPE-PE ₄₁ - <i>b</i> -PS ₃₈	5600	12900	41	38	1.10
6	TPE-PE ₉₇ - <i>b</i> -PCL ₂₃	5700	9000	97	23	1.21
7	TPE-PE ₈₂ - <i>b</i> -PtBA ₂₉	6500	9500	82	29	1.23
8	TPE-PE ₈₂ - <i>b</i> -PtBA ₈₀	13000	21400	82	80	1.32
9	TPE-PE ₈₂ - <i>b</i> -PtBA ₁₅₀	22000	41800	82	150	1.37

^a $M_{n, \text{NMR}}$ and DP were calculated from ¹H NMR spectra (600 MHz, C₂D₂Cl₄, 90 °C); ^b $\bar{D}$ (M_w/M_n) and $M_{n, \text{GPC}}$, determined by HT-GPC (1,2,4-trichlorobenzene, 150 °C, PS standards). $M_{n, \text{NMR, TPE-PE}} = (\text{DP}_{\text{PE}} + 1) \times 28 + \text{MW}_{\text{TPE}} + \text{MW}_{\text{OH}}$; $M_{n, \text{NMR, coblock polymer}} = (\text{DP}_{\text{coblock}}) \times \text{MW}_{\text{monomer of coblock}} + M_{n, \text{NMR, TPE-PE}}$.

Figure 2. ^1H NMR spectra of the: (a) TPE-alkene (CDCl_3 , 25 °C, 500 MHz); (b) TPE-PE₄₁ ($\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C, 600 MHz).

With the successful results on TPE-PE synthesis in hand, a series of TPE-PE-based block copolymers were synthesized (Scheme 2). The hydroxyl group of TPE-PE was utilized to initiate the ROP of ϵ -caprolactone with the phosphazene superbase $^t\text{Bu-P}_2$ as the catalyst in toluene at 80 °C to form TPE-PE-*b*-PCL. The hydroxyl group of TPE-PE was also 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 styrene or *tert*-butyl acrylate affording the corresponding block copolymers TPE-PE-*b*-PS or TPE-PE-*b*-PtBA. The molecular characteristics and HT-GPC traces of block copolymers are shown in Table 1, Figure 3, Figure S2 and S3 (ESI†). Three block copolymers TPE-PE₈₂-*b*-PtBA_x with different DP (x) of *tert*-butyl acrylate, were synthesized from the same macroinitiator TPE-PE₈₂-Br (Table 1, line 7-9). As shown in Figure 3

all block copolymers TPE-PE₈₂-*b*-PtBA_x are eluted earlier (higher molecular weight) than the corresponding precursor TPE-PE₈₂. Similar results are observed from HT-GPC traces of the other block copolymers (Figure S2 and S3, ESI[†]). As shown in the ¹H NMR spectra, both signals due to PCL, PS and PtBA blocks as well as TPE group can be identified (Figure 4).

Scheme 2. Synthesis of TPE-terminated block copolymers

Figure 3. HT-GPC (TCB at 150 °C) traces of TPE-PE-*b*-PtBAs.

Figure 4. ^1H NMR (600 MHz) spectra of the : (a) TPE-PE₄₁; (b) TPE-PE₉₇-*b*-PCL₂₃; (c) TPE-PE₄₁-*b*-PS₃₈; (d) TPE-PE₈₂-*b*-PtBA₁₅₀ in $\text{C}_2\text{D}_2\text{Cl}_4$ at 90 °C.

Aggregation-Induced Emission. The emission characteristics of the solutions of TPE-PE-based polymers were then investigated. The AIE behavior of TPE-PE₈₂ was investigated in toluene/*n*-hexane mixture at a concentration of 0.1 g/L. As shown in Figure 5a and Figure S5, the addition of *n*-hexane into the toluene solution induced the molecular aggregation and gradually enhanced its photoluminescence (PL) intensities. At 90 vol % *n*-hexane fraction, the highest intensity was observed (4.5-fold compared to that of pure toluene solution) (Figure S5, ESI[†]). For the block copolymers, THF/H₂O were selected as solvent and similar results were observed, whereas addition of non-solvent (H₂O) to good solvent (THF) also resulted in a rapid increase of the

emission (Figure 5b-d and S4, ESI†). The PL intensities of TPE-PE₈₂-*b*-PtBA_x are summarized in Figure 5c. The lower TPE content in TPE-PE₈₂-*b*-PtBA₈₀ and TPE-PE₈₂-*b*-PtBA₁₅₀ resulted in the lower PL intensity in comparison to TPE-PE₈₂-*b*-PtBA₂₉ solution. Solutions of TPE-PE₈₂-*b*-PtBA₂₉ with low H₂O fraction (<60 vol %) have low PL intensity which increases abruptly to reach its highest value for the 90 vol %-H₂O solution, which is about 12-fold compared with that in pure THF, because of the strong aggregation (Figure 5b and 5d). The aggregation was also confirmed by the decreasing transmittance of the solutions. As shown in Figure 5d, the transmittance of the TPE-PE₈₂-*b*-PtBA₂₉ solutions decreases when the amount of H₂O increases, along with the increase of PL intensity as the macromolecular aggregate. DLS was used to check the nanoparticle size in the TPE-PE₈₂-*b*-PtBA₂₉ solutions (Figure S7). Clearly, the average hydrodynamic diameter (D_h) of the nanoparticles increased with the H₂O fraction. D_h value was 360 nm in 30 vol % of H₂O, 684 nm in 70 vol % of H₂O, and 841 nm in 90 vol % of H₂O, along with the increase of PL intensity as the macromolecular aggregate.

Figure 5. (a) Photoluminescence (PL) spectra of TPE-PE₈₂ in toluene/*n*-hexane mixtures with different *n*-hexane fractions at a concentration of 0.1 g/L; (b) PL spectra of TPE-PE₈₂-*b*-PtBA₂₉ in THF/H₂O mixtures with different H₂O fractions at a concentration of 0.1 g/L; (c) Plot of PL intensity of TPE-PE₈₂-*b*-PtBA_x at 483 nm versus H₂O fraction in THF/H₂O mixture; (d) Plot of I/I_0 and transmittance of TPE-PE₈₂-*b*-PtBA₂₉ versus H₂O fraction in the THF/H₂O mixture; I is PL intensity in THF/H₂O mixtures with different H₂O fractions, I_0 is PL intensity in pure THF solution.

Self-Assembly of Block Copolymers. PE-based block copolymers in selective solvents for the one block self-assemble to form micellar structures. For example, in the case of TPE-PE-*b*-PtBA, DMF is a selective solvent for PtBA and therefore the DMF-phobic TPE-PE block will form the core while PtBA the corona. As a consequence, the aggregated polyethylene chains will restrict the intramolecular rotation of TPE and thus enhance the FL intensity. To investigate the relationship between the FL intensity and self-assembled behavior, a series of TPE-PE₈₂-*b*-PtBA_x

DMF solutions with different concentration were prepared and the AIE behaviors were checked (Figure S8).

Figure 6. (a) PL spectra of TPE-PE₈₂-b-PtBA_x in DMF solutions at a concentration of 0.25 g/L; (b) Plot of peak intensity of TPE-PE₈₂-b-PtBA_x solutions at 483 nm as a function of the TPE concentration in mmol/L from Figure S8.

All solutions of TPE-PE₈₂-b-PtBA_x copolymers shown strong emission intensities. Comparing the emission intensities of DMF solutions (Figure 6a) to those in THF/ H₂O mixtures (Figure 5d), it is obvious that as in the case of THF/H₂O, the higher TPE content of the block copolymer (lower molecular weight) the higher intensity. As shown in figure 6b, the intensity is plotted against the concentration in mmol/L, concentration in mmol/L was used in order to normalize the TPE concentration in each case. The solution of TPE-PE₈₂-b-PtBA₂₉ still has the highest emission intensity comparing to other two block copolymers, although the concentration of TPE group was the same.

Figure 7. Size distribution of TPE-PE₈₂-*b*-PtBA_x in DMF (a) TPE-PE₈₂-*b*-PtBA₁₅₀; (b) TPE-PE₈₂-*b*-PtBA₈₀; (c) TPE-PE₈₂-*b*-PtBA₂₉.

The size distribution of the formed micelles in DMF were measured by dynamic light scattering (DLS) at room temperature (Figure 7). It is obvious that the lower the molecular weight of the PtBA block the higher the size of the micelles, due to the higher PE content of block copolymer. This is in agreement with the PL intensity results since the lower molecular weight copolymer has the higher aggregation (TPE-PE: fixed molecular weight).

Critical Micelle Concentration (CMC) of TPE-PE-*b*-PtBA in DMF. CMC is defined as the concentration below which only single chains are present and above the single chains can self-assemble into micelles. At concentration above CMC, the aggregation of TPE-PE chain in the core

region should exert AIE-operative emission, while at a concentration below CMC, the polymer chain are isolated in the dilute solution and there should be no emission expected in this case.

Figure 8. (a-c) Plot of emission intensity at 483 nm versus the logarithm of the concentration of TPE-PE₈₂-*b*-PtBA_x; (d) Plot of Log CMC versus the molar fraction of PtBA block.

The relationship of fluorescence intensity toward the concentration of the TPE-PE₈₂-*b*-PtBA_x solution in DMF was used to locate the CMC. A series of TPE-PE₈₂-*b*-PtBA_x solutions in DMF were prepared and all the AIE behaviors were investigated. The PL spectra are shown in Figure S6. The aggregate emission intensity at 483 nm was plotted against the logarithm of the concentration of the DMF solutions (Figure 8, a-c), the emission intensities remain very low when the concentration is below CMC and increase sharply above the CMC in all block polymers. The

CMC values of the block copolymer solutions are in the range of $(0.5-1.5) \times 10^{-2}$ mg/mL, indicating an obvious effect of the PtBA lengths on the CMC values. With the highest PtBA content, TPE-PE₈₂-*b*-PtBA₁₅₀ has the highest CMC value (1.47×10^{-2} mg/mL) compared to the other two block polymers. This result is reasonable because the longer PtBA chain will prevent PE block to aggregate, so the one who has longer PtBA chain will form micelle later than others. As depicted in Figure 8d, a linear relationship between logarithm CMC and molar fraction of PtBA chain in the block copolymer ($DP_{PtBA}/(DP_{PE}+DP_{PtBA})$) are observed, and the CMC value increases as the molar fraction of PtBA chain increases at constant PE length.

CONCLUSION

In summary, a series of TPE-functionalized PE-based homo/copolymers were synthesized by using polyhomologation. Tris(3-(4-(1,2,2-triphenylvinyl)phenoxy)propyl)borane was used as initiator for the polyhomologation of dimethylsulfoxonium methylide to give TPE-terminated linear polyethylene. Combining this method with ROP or ATRP, more TPE-active PE-based block copolymers were synthesized. All synthesized polymers showed AIE-behavior either in solution or in bulk. The DMF solution of block copolymer TPE-PE-*b*-PtBA can undergo self-assembly to give micelle solutions with strong emission. The TPE-PE-core in the micelle restricts the intramolecular rotation of TPE and thus enhances FL emission intensity. The block copolymer with lower PtBA block composition forms micelle with the larger size, which results in higher PL emission intensity. CMC value of TPE-PE-*b*-PtBA was determined by using the response of the AIE behavior toward the concentration of the block polymer solutions. This research opens new horizons toward potential application of PE-based polymer in AIE materials.

ASSOCIATED CONTENT

Supporting Information. Additional figures are presented in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

* (N.H.) Telephone: + 966-(0)12-8080789. E-mail: nikolaos.hadjichristidis@kaust.edu.sa.

ORCID

Yu Jiang: 0000-0002-8781-6381

Nikos Hadjichristidis: 0000-0003-1442-1714

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors like to thank Dr. Panagiotis Bilalis for his help on the investigation of self-assembly.

The research reported in this publication was supported by King Abdullah University of Science and Technology (KAUST).

REFERENCES

1. Bredol, M.; Kynast, U.; Ronda, C., Designing luminescent materials. *Adv. Mater.* **1991**, *3*, 361-367.
2. Schmidt, A.; Anderson, M.; Armstrong, N., Electronic states of vapor deposited electron and hole transport agents and luminescent materials for light-emitting diodes. *J. Appl. Phys.* **1995**, *78*, 5619-5625.
3. Jüstel, T.; Nikol, H.; Ronda, C., New developments in the field of luminescent materials for lighting and displays. *Angew. Chem., Int. Ed.* **1998**, *37*, 3084-3103.
4. Bünzli, J.-C. G., Lanthanide luminescence for biomedical analyses and imaging. *Chem. Rev.* **2010**, *110*, 2729-2755.
5. Förster, T.; Kasper, K., Ein konzentrationsumschlag der fluoreszenz des pyrens. *Z. Phys. Chem. (Muenchen, Ger.)* **1955**, *59*, 976-980.
6. 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.
7. Hong, Y.; Lam, J. W.; Tang, B. Z., Aggregation-induced emission. *Chem. Soc. Rev.* **2011**, *40*, 5361-5388.
8. Mei, J.; Hong, Y.; Lam, J. W.; Qin, A.; Tang, Y.; Tang, B. Z., Aggregation-induced emission: the whole is more brilliant than the parts. *Adv. Mater.* **2014**, *26*, 5429-5479.
9. 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.
10. Kwok, R. T.; Leung, C. W.; Lam, J. W.; Tang, B. Z., Biosensing by luminogens with aggregation-induced emission characteristics. *Chem. Soc. Rev.* **2015**, *44*, 4228-4238.
11. Feng, H.-T.; Yuan, Y.-X.; Xiong, J.-B.; Zheng, Y.-S.; Tang, B. Z., Macrocycles and cages based on tetraphenylethylene with aggregation-induced emission effect. *Chem. Soc. Rev.* **2018**, *47*, 7452-7476.
12. Hu, R.; Kang, Y.; Tang, B. Z., Recent advances in AIE polymers. *Polymer Journal* **2016**, *48*, 359.
13. Hu, R.; Leung, N. L.; Tang, B. Z., AIE macromolecules: syntheses, structures and functionalities. *Chem. Soc. Rev.* **2014**, *43*, 4494-4562.
14. Qin, A.; Lam, J. W.; Tang, B. Z., Luminogenic polymers with aggregation-induced emission characteristics. *Prog. Polym. Sci.* **2012**, *37*, 182-209.
15. Schatz, C.; Louguet, S.; Le Meins, J. F.; Lecommandoux, S., Polysaccharide-block-polypeptide copolymer vesicles: towards synthetic viral capsids. *Angew. Chem., Int. Ed.* **2009**, *48*, 2572-2575.
16. Wang, Y.; Xu, H.; Zhang, X., Tuning the amphiphilicity of building blocks: controlled self-assembly and disassembly for functional supramolecular materials. *Adv. Mater.* **2009**, *21*, 2849-2864.
17. Meng, F.; Zhong, Z.; Feijen, J., Stimuli-responsive polymersomes for programmed drug delivery. *Biomacromolecules* **2009**, *10*, 197-209.
18. Vriezema, D. M.; Comellas Aragonès, M.; Elemans, J. A.; Cornelissen, J. J.; Rowan, A. E.; Nolte, R. J., Self-assembled nanoreactors. *Chem. Rev.* **2005**, *105*, 1445-1490.
19. Zhang, X.; Zhang, X.; Tao, L.; Chi, Z.; Xu, J.; Wei, Y., Aggregation induced emission-based fluorescent nanoparticles: fabrication methodologies and biomedical applications. *J. Mater. Chem. B* **2014**, *2*, 4398-4414.

20. Wang, J.; Wang, S.; Zhou, Y.; Wang, X.; He, Y., Fast photoinduced large deformation of colloidal spheres from a novel 4-arm azobenzene compound. *ACS Appl. Mater. Interfaces* **2015**, *7*, 16889-16895.
21. Yan, L.; Zhang, Y.; Xu, B.; Tian, W., Fluorescent nanoparticles based on AIE fluorogens for bioimaging. *Nanoscale* **2016**, *8*, 2471-2487.
22. Zhao, Y.; Wu, Y.; Chen, S.; Deng, H.; Zhu, X., Building single-color AIE-active reversible micelles to interpret temperature and pH stimuli in both solutions and cells. *Macromolecules* **2018**, *51*, 5234-5244.
23. Wang, H.; Wu, C.; Xia, G.; Ma, Z.; Mo, G.; Song, R., Semi-crystalline polymethylene-b-poly (acrylic acid) diblock copolymers: aggregation behavior, confined crystallization and controlled growth of semicrystalline micelles from dilute DMF solution. *Soft matter* **2015**, *11*, 1778-1787.
24. Schöbel, J.; Karg, M.; Rosenbach, D.; Krauss, G.; Greiner, A.; Schmalz, H., Patchy Wormlike micelles with tailored functionality by crystallization-driven self-assembly: A versatile platform for mesostructured hybrid materials. *Macromolecules* **2016**, *49*, 2761-2771.
25. Fan, B.; Liu, L.; Li, J.-H.; Ke, X.-X.; Xu, J.-T.; Du, B.-Y.; Fan, Z.-Q., Crystallization-driven one-dimensional self-assembly of polyethylene-b-poly (tert-butylacrylate) diblock copolymers in DMF: effects of crystallization temperature and the corona-forming block. *Soft Matter* **2016**, *12*, 67-76.
26. Fan, B.; Xue, J.-Q.; Guo, X.-S.; Cao, X.-H.; Wang, R.-Y.; Xu, J.-T.; Du, B.-Y.; Fan, Z.-Q., Regulated fragmentation of crystalline micelles of block copolymer via monoamine-induced corona swelling. *Macromolecules* **2018**, *51*, 7637-7648.
27. Gilroy, J. B.; Gädt, T.; Whittell, G. R.; Chabanne, L.; Mitchels, J. M.; Richardson, R. M.; Winnik, M. A.; Manners, I., Monodisperse cylindrical micelles by crystallization-driven living self-assembly. *Nat. Chem.* **2010**, *2*, 566.
28. Hudson, Z. M.; Boott, C. E.; Robinson, M. E.; Rupar, P. A.; Winnik, M. A.; Manners, I., Tailored hierarchical micelle architectures using living crystallization-driven self-assembly in two dimensions. *Nat. Chem.* **2014**, *6*, 893.
29. He, W.-N.; Xu, J.-T., Crystallization assisted self-assembly of semicrystalline block copolymers. *Prog. Polym. Sci.* **2012**, *37*, 1350-1400.
30. Yang, J.; Liu, L.; Xu, J., Crystalline micelles of block copolymers. *Prog. Chem.* **2014**, *26*, 1811-1820.
31. Luo, J.; Shea, K. J., Polyhomologation. A living C1 polymerization. *Acc. Chem. Res.* **2010**, *43*, 1420-1433.
32. Shea, K.; Walker, J.; Zhu, H.; Paz, M.; Greaves, J., Polyhomologation. A living polymethylene synthesis. *J. Am. Chem. Soc.* **1997**, *119*, 9049-9050.
33. Shea, K. J., Polyhomologation: The living polymerization of ylides. *Chem. – Eur. J.* **2000**, *6*, 1113-1119.
34. Wang, D.; Zhang, Z.; Hadjichristidis, N., C1 polymerization: a unique tool towards polyethylene-based complex macromolecular architectures. *Polym. Chem.* **2017**, *8*, 4062-4073.
35. Li, Q. Z.; Zhang, G. Y.; Chen, J. Z.; Zhao, Q. L.; Lu, H. C.; Huang, J.; Wei, L. H.; D'agosto, F.; Boisson, C.; Ma, Z., Well - defined polyolefin/poly (ϵ -caprolactone) diblock copolymers: New synthetic strategy and application. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 511-517.
36. Lu, H. C.; Xue, Y.; Zhao, Q. L.; Huang, J.; Xu, S. G.; Cao, S. K.; Ma, Z., Well - defined amphiphilic polymethylene-b-poly (acrylic acid) diblock copolymers: New synthetic strategy and their self-assembly. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 3641-3647.

37. Xue, Y.; Lu, H.-C.; Zhao, Q.-L.; Huang, J.; Xu, S.-G.; Cao, S.-K.; Ma, Z., Polymethylene-*b*-poly (styrene-*co*-2, 3, 4, 5, 6-pentafluoro styrene) copolymers: synthesis and fabrication of their porous films. *Polym. Chem.* **2013**, *4*, 307-312.
38. Li, J.; Zhao, Q.-L.; Chen, J.-Z.; Li, L.; Huang, J.; Ma, Z.; Zhong, Y.-W., Highly ordered microporous films containing a polyolefin segment fabricated by the breath-figure method using well-defined polymethylene-*b*-polystyrene copolymers. *Polym. Chem.* **2010**, *1*, 164-167.
39. Zhang, H.; Gnanou, Y.; Hadjichristidis, N., Well-defined polyethylene molecular brushes by polyhomologation and ring opening metathesis polymerization. *Polym. Chem.* **2014**, *5*, 6431-6434.
40. Zapsas, G.; Ntetsikas, K.; Kim, J.; Bilalis, P.; Gnanou, Y.; Hadjichristidis, N., Boron “stitching” reaction: a powerful tool for the synthesis of polyethylene-based star architectures. *Polym. Chem.* **2018**, *9*, 1061-1065.
41. Shea, K. J.; Busch, B. B.; Paz, M. M., Polyhomologation: Synthesis of novel polymethylene architectures by a living polymerization of dimethylsulfoxonium methylide. *Angew. Chem., Int. Ed.* **1998**, *37*, 1391-1393.
42. Zhang, Z.; Zhang, H.; Gnanou, Y.; Hadjichristidis, N., Polyhomologation based on in situ generated boron-thexyl-silaboracyclic initiating sites: a novel strategy towards the synthesis of polyethylene-based complex architectures. *Chem. Commun.* **2015**, *51*, 9936-9938.
43. Zhang, Z.; Gnanou, Y.; Hadjichristidis, N., Well-defined 4-arm stars with hydroxy-terminated polyethylene, polyethylene-*b*-polycaprolactone and polyethylene-*b*-(polymethyl methacrylate)₂ arms. *Polym. Chem.* **2016**, *7*, 5507-5511.
44. Zhang, Z.; Altaher, M.; Zhang, H.; Wang, D.; Hadjichristidis, N., Synthesis of well-defined polyethylene-based 3-miktoarm star copolymers and terpolymers. *Macromolecules* **2016**, *49*, 2630-2638.
45. Zhang, H.; Banerjee, S.; Faust, R.; Hadjichristidis, N., Living cationic polymerization and polyhomologation: an ideal combination to synthesize functionalized polyethylene-polyisobutylene block copolymers. *Polym. Chem.* **2016**, *7*, 1217-1220.
46. Wang, D.; Hadjichristidis, N., Allyl borates: a novel class of polyhomologation initiators. *Chem. Commun.* **2017**, *53*, 1196-1199.
47. Xue, Y.; Zhang, S.-S.; Cui, K.; Huang, J.; Zhao, Q.-L.; Lan, P.; Cao, S.-K.; Ma, Z., New polymethylene-based AB₂ star copolymers synthesized *via* a combination of polyhomologation of ylides and atom transfer radical polymerization. *RSC Adv.* **2015**, *5*, 7090-7097.
48. Wang, H.; Xu, F.; Cui, K.; Zhang, H.; Huang, J.; Zhao, Q.; Jiang, T.; Ma, Z., Synthesis of polymethylene-*b*-poly(vinyl acetate) block copolymer *via* visible light induced radical polymerization and its application. *RSC Adv.* **2017**, *7*, 42484-42490.
49. He, Q.; Ren, J.; Ren, J.; Pang, K.; Ma, Z.; Zhu, X.; Song, R., Polymethylene-*b*-poly (acrylic acid) diblock copolymers: Aggregation and crystallization in the presence of CaCl₂. *European Polymer Journal* **2017**, *95*, 174-185.
50. Jiang, Y.; Zhang, Z.; Wang, D.; Hadjichristidis, N., An Efficient and general strategy toward the synthesis of polyethylene-based cyclic polymers. *Macromolecules* **2018**, *51*, 3193-3202.
51. Corey, E.; Chaykovsky, M., Dimethyloxosulfonium methylide ((CH₃)₂SOCH₂) and dimethylsulfonium methylide ((CH₃)₂SCH₂). Formation and application to organic synthesis. *J. Am. Chem. Soc.* **1965**, *87*, 1353-1364.

52. Zhang, H.; Alkayal, N.; Gnanou, Y.; Hadjichristidis, N., Anionic polymerization and polyhomologation: an ideal combination to synthesize polyethylene-based block copolymers. *Chem. Commun.* **2013**, *49*, 8952-8954.

For Table of Contents Use Only

Tetraphenylethene-Functionalized Polyethylene-based Polymers with Aggregation-Induced Emission

Yu Jiang, Nikos Hadjichristidis*

Table of Contents Graphic