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Aggregation-Induced Emission and Photocyclization of Poly(hexaphenyl-1,3-butadiene)s Synthesized from "1 + 2" Polycoupling of Internal Alkynes and Arylboronic Acids

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S Supporting Information

ABSTRACT: A new polymerization method for *in situ* generation of luminescent polymers with aggregation-induced emission characteristics from readily prepared or commercially available reactants was developed in this work. The "1 + 2" polycoupling of internal alkynes and arylboronic acids took place under mild reaction conditions and was tolerant to moisture, air, and monomer stoichiometric imbalance, furnishing poly(hexaphenyl-1,3-butadiene)s (PHBs) with partially or wholly conjugated structures in satisfactory yields. All the PHBs showed good solubility, thermal stability, and filmforming ability. Their optical properties could be easily tuned by proper monomer design and external perturbation. The PHBs underwent active photocyclization in both solution and



solid states, converting them to poly(dihydronaphthalene)s. Such a property made them promising materials for fabricating luminescent photopatterns. A new mechanistic pathway was proposed as supplementary to explain the aggregation-induced emission (AIE) phenomenon by studying the emission of PHBs and the corresponding model compound.

INTRODUCTION

Luminescent materials play a vital role in real-world applications and high-tech innovations. Most of the luminescent materials are used in the solid state, such as those for lighting and display devices, or in physiological environment for bioimaging agents or bioprobes. However, a majority of the luminescent materials are organic molecules composed of hydrophobic aromatics, which normally form aggregates in aqueous media. It is known that aggregate formation can partially or completely quench the emission of luminophores. Such aggregation-caused quenching (ACQ) effect has limited their applications in some areas. Aggregation-induced emission (AIE) is a photophysical phenomenon that is exactly opposite of the ACQ effect. Luminogens with AIE features (AIEgens) are weakly or nonemissive in the monodispersed state but are induced to emit intensely in the aggregate state.¹ Such a property enables AIEgens to find many applications in various

fields such as organic light-emitting diodes,² organic field-effect transistors,³ chemosensors,⁴ biosensors,⁵ and biomedical imaging agents.⁶ Compared with their small molecule counterparts, polymeric materials enjoy a wider scope of industrial applications due to their easy fabrication into large-area panel films by simple, cheap, and energy-saving techniques such as spin-coating. Their structure, topology, and functionality can be readily tuned by molecular engineering, which is sometimes difficult with low molecular weight materials. Because of such attractive perspectives, various synthetic strategies have been proposed to prepare AIE polymers.⁷

Scheme 1 shows the commonly adopted methodologies for synthesizing AIE polymers. Direct polymerization of AIEgen-

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Scheme 1. Polymerization Strategies toward AIE Polymers



Scheme 2. Polycoupling of Internal Diynes, Aryl Diiodides, and Arylboronic Acids



containing monomers or their copolymerization with other monomers generate (co)polymers with AIEgens embedded in the main chain (Scheme 1A). Alternatively, an AIEgen is attached to a polymerizable monomer, whose homopolymerization or copolymerization produces polymers with AIEgens as side chains (Scheme 1B). In addition to these routes, AIEinactive polymers can be endowed with AIE characteristics through postmodification (Scheme 1C). While these methods are versatile to generate AIE polymers with different structures, properties, and applications, functional AIEgen-containing monomers need to be presynthesized in time-consuming synthetic steps,⁸ and polymers with irregular structures may be generated as the polymer effect tends to prevent postpolymerization from proceeding to completion. Thus, the development of new synthetic tools for facile preparation of AIE polymers is of great importance to polymer chemists and materials scientists.

Recent studies have shown that AIEgens such as 1cyanotriarylethene and tetraarylethene with high regio- and stereoregularity can be generated from commercially available, non-AIE, functional reactants (aromatic internal alkynes, aromatic halides, and potassium ferrocyanide or arylboronic acids or aryl magnesium bromides) in the presence of transition-metal catalyst under mild reaction conditions.⁹ Thus, these organic reactions may provide conceptually new, operationally simple, and practical protocols for synthesizing AIE polymers. However, such possibility is less explored by polymer scientists. Tomita synthesized wholly aromatic poly-(arylene vinylene)s containing tetra-aryl-substituted olefin units in the main chain by the three-component coupling polymerization of dihaloarenes, aryldiboronic acids, and diphenylacetylene derivatives catalyzed by PdCl₂(CN)₂ and KHCO₃ in DMF/H₂O at 100 °C.¹⁰ Although soluble polymers were isolated in high yields, their molecular weights were low ($M_w \sim$ 4000). We also made efforts to prepare polymers with AIEgens generated *in situ* during the polymerization.¹¹ In the presence of PdCl₂ and NaF, the reaction of diynes, aryl diiodides, and arylboronic acids proceeded in a more efficient fashion, generating triarylphenyethene-containing polymers with higher molecular weights (M_w up to 18 000) and novel materials properties (Scheme 2). Although such a method is versatile for synthesizing AIE-active polymer, we would like to enrich the synthetic toolbox by developing systems using more simple reactants.

Recently, Miura and co-workers reported a palladiumcatalyzed oxidative coupling reaction of internal alkynes and arylboronic acids to produce multisubstituted 1,3-butadienes (Scheme 3).¹² Since hexaaryl-1,3-butadiene derivatives were reported as excellent AIE-active materials,¹³ we believed that

Scheme 3. Oxidative Coupling of Alkynes with Arylboronic Acids To Produce 1,4-Diaryl-1,3-butadienes





this reaction could be utilized for *in situ* generation of AIE units in the polymer chain. As this coupling occurs in a reactant ratio of 2:2,¹¹ polymers can be readily obtained by replacing one of the monomers from mono- to difunctionality. As internal alkynes and arylboronic acids can be readily functionalized, the properties of their associated polymers can be easily tuned.

In this work, we developed two new systems for preparing AIE polymers: (A) polycoupling of internal diynes with arylboronic acid and (B) polycoupling of diphenylacetylene with benzene-1,4-diboronic acid (Scheme 4). These polymerization reactions can be performed under mild and monomer stoichiometric imbalanced conditions in open air. They are also tolerant to various functional groups in the monomers. The obtained poly(hexaphenyl-1,3-butadiene)s (PHBs) possess good solubility in common organic solvents and high thermal stability. PHBs serve as ideal models for the mechanistic study of the AIE phenomenon. Investigation on the photocyclization reactions of PHBs let us gain further insight into the alternative pathways of the AIE process. In addition to the mechanism of restriction of intramolecular motion (RIM)^{1,4} proposed in our previous reports, here we identified that the restriction of intramolecular cyclization (RIC) is another elementary step in the AIE process, especially for olefin-based AIE systems.

EXPERIMENTAL SECTION

Materials and Instruments. Palladium acetate, silver carbonate, arylboronic acids, diphenylacetylene, and other reagents were purchased from Aldrich and used as received without further purification. Toluene, 1-butanol, tetrahydrofuran (THF), water, and other solvents were distilled before use. Monomers **1a**–**1c** were synthesized according to the procedures reported previously.¹¹

Details about the instruments for obtaining the high-resolution mass spectra (HRMS), gel permeation chromatography (GPC) curves, IR spectra, ¹H and ¹³C NMR spectra, thermogravimetric analysis (TGA) thermograms, UV spectra, and photoluminescence (PL) spectra are

given in the Supporting Information. Photocyclization and photopatterning were conducted in air at room temperature using 365 nm light obtained from a Spectroline ENF-280C/F UV lamp with a working power of 180 W.¹⁴

Polymer Synthesis. A typical procedure for the polymerization of 1a and 2a is given below as an example. Into a 25 mL tube with a magnetic stirrer were placed 0.1 mmol of 1a, 0.3 mmol of 2a, 0.01 mmol of Pd(OAc)₂, and 0.3 mmol of Ag₂CO₃ in 3 mL of solvent mixture (1.4 mL of toluene, 1.5 mL of 1-butanol, and 0.1 mL of H₂O). The mixture was stirred in open air at 120 °C for 13 h. The polymerization was terminated by pouring the mixture into a large quantity of methanol through a dropper filled with neutral Al₂O₃ to remove, if any, the catalyst residue and insoluble substrates. The precipitate was collected by filtration through a sand-core funnel. The crude product was then dissolved in THF, reprecipitated in methanol, and washed repeatedly before being dried under vacuum to a constant weight. Yellow powder of polymer Pla/2a was obtained in 56.9% yield (Table 5, entry 1). M_w 10 580; M_w/M_n 1.57. IR (film), v (cm⁻¹): 3024 (CH₃), 2940 (CH₂), 2866, 1602, 1507, 1245, 1175, 1021. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.21–6.46 (26H, aromatic protons), 3.85 (4H, CH₂ protons), 2.23 (6H, CH₃ protons), 1.71 (4H, CH₂ protons), 1.42 (4H, CH₂ protons). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 157.69, 145.28, 142.76, 132.01, 131.71, 128.94, 124.14, and 115.12 (aromatic carbons), 68.55, 29.69, and 26.35 (CH₂ carbons), 21.41 (CH₃ carbons).

P1a/2b. Yellow powder; yield 56.4% (Table 5, entry 2). M_w 6410; M_w/M_n 1.83. IR (film), v (cm⁻¹): 3054, 2930, 2857, 2730, 1670, 1560, 1508, 1387, 1285, 1210, 1174, 1015. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 9.87 (2H, CHO protons), 7.57–6.49 (26H, aromatic protons), 3.86 (4H, CH₂ protons), 1.71 (4H, CH₂ protons), 1.44 (4H, CH₂ protons). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 192.25 (CHO carbons), 158.92, 141.68, 134.94, 132.94, 131.97, 129.29, 126.29, 126.96, and 115.11 (aromatic carbons), 68.32, 29.70, and 26.35 (CH₂ carbons).

P1a/2c. Yellow powder; yield 62.6% (Table 5, entry 3). M_w 6420; M_w/M_n 1.19. IR (film), v (cm⁻¹): 3054, 2925, 2855, 1659, 1633, 1505, 1489, 1242, 1174, 1027. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.50–6.48 (26H, aromatic protons), 3.86 (4H, CH₂ protons), 1.71

(4H, CH₂ protons), 1.44 (4H, CH₂ protons). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 160.91, 159.90, 158.83, 157.92, 142.20, 140.79, 133.51, 131.88, 130.29, 128.94, 128.32, 127.18, 126.42, 124.14, 115.52, 114.54, and 113.90 (aromatic carbons), 68.36, 29.73, and 26.36 (CH₂ carbons).

P1b/2a. Yellow powder; yield 79.9% (Table 5, entry 4). M_w 8040; M_w/M_n 1.30. IR (film), v (cm⁻¹): 3051, 3021, 2955, 2924, 2868, 1655, 1604, 1508, 1284, 1240, 1174, 1110. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.37–6.47 (26H, aromatic protons), 3.88 (4H, CH₂ protons), 2.23 (6 H, CH₃ protons), 1.81 (4H, CH₂ protons). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 158.90, 142.03.68, 136.60, 133.15, 131.64, 130.35, 128.82, 128.04, 126.15, 115.17, and 113.82 (aromatic carbons), 67.96 and 26.56 (CH₂ carbons), 21.44 (CH₃ carbons).

P1c/2a. Yellow powder; yield 85.4% (Table 5, entry 5). M_w 6200; M_w/M_n 1.43. IR (film), v (cm⁻¹): 3076, 2053, 3022, 2923, 2854, 1670, 1681, 1597, 1387, 1505, 1442, 1182, 1111. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.05–6.85 (36H, aromatic protons), 2.25 (6H, CH₃ protons). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 149.53, 141.65, 134.94, 136.98, 131.79, 130.52, 128.41, 127.91, 126.74, 123.29, and 122.52 (aromatic carbons), 21.43 (CH₃ carbons).

P3/4. Yellow powder; yield 57.5% (Table 5, entry 6). M_w 2030; M_w/M_n 1.25. M_w/M_n 1.25. IR (film), v (cm⁻¹): 3076, 3025, 2957, 2924, 2858, 1643, 1491, 1442. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.25–6.94 (aromatic protons). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 144.72, 143.84, 142.20, 141.13, 132.02, 131.78, 130.83, 129.39, 128.13, 127.92, 127.02, and 126.54 (aromatic carbons).

Model Reaction. Model compound **5** was synthesized by the oxidative coupling of diphenylacetylene with *p*-tolylboronic acid. The experimental procedure was similar to the preparation of P1a/2a. Yellow solid was obtained in 49.6% yield (after purification by column chromatography). IR (film), *v* (cm⁻¹): 3078, 3052, 3021, 2921, 1597, 1509, 1489, 1443, 1346, 1181, 1028. ¹H NMR (400 MHz, CD₂Cl₂), δ (ppm): 7.22 (d, *J* = 7.2, 4H), 7.21 (s, 6H), 6.91 (m, 14H), 6.81 (d, *J* = 7.6, 4H), 2.24 (s, 6H). ¹³C NMR (100 MHz, CD₂Cl₂), δ (ppm): 144.92, 143.40, 142.38, 141.43, 140.44, 136.88, 131.77, 130.19, 128.47, 127.67, 126.84, and 126.30 (aromatic carbons), 21.41 (CH₃ carbons). HRMS (MALDI-ToF): *m/z* 538.2677 (M⁺, calcd 538.2661) (Figure S1 in the Supporting Information).

RESULTS AND DISCUSSION

Polymerization. To develop the oxidative coupling of alkynes and arylboronic acids into a facile tool for the synthesis

 Table 1. Effect of Reactant Ratio on the Polymerization of 1a

 and 2a^a

entry	$[1a]:[2a]:[Pd(OAc)_2]:[Ag_2CO_3]$	yield (%)	$M_{\rm w}$	$M_{\rm w}/M_{\rm n}$
1	1.0:3.0:0.10:3.0	36.2	7140	2.85
2	1.0:2.0:0.10:2.0	11.6	1510	1.09
3	1.2:2.0:0.10:2.0	6.1	1480	1.07
4	1.0:3.0:0.05:3.0	36.8	4030	2.16
5	1.0:3.0:0.10:2.5	39.9	5980	2.37

"Polymerization at 120 °C for 4 h in open air in the presence of $Pd(OAc)_2$ and Ag_2CO_3 . [1a] = 0.033 M. Solvent composition: THF/ 1-butanol/ $H_2O = 4/5/1$.

of AIE polymers, we synthesized or purchased such molecules 1-4 with mono- or bifunctional groups and optimized the reaction conditions with respect to reactant ratio, reaction time, temperature, ligand, and solvent composition by using 1a and 2a as model monomers. The polymerization of 1a and 2a was catalyzed by palladium acetate and silver carbonate in a mixture of THF/1-butanol/H₂O at 120 °C for 4 h in an open atmosphere with varied monomer ratio, catalyst loading, and oxidant content.¹² The effects of an excess amount of 2a (entry 1) and 1a (entry 3) and their ratio are shown in Table 1, entries

Table 2. Time Course and Other Effects on the Polymerization of 1a and $2a^{a}$

entry	time (h)	yield (%)	$M_{ m w}$	$M_{\rm w}/M_{\rm n}$
1	1	15.0	1810	1.11
2 ^b	4	36.2	7140	2.85
3 ^c	4	14.7	2990	1.43
4	13	48.5	14720	3.83
5 ^d	13	31.1	6210	1.83
6	18	32.8 ^e	10240	4.11

^{*a*}Polymerization at 120 °C in open air in the presence of $Pd(OAc)_2$ and Ag_2CO_3 . [1a]:[2a]:[Pd(OAc)_2]:[Ag_2CO_3] = 1:3:0.1:3. [1a] = 0.033 M. Solvent composition: THF/1-butanol/H₂O = 4/5/1. ^{*b*}Data taken from Table 1, entry 1. ^{*c*}Polymerization performed in a sealed system. ^{*d*}[1a] = 0.05 M. ^{*e*}Soluble fraction.

Table 3. Temperature and Ligands Effect on the Polymerization of 1a and $2a^{a}$

entry	temp (°C)	ligand	yield (%)	$M_{ m w}$	$M_{\rm w}/M_{\rm n}$
1	65		54.3	4820	2.07
2	95		42.3	5480	2.52
3 ^b	120		48.5	14720	3.83
4	120	L1	47.2	3910	1.79
5	120	L2	7.5	2540	1.19

^{*a*}Polymerization for 13 h in open air in the presence of Pd(OAc)₂ and Ag₂CO₃. [1a]:[2a]:[Pd(OAc)₂]:[Ag₂CO₃] = 1:3:0.1:3. [1a] = 0.033 M. Solvent composition: THF/1-butanol/H₂O = 4/5/1. ^{*b*}Data taken from Table 2, entry 4.

Table 4. Solvent Composition Effect on the Polymerization of 1a and $2a^a$

entry	THF/1-buOH/H ₂ O	$conc \ (M)$	yield (%)	$M_{ m w}$	$M_{\rm w}/M_{\rm n}$
1	1/2/0	0.033	trace		
2	0/10/1	0.036	51.0	7640	3.52
3 ^b	8/10/2	0.033	48.5	14720	3.83
4	$14/15/1^{c}$	0.033	56.9	10580	1.57

^{*a*}Polymerization at 120 °C for 4 h in open air in the presence of $Pd(OAc)_2$ and Ag_2CO_3 . [1a]:[2a]:[Pd(OAc)_2]:[Ag_2CO_3] = 1:3:0.1:3. [1a] = 0.033 M. ^{*b*}Data taken from Table 2, entry 4. ^{*c*}Solvent composition: toluene/1-buOH/H₂O = 14/15/1.

Table 5. Polymerization of Different Monomers^a

entry	polymers	yield (%)	$M_{ m w}$	$M_{\rm w}/M_{\rm n}$
1 ^b	P1a/2a	56.9	10580	1.57
2	P1a/2b	56.4	6410	1.83
3	P1a/2c	62.6	6420	1.19
4	P1b/2a	79.9	8040	1.30
5	P1c/2a	85.4	6200	1.43
6 ^c	P3/4	57.5	2030	1.25

^aPolymerization at 120 °C for 13 h in open air in the presence of $Pd(OAc)_2$ and Ag_2CO_3 . [1]:[2]:[Pd(OAc)_2]:[Ag_2CO_3] = 1:3:0.1:3. [1] = 0.033 M. Solvent composition: toluene/1-butanol/H₂O = 14/ 15/1. ^bData taken from Table 4, entry 5. ^c[3]:[4]:[Pd(OAc)_2]: [Ag_2CO_3] = 2:1.5:0.1:1.5. [4] = 0.1 M.

1–3. Results show that an excess amount of boronic acid led to the generation of a higher molecular weight polymer in a higher yield. This suggests that the polymerization can be carried out under stoichiometric imbalanced condition. Reducing the catalyst loading from 10% (entry 1) to 5% (entry 4) had lowered the molecular weight. Although lowering the oxidant

Scheme 5. Synthesis of Model Compound from Diphenylacetylene and p-Tolylboronic Acid





Figure 1. Photographs of single crystals of 5 taken under (A) bright field and (B) UV irradiation. (C) Molecular geometry of 5 in the crystal state.



Figure 2. ¹H NMR spectra of (A) 1a, (B) 2a, (C) 5, and (D) P1a/2a in (A, C, and D) CD_2Cl_2 and (B) D_2O . The solvent peaks are marked with asterisks.

content from 3.0 equiv (entry 1) to 2.5 equiv (entry 5) had slightly improved the yield (39.9%), it had decreased the molecular weight of the resulting polymer. Therefore, the reactant ratio in entry 1 was adopted for the below investigation.



Figure 3. ¹³C NMR spectra of (A) 1a, (B) 2a, (C) 5, and (D) P1a/2a in (A, C, and D) CD_2Cl_2 and (B) D_2O . The solvent peaks are marked with asterisks.



Figure 4. Absorption spectra of 5, P1a/2a, P1a/2b, P1c/2a, and P3/4 in THF solutions. Solution concentration: 10 μ M.

At a fixed reactant ratio, we tracked the time course on the polymerization (Table 2). When the reaction time was prolonged from 1 h (entry 1) to 4 h (entry 2) and then 13 h

Table 6. Optical Properties of PHBs and 5^{a}

	$\lambda_{\rm abs}~({\rm nm})$	$\varepsilon/10^4 \text{ (mol}^{-1} \text{ L cm}^{-1}\text{)}$	$\lambda_{\rm em}~({\rm nm})$		
P1a/2a	362	0.353	444		
P1a/2b	359	1.094	472		
P1c/2a	354	2.893	522		
P3/4	360	1.307	392		
5	349	1.315	432		
^{<i>a</i>} In THF solution. Abbreviation: λ_{abs} = absorption maximum, λ_{em} =					
emission maximum.					

(entry 4), both the molecular weight and yield of the obtained polymer were improved. Further lengthening the reaction time to 18 h, surprisingly, gave rise to insoluble gel (entry 6). The polymer may readily undergo intramolecular cyclization in such a long reaction time, converting to poly(dihydronaphthalene) with a poorer solubility. Details of photocyclization of Pla/2a will be discussed in the later section. Therefore, all the polymerization reactions were terminated at 13 h. Interestingly, when the polymerization was performed in open air (entry 2) rather than in a sealed tube (entry 3), the reaction efficiency was much higher. Such difference may be attributed to oxygen in air that facilitates the oxidation process in the reaction mechanism. Thus, the air-insensitive feature of this reaction largely simplifies the experimental operation. Increasing the monomer concentration from 0.033 M (entry 4) to 0.05 M (entry 5) had narrowed the polydispersity $(M_w/M_p = 1.83)$ but resulted in lower molecular weight and yield. Thus, the reaction condition was set at a monomer concentration of 0.033 M in open air and a reaction time of 13 h.

Temperature exerts a strong effect on the reaction efficiency from a thermodynamic point of view. For energy conservation, we tried to lower the reaction temperature from 120 to 95 °C or 65 °C (Table 3). However, in doing so, the molecular weight of the corresponding polymer (entries 1 and 2) was progressively lowered. Obviously, a higher temperature was more suitable for the polymerization. In previous studies,^{12b} phosphite or phosphate ligands had been found to increase the lifetime of catalysts and hence improve the polymerization result for this reaction system. Thus, the effect of tri-*p*-tolyl phosphite (L1) or triphenyl phosphate (L2) on the polymerization was tested. From the data shown in entries 4 and 5, neither of them could enhance the molecular weight and yield. Apparently, ligands are not necessary for this polymerization reaction.

Solvent is another crucial factor affecting the polymerization efficiency. According to the literature,¹¹ this reaction performs well in THF and is tolerant to moisture. Occasionally, water can even assist the reaction. This also was true in the polymerization system: only a trace amount of product was generated in the absence of water (Table 4, entry 1). On the other hand, THF possesses a high solvating power, which allows the propagating polymer chain to grow longer. Indeed, the final molecular weight of the resulting polymer will be lowered without its presence (entry 2, Table 4). Interestingly, it was later discovered that toluene outperformed THF as polymerization solvent (Table 4, entry 5) because a polymer with a narrower polydispersity was isolated in a higher yield (56.9%) under the same conditions. As a result, further experiments were carried out in a solvent mixture of toluene/1 $buOH/H_2O$ at a volume ratio of 14/15/1.

On the basis of the optimization result, we explored the monomer scope by using different internal diynes and arylboronic acids to construct PHBs with various structures. The results are summarized in Table 5. PHBs abbreviated as Pla/2a-c were synthesized from internal divne la and arylboronic acids with an electron-donating or electronwithdrawing group such as methyl (2a), aldehyde (2b), or fluoride (2c) substituents (entries 1–3). Among them, P1a/2a was obtained with the highest molecular weight, which was in accordance with the previous observation that electrondonating boronic acid was a preferred reactant for such reaction.¹² The obtained yields of all the PHBs were only moderate, probably due to the formation of bis-phenyl derivatives as byproducts. P1a-c/2a were prepared from internal divnes with different conjugation degree (entries 1, 4, and 5) and p-tolylboronic acid. The longer alkyl chain in P1a/ 2a made its growing chain more soluble in the solvent mixture during the polymerization, leading to its higher molecular weight than P1b/2a. The polymerization of 1,2-diphenylethyne (3) and 1,4-phenylenediboronic acid (4) generated P3/4, which contained solely phenylene and butadiene moieties along its backbone (entry 6). The close proximity of rings may lead to severe steric congestion, preventing the polymer chain to grow further and hence lead to low polymerization degree. On the other hand, the GPC result is obtained based on a calibration



Figure 5. (A) PL spectra of **5** in THF and THF/H₂O mixtures with different water fractions (f_w). Concentration: 10⁻⁵ M; excitation wavelength: 349 nm. (B) Plot of relative PL intensity (I/I_0) versus the composition of the THF/H₂O mixture of **5**. Inset: fluorescent photograph of THF/H₂O mixtures of **5** with water fractions of 70% and 80% taken under 365 nm UV irradiation from a hand-held UV lamp.



Figure 6. (A) Normalized PL spectra of model compound **5** in THF solution, solid, and THF/H₂O mixture with 99% water fraction. Excitation wavelength: 349 nm. (B) Relative brightness (B/B_0) of the fluorescent photographs of 99% aqueous mixture, THF solution, and powder of **5** taken under 365 nm UV irradiation from a hand-held UV lamp. B_0 = brightness of the THF solution. The relative brightness of the photographs was analyzed by a MATLABV program. Camera parameters: f/5.6, 1/10s, ISO 800.

curve of polystyrene. Considering the quite large structural difference between P3/4 and polystyrene, the actual molecular weight of P3/4 should be higher than the present value. Nevertheless, the ¹H NMR spectrum of P3/4 shown in Figure S6 exhibits broad aromatic proton resonances, which was suggestive of its polymeric nature. All the polymers including those with fully conjugated structures such as P1c/2a and P3/4 are completely soluble in common organic solvents such as THF, toluene, chloroform, and dimethylformamide.

Model Reaction. Model reaction was carried out to assist the structural characterization and property investigation of the PHBs. By coupling diphenylacetylene (3) with *p*-tolylboronic acid under conditions similar to those for the polymerization, model compound 5 was obtained (Scheme 5). The crystals of 5 emitted intense green light under UV irradiation (Figure 1). Analysis by X-ray crystallography revealed that the phenyl rings in 5 twisted in different extents around the butadiene core, suggesting a helical *s-cis* conformation (Figure 1C, Figure S2 and Table S2).

Structural Characterization. The structures of the PHBs and the model compound were analyzed by IR and NMR spectroscopies. The IR spectra of P1a/2a and its corresponding monomers 1a and 2a and model compound 5 are given in Figure S3 as an example. The absorption peaks at 2937 and 3078 cm^{-1} in the spectrum of Pla/2a were assigned to the stretching vibration of CH₂ and CH₃ groups in 1a and 2a, respectively. On the other hand, the absorption band at 1337 cm^{-1} in **2a** ascribed to B–O stretching vibration disappeared in the spectra of 5 and P1a/2a. More informative structural data were obtained from the ¹H NMR spectra (Figure 2). The methylene protons of 1a resonating at δ 3.99, 1.84, and 1.55 were all located at the same chemical shifts in the spectrum of Pla/2a. The resonance peak at δ 2.44 for the methyl protons of **2a** underwent an upfield shift to δ 2.23 in the spectra of **5** and P1a/2a. Neither 5 nor P1a/2a showed the resonance peak at δ 4.79 associated with the resonance of the boronic acid protons, demonstrating a complete consumption of such functional group by the polymerization reaction. Since the polymerization does not proceed in a regioselective fashion, regioisomeric units thus exist in the resulting polymers (Scheme 4). The change in the local electron environment will lead to peak shift. Therefore, the resonance of the methylene protons next to

the oxygen atom of 1a was splitted into a doublet at δ 3.86 and δ 3.77 in P1a/2a. Similarly, the aromatic protons ortho to the oxygen atom were now resonated at δ 6.58 and 6.44. The methylene proton resonances "b" and "c" in 1a were less affected as they were far away from the unsaturated moieties.

Likewise, the ¹³C NMR spectrum of P1a/2a inherited the resonance peaks for the methylene carbon absorptions of 1a at δ 68.85, 29.52, and 26.27 and the absorption peak of methyl carbon of 2a at δ 21.54. The signals for the triple bond carbon absorptions of 1a locating at δ 88.96 and 88.05 were absent in the spectra of both 5 and P1a/2a. Thus, the IR and NMR analyses have convincingly demonstrated the occurrence of the polymerization and clarified the polymer structure. The IR and NMR data for other PHBs are provided in the Experimental Section, which all confirm their structures as illustrated in Scheme 4.

Optical Properties. Measurement on the absorption and photoluminescence (PL) of the polymers enables us to better understand the photophysical properties of the PHBs and their structural features. As shown in Figure 4, the absorption maximum of the polymers fell in the range of 354–362 nm, which was in accordance with the reported values (Table 6).¹⁵ P1a/2b showed a redder emission than P1a/2a, probably due to the intramolecular charge transfer effect from the electronrich backbone to the electron-deficient aldehyde groups. Although P3/4 possessed a conjugated structure, it emitted at a shorter wavelength (392 nm) than other PHBs, presumably owing to its twisted molecular conformation caused by the steric hindrance between the phenyl rings.

Since hexaphenyl-1,3-butadiene (HPB) is a typical AIEgen,¹² model compound 5 and PHBs are anticipated to be AIE-active as well. As shown in Figure 5, the dilute THF solution of 5 was barely emissive under UV illumination. When its hydrophobic molecules formed nanoaggregates in THF/water mixtures with water fractions (f_w) of 80% or higher,¹⁴ their emission was turned on, with the intensity at 95% water content being ~9-fold higher than that in pure THF solution. The photographs of THF solution, suspended aggregates, and solid powders of 5 taken under UV irradiation are given in Figure 6, in which the emission of the solid powders captured by a camera and analyzed by a MATLAB program¹⁵ is 10-fold brighter than its solution. Likewise, P1a/2a, P1a/2b, and P1c/2a exhibited



Figure 7. PL spectra of (A) Pla/2a, (C) Pla/2b, and (E) Plc/2a in THF and THF/H₂O mixtures with different water fractions (f_w) . Concentration: 10^{-5} M; excitation wavelength (nm): (A) 362, (C) 359, and (E) 354. Plot of relative PL intensities (I/I_0) versus the compositions of the THF/H₂O mixtures of (B) Pla/2a, (D) Pla/2b, and (F) Plc/2a. Insets: fluorescent photographs of THF/H₂O mixtures of (B) Pla/2a, (D) Pla/2b, and (F) Plc/2a. Insets: fluorescent photographs of THF/H₂O mixtures of (B) Pla/2a, (D) Pla/2b, and (F) Plc/2a.

similar AIE or aggregation-enhanced emission (AEE) phenomenon (Figure 7), demonstrating that this polymerization method was highly efficient for *in situ* generation of AIE polymers. Besides, the varied emission colors of the PHBs proved the efficacy of the functional groups in tuning the photophysical properties of the polymers (insets in Figure 7B, D, F).

Notably, the emission of 5 (Figure 6A), P1a/2a (Figure 7A), P1a/2b (Figure 7C), and P3/4 (Figure 8) all experienced a bathochromic shift when aggregates formed. For example, 5 emitted at 432 and 489 nm in THF and 99% aqueous mixture,

respectively. Considering that the amorphous powder of HPB was reported to emit at 493 nm,¹² the much bluer emission observed in the solution state seemed abnormal. Crystal analysis and theoretical calculation (Table S2) suggested that the molecules of **5** showed similar dihedral angles in the solution and crystal states. Thus, such a phenomenon did not likely result from their conformational difference. On the other hand, P3/4 exhibited two distinct emission bands at about 392 and 527 nm in THF and THF/water mixtures, whose intensities varied with the water content (Figure 8A). Since the absorption maximum changed little with the composition of



Figure 8. (A) PL spectra of P3/4 in THF and THF/H₂O mixtures with different water fractions (f_w). Concentration: 10⁻⁵ M; excitation wavelength: 360 nm. (B) Plot of relative PL intensity (I/I_0) at 528 nm versus the composition of the THF/H₂O mixture of P3/4.





the THF/water mixture (Figure S4), excimer formation seems to be ruled out for such possibility.¹⁷ On the other hand, we noticed that the PL spectrum of tetraphenylethene (TPE) exhibited a similar phenomenon,¹⁸ and the emission at the bluer region was proved to be caused by its photocyclization in the presence of UV irradiation, producing 9,10-diphenyl-phenanthrene as the product. We further noticed that HPB derivatives could undergo photoinduced cyclization to generate

their cycloisomers, namely dihydronaphthalene (DHN).¹⁹ Thus, there is a large possibility that the shorter-wavelength emission in the PL spectra of **5**, P1a/2a, P1a/2b, and P3/4 arise from the DHN moieties in their backbones.

With such presumption, the PL spectra of 5, P1a/2a, P1a/ 2b, and P1c/2a can be better explained. In the presence of UV irradiation, 5 and the hexaphenylbutadiene moieties in PHBs undergo photocyclization, generating DHN which is highly



Figure 9. ¹H NMR spectra of **5** in CD_2Cl_2 before and after UV irradiation for 0, 30, 60, 90, and 120 min. The solvent peaks are marked with asterisks.



Figure 10. ¹H NMR spectra of P1c/2a in CD_2Cl_2 before and after UV irradiation at different times. The solvent peaks are marked with asterisks.

emissive in the bluer region in solutions. During the gradual addition of water into their THF solutions, their PL spectra showed a superficial bathochromic shift due to the mathematic superposition of the emission bands of both HPB and DNH. In P1c/2a, the emission of the TPE units in the aggregate state was so intense that the PL of DHN was neglected.

Photocyclization. In order to verify our hypothesis, we further investigated the photocyclization of **5** and PHBs. The proposed mechanism is illustrated in Scheme 6.¹⁸ Because of the steric effect of the periphery phenyl rings, **5** took a twisted *s-cis* conformation. The close proximity of the alkene and the *ortho* phenyl carbons led to facile cyclization followed by a subsequent irreversible [1,5]-hydrogen shift, affording pentaphenyl DHN **6**. Likewise, P1/2a and P3/4 could be cyclized into poly(dihydronaphthalene)s (PDHNs, P7–9). Since the



Figure 11. Conversion for the photocyclization of 5, P1a/2a, P1c/2a, and P3/4 at different irradiation times.



Figure 12. ¹H NMR spectra of a solution of tetraphenylethene before and after UV irradiation for different times in DMSO- d_6 . The conversion was calculated from the peak integral and was determined to be 0%, 3.5%, 4.5%, and 5.0% at 0, 30, 60, and 120 min, respectively.

reaction condition is fairly mild for this reaction (UV irradiation in air at room temperature), it is possible that some photocyclized products have already been formed during the material preparation.

¹H NMR spectroscopy is a facile tool for monitoring the structural change. The solutions of **5**, P1a/2a, P1c/2a, and P3/4 (~20 mg/mL) were irradiated by UV light and analyzed by NMR spectroscopy at different times. The time-dependent ¹H NMR spectra of **5**, P1a/2a, P1c/2a, and P3/4 are given in Figures 9 and 10 and Figures S5 and S6. In Figure 9, the newly emerged resonance peak at δ 4.30 was attributed to the methine protons of **6**, whose intensity kept increasing with the irradiation time. The peak located at δ 2.25 was assigned to the methyl protons of **5**, which shifted into several peaks after UV irradiation and was indicative of the gradual conversion of **5** to **6**. Similarly, the resonance peaks for the methine protons of the DHN units in P7, P8, and P9 were located at δ 4.22, 4.19, and 4.41, respectively, and their intensities were gradually augmented during the irradiation process.

By calculating the integration of the resonance peaks for the methine and methyl/aromatic protons, we can estimate the



Figure 13. (A) Normalized absorption and emission spectra of P1a/2a and P7 in THF solutions. Concentration: 10^{-5} M; excitation wavelength: 362 nm. Inset: fluorescent photos of (left) P1a/2a and (right) P7 in THF solutions taken under 365 nm UV irradiation from a hand-held UV lamp. Concentration: 10^{-3} M. (B) PL spectra of THF solutions of P1a/2a and P7 and THF/water mixture of P7 (1:99, v/v). Inset: fluorescent photos of (left) THF solution and (right) 99% aqueous mixture of P7 taken under 365 nm UV irradiation from a hand-held UV lamp.



Figure 14. ¹H NMR spectra of P1a/2a (A) before and (B, C) after UV irradiation for 90 min in the (B) solution and (C) solid thin film states for 90 min in (A, B) CD_2Cl_2 and (C) $CDCl_3$.



Figure 15. Fluorescent photo of P1a/2a dip-coated on a piece of filter paper after UV irradiation for 2 h through a cardboard mask.

efficiency of the photocyclization. As shown in Figure 11, the ultimate conversion of 5, P1a/2a, P1c/2a, and P3/4 are 76.2%

at 120 min, 54.0% at 90 min, 66.8% at 240 min, and 61.5% at 160 min, respectively. Such difference is closely related to their structures. Compared to the low molecular weight model compound, the polymer backbones are more difficult to twist. This has lowered the chance for the reaction sites to approach each other for cyclization.

A control experiment was carried out to study the potential photocyclization reaction of the TPE moieties in P1c/2a. Analysis by ¹H NMR spectroscopy of a solution of TPE (Figure 12) suggested that only 5.0% of TPE were photocyclized into 9,10-diphenylphenanthrene after UV irradiation for 120 min. Such value was much lower than that achieved by HPB. The characteristic resonance peak for 9,10-diphenylphenanthrene at δ 8.96 in Figure 12 was absent in the spectra of P1c/2a (Figure 10), suggesting that the major photocyclized product was DHN (Figure 10).

Owing to the structural change, the optical properties of the PHBs are tuned after UV-induced cyclization. The normalized absorption and emission spectra of Pla/2a before and after photocyclization, for example, are obviously different (Figure 13A). The absorption band attributed to the HPB moiety was located at 362 nm in P1a/2a, which became much weaker in P7. The emission spectrum of P7, on the other hand, was 30 nm blue-shifted from that of Pla/2a with a narrower bandwidth because the latter polymer was more conjugated and its spectrum also combined the spectrum of DHN. Notably, unlike P1a/2a, P7 was no longer AIE-active. As shown in Figure 13B, the solution of P7 was much more emissive than its suspended aggregates. Such aggregation-caused quenching effect may be due to the $\pi - \pi$ stacking of the DHN cores in the aggregate state. Although the HPB units in P1c/2a also underwent photocyclization upon UV light irradiation, the emission of its photocyclized product P8 was still dominated by the TPE units in the backbone. Thus, P8 preserved the AIE characteristic of P1c/2a (Figure S7).

The efficient photocyclization of PHBs' solutions spurs us to investigate whether such reaction can be carried out in the solid state. Thus, a thin film of P1a/2a was spin-coated on silica wafer, and after being UV irradiated in air for 90 min, NMR analysis was carried out. The appearance of the resonance peak for the methine protons in solution at δ 4.20 was also found in the UV-irradiated film, indicating that the photocyclization



Figure 16. Restriction of intramolecular cyclization: AIE mechanism in butadiene-containing materials.



Figure 17. TGA thermograms of P1/2 and P3/4.

reaction could readily took place in the solid state (Figure 14B). The conversion estimated from the peak integral was approximately 49.1% according to the integration, making this reaction a simple tool to change the polymer structure and property.

Photopatterning. Because of the high photosensitivity of P1a/2a and the ACQ feature of P7, we explored the potential application of P1a/2a as a photopatterning material. We fabricated a thin film of P1a/2a on a piece of filter paper by dipcoating and then shielded part of paper by black cardboard in the letter form of "AIE". After UV irradiation for 2 h, the cardboard was removed. While the unexposed or covered region exhibited blue emission, the irradiated part appeared dark under UV illumination (Figure 15). This is because in the presence of UV light the AIE-active P1a/2a is photocyclized into P7 with ACQ effect. Such a result demonstrates a facile approach for the microfabrication of photopatterns by UV lithography.

Restriction of Intramolecular Cyclization. From the study above and the literature reports,^{18,20} we can gain some mechanistic insight into the AIE process. As we know, RIM, including intramolecular rotation and vibration, is responsible for the AIE or AEE of some molecules.^{1,4} Here, we propose that for hexaarylbutadiene derivatives and polymers containing butadiene skeletons RIC is the cause for their AIE feature. As

illustrated in Figure 16, the butadiene derivatives could undergo intramolecular twist to a *cis* conformation in the solution state, subsequent photocyclization of which generated dihydronaphthalene. The photocyclized products may suffer π – π stacking or excimer/exciplex formation in the aggregate state, which quench their emission. However, the intramolecular rotation of the butadiene core is much difficult in the aggregate state. As a result, photocyclization is less likely to occur, leading to the preservation of the strong emission. In PHBs, the butadiene units may adopt a predominant *trans* conformation to prevent steric hindrance between segments; coupled with their high molecular weight and hence slow rotation, butadienebearing polymers should be more difficult to be photocyclized, which is consistent with our result on the different conversion for molecules and polymers with different structures.

Thermal Stability. Polymers with high thermal stability are good candidates as heat-resistant materials. As shown in Figure 17, all the PHBs lose merely 5% of their weight at high temperatures of 380-445 °C. In particular, P1c/2a (445 °C) showed a much higher heat resistance than other polymers, thanks to its high aromatic content. The high thermal stability of the PHBs makes them promising functional materials for real-world applications.

CONCLUSIONS

In this work, we have demonstrated an efficient method to prepare PHBs by a palladium-catalyzed oxidative polycoupling of internal alkynes and arylboronic acids. This polymerization reaction realized *in situ* generation of AIEgens in the polymer backbones from a wide monomer scope. PHBs with electrondonating or -withdrawing pendants were readily obtained under mild and monomer nonstoichiometric conditions in the presence of moisture and oxygenic species. The PHBs enjoyed good film-forming capability and high thermal stability. The strong solid-state emission of the PHBs enabled their films to serve as high-contrast photopatterning materials. The PHBs could undergo facile photocyclization in air under UV irradiation, during which the optical properties of the polymers were tuned. By analysis of such process, deeper mechanistic insights into the AIE phenomenon could be obtained.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.6b01148.

Details of the instrumental analysis, HRMS spectrum of 5, crystal data and structure refinement of 5, computational calculation of 5, dihedral angles of 5 in single crystal, solution and gas states, IR spectra of 1a, 2a, 5, and P1a/2a, absorption spectra of P3/4, ¹H NMR spectra of P1a/2a and P3/4 before and after photocyclization, PL spectra of P8 (PDF)

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Notes

The authors declare no competing financial interest.

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