

Regio- and Stereoselective Polymerization of Diynes with Inorganic Comonomer: A Facile Strategy to Conjugated Poly(*p*-arylene dihalodiene)s with Processability and Postfunctionalizability

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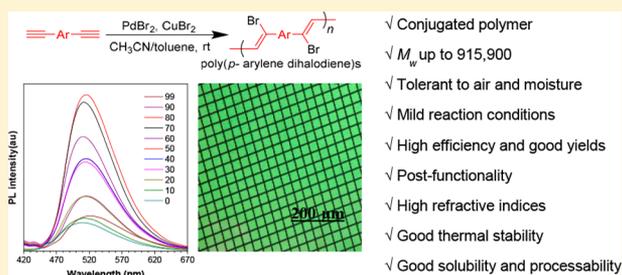
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Supporting Information

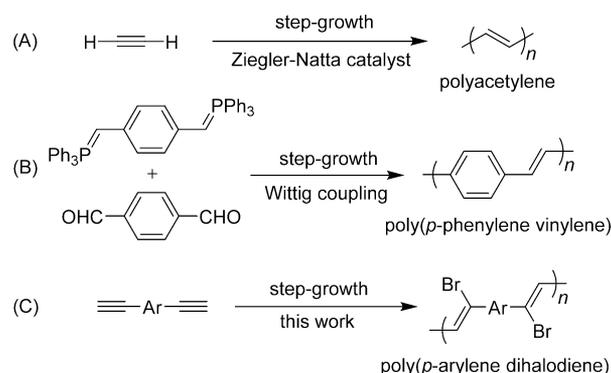
ABSTRACT: Development of new methodologies for synthesizing polymers with novel structures and unique properties is a fundamentally important area in polymer science. Herein, a novel synthetic strategy to conjugated poly(*p*-arylene dihalodiene)s (PADs) with high regio- and stereoselectivity was developed. In the presence of PdBr₂ and CuBr₂, the polymerizations of terminal alkynes proceeded smoothly in air without heating to generate PADs in high yields (up to 95.3%) with high molecular weights (*M_w* up to 915 900). Low-cost inorganic CuBr₂ played dual roles as cocatalyst and comonomer. The PADs possessed good solubility and film-forming ability. Their thin films exhibited high refractive indices (1.7149–1.7245) and would be fabricated into well-resolved fluorescent photopatterns by photolithography. Thanks to the vinyl bromine functionality, the PADs could undergo efficient postmodification to afford polymers with more sophisticated structures and applications.



INTRODUCTION

Polyolefins such as polyethylene and polypropene are synthetic polymers known for their excellent mechanical properties. However, they are electronically nonconjugated, which limits their advanced applications.^{1–3} On the contrary, conjugated polymers constructed from alkyne monomers show novel electronic and optical properties due to the unsaturated repeating units in the main chain, allowing them to serve as specialty materials. Among them, polyacetylene (PA) is the most pioneering and classical conjugated polymer and shows a high conductivity upon doping (Scheme 1A).⁴ Various catalysts have been developed to polymerize PA and its derivatives. For example, in the early stage, Ziegler-type catalysts can only polymerize unsubstituted and monosubstituted acetylenes to produce insoluble polymers or soluble oligomers.^{5–9} Metathesis catalysts based on group 5 and 6 transition metals (Nb, W, Mo, Ta) were developed to synthesize sterically crowded substituted PAs with improved solubility and enhanced functionalities.^{10–14} Unfortunately, these catalysts need to perform under harsh conditions, such as inert gas protection and high temperature; thus, they show little tolerance to functional groups of the monomers.^{13–17} Therefore, develop-

Scheme 1. Polymerization Routes to Conjugated Polymers

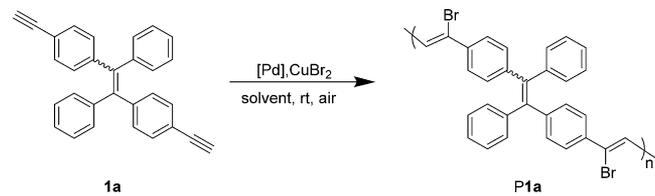


ment of new catalysts without such constraints is important for conjugated polymer research.

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Table 1. Optimization of Polymerization Conditions^a


entry	[Pd]	solvent ^b	yield (%)	M_w^c	M_w/M_n^c	S ^d
1	PdBr ₂	toluene/MeCN	81.8	166900	4.9	✓
2	PdCl ₂	toluene/MeCN	49.9	35700	3.7	✓
3	Pd(PPh ₃) ₂ Cl ₂	toluene/MeCN	trace			✓
4	Pd(OAc) ₂	toluene/MeCN	86.1	10400 ^e	2.3	▲
5	PdBr ₂	toluene	92.4	144900 ^e	2.5	▲
6	PdBr ₂	THF/MeCN	55.2	12500	1.9	✓
7	PdBr ₂	chloroform/MeCN	51.3	43400	3.8	✓
8	PdBr ₂	DCE/MeCN	52.1	92700	1.9	✓

^aCarried out at room temperature for 6 h in the presence of different catalysts, different solvents, and CuBr₂. [1a] = 0.04 M, [catalyst] = 0.004 M, [CuBr₂] = 0.24 M. ^bWhen mixed solvent system was used, the volume ratio was 50:1. Abbreviations: MeCN = acetonitrile, THF = tetrahydrofuran, DCM = dichloromethane, and DCE = 1,2-dichloroethane. ^cDetermined by GPC in THF on the basis of a linear polystyrene calibration. ^dSolubility (S) tested in common organic solvents, such as DCM, chloroform, and THF: ✓ = completely soluble; ▲ = partially soluble; × = insoluble. ^eSoluble fraction.

Another breakthrough in the field of conjugated polymer is the development of novel polymers with diverse structures. Thanks to the rapid progress of coupling chemistry, various kinds of conjugated polymers have been developed as alternatives for PA, among which poly(*p*-phenylene vinylene) (PPV) is one of the raising stars (Scheme 1B).¹⁸ Except for its electrical conductivity, PPV is famous for its excellent electroluminescence and has been used as emissive layer for the first polymer-based light-emitting diode in 1990.¹⁹ Similar to unsubstituted PA, unmodified PPV suffers from the solubility issue due to the strong interchain π - π stacking interactions. Fortunately, such a problem is easy to be solved in PPV by introducing long alkyl chains to its phenyl rings, albeit with a slight loss of conjugation. Different from PA, PPV is generally synthesized by two-component condensation polymerization such as Wittig coupling, Knoevenagel condensation, and Heck coupling.^{20–26} As a result, the stoichiometric balance of two monomers needs to be strictly followed to obtain high molecular weight polymers.

Despite significant achievements mentioned above, novel synthetic routes for synthesizing conjugated polymers with good solubility and functionalities under mild conditions are still in great demand. In 2004, Li et al. reported the dimerization of terminal alkynes by palladium catalyst to yield regio- and stereoselective (*Z,Z*)-1,4-dihalo-1,3-dienes in high yields under mild conditions.²⁷ The *cis*-addition of alkyne and PdX₂ proceeds to form a *cis*-halopalladation intermediate, which undergoes a consecutive *cis*-addition with alkyne to generate the final product with high regio- and stereoselectivity. Notably, symmetrical arylene diene structure similar to the repeating unit of PPV would be obtained efficiently. Therefore, this dimerization reaction is promising for constructing novel conjugated polymers.

In this work, a novel synthetic strategy to conjugated poly(*p*-arylene dihalodienes) (PADs) with high molecular weight and regio- and stereoselectivity was successfully developed (Scheme 1C). The polymerization suffered no strict control on the monomer stoichiometric balance. Inexpensive, nontoxic inorganic CuBr₂ was used as cocatalyst and comonomer. Because

of the presence of vinyl bromide functionality in the structure, the PADs could undergo postfunctionalization to generate polymers with high conversion rate. Such attributes make this polymerization route a promising tool for synthesizing conjugated and luminescent materials for various high-tech applications.

RESULTS AND DISCUSSION

To develop the dimerization of terminal alkynes into a facile polymerization tool to poly(*p*-phenyl dihalodienes), the reaction conditions should be optimized first. Except for introducing long alkyl chain, another strategy to improve the solubility of the resulting polymers is to utilize monomers with twisted structures to introduce large free volume between polymer strands. Recently, a new kind of luminogens with twisted structures and aromatic rotors has attracted great attention for their unusual photophysical phenomenon of aggregation-induced emission (AIE).²⁸ Luminogens with AIE characteristics (AIEgen) such as tetraphenylethene (TPE) are weakly or nonemissive in solution but display enhanced emission upon aggregation. Therefore, TPE-containing diyne 1a was used as monomer to impart the prepared polymer with good solubility and strong luminescence in the aggregated states.^{29,30} First, the catalytic effect was investigated (Table 1, entries 1–4) of different palladium(II) complexes. As suggested by the small molecular reaction, benzene is a good solvent for the dimerization. In this work, toluene was used instead because of its similar properties with benzene but much lesser toxicity. The polymerization of 1a was carried out in toluene in the presence of 2 vol % of acetonitrile with PdBr₂ and CuBr₂ at room temperature and afforded P1a with exceptionally high weight-average molecular weight (M_w) of 166 900 in 81.8% yield after merely 6 h (Table 1, entry 1). Replacing the catalyst to PdCl₂, however, had lowered the molecular weight (M_w of 35 700) of the resulting polymer in a much lower yield (49.9%) (Table 1, entry 2). A trace amount of polymeric product was obtained when Pd(PPh₃)₂Cl₂ was used as catalyst (Table 1, entry 3). Surprisingly, the polymerization proceeded vigorously with Pd(OAc)₂ to yield almost gelation product and polymer

Table 2. Polymerization of Different Monomers^a

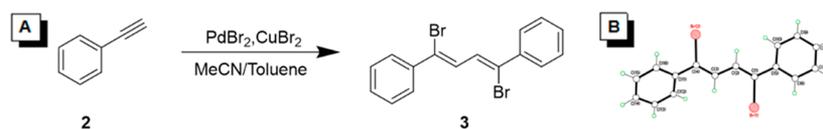
1a-d → P1a-d

R = 1a, 1b, 1c, 1d

entry	polymer	yield (%)	M_w^b	M_w/M_n^b	S^c
1 ^d	P1a	82.7	413100	5.0	✓
2	P1b	83.0	86100	2.0	✓
3	P1c	80.0	6400	1.5	✓
4	P1d				×

^aCarried out in toluene/MeCN mixture (50:1, v/v) at room temperature for 12 h in the presence of PdBr₂ and CuBr₂, [1] = 0.04 M, [PdBr₂] = 0.004 M, and [CuBr₂] = 0.24 M. ^bDetermined by GPC in THF on the basis of a linear polystyrene calibration. ^cSolubility (S) tested in common organic solvents, such as dichloromethane, chloroform, and tetrahydrofuran: ✓ = completely soluble; ▲ = partially soluble; × = insoluble. ^dData taken from Table S2, entry 3.

Scheme 2. Synthetic Route to Model Compound 3 and Its Crystal Structure



with low molecular weight ($M_w = 10\,400$) (Table 1, entry 4). The above results suggested that PdBr₂ was the most suitable candidate for the polymerization.

Afterward, the solvent effect on the polymerization was studied using PdBr₂ as catalyst (Table 1, entries 5–8). Although PAD with high molecular weight ($M_w = 144\,900$) would be obtained in pure toluene, its poor solubility in common organic solvents hindered its structural characterization (Table 1, entry 5). On the other hand, as shown in Table 1, entries 6–8, PADs obtained in THF/MeCN, chloroform/MeCN, and DCE/MeCN possessed only moderate to high molecular weights (12 500–92 700) and were synthesized in low yields (51.3%–55.2%). These results indicated that the solvent exerted strong influence on the polymerization. Among the solvents tested, toluene/MeCN mixture was identified as the best solvent system.

Then we tested the influence of monomer concentration, as shown in Table S1 of the Supporting Information, on the polymerization catalyzed by PdBr₂ in toluene/MeCN mixture. Partially soluble product with high molecular weight ($M_w = 374\,700$) was formed when the monomer concentration was slightly increased from 0.04 to 0.05 M (Table S1, entry 5). On the other hand, when the monomer concentration was lowered to 0.01 M, polymer with decreased molecular weight were obtained in low yield. Therefore, 0.04 M was chosen as the optimized monomer concentration as PAD with high molecular weight ($M_w = 166\,900$), and good solubility in common organic solvents could be generated in high yield (81.8%) at this concentration. CuBr₂ played a dual role as cocatalyst and monomer; thus, the effect of its feeding ratio on the polymerization was also studied. As shown in Table S1, entries 4, 6, and 7, although polymers with higher molecular weight were isolated at a lower feeding ratio of CuBr₂, they were

partially soluble in common organic solvents. Instead, high molecular weight polymers with good solubility were generated at an excess amount of CuBr₂ (6 equiv), suggesting that this polymerization does not constrained by strict monomer stoichiometric balance as required in traditional two-component polycondensation and polyaddition.

A series of experiments were conducted to investigate the time course of the polymerization under optimized conditions (Table S2). The yields increased considerably from 3 to 6 h (from 39.9% to 81.8%) and kept almost constant after 12 and 24 h. Besides, the molecular weight of the polymer increased linearly with the polymerization time, indicating a step-growth mechanism. After 24 h, partially soluble products with extremely high molecular weights ($M_w = 915\,900$) were obtained (Table S2, entry 4).

We then explored the monomer scope under optimized polymerization conditions. Monomer 1b is the structural isomer of monomer 1a with two alkyne groups located at the same side of the phenyl rings of TPE. Its polymerization generated polymer P1b with a much lower molecular weight than P1a (Table 2, entries 1 and 2). This might due to its higher steric crowded structure. This speculation was further supported by the low molecular weight of P1c formed by the polymerization of bulky tetraphenylpyrazine (TPP)-containing monomer 1c (Table 2, entry 3). P1d was obtained as a black powder by the polymerization of rodlike diyne 1d. It was completely insoluble in common organic solvents due to its rigid, linear, and fully conjugated structure (Table 2, entry 4).

Except for linear polymers mentioned above, functional hyperbranched polymers would demonstrate unique and interesting optical and electronic properties derived from their highly branched topological structures.^{31,32} Thus, we also tried to polymerize monomer 4 with four alkyne groups to

generate hyperbranched conjugated polymer (Scheme S1). However, due to the high efficiency of this polymerization, gel forms when we carried out the polymerization in toluene/MeCN mixture (50:1, v/v) at room temperature for 10 min in the presence of PdBr₂ and CuBr₂.

Model Reaction. Model compound **3** was synthesized according to the same reaction conditions for the polymer by dimerization of phenylacetylene **2** to verify the polymer structure and regio-/stereoselectivity (Scheme 2A). Compound **3** was isolated as a white solid in an almost quantitative yield (98%) and was fully characterized by standard spectroscopic techniques. Single crystals of **3** were obtained by slow diffusion of hexane into a dichloromethane solution of **3** at room temperature. Analysis by single-crystal X-ray diffraction confirmed the high regio-/stereoselectivity of the reaction as only structure of the (*Z,Z*)-isomer was obtained (Scheme 2B). Details of the crystal data and the high-resolution mass spectrum of the compound are given in Table S3 and Figures S1 and S2.

Structural Characterization. All the obtained polymers were fully characterized by standard NMR and IR spectroscopic techniques. The IR and NMR spectra of monomer **1a**, the model compound **3**, and the corresponding polymer **P1a** were selected and are given in Figure 1 for discussion. The ≡C–H

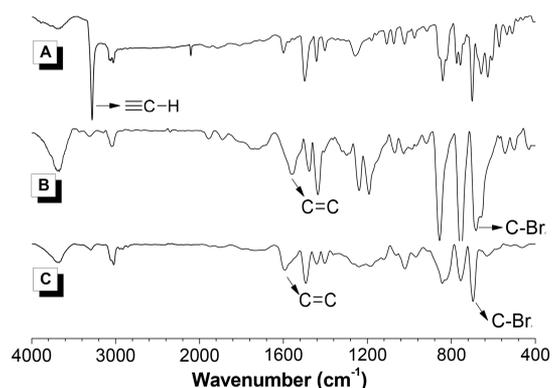


Figure 1. IR spectra of (A) **1a**, (B) **3**, and (C) **P1a**.

and C≡C stretching vibrations of monomer **1a** occurred at 3275 and 2106 cm⁻¹, respectively, which completely disappeared in the IR spectrum of **P1a**. On the other hand, new bands associated with C=C and C–Br stretching vibrations appeared in the spectra of model compound **3** and **P1a** at 1591 and 754 cm⁻¹. All these suggested the complete consumption of the monomer and the transformation of the C≡C bond of **1a** to vinyl bromide C=C–Br functionality of **P1a**.

Comparison between the ¹H NMR spectra of monomer **1a**, model compound **3**, and **P1a** provided a more detailed information on the polymer structure (Figure 2). The acetylene proton (a) of **1a** resonated at δ 3.03, which disappeared in the spectra of **3** and **P1a**. The peaks located at δ 7.40 were associated with the alkene proton absorption of **3** (b) and **P1a** (c) and suggested the generation of olefin double bond after dimerization. On the other hand, the peaks at δ 7.04–7.31 in **P1a** were associated with the resonances of the TPE unit. The ¹³C NMR spectra of **1a**, **3**, and **P1a** are given in Figure 3. The signal (a) at δ 84.0 was related to the absorption of the acetylene carbon of **1a**, which was not observed in the spectrum of **3** and **P1a**. Besides, the peak at δ 120.00 in monomer **1a** was

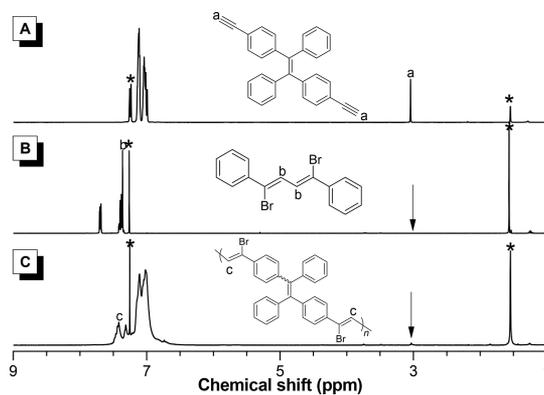


Figure 2. ¹H NMR spectra of (A) **1a**, (B) **3**, and (C) **P1a** in CDCl₃. The solvent peaks are marked with asterisks.

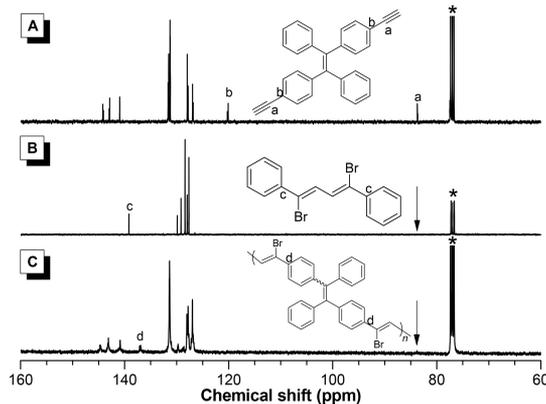


Figure 3. ¹³C NMR spectra of (A) **1a**, (B) **3**, and (C) **P1a** in CDCl₃. The solvent peaks are marked with asterisks.

associated with the resonance of the aromatic carbon (b) connected with triple bond, which shifted to δ 138.66 (c) and δ 136.91 (d) in **3** and **P1a**, respectively, due to the transformation of the triple bond to the olefin double bond by the dimerization reaction. The ¹H and ¹³C NMR spectra of **P1a** largely resembled those of **3**, suggesting that **P1a** possessed high regio- and stereoselectivity as well. The characterization data of other polymers are summarized in the Supporting Information and all solidly confirmed their corresponding structures (Figures S3–S8).

Solubility, Thermal Stability, and Light Refraction. Despite their conjugated backbone, all the PADs except **P1d** possessed good solubility. Such good solubility can be explained by the twisted conformations of TPE and TPP unit, which endowed a large free volume between polymer chains to accommodate more solvent molecules for solvation. On the contrary, the linear and rigid structure of **P1d** resulted in poor solubility as expected. Besides, the thermal properties of **P1a–c** were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis. All the polymers enjoyed high thermal stability, losing 5% of their weight at temperature ranging from 288 to 325 °C (Figure 4A). No signals associated with glass transition were detected in the DSC thermograms of **P1a–c** (Figure S9),³³ presumably due to their rigid structures.

High refractive indices polymers (HRIPs) are in high demand as they may serve as advanced optoelectronic materials. The real-world applications of HRIPs include high performance substrates for display devices, optical adhesives,

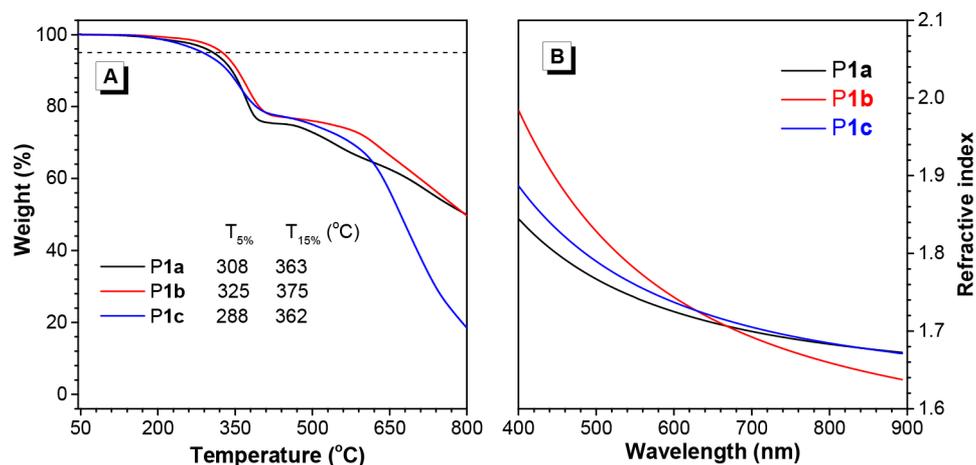


Figure 4. (A) TGA thermograms of PADs, recorded under N₂ at a heating rate of 10 °C/min. (B) Light refraction spectra of thin solid films of P1.

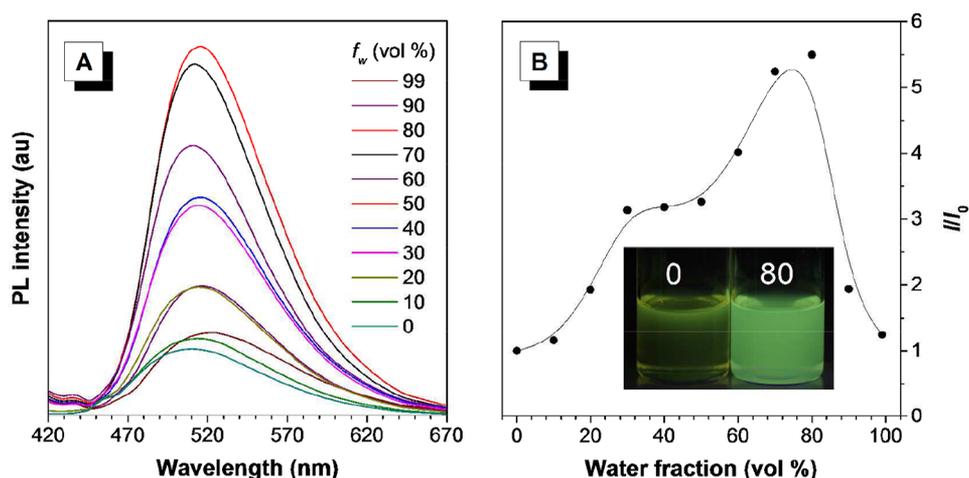
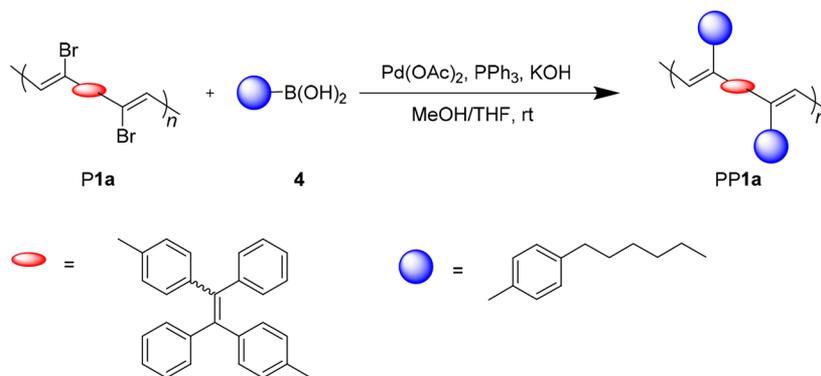


Figure 5. (A) Emission spectra of P1a in THF/water mixtures with different water fractions (f_w). Solution concentration: 10 μ M; excitation wavelength: 390 nm. (B) Plot of relative emission intensity (I/I_0) versus composition of the THF/water mixture of P1a. Inset: fluorescent photographs of P1a in THF solution and THF/water mixture with 80% water fraction taken under 365 nm UV illumination from a hand-held UV lamp.

Scheme 3. Synthetic Route to Postfunctionalized Polymer PP1a



encapsulants for organic light-emitting diode devices, and microlens components for the charge coupled device. Thanks to their good solubility, P1a–c could form tough films by spin-coating of their solutions. Their refractive indices (RI) were measured, and the results are shown in Figure 4B. The RI values of the polymer films at 632.5 nm (1.7149–1.7245) were all higher than conventional polymers (1.30–1.70). Such high values should be attributed to their conjugated structures

possessing bromide atoms, double bonds, and phenyl rings. Coupled with their good processability and high thermal stability, PADs clearly are promising materials for optoelectronic applications.

Photophysical Properties. The absorption and emission spectra of PADs in dilute THF solutions (10 μ M) are given in Figure S10. The absorption maximum (λ_{abs}) of P1a was located at 375 nm, while that of P1b was blue-shifted 40 nm due to its

weak conjugation. On the contrary, red-shifted λ_{abs} was observed in P1c because the TPP unit has stronger electronic interaction with the bromide atom than the TPE one.

Since TPE and TPP are typing AIEgens, polymers carrying these units are expected to be AIE-active as well.^{34,35} The emission behavior of P1a was investigated in THF and THF/water mixtures with different water fractions (f_w) as an example (Figure 5). Different from small molecular AIEgen, P1a already showed weak emission at 510 nm in pure THF solution. This was due to the partial restriction of the molecular motion of the TPE unit by the rigid polymer chain. Upon addition of poor solvent such as water into the THF solution, the P1a had enhanced its light emission gradually due to the aggregate formation. Further increasing the water fraction led to dramatic emission annihilation owing to the precipitation of large-sized aggregates at high water fraction.

Postfunctionalization. Generally, polymers with complicated structures and various functionalities are difficult to synthesize through direct polymerization of their corresponding monomers. Consequently, postfunctionalization of polymers is a powerful strategy to endow synthetic polymers with more sophisticated structures and tunable functionalities. The vinyl bromine functionality of P1 enables it to undergo various postfunctionalization via efficient named organic reactions such as Suzuki coupling. To demonstrate such possibility, we reacted P1a with boronic acid derivative 4 in the presence of Pd(OAc)₂, PPh₃, and KOH to generate PP1a in high yield (Scheme 3). To confirm the structure of PP1a, postfunctionalized model compound 5 was also synthesized and fully characterized (Scheme S2 and Figures S11 and S12). Comparing the spectroscopic data of 5 with PP1a demonstrated the success of the postfunctionalization (Figure 6). According to integrations of the ¹H NMR peaks, the conversion yield was calculated to be 80.0%, suggesting that P1a could serve as a versatile platform for postfunctionalization.

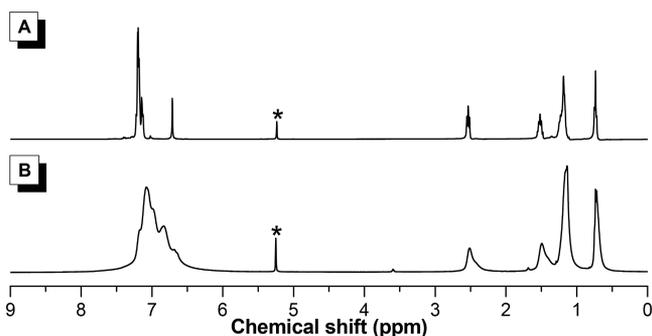


Figure 6. ¹H NMR spectra of (A) 5 and (B) PP1a in dichloromethane-d₂. The solvent peaks are marked with asterisks.

Besides, the long alkyl chain of PP1a also endowed it with an even better solubility than P1a. Both P1a and PP1a could form uniform thin films on silica wafers by spin-coating of their toluene solutions ($\sim 10 \text{ mg mL}^{-1}$). However, as shown in Figure S13A, although P1a was AIE-active, its thin film emitted weakly due to the heavy atom effect of the bromine atom. After postfunctionalization, 80.0% of bromine atoms were substituted by alkyl chains to relieve the heavy atom effect. Therefore, the film of PP1a demonstrated strong fluorescence (Figure S13B) and could be fabricated into a well-resolved fluorescent photopattern by irradiating with strong UV light (power = 180 W, intensity = $\sim 18.5 \text{ mW/cm}^2$) for 20 min in air through a

copper photomask. After irradiation, the fluorescence of the exposed parts (dark lines) was quenched due to photobleaching by photo-oxidation reaction, while the covered parts (squares) remained emissive. As shown in Figure S13C, a two-dimensional fluorescent photopattern with high resolution and sharp edges was fabricated without a complicated process.

CONCLUSION

In summary, we developed a novel and efficient synthetic strategy to poly(*p*-arylene dihalodiene)s with AIE characteristics. In the presence of PdBr₂ and CuBr₂, the polymerization of terminal alkynes proceeded smoothly without heating to generate PADs with high molecular weight and high thermal stability. The polymerization had various advantages such as mild conditions, tolerance to air and moisture, high efficiency, and good yield. An excessive amount of CuBr₂ could be used for the polymerization without strict control on the monomer stoichiometric balance as required in traditional two-component polycondensation and polyaddition. Monomers with twisted structures endowed the resulting polymers with good solubility and processability. The thin films of PADs showed high refractive indices and could be utilized for fabricating well-resolved fluorescent photopatterns by photolithography. The vinyl bromine functionality of PADs enables them to undergo postfunctionalization to afford materials with more sophisticated structures and applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b00435.

Materials and instrumentation, polymer synthesis, optimization of polymerization, structural characterization data of P1, model reaction, postfunctionalization reaction, HRMS spectra of 3 and PP1a, structural characterization (IR, ¹H NMR, and ¹³C NMR spectra) of P1b and P1c, DSC thermograms of P1, and single-crystal data of 3 (CCDC 1814311) (PDF)
X-ray crystallographic data of 3 (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Wang, J.-S.; Matyjaszewski, K. Controlled/"Living" Polymerization. Halogen Atom Transfer Radical Polymerization Promoted by a Cu(I)/Cu(II) Redox Process. *Macromolecules* **1995**, *28*, 7901–7910.
- (2) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process. *Macromolecules* **1998**, *31*, 5559–5562.
- (3) Guo, L.; Liu, W.; Chen, C. Late Transition Metal Catalyzed α -Olefin Polymerization and Copolymerization with Polar Monomers. *Mater. Chem. Front.* **2017**, *1*, 2487–2494.
- (4) Shirakawa, H. The Discovery of Polyacetylene Film: The Dawning of an Era of Conducting Polymers (Nobel Lecture). *Angew. Chem., Int. Ed.* **2001**, *40*, 2574–2580.
- (5) Watson, W. H., Jr.; Mcmordie, W. C., Jr.; Lands, L. G. Polymerization of Alkynes by Ziegler-Type Catalyst. *J. Polym. Sci.* **1961**, *55*, 137–144.
- (6) Aldissi, M. Review of the Synthesis of Polyacetylene and Its Stabilization to Ambient Atmosphere. *Synth. Met.* **1984**, *9*, 131–141.
- (7) Schrock, R. R. Multiple Metal-Carbon Bonds for Catalytic Metathesis Reactions (Nobel Lecture). *Angew. Chem., Int. Ed.* **2006**, *45*, 3748–3759.
- (8) Shiotsuki, M.; Sanda, F.; Masuda, T. Polymerization of Substituted Acetylenes and Features of The Formed Polymers. *Polym. Chem.* **2011**, *2*, 1044–1058.
- (9) Masuda, T.; Hasegawa, K.; Higashimura, T. Polymerization of Phenylacetylene. I. Polymerization of Phenylacetylene Catalyzed by WCl_6 and $MoCl_5$. *Macromolecules* **1974**, *7*, 728–731.
- (10) Masuda, T.; Higashimura, T. Polyacetylenes with Substituents: Their Synthesis and Properties. *Adv. Polym. Sci.* **1986**, *81*, 121–165.
- (11) Masuda, T. Substituted Polyacetylenes. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 165–180.
- (12) Wiberg, K. B.; Rablen, P. R. Substituent Effects. 5. Vinyl and Ethynyl Derivatives. An Examination of The Interaction of Amino and Hydroxy Groups with Carbon-Carbon Double and Triple Bonds. *J. Am. Chem. Soc.* **1993**, *115*, 9234–9242.
- (13) Furstner, A.; Davies, P. W. Alkyne Metathesis. *Chem. Commun.* **2005**, *18*, 2307–2320.
- (14) Melloni, G.; Modena, G.; Tonellato, U. Relative Reactivities of Carbon-Carbon Double and Triple Bonds toward Electrophiles. *Acc. Chem. Res.* **1981**, *14*, 227–233.
- (15) Schrock, R. R.; Czekelius, C. Recent Advances in The Syntheses And Applications of Molybdenum and Tungsten Alkylidene and Alkylidyne Catalysts for The Metathesis of Alkenes and Alkynes. *Adv. Synth. Catal.* **2007**, *349*, 55–77.
- (16) Bunz, U. H. F.; Kloppenburg, L. Alkyne Metathesis as a New Synthetic Tool: Ring-Closing, Ring-Opening, and Acyclic. *Angew. Chem., Int. Ed.* **1999**, *38*, 478–481.
- (17) Astruc, D. The Metathesis Reactions: From A Historical Perspective to Recent Developments. *New J. Chem.* **2005**, *29*, 42–56.
- (18) Shi, L.; Guo, Y.; Hu, W.; Liu, Y. Design and Effective Synthesis Methods For High-Performance Polymer Semiconductors in Organic Field-Effect Transistors. *Mater. Chem. Front.* **2017**, *1*, 2423–2456.
- (19) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. Light-Emitting Diodes Based on Conjugated Polymers. *Nature* **1990**, *347*, 539–541.
- (20) Babudri, F.; Farinola, G. M.; Lopez, L. C.; Martinelli, M. G.; Naso, F. A Synthetic Strategy Leading to Monodisperse PPV Oligomers by Coupling Reactions of Vinyltrimethylsilanes. *J. Org. Chem.* **2001**, *66*, 3878–3885.
- (21) Pan, M.; Bao, Z.; Yu, L. Regiospecific, Functionalized Poly(phenylenevinylene) Using the Heck Coupling Reaction. *Macromolecules* **1995**, *28*, 5151–5153.
- (22) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. Conjugated Liquid Crystalline Polymers-Soluble and Fusible Poly(phenylenevinylene) by the Heck Coupling Reaction. *Macromolecules* **1993**, *26*, 5281–5286.
- (23) Liao, J.; Wang, Q. Ruthenium-Catalyzed Knoevenagel Condensation: A New Route toward Cyano-Substituted Poly(p-phenylenevinylene)s. *Macromolecules* **2004**, *37*, 7061–7063.
- (24) Grisorio, R.; Mastrorilli, P.; Nobile, C. F.; Romanazzi, G.; Suranna, G. P. A Novel Synthetic Protocol for Poly-(fluorenylenevinylene)s: A Cascade Suzuki-Heck Reaction. *Tetrahedron Lett.* **2005**, *46*, 2555–2558.
- (25) Nomura, K.; Haque, T.; Onuma, T.; Hajjaj, F.; Asano, M. S.; Inagaki, A. Precise One-Pot Synthesis of End-Functionalized Conjugated Multi-Block Copolymers via Combined Olefin Metathesis and Wittig-type Coupling. *Macromolecules* **2013**, *46*, 9563–9574.
- (26) Becker, H.; Spreitzer, H.; Kreuder, W.; Kluge, E.; Schenk, H.; Parker, I.; Cao, Y. Soluble PPVs with Enhanced Performance – A Mechanistic Approach. *Adv. Mater.* **2000**, *12*, 42–48.
- (27) Li, J. H.; Liang, Y.; Xie, Y. X. Mild and Selective Palladium-Catalyzed Dimerization of Terminal Alkynes To Form Symmetrical (Z,Z)-1,4-Dihalo-1,3-dienes. *J. Org. Chem.* **2004**, *69*, 8125–8127.
- (28) Mei, J.; Leung, N. L. C.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem. Rev.* **2015**, *115*, 11718–11940.
- (29) Huang, H.; Qiu, Z.; Han, T.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. Synthesis of Functional Poly(propargyl imine)s by Multicomponent Polymerizations of Bromoarenes, Isonitriles, and Alkynes. *ACS Macro Lett.* **2017**, *6*, 1352–1356.
- (30) Deng, H.; Zhao, E.; Li, H.; Lam, J. W. Y.; Tang, B. Z. Multifunctional Poly(N-sulfonylamidine)s Constructed by Cu-Catalyzed Three-Component Polycouplings of Diynes, Disulfonyl Azide, and Amino Esters. *Macromolecules* **2015**, *48*, 3180–3189.
- (31) Mezzenga, R.; Boogh, L.; Manson, J. E. A Review of Dendritic Hyperbranched Polymer as Modifiers in Epoxy Composites. *Compos. Sci. Technol.* **2001**, *61*, 787–795.
- (32) Wu, W.; Tang, R.; Li, Q.; Li, Z. Functional Hyperbranched Polymers with Advanced Optical, Electrical and Magnetic Properties. *Chem. Soc. Rev.* **2015**, *44*, 3997–4022.
- (33) Qiu, Z.; Han, T.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. Polyarylcyanation of Diyne: A One-Pot Three-Component Convenient Route for In Situ Generation of Polymers with AIE Characteristics. *Macromolecules* **2016**, *49*, 8888–8898.
- (34) Liu, Y.; Roose, J.; Lam, J. W. Y.; Tang, B. Z. Multicomponent Polycoupling of Internal Diynes, Aryl Diiodides, and Boronic Acids to Functional Poly(tetraarylethene)s. *Macromolecules* **2015**, *48*, 8098–8107.
- (35) Chen, M.; Li, L.; Nie, H.; Tong, J.; Yan, L.; Xu, B.; Sun, J. Z.; Tian, W.; Zhao, Z.; Qin, A.; Tang, B. Z. Tetraphenylpyrazine-based AIEgens: facile preparation and tunable light emission. *Chem. Sci.* **2015**, *6*, 1932–1937.
- (36) Palma-Cando, A.; Woitassek, D.; Brunklaus, G.; Scherf, U. Luminescent Tetraphenylethene-Cored, Carbazole- And Thiophene-Based Microporous Polymer Films for The Chemosensing of Nitroaromatic Analytes. *Mater. Chem. Front.* **2017**, *1*, 1118–1124.