

# Synthesis of Functional Disubstituted Polyacetylenes Bearing Highly Polar Functionalities via Activated Ester Strategy

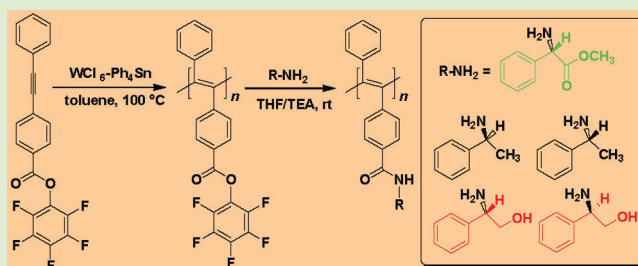
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## Supporting Information

**ABSTRACT:** We demonstrate a facile synthetic route to functional disubstituted polyacetylenes bearing highly polar groups based on polymer reactions. A pentafluorophenyl (PFP) ester-containing diphenylacetylene was designed and polymerized to obtain PFP activated ester-functionalized disubstituted polyacetylene (P1). P1 was used as a parent polymer to further react separately with diverse amines, giving rise to a series of functional disubstituted polyacetylenes with a chiral moiety and hydroxyl and carboxyl groups in high yields under mild condition. Spectral characterization data indicated that the polymers' structures were well consistent with the expected results. The helicity and emission property of polymers were also studied.



Owing to their potential applications in conducting materials, optoelectronics, biomedicine, and sensor, much attention has been paid to the design and synthesis of functional polyacetylenes.<sup>1–3</sup> The polymerization of mono-substituted acetylenic monomers was greatly facilitated by the development of Rh-based catalysts,<sup>4,5</sup> which are tolerant to various polar functional groups in the monomers and different solvents; thus, a series of monosubstituted functional polyacetylenes, such as poly(phenylacetylenes),<sup>6–10</sup> poly(1-alkynes),<sup>11–13</sup> poly(propiolates),<sup>14,15</sup> and poly(*N*-propargylamides),<sup>16–19</sup> have been successfully prepared. Disubstituted polyacetylenes have shown superior properties such as thermal stability and photoluminescence to their monosubstituted counterparts.<sup>20–26</sup> However, the synthesis of disubstituted polyacetylenes through a direct polymerization route proves difficult, for the polar functional groups tend to poison the early transition-metal-based metathesis catalyst systems, which are only effective for the polymerization of only a few disubstituted acetylenic monomers.<sup>1–3</sup> Alternatively, postpolymerization reactions,<sup>27–35</sup> such as ionization, deprotection reaction, click reaction, hydrazinolysis, and nucleophilic substitution, have been used to prepare functional disubstituted polyacetylenes. But these reactions are only suitable for very limited disubstituted acetylenic monomers. Exploring facile and ubiquitous synthetic routes toward disubstituted functional polyacetylenes is still a challenging task.

Recently, an activated ester strategy has been employed to modify the side chain of monosubstituted polyacetylenes by Theato's and our groups.<sup>36,37</sup> This strategy has shown great power in deriving a series of functional monosubstituted

polyacetylenes from the same precursor polymer. Using this strategy to prepare disubstituted polyacetylenes, however, is an untouched field. Inspired by the previous achievements, in this work, we report the synthesis of a pentafluorophenyl (PFP)-activated ester-functionalized poly(diphenylacetylene) (P1, Scheme 1). We used P1 as a precursor polymer to react stepwise with diverse chiral amines, which gives rise to disubstituted polyacetylenes with amide and other polar groups such as hydroxyl and carboxyl in high efficiency under mild reaction conditions.

The synthetic route toward poly(diphenylacetylenes) is shown in Scheme 1 (the detailed synthesis and characterization data are included in Supporting Information). Monomer **1** was synthesized according to Scheme S1 in a high yield of 85.8%. In our previous study, we succeeded in polymerizing diphenylacetylenes containing ester unit by  $WCl_6-Ph_4Sn$ .<sup>38,39</sup> We thus selected the same catalyst system to polymerize monomer **1**. The experiment data (Table S1) indicate that the polymerization of **1** proceeded smoothly and the derived polymer, or P1, was obtained in high yields (up to 64.7%) with high molecular weight ( $M_w \sim 247800$ ) and moderate polydispersity index (around 3.00) provided careful and elaborate procedures were followed.

NMR and FTIR spectroscopy were utilized to characterize the chemical structure of P1. The results are quite satisfactory corresponding to the expected molecular structures. Figure 1

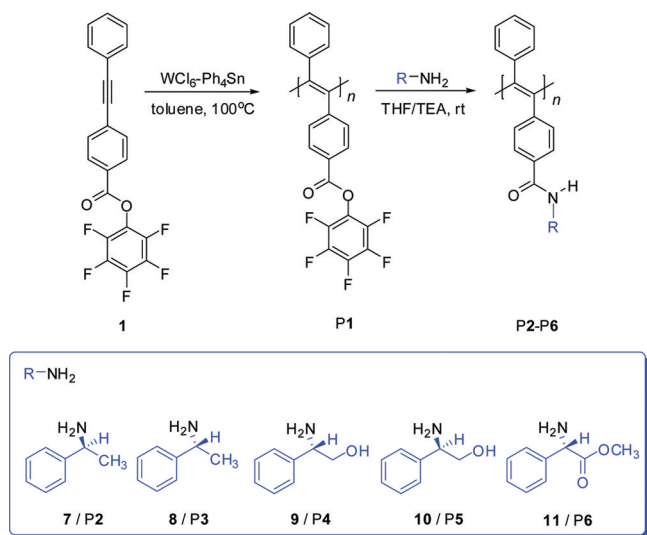
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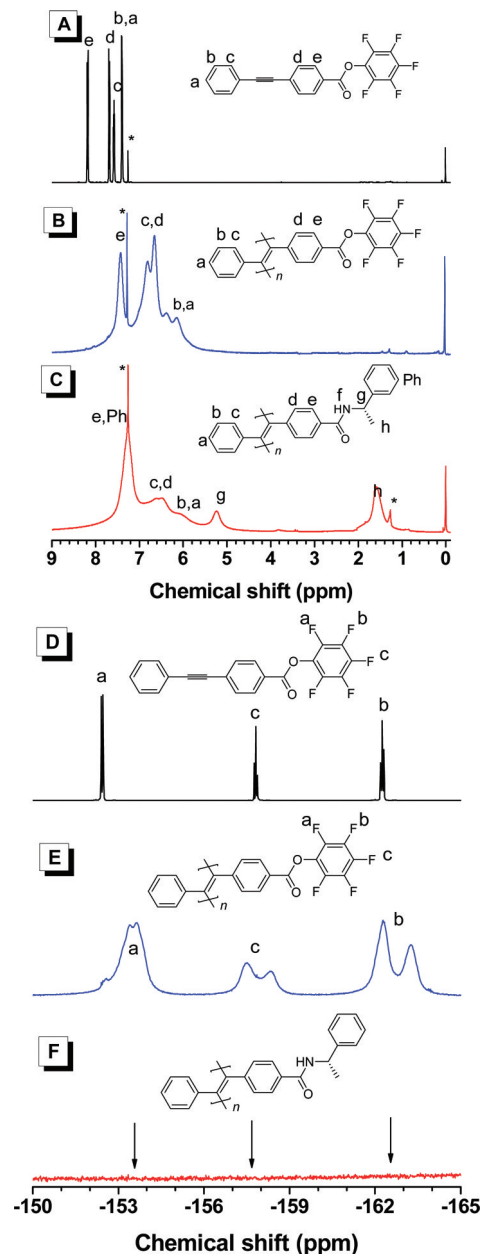


## Scheme 1



shows the  $^1\text{H}$  NMR spectra of P1 and its monomer **1**. For the polymer, there is no sharp resonance peaks at  $\delta \sim 8.19$ , 7.70, 7.57, and 7.40, which are associated with the phenyl protons linked to the triple bond of **1**, indicative of complete consumption of the monomer. The phenyl proton resonances of P1 are upfield shifted to  $\delta \sim 7.43$ , 6.82, 6.66, 6.38, and 6.15, owing to the transformation of the triple bond of **1** to the double bond of P1 by the polymerization. The broad peaks prove that the aromatic rings are directly linked to rigid polymer backbones. Both FTIR (Figure S1B) and  $^{13}\text{C}$  NMR (Figure S4B) data witness the disappearance of the carbon–carbon triple bond, and the peaks in the  $^{19}\text{F}$  NMR spectra of P1 are broadened as well in comparison with that of **1** (Figure 1D,E), further indicating that the polymerization proceeds and pure polymer is obtained.

It has been proven that the PFP ester can be easily and completely substituted by stronger nucleophilic reagents such as amines and alcohols.<sup>40–43</sup> Accordingly, P1 reacted separately with diverse chiral amines, including *L*- and *D*-2-phenylethyl amines (**7** and **8**), hydroxyl-containing *L*- and *D*-phenylalanylols (**9** and **10**), and carboxyl ester-containing *L*-methyl 2-amino-2-phenylacetate (**11**). After simply stirring the mixture of P1 and amine (P1/amine = 1:1.1, by molar ratio) in their THF solution at room temperature under nitrogen for 12 h (see Experimental Section in Supporting Information for details), the target polymers (P2–P6) were obtained in high yields (up to 95.4%) with similar molecular weights to that of their parent polymer P1 (Table S2). Compared with P1, in the  $^{19}\text{F}$  NMR spectra of P2, P4, and P6, the resonance peaks corresponding to F atoms disappeared completely (Figure 1F, Figures S3D and S3E); while in the  $^1\text{H}$  NMR spectrum of P2 (Figure 1C), two resonance peaks appear at  $\delta \sim 5.25$  and 1.59, which are associated with the protons on the chiral carbon and the adjacent methyl, respectively. The NMR data of all polymers (see Experimental Section for details) indicate that the activated PFP ester was fully substituted by amines. In addition, FTIR spectra provide further evidence. The stretching band of carbonyl group in PFP ester moiety of P1 appears at  $\sim 1764\text{ cm}^{-1}$  (Figure S1B), while for polymers P2, P4, and P6, this band totally disappears, indicating the full consumption of the activated PFP ester groups. Meanwhile, there emerges a new



**Figure 1.**  $^1\text{H}$  NMR spectra of (A) **1**, (B) P1 (Table S1, no. 3), (C) P2 (Table S2, no. 1), and  $^{19}\text{F}$  NMR spectra of (D) **1**, (E) P1 (Table S1, no. 3), (F) P2 (Table S2, no. 1) in chloroform-*d*. The solvent peaks are marked with asterisks.

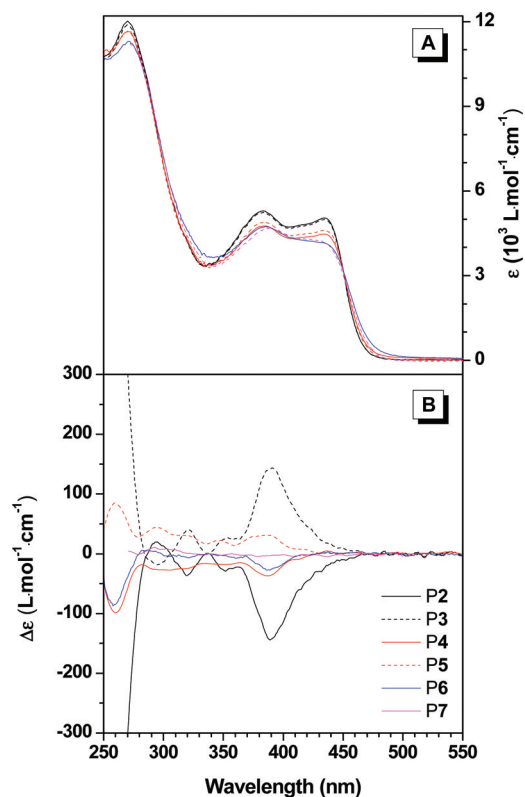
band at  $\sim 1640\text{ cm}^{-1}$ , corresponding to the stretching band of the carbonyl group in amide group.

Carboxyl-bearing disubstituted polyacetylene, or P7, was transformed from P6 via the hydrolysis of its pendant ester according to Scheme S2.<sup>44</sup> Owing to strong hydrogen bonding interactions among carboxyl groups, P7 cannot be dissolved in common solvents such as THF, chloroform, dichloromethane, and DMF which are good solvents for P1–P6. Luckily, DMSO was found to be a good solvent for P7. In its FTIR spectrum, the stretching band of carbonyl shifts to low frequency ( $\sim 1600\text{--}1640\text{ cm}^{-1}$ ), owing to the possible hydrogen bonding formation of carboxyl, while the band at  $\sim 1749\text{ cm}^{-1}$  in the spectrum of its precursor P6 is ascribed to the stretching band of the carbonyl group in  $\text{COOCH}_3$ . Successful and complete hydrolysis of ester was further confirmed by the  $^1\text{H}$  NMR

spectrum of P7 (Figure S2C), which show the disappearance of resonance peak associated with methyl protons of ester. Ionization of P7 by sodium hydroxide furnishes polyanion P7<sup>-</sup> (Scheme S2), a disubstituted polyacetylene-based polyelectrolyte that is soluble in water to give a clear yellow solution. Further studies on P7<sup>-</sup> are in progress.

It is known that disubstituted polyacetylenes have higher thermal stability than their monosubstituted counterparts. As shown in Figure S5, the three polymers (P1, P2, and P3) lose merely 5% of their weight when heated to ~415 °C ( $T_5$ ). The high thermal stability can be ascribed to the fact that the polymer backbone was wrapped by bulky and thermal stable phenyl groups. In addition, P1, P2, and P3 own very high molecular weight ( $M_w > 240000$ , see Tables S1 and S2), which plays a positive role in the thermal stability. In contrast, both P5 and P6 were prepared from P1 with relatively lower molecular weight ( $M_w \sim 70900$ , see Table S2), which imparts these polymers with a lower  $T_5$  of 329 °C (Figure S6).

The chiral pendants are believed to be able to induce backbone helicity if they are directly attached to monosubstituted polyacetylenes with highly stereoregular head-to-tail *cis-transoidal* conformation.<sup>45–48</sup> Recently, we discovered the helix induction of chiral pendant in disubstituted polyacetylenes,<sup>33</sup> although the polymers were prepared by W-catalyzed polymerization and thus took irregular stereostructures. Herein, we measured the circular dichroism (CD) spectra of P2–P6 in THF and P7 in DMSO, and the data are depicted in Figure 2B



**Figure 2.** UV (A) and CD (B) spectra of P2, P3, P4, P5, and P6 in THF and P7 in DMSO at room temperature. Concentration: 100  $\mu$ M. The spectral data in DMSO below 270 nm were not taken due to the interference of the solvent.

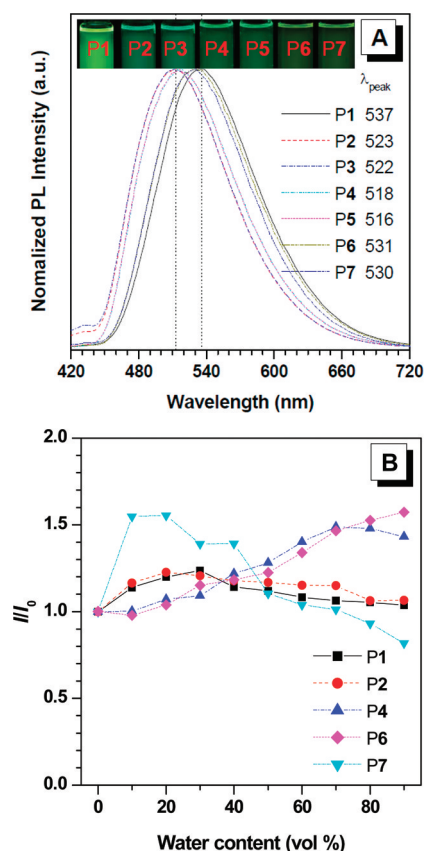
(detailed UV and CD spectra of the polymers in various solvents are displayed in Supporting Information). It is obvious that monomer 1 does not absorb at wavelength longer than 350

nm (Figure S7). Therefore, the absorption peaks of all polymers at 384 and 435 nm should be ascribed to the  $\pi$ – $\pi^*$  transition of the polyene backbone. Coincidentally, both P2 and P3 in THF display intense CD band at 390 nm with  $\Delta\epsilon$  ( $L\cdot mol^{-1}\cdot cm^{-1}$ ) of  $-145$  and  $144$ , respectively, owing to their opposite chiral pendants. Thus, the strong negative and positive Cotton effect observed at 390 nm are related to the absorption of the polymer backbone, offering articulate evidence that the main chain takes a helical conformation with a large excess of one-handedness. Similar to P2(P3), P4, and P5 in THF exhibit negative and positive Cotton effect at 390 nm as well, but with  $\Delta\epsilon$  ( $L\cdot mol^{-1}\cdot cm^{-1}$ ) as low as  $-32$  and  $34$ , respectively. Now that all polymers own stiff backbones with the same stereostructure, the difference in the intensity of Cotton effect is ascribed to the ability of the chiral pendant to induce the helicity. As a consequence, P6 in THF shows a weaker CD band, and P7 in DMSO exhibits no CD signals at the wavelength where the backbone absorbs. Solvent dependence of UV and CD spectra were also studied. Little spectral change was observed when the UV measurement was conducted in other solvents such as dichloromethane and DMF (Figures S8–S11), indicating that the ground-state electronic transitions of the polymers vary little with the solvent. Similar CD bands in various solvents are ascribed to the same helical conformation of the polymers.

The important characteristic of disubstituted polyacetylenes is their emission property. Figure 4A depicts the PL spectra of P1–P6 in THF and P7 in DMSO. In pure THF, P1 emits a yellowish green light at 537 nm when photoexcited at 394 nm. The fluorescence quantum ( $\Phi_F$ ) determined by using fluorescein ( $\Phi_F = 79\%$  in 0.1 M NaOH solution) is 22.4% (Table S3). Polymers P2–P5 in THF emit green light around 520 nm and P6 and P7 emit yellowish green light around 530 nm. The light color variation was caused by different conjugation length of the according polymer. Thus, we successfully tune the emission color through the substitution of PFP ester pendant with diverse chiral moieties. Addition of water into the polymer solution leads to PL intensity change and spectral red-shift (Figures 3B and S12). Indeed, as extreme aggregated state, polymer films of P1–P6 emit greenish yellow light (Figure S17). As a nonsolvent, water can cause the polymer chains to aggregate. Aggregation, on one hand, quenches the PL intensity of fluorophores due to the increase in the short-range interactions. On the other hand, aggregation could restrict the intramolecular motions of the phenyl fluorophores and, thus, would block the nonradiative decay of the excitons and boost the PL intensity. For P1 and P2, The first effect may be predominant and PL intensity begins decreasing when the water content is 30% and 20%, respectively (Figure 3B). As for P4 and P6, however, this critical water content changes to 70% and 80% due to lower molecular weight of polymers and moderate hydrogen bonding. With carboxylic pendant, P7 is so easy to aggregate that  $I/I_0$  value is below 1 when the water content is over 80%.

In summary, the activated ester-functionalized poly(diphenylacetylene) P1 has been successfully synthesized with desirable yield and high molecular weight. The activated ester groups in P1 were easy to be substituted with diverse amines and resulted in a series of disubstituted polyacetylenes with highly polar groups such as amide, carboxyl, and hydroxyl, which are incapable of being prepared by direct polymerization of respect monomers using Mo–W-based catalysts. Spectroscopic techniques including  $^1H$ ,  $^{13}C$ , and  $^{19}F$  NMR and FTIR





**Figure 3.** (A) PL spectra of polymers P1–P6 in THF and P7 in DMSO. (B) Change in the PL intensity ( $I$ ) of polymers P1, P2, P4, P6, and P7 at  $\lambda_{\text{max}}$  with water content;  $I_0$  is the intensity in pure THF (P7 in DMSO): concentration, 10  $\mu\text{M}$ ;  $\lambda_{\text{ex}}$  394 nm for P1 and 384 nm for P2, P4, P6, and P7.

were used to characterize the obtained polymers and the analysis data were well consistent with the expected molecular structures. A significant feature is that the activated ester route imparts some intrinsic properties of P1, such as similar molecular weight and polydispersity index, high thermal stability, and fluorescence, to the obtained disubstituted polyacetylenes. In addition, CD spectra reveal that the substitution of activated ester with asymmetric amines transfers the chirality to the polyacetylene backbone, and the polymers in solution show distinct helical conformation, for different chiral moieties have different abilities to induce helix. Considering that the substitution of activated ester by amines takes place in mild reaction condition and there is a library of amine compounds, the present work provides a promising strategy for design and synthesis of various functional disubstituted polyacetylenes.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental section, synthetic route to monomer **1** (Scheme S1) and compound **7** (Scheme S2), polymerization of monomer **1** (Table S1), polymer reactions of P1 with amines (Table S2), FTIR spectra of **1**, P1, P2, P4, P6, and P7 (Figure S1),  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR spectra of monomer **1** and polymers (Figure S2–S4), TGA thermograms of P1, P5, and P6 (Figure S6), UV spectra of **1** and P1 (Figure S7), UV and CD spectra of P2–P7 in different solvents (Figures S8–S11),  $\Phi_{\text{F}}$  value of polymers P1–P6 in THF and P7 in DMSO (Table

S3), PL spectra of polymers P1, P2, P4, and P6 in THF/water and P7 in DMSO/water mixtures (Figures S12–S16), PL and UV spectra of polymer films of P1–P6 (Figures S17 and S18), and mass spectrum of monomer **1** (Figure S19). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

PFPh, pentafluorophenyl; NMR, nuclear magnetic resonance; FTIR, Fourier transform infrared spectroscopy; PL, photoluminescence; UV, ultraviolet; CD, dichromism; THF, tetrahydrofuran; DMSO, dimethyl sulfoxide; DMF, dimethylformamide

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