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Helical and Luminescent Disubstituted Polyacetylenes: Synthesis, Helicity, and Light Emission of Poly(diphenylacetylene)s Bearing Chiral Menthyl Pendant Groups

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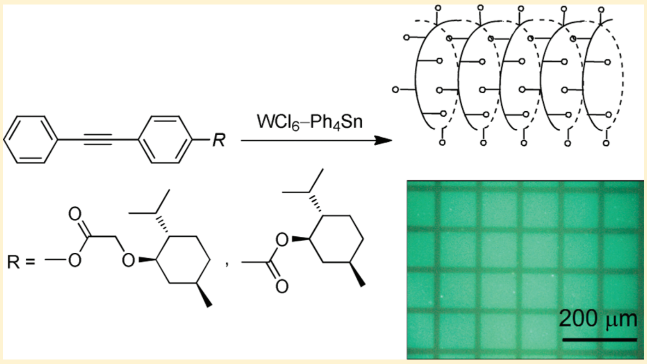
ABSTRACT: Diphenylacetylenes containing chiral menthyl groups [$C_6H_5C{\equiv}C{-}C_6H_4OCOCH_2OR^*$ and $C_6H_5C{\equiv}C{-}C_6H_4CO_2R^*$, R* = (1*R*,2*S*,5*R*)-(−)-menthyl] are synthesized and polymerized by $WCl_6{-}Ph_4Sn$ catalyst. The structures and properties of the polymers are characterized and evaluated by IR, NMR, TGA, UV, CD, and PL analyses. All the polymers are thermally stable, losing little of their weights when heated to ≥250 °C. They also enjoy high photostability, suffering no change in the molecular weight when exposed to UV irradiation in air for 24 h. The backbones of the polymers are induced to helically rotate by the chiral pendants, as verified by their large specific optical rotations and strong Cotton effects in the backbone absorption region in the solution and aggregate states. The polymers emit green light of 493 and 520 nm when their solutions and nanoparticle suspensions in poor solvents are photoexcited. UV irradiation of the polymer films in air photooxidizes the exposed regions, generating two-dimensional luminescent photopatterns.



INTRODUCTION

Optically active polymers with extended π-electron conjugations are under hot pursuit of scientists because the development of such polymers may lead to technological innovations in nonlinear optics, asymmetric electrodes, photonic switching, and so forth.[1,2] One such conjugated polymer is represented by polyacetylenes, whose conjugated backbones can be induced to helically rotate when the surrounding environments exert chiral forces on the polymer chains or when the chiral substituents internally perturb the polymer strands in an asymmetric fashion.[3−9]

Most of the optically active polyacetylenes prepared so far are monosubstituted, with an overwhelming majority of them being poly(phenylacetylene) (PPA) and polypropargyl derivatives.[7−9] While the monosubstituted polyacetylenes are more stable than their unsubstituted polyacetylene parent, their stabilities are still of concern for many practical applications.[10] One way to further boost the polymer stability is to make a disubstituted polyacetylene, which is generally more stable than its monosubstituted homologue. For example, poly(1-chloro-2-phenylacetylene), a disubstituted derivative of PPA is so stable that it does not suffer any decrease in its molecular weight when heated to 200 °C in air for 20 h. In sharp contrast, PPA decomposes readily when heated under the same conditions.[11] It is envisioned that chiral disubstituted polyacetylenes should be thermally stable, thus enabling them to find useful practical applications such as chiral stationary phase in the chromatographic drug enantioseparation.[12]

The synthesis of chiral disubstituted polyacetylenes has, however, been difficult due to the lack of effective polymerization systems for disubstituted acetylenes containing functional groups. So far, only a few helical disubstituted polyacetylenes have been prepared.[13] The chiral groups are incorporated into the polymer structures through multistep silicon chemistry, possibly because of the need to avoid the use of polar functional groups, which are poisoning to $TaCl_5$ and $NbCl_5$, the most widely used catalysts for the polymerizations of disubstituted acetylenes.[14] If the stereogenic groups can be attached to the polyacetylene strands via "normal" functional groups such as ester, it will greatly facilitate the molecular design and polymer synthesis and significantly enrich the research field of helical disubstituted polyacetylenes because a vast variety of acetylenes and chiral building blocks with ester-forming hydroxyl and carboxyl groups is commercially available.[15]

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Scheme 1

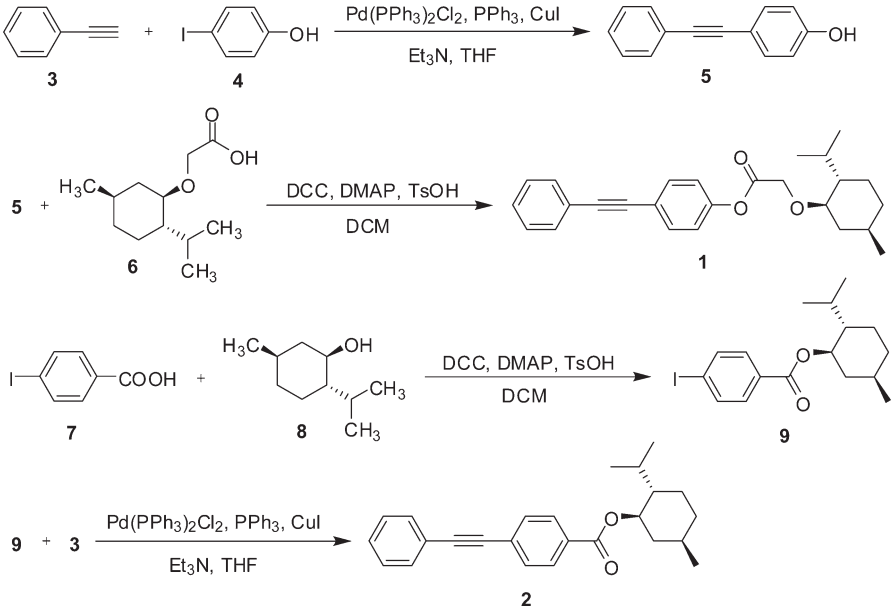
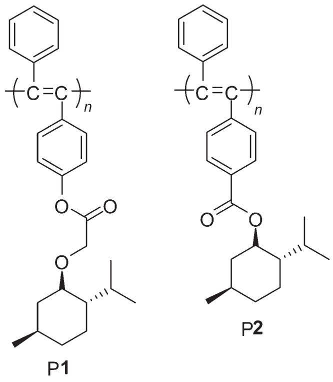


Chart 1



In our previous work, we succeeded in preparing a group of chiral disubstituted polyacetylenes bearing ester functionalities, i.e., poly(phenylpropiolate)s, by inexpensive, "classic" metathesis catalysts of WCl_6– and $MoCl_5$–Ph_4Sn.[16] Whereas the few known examples of helical disubstituted polyacetylenes show Cotton effects in the backbone absorption spectral region with molar ellipticities ([θ]) smaller than 35 000 deg cm^2 $dmol^{-1}$, our chiral poly(phenylpropiolate)s, however, exhibit much higher Cotton effects in the similar spectral region ([θ] up to 115 000 deg cm^2 $dmol^{-1}$).[16a,b] Unfortunately, the polymers are not emissive as luminogenic materials with helical conformations may emit polarized light upon photoexcitation, which may be utilized for the construction of lightning and orientating layers in liquid crystal optical display devices, thus obviating the use of backlight lamps, polyimide films, and polarizing sheets.

Disubstituted polyacetylenes such as poly(1-phenyl-1-alkyne)s and poly(diphenylacetylene)s are found to be capable of emitting strong light upon photoexcitation.[17] Thus, attachment of stereogenic groups to the backbones of these polymers is anticipated to generate materials with both fluorescence and helicity. With such regard, we have worked on the synthesis of poly(1-phenyl-1-octyne)s carrying different chiral substituents.[18] Disappointedly, the stereogenic polymers exhibit only weak helicity though they emit intensely in the solution and solid states. In this paper, we continued our research on helical and luminescent polyacetylenes. We attached (−)-menthol, a naturally occurring species, to diphenylacetylene via ester functionality. The synthesis is straightforward, involves no complicated procedures under stringent controlled conditions, and gives products **1** and **2** in high yields (Scheme 1). In this report, we tell how the new monomers can be polymerized and report what the properties of the resultant poly(diphenylacetylene)s exhibit (**P1** and **P2**; Chart 1).

■ EXPERIMENTAL SECTION

Materials and Instrumentation. Tetrahydrofuran (THF; Labscan) and toluene (BDH) were distilled under nitrogen from sodium benzophenone ketyl immediately prior to use. Dichloromethane (DCM) was distilled under nitrogen over calcium hydride. All other solvents were purified using standard procedures. Phenylacetylene (**3**), 4-iodophenol (**4**), (−)-menthoxyacetic acid (**6**), 4-iodobenzoic acid (**7**), (1*R*,2*S*,5*R*)-(−)-menthol (**8**), 1,3-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), *p*-toluenesulfonic acid monohydrate (TsOH), and other chemicals were purchased from Aldrich and used as received without further purification.

Number (M_n)- and weight (M_w)-averaged molecular weights and polydispersity indices (M_w/M_n) of the polymers were estimated by a Waters Associates gel permeation chromatography (GPC) system equipped with refractive index and UV detectors. THF was used as eluent at a flow rate of 1.0 mL/min. A set of linear polystyrenes was used for the molecular weight calibration. IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a Bruker ARX 300 NMR spectrometer using $CDCl_3$ as solvents. Thermogravimetric analysis (TGA) measurements were carried out under nitrogen on a Perkin-Elmer TGA 7 analyzer at a heating rate of 10 °C/min.

UV spectra were measured on a Milton Roy Spectronic 3000 array spectrophotometer, and the molar absorptivity of the polymers was calculated on the basis of their monomer repeat units. High-resolution mass spectra (HRMS) were recorded on a Finnigan TSQ 7000 operating in a MALDI-TOF mode. Specific optical rotations ($[\alpha]_D$) were measured on a Perkin-Elmer 241 polarimeter at room temperature (~23 °C) with a beam of plane-polarized light of the D line of a sodium lamp (589.3 nm) as the monochromatic source. Circular dichroism (CD) measurements were recorded on a Jasco J-720 spectropolarimeter in 1 mm quartz cuvettes with a step resolution of 0.2 nm, a scan speed of 50 nm/min, a sensitivity of 0.1°, and a response time of 9.5 s. Each spectrum was the average of 5−10 scans. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS55 spectrofluorometer with a xenon discharge lamp excitation.

Monomer Preparation. The (−)-menthol-containing diphenylacetylenes (**1** and **2**) were synthesized according to Scheme 1. Typical procedures for their syntheses are shown below.

*1-(4-Hydroxyphenyl)-2-phenylacetylene (**5**).* Into a 500 mL round-bottom flask equipped with septum and stirring bar were added 4.40 g (20 mmol) of **4**, 0.2 g (0.29 mmol) of Pd(PPh$_3$)$_2$Cl$_2$, 55.1 mg (0.29 mmol) of CuI, and 75.4 mg (0.29 mmol) of PPh$_3$. Dry Et$_3$N (150 mL) and THF (150 mL) and 2.75 mL (2.56 g, 25 mmol) of **3** were then injected by hypodermic syringes. After stirring at room temperature for 12 h, the mixture was filtered and the precipitates were washed with diethyl ether. The filtrate was collected, and after solvent evaporation under reduced pressure, the crude product was purified by silica gel column chromatography using chloroform as eluent. A white solid of **5** was obtained in 81% yield. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.50 (m, 2H), 7.42 (d, 2H), 7.32 (m, 3H), 6.82 (d, 2H), 4.85 (s, 1H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 155.6, 133.3, 131.4, 128.4, 127.9, 123.4, 115.7, 115.6, 89.4, 88.1.

*1-{[(1R,2S,5R)-(−)-Menthoxymethylcarbonyloxy]phenyl}-2-phenylacetylene (**1**).* Into a 250 mL round-bottom flask equipped with a stirring bar were dissolved 3.88 g (20 mmol) of **5**, 6.24 g (30 mmol) of DCC, 0.49 g (4 mmol) of DMAP, and 0.77 g (4 mmol) of TsOH in 100 mL of dry DCM/THF mixture (5:1 v/v). The solution was cooled to 0 °C with an ice bath, into which 4.29 g (20 mmol) of **6** dissolved in 50 mL of DCM/THF mixture (5:1 v/v) was added under stirring via a dropping funnel. The reaction mixture was stirred overnight. After filtration, the solution was concentrated by a rotary evaporator. The crude product was purified by a silica gel column using chloroform/hexane mixture (1:2 v/v) as eluent. White solid; yield 79.2%. IR (thin film), ν (cm^{-1}): 2954, 2924, 2830, 1784, 1594, 1572, 1506, 1445, 1407, 1383, 1368, 1343, 1277, 1234, 1203, 1166, 1119, 1041, 1013. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.54 (m, 4H), 7.34 (m, 3H), 7.14 (d, 2H), 4.38 (d, 2H), 3.28 (m, 1H), 2.34 (m, 1H), 2.12 (d, 1H), 1.66 (m, 2H), 1.56 (2, 1H), 1.34 (m, 2H), 0.98 (m, 7H), 0.83 (d, 3H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 169.2, 150.1, 132.8, 131.6, 128.3, 123.0, 121.6, 121.1, 89.5 ($\equiv$C−PhO), 88.5 (PhC$\equiv$), 80.5, 65.9, 48.2, 40.0, 34.4, 31.5, 25.5, 23.3, 22.3, 21.0, 16.3. HRMS (MALDI-TOF): m/z 391.2266 [(M + 1)$^+$, calcd 391.2195].

*(1R,2S,5R)-(−)-Menthyl-4-iodobenzoate (**9**).* Into a 250 mL round-bottom flask equipped with a stirring bar were dissolved 3.15 g (20 mmol) of **8**, 6.24 g (30 mmol) of DCC, 0.49 g (4 mmol) of DMAP, and 0.77 g (4 mmol) of TsOH in 100 mL of dry DCM/THF mixture (4:1 v/v). The solution was cooled to 0 °C with an ice bath, into which 5.00 g (20 mmol) of **7** dissolved in 50 mL of DCM/THF (4:1 v/v) was added under stirring via a dropping funnel. The reaction mixture was stirred overnight. After filtration, the solution was concentrated by a rotary evaporator. The crude product was purified by a silica gel column using chloroform/hexane mixture (1:2 v/v) as eluent. A white solid of **9** was obtained in 83.4% yield. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.78 (d, 2H), 7.76 (d, 2H), 4.93 (t, 1H), 2.09 (d, 1H), 1.92 (m, 1H), 1.71 (m, 2H), 1.49 (m, 2H), 1.11 (m, 2H), 0.94 (m, 6H), 0.79 (d, 3H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 165.6, 137.6, 131.0, 130.3, 100.4, 75.2, 47.2, 40.9, 34.2, 31.6, 31.4, 26.5, 23.6, 22.0, 20.7, 16.5.

*1-{[(1R,2S,5R)-(−)-Menthoxycarbonyl]phenyl}-2-phenylacetylene (**2**).* Into a 500 mL round-bottom flask equipped with a septum and a stirring bar were added 7.72 g (20 mmol) of **9**, 0.2 g (0.29 mmol) of Pd(PPh$_3$)$_2$Cl$_2$, 55.1 mg (0.29 mmol) of CuI, and 75.4 mg (0.29 mmol) of PPh$_3$. Dry Et$_3$N (150 mL) and THF (150 mL) and 3.29 mL (3.06 g, 30 mmol) of **3** were then injected by hypodermic syringes. After stirring at room temperature for 12 h, the mixture was filtered and the precipitates were washed with diethyl ether. The filtrate was collected, and after solvent evaporation under reduced pressure, the crude product was purified by silica gel column chromatography using chloroform/hexane mixture (1:2 v/v) as eluent. White solid; yield 82.0%. IR (thin film), ν (cm^{-1}): 3060, 2958, 2928, 2870, 2218, 1932, 1806, 1714, 1606, 1560, 1510, 1488, 1456, 1404, 1387, 1368, 1327, 1305, 1290, 1270, 1175, 1140, 1115, 1036, 1017. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.04 (d, 2H), 7.56 (m, 4H), 7.35 (m, 3H), 4.95 (m, 1H), 2.11 (d, 1H), 1.96 (m, 1H), 1.71 (d, 2H), 1.56 (m, 2H), 1.15 (m, 2H), 0.95 (m, 7H), 0.81 (d, 3H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 165.5, 131.7, 131.4, 130.1, 129.5, 128.7, 128.4, 127.7, 122.7, 92.1 ($\equiv$C−PhCO$_2$), 88.7 (PhC$\equiv$), 75.0, 47.2, 40.9, 34.3, 31.4, 26.5, 23.6, 22.0, 20.8, 16.5. HRMS (MALDI-TOF): m/z 361.2176 [(M + 1)$^+$, calcd 361.2089].

Polymer Synthesis. All the polymerization reactions were carried out under dry nitrogen using the standard Schlenk technique, unless otherwise specified. A typical procedure for the polymerization of **1** is given below as an example.

Into a baked 15 mL Schlenk tube with a stopcock in the side arm was added 0.31 g of **1**. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the side arm. Freshly distilled toluene (2 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tune by dissolving 16 mg of tungsten(VI) chloride and 17 mg of tetraphenyltin in 2 mL of toluene. The catalyst solution was aged at room temperature for 15 min and was transferred to the monomer solution using a hypodermic syringe. The reaction mixture was stirred at 100 °C for 24 h. The solution was cooled to room temperature, diluted with 15 mL of chloroform, and added dropwise to 500 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and then collected by filtration. The polymer was washed with methanol and dried under vacuum at room temperature to a constant weight.

Characterization data for **P1**: Yellow powder; yield 66.3%. M_w 28 800; M_w/M_n 1.3 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3084, 3052, 3023, 2952, 2920, 2868, 1780, 1755, 1598, 1503, 1455, 1444, 1400, 1384, 1370, 1342, 1265, 1200, 1165, 1116, 1016. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 6.63, 6.50, 6.23, 6.16, 4.24, 3.20, 2.36, 2.13, 1.66, 1.34, 0.92, 0.78. ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 168.5, 148.0, 145.4 (=CPhO), 143.1 (PhC=), 141.3, 131.1, 126.1, 119.4, 80.2, 65.8, 48.1, 40.0, 34.4, 31.5, 25.3, 23.2, 22.3, 21.1, 16.2.

Characterization data for **P2**: Yellow powder; yield 30.9%. M_w 12 300; M_w/M_n 3.1 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3056, 3028, 2953, 2926, 2868, 1716, 1640, 1606, 1490, 1453, 1404, 1387, 1368, 1288, 1272, 1179, 1108, 1017. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 7.26, 7.20, 6.98, 6.79, 6.16, 4.86, 2.26, 1.70, 1.43, 1.25, 0.90. ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 165.8, 150.4 (=CPhCO$_2$), 146.5 (PhC=), 128.9, 128.4, 126.0, 74.8, 47.2, 41.9, 41.0, 34.3, 31.4, 30.0, 26.4, 23.6, 22.0, 20.8, 18.5, 16.5.

Photopatterning. Photooxidation reactions of the polymer films were conducted in air at room temperature using 365 nm light obtained from a Spectroline ENF-280C/F UV lamp at a distance of 1 cm as light source. The incident light intensity was ~18.5 mW/cm^2. The film was prepared by spin-coating the polymer solution (10% w/w in

Table 1. Polymerizations of 1 and 2[a]

run	monomer	temp (°C)	yield (%)	M_n[b]	M_w[b]	M_w/M_n[b]
1	**1**	80	17.1	5300	7900	1.5
2	**1**	100	66.3	9600	28800	3.0
3	**2**	100	30.9	4000	12300	3.1

[a] Catalyzed by WCl_6-Ph_4Sn in toluene under nitrogen for 24 h; $[M]_0$ = 0.2 M, $[WCl_6]$ = $[Ph_4Sn]$ = 10 mM. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration.

1,2-dichloroethane) at 2000 rpm for 1 min on a silicon wafer. The polymer film was dried in a vacuum oven at room temperature overnight. The photopatterns were generated using a copper photomask and taken on an optical microscopy (Nikon 80i equipped with Nikon Digital Sight DS-5Mc-L2 Cooled CCD camera) using UV light source.

RESULTS AND DISCUSSION

Monomer Synthesis. With a view to synthesizing polymers with both fluorescence and helicity, we designed two diphenylacetylene derivatives containing chiral menthyl units according to the synthetic routes shown in Scheme 1. The Pd-catalyzed cross coupling of **3** and **4** gave **5**, whose esterification reaction with **6** in the presence of DCC, DMAP, and TsOH furnished the desirable product **1**. Monomer **2** was obtained by esterification reaction of **7** with **8**, followed by Sonogashira coupling of the resultant compound (**9**) with **3**. All the reactions could be carried out at ambient conditions, and all the intermediates and monomers were obtained in high yields. We characterized their molecular structures by standard spectroscopic methods and obtained satisfactory analysis results (see Experimental Section for details).

Polymerization. In our previous study, we succeeded in polymerizing diphenylacetylenes containing ester unit by WCl_6-Ph_4Sn.[19] We thus tested whether the same catalyst can initiate the polymerizations of **1** and **2**. Stirring a toluene solution of **1** at 80 °C in the presence of WCl_6-Ph_4Sn under nitrogen for 24 h gives a polymeric product with M_w of 7900 in a low yield (~17%) (Table 1, run 1). GPC analysis of the residue by evaporation of the filtrate shows that it is oligomeric species with molecular weights of several hundreds. Raising the temperature to 100 °C has improved the polymerization result significantly: the yield and molecular weight of the polymer are more than 3.5-fold higher than those obtained at 80 °C. A higher temperature may make the catalyst more active and thus greatly accelerates the polymerization reaction.

Under the same experimental conditions, **2** was converted into a polymer with a lower molecular weight in a lower yield (Table 1, no. 3). Why the polymerization behavior of **2** is different from that of **1** is unclear at present but may be related to the difference in the steric crowdedness around the triple bond. Attachment of (−)-menthyl pendant to the diphenylacetylene structure directly through the ester functionality generates sterically more bulky monomer **2**, making it more difficult to be polymerized into high molecular weight polymer in high yield by the tungsten catalyst. On the other hand, the polar ester group in **1** may be well shielded by the methylene group. This reduces its toxic interaction with the transition-metal catalyst and hence enhances the polymerizability of the monomer.

Structural Characterization. The molecular structures of the polymers are characterized by spectroscopic methods, and all give satisfactory data corresponding to their expected molecular structures (see Experimental Section for details). An example of the IR spectrum of **P1** is shown in Figure 1, with that of its monomer (**1**) given in the same figure for comparison. The spectrum of **P1** resembles that of **1**, exhibiting a strong band at 1740 cm^{-1} associated with C═O stretching vibration. This result indicates that the ester functionality remains intact after the polymerization. Since no peaks related to C≡C stretching vibration at ~2222 cm^{-1} are observed in the spectra of the monomers, no further information on the structures of the polymers can be obtained. We thus characterized the polymers

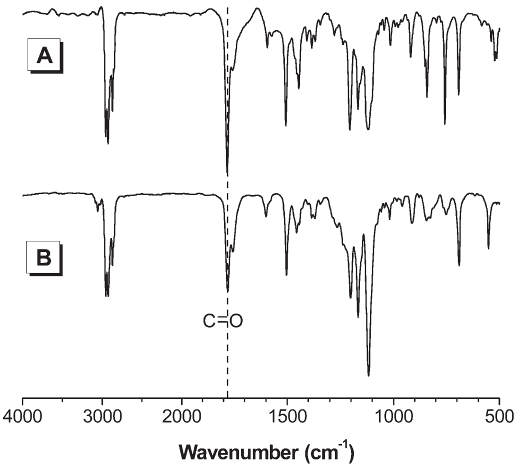


Figure 1. IR spectra of (A) monomer **1** and (B) its polymer **P1** (Table 1, run 2).

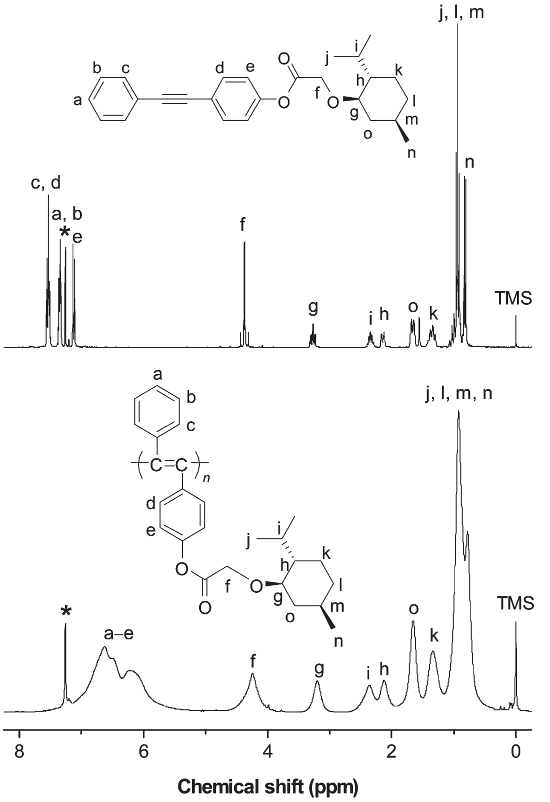


Figure 2. ^1H NMR spectra of **1** and its polymer **P1** (Table 1, run 2) in $CDCl_3$. The solvent peaks are marked with an asterisk.

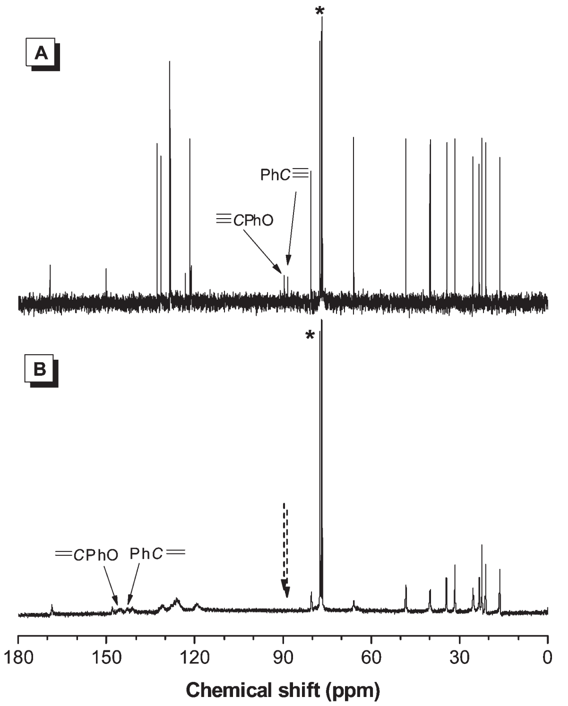


Figure 3. ^{13}C spectra of (A) **1** and (B) its polymer **P1** (Table 1, run 2) in $CDCl_3$. The solvent peaks are marked with an asterisk.

by NMR analyses, which prove that the acetylenic triple bonds of the monomers have been consumed and transformed to the polyene double bonds of the polymers by the polymerization reactions.

Figure 2 shows the ^{1}H NMR spectra of **1** and its polymer **P1** in chloroform-*d*. The phenyl protons linked to the acetylene triple bond of **1** resonate at δ 7.54, 7.34, and 7.14. These absorption peaks, however, disappear after polymerization. The transformation of the acetylene triple bond of **1** to the double bond of **P1** by the polymerization reaction downfield shifts the phenyl proton resonances, which are now observed at δ 6.63, 6.50, and 6.16. The peaks are broad because the aromatic rings are directly attached to a rigid polymer backbone. No other unexpected signals are observed, and all the peaks can be readily assigned, verifying the high purity of its molecular structure. Similar results are obtained when compared the spectrum of **P2** with that of **2**, proving that the molecular structure of the polymeric product is indeed **P2**, as shown in Chart 1.

The ^{13}C NMR spectroscopy offers more informative characterization data. For example, the spectrum of **P1** shows no acetylene carbon resonances of **1** at δ 89.5 and 88.5 (Figure 3). On the other hand, two new peaks appear at δ 145.4 to 143.1. Since the resonance peaks of the backbone carbons of poly(diphenylacetylene)s carrying naphthalene pendants have been reported to locate at δ 145.2 and 143.7.[19a] It thus seems reasonable to assign the peaks at δ 145.4 and 143.1 to the backbone olefin carbon resonances of **P1**. Similarly, **P2** displays no peaks associated with the acetylene carbon absorptions of **2** at δ 92.1 and 88.7 but exhibits backbone olefin carbon resonances at δ 150.4 and 146.5. This also once again proves that the diphenylacetylene polymerization is realized through the conversion of the triple bonds to the double bonds.

Solubility and Thermal Stability. It is known that monosubstituted polyacetylenes without functional bridges and/or bulky groups are unstable.[11] The first examples of optically active polyacetylenes are a group of poly(1-alkyne)s with small chiral groups, which are very sensitive to oxygen, light, and heat and must be stored in a refrigerator under nitrogen in the dark.[3] Thanks to the stable aromatic rings along the polymer backbone, our polymers can be stored under ambient temperatures in vials in air, with no observable color and morphology changes.

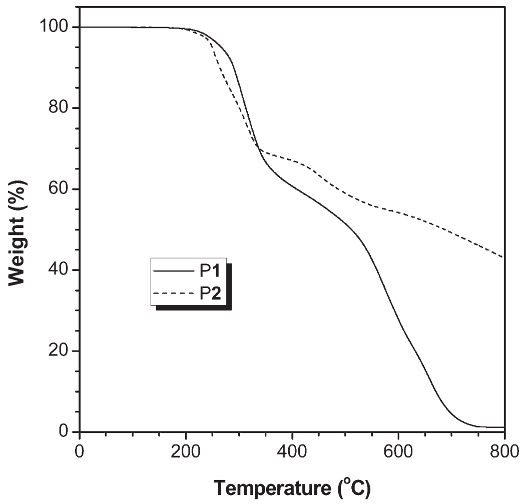


Figure 4. TGA thermograms of **P1** (Table 1, run 2) and **P2** recorded under nitrogen at a heating rate of 10 °C/min.

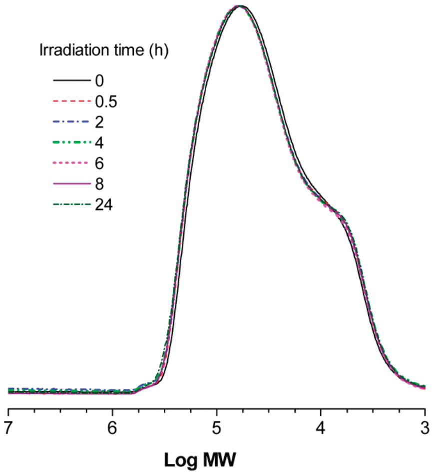


Figure 5. GPC traces of **P1** before and after UV irradiation in air for different time intervals.

Both **P1** and **P2** are completely soluble in common organic solvents, such as THF, DCM, chloroform, and dioxane and can be readily fabricated into tough solid films by spin-coating or solution-casting process. They enjoy high thermal stability. As shown in Figure 4, **P1** loses merely 5% of its weight when heated to ~300 °C (T_d). The polymer strand is well wrapped by the bulky, stable phenyl rings, which imparts **P1** with high resistance to thermolysis. The T_d (~250 °C) of **P2** is lower than **P1**, presumably due to its lower molecular weight.

We also investigated the photostability of the polymers. We irradiated the solid powders of **P1** in air under stirring by UV light from a Spectroline ENF-280C/F UV lamp placed ~5 cm away from the center of the Schlenk tube (incident light intensity = 13 mW/cm^2). The change in the molecular weight of the polymer at different time intervals was followed by GPC analysis. As shown in Figure 5, the polymer suffers no degradation after exposure to UV irradiation for 0.5 h. Even prolonging the time to 24 h, practically no change was observed in its GPC curve, suggesting that it possesses a high photostability. **P1** contains many aromatic rings, which may act as radical sponges to trap, deactivate, and/or annihilate the destructive radical species formed in the UV irradiation process.

Chiroptical Properties. Acetylene polymerizations initiated by Mo- and W-based catalysts are known to yield polymers with irregular or random stereostructures, containing chain segments with cis–transoid and trans–cisoid conformations.[16] Many research groups have formed that stereoregular cis geometrical structure is indispensable for helix induction.[5,6,8] Will our chiral poly(diphenylacetylene)s (**P1** and **P2**) prepared from tungsten catalyst take helical conformation? To check this, we measured the $[\alpha]_D$ values of the polymers at room temperature (Table 2). The $[\alpha]_D$ value of **P1** in $CHCl_3$ is very large (−1728.6°) and is more than 90-fold higher than its monomer **1** (−19.3°) in the same solvent, suggestive of chirality contribution from the polyene backbone and the formation of helical conformation with an excess in one handedness. The $[\alpha]_D$ value of the polymer changes with solvent, but the direction remains unchanged, in contrast to our previous observation that not only the magnitudes of $[\alpha]_D$'s of the solutions of chiral monosubstituted poly(phenylacetylene)s change but also their signs reverse even when the polarities of the solvents are similar.[9f,g] A disubstituted polyacetylene chain is generally more rigid than a monosubstituted one,[20] and it is envisioned that the high chain stiffness of **P1** has helped keep its helical-sense preference unaltered by the solvent perturbation.

Similarly, the $[\alpha]_D$ value of **P2** is much higher than its monomer. Its magnitude varies with solvent but its sign remains unchanged. There is also no correlation between the $[\alpha]_D$ value and the solvent polarity. Interestingly, however, although both **P1** and **P2** possess the same kind of chiral moiety [i.e., (1*R*,2*S*,5*R*)-(−)-menthyl], the $[\alpha]_D$ of the former is up to 3-fold larger than that of the latter in magnitude and opposite to that of the latter in sign, demonstrating that the chiroptical properties of polyacetylenes can be readily tuned by changing their molecular structures.

To confirm whether the macromolecular chains are really spiraling in a helical sense, we measured the circular dichroism (CD) spectra of the polymer solutions. Before the CD analysis, we performed UV measurements to check where the backbone absorbs. The upper panels of Figures 6 and 7 show the UV spectra of **P1** and **P2** in different solvents. In THF, **P1** exhibits absorption peaks centered at 270, 370, and 425 nm. Since its monomer does not absorb at wavelengths longer than 310 nm, the peaks at 370 and 425 nm should be associated with the absorptions of the polyacetylene backbone. The ground-state electronic transitions vary little with the solvent: the UV spectra measured in DCM, toluene, and $CHCl_3$ are basically the same as that performed in THF. Similarly, the backbone of **P2** absorbs at wavelengths longer than 330 nm. No spectral change was observed when the measurement was carried out in other solvents.

The CD spectra of **P1** and **P2** measured in different solvents are shown in the lower parts of Figures 6 and 7. The THF solution of **P1** displays a strong CD band at 380 nm with a molar ellipticity as high as −74 500 deg cm^2 dmol^{-1}, whereas its monomer (**1**) is CD-inactive, giving a flat line parallel to the abscissa. Thus, the strong Cotton effect observed at 380 nm should be related to the absorption of the polyene backbone, unambiguously confirming that the main chain indeed takes a helical conformation with a large excess of one-handedness. To check how the chain conformation of **P1** varies with response to

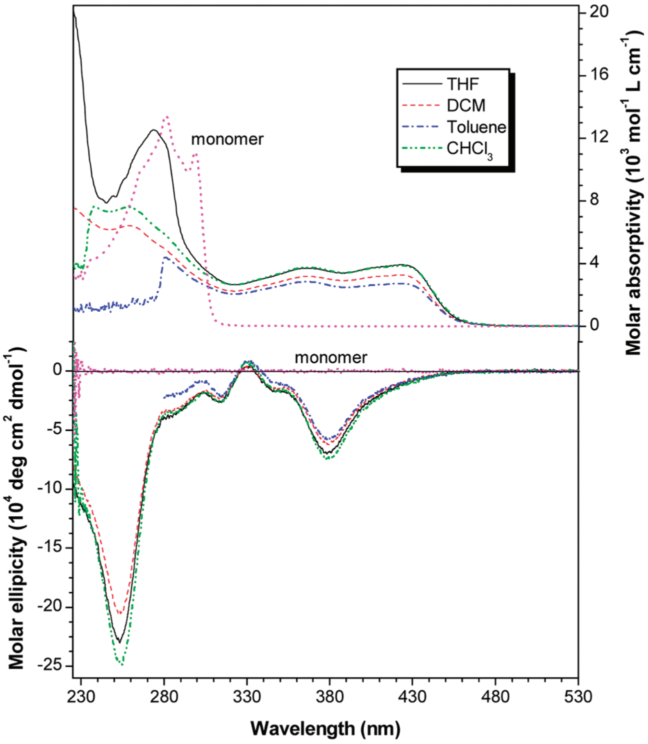


Figure 6. UV (upper panel) and CD (lower panel) spectra of monomer **1** in $CHCl_3$ and **P1** in different solvents at room temperature. Concentration (mM): ~0.38 (CD) and 0.12 (UV). The spectral data in toluene below 290 nm were not taken because of the interference by the solvent absorption.

Table 2. Specific Optical Rotations of Monomers and Polymers in Different Solvents

	$[\alpha]_D$, deg (*c*, g/dL)			
solvent[a]	1	P1	2	P2
$CHCl_3$	−19.3 (0.015)	−1728.6 (0.014)	−17.0 (0.125)	+765.7 (0.042)
DCM		−1450.0 (0.018)		+694.7 (0.036)
THF		−1718.8 (0.016)		+690.6 (0.036)
toluene		−1212.5 (0.016)		+573.0 (0.050)

[a] Debye solvent polarizability functions of the solvents: 0.71 ($CHCl_3$), 0.73 (DCM), 0.68 (THF), and 0.31 (toluene).

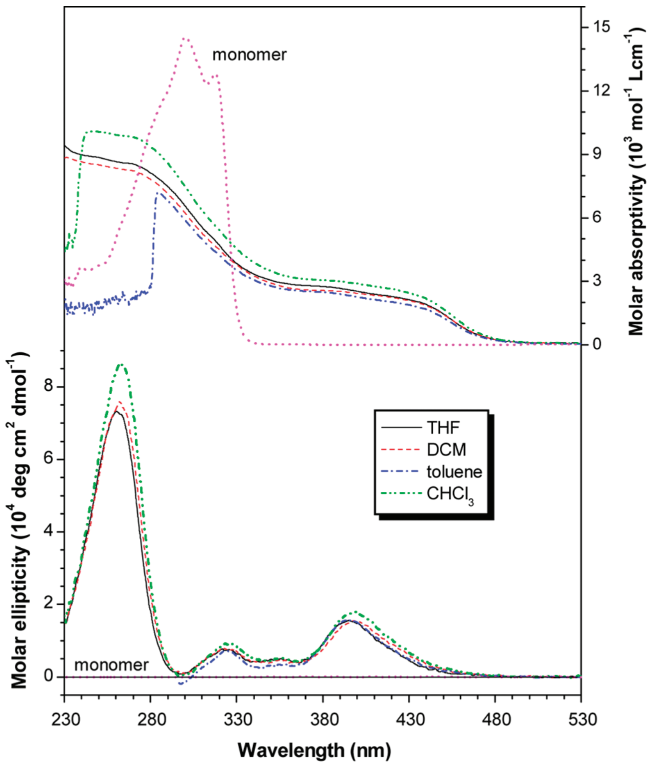


Figure 7. UV (upper panel) and CD (lower panel) spectra of monomer **2** in $CHCl_3$ and **P2** in different solvents at room temperature. Concentration (mM): ∼1 (CD), 0.1 (UV). The spectral data in toluene below 290 nm were not taken because of the interference by the solvent absorption.

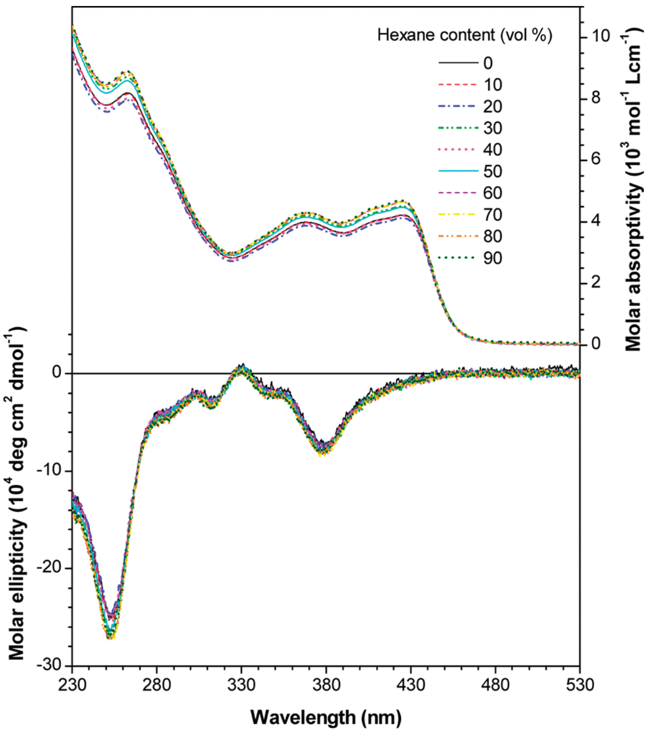


Figure 8. UV (upper panel) and CD (lower panel) spectra of **P1** in THF and THF/hexane mixtures with different hexane fractions at room temperature. Concentration (mM): ∼0.13 (CD and UV).

the change in its surrounding environment, we carried out the CD measurement in different solvents. The spectral pattern of **P1** remains the same when the solvent is changed from THF to DCM, toluene, and $CHCl_3$, indicating the same screw sense dominates in these solvents. The Cotton effects measured in DCM and toluene, are, however, slightly lowered, suggesting that some of the helical chains have reversed their screw sense.

CD analysis verifies that **P2**, like its cousin **P1**, possesses a helical conformation. In THF, it shows a $[\theta]$ value of $+17\,900$ deg cm^2 dmol^{-1} at ∼400 nm associated with the helicity of the polymer chain. Thanks to the stiff backbone, the polymer possesses a stable helical conformation and is thus less susceptible to the solvent perturbation, as revealed by the large similarity in the CD spectra obtained in DCM, toluene, and $CHCl_3$.

Some chiral molecules and polymers are found to exhibit lower or amplified CD signals when aggregated in poor solvents or fabricated as thin films in the solid state.[21] Which case can be best described for our system? To address this question, we studied the chiroptical properties of the polymers in THF/hexane and/or THF/H_2O mixtures. Since hexane and water are nonsolvents for **P1** and **P2**, their polymer chains must have been aggregated in the solvent mixtures with high fractions of these solvents. Dilute polymer solutions are used for the investigation to prevent the precipitation of the polymers. As shown in Figure 8, addition of small amount of hexane (<50%) into the THF solution of **P1** causes no significant change in its UV spectrum. Afterward, the peak intensity increases slightly, but the spectral pattern remains unchanged. Similar results are also obtained in the CD analyses. The CD spectrum suffers little change when up to 40% of hexane is added to the THF solution, but the peak ellipticity increases slightly (in absolute term) afterward.

The effect of water on the optical and chiroptical properties of **P1** is more pronounced. The UV spectra measured in THF/H_2O mixtures are resembled to that in THF, irrespective of the water content (Figure 9). A level-off tail is observed in THF/H_2O mixtures with water fractions larger than 10%, due to the light scattering or Mie effect of the polymer aggregates.[22] The mixtures are, however, visually transparent and macroscopically homogeneous, suggesting that the polymer aggregates are nanometer sized.[23] Addition of 10% of water in the THF solution of **P1** alters little its helicity. When the water content is increased to 20%, the Cotton effect at 388 nm is intensified by more than 2-fold and a new peak is emerged at 430 nm. Further increment of the amount of water in the solvent mixture weakens the backbone CD absorptions, but their ellipticities are still higher than those in pure THF.

Why the polymer shows different responses to the presence of hexane and water? Being hydrophobic in nature, **P1** should aggregate more readily in THF/H_2O mixtures even at low water contents. In the aggregates, the polymer chains are located in the close vicinity, which promotes exciton coupling[24] and hence results in the emergence of a new CD peak at the longer wavelength region. The steric effect and/or hydrophobic interaction imposed by the neighboring strand, on the other hand, have stabilized the helical conformation and thus intensified the CD signals. In a mixture with a "lower" water fraction, the polymer stands of **P1** may slowly assemble to form more regular or ordered aggregates, while in a mixture with a "higher" water content, the fast agglomeration of the polymer strands may generate aggregates with more random structures, which weakens the interstrand interaction and the associated Cotton effects.

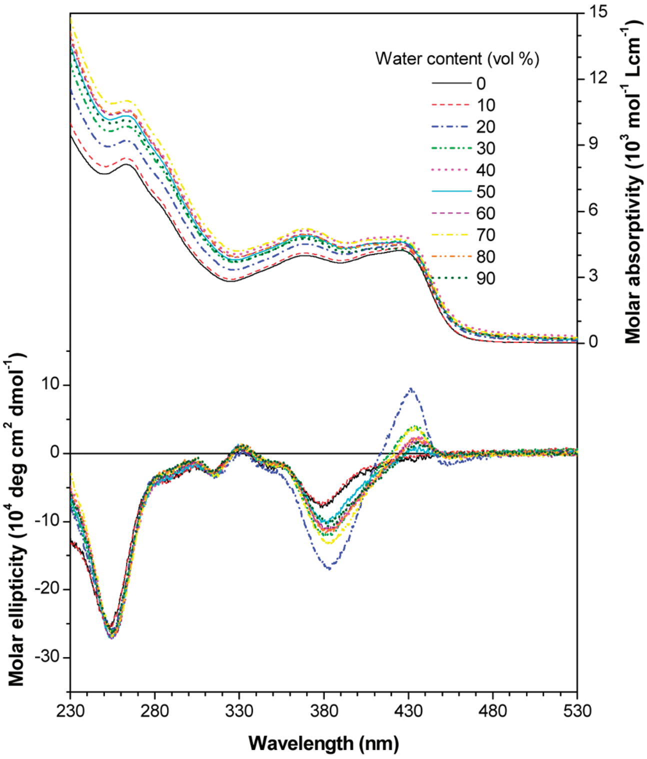


Figure 9. UV (upper panel) and CD (lower panel) spectra of **P1** in THF and THF/water mixtures with different water fractions at room temperature. Concentration (mM): ~0.13 (CD and UV).

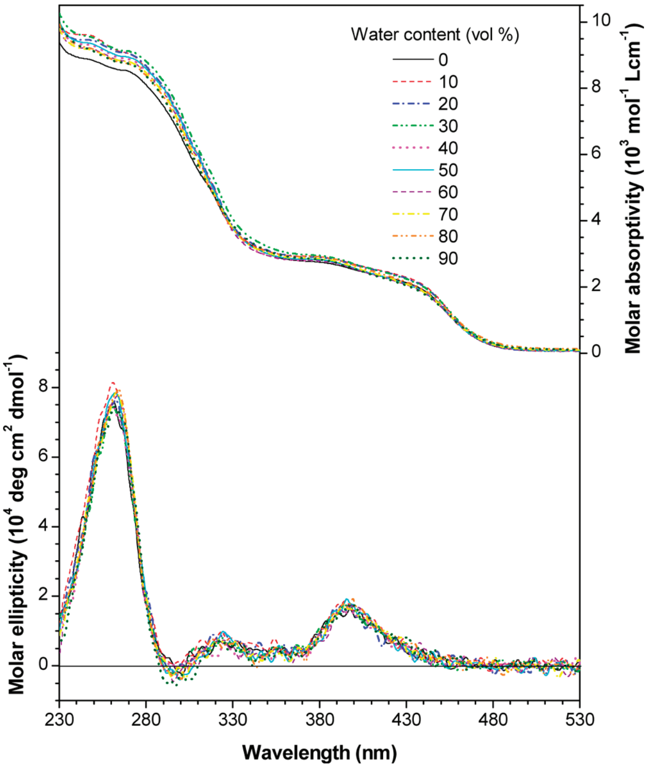


Figure 10. UV (upper panel) and CD (lower panel) spectra of **P2** in THF and THF/water mixtures with different water fractions at room temperature. Concentration (mM): ~0.10 (CD and UV).

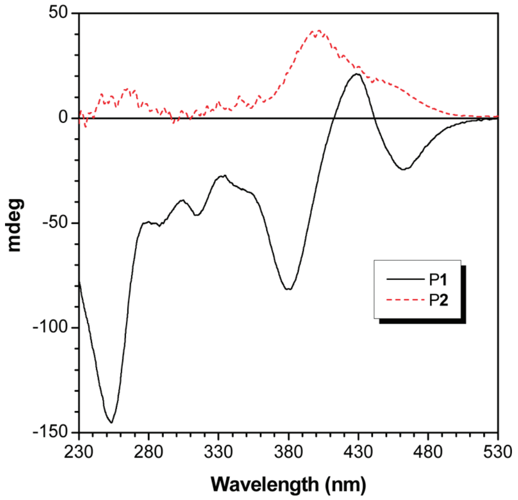


Figure 11. CD spectra of thin films of **P1** and **P2** at room temperature.

Figure 10 depicts the UV and CD spectra of **P2** in THF and THF/water mixtures with different water fractions. The UV spectrum of **P2** shifts slightly upward even when a large amount of water is added to its THF solution. Unlike **P1**, the CD spectrum of **P2** changes little upon aggregate formation, presumably due to its relatively lower molecular weight, which forms fewer aggregates with smaller sizes in the aqueous mixtures.

Similar to those in THF and THF/H_2O mixtures, the spectra of thin films of the polymers depict strong CD bands associated with the helicity of the polyacetylene chains (Figure 11). New Cotton effects are observed at the longer wavelengths due to the stronger interstrand interaction in the solid state.

Light Emission. It now becomes clear that the present polymers are optically active in both solution and aggregate state. The next question is: will they emit strong light upon UV exposure? Figure 12A depicts the PL spectra of **P1** in THF and THF/hexane mixtures. In pure THF, **P1** emits a green light at 493 nm when photoexcited at 424 nm. The fluorescence quantum yield (Φ_F) determined by using fluorescein (Φ_F = 79% in 0.1 M NaOH solution) is 25.4%. Addition of hexane into its THF solution causes little spectral change but increases slightly the light emission. The PL intensity remains unchanged when up to 80% of hexane is added but drops afterward. Generally, aggregation quenches the PL of fluorophores due to the increase in the short-range interactions.[25,26] On the other hand, aggregation can positively restrict the intramolecular motions of the fluorophores, which block the channels for the excitons to decay nonradiatively. Whether aggregation quenches or boosts the PL of fluorophores depends on their molecular structures. In **P1**, the first effect seems to be prevailed, and its PL thus becomes lower in THF/hexane mixtures with high hexane contents.

The destructive effect of aggregation on the PL of **P1** is more obvious in THF/H_2O mixture. Since water is such a nonsolvent for **P1**, addition of 20% of water into its THF solution has already aggregated its chains and weakened its PL (Figure 12B). The higher the water content, the weaker is the light emission. Although aggregation reaches its maximum in the solid state, the thin film of **P1** shows reasonable strong green light upon UV irradiation.

The phenomenon observed in **P1** is not an isolated case but is also found in **P2**. In THF, **P2** emits at 520 nm with an Φ_F value of

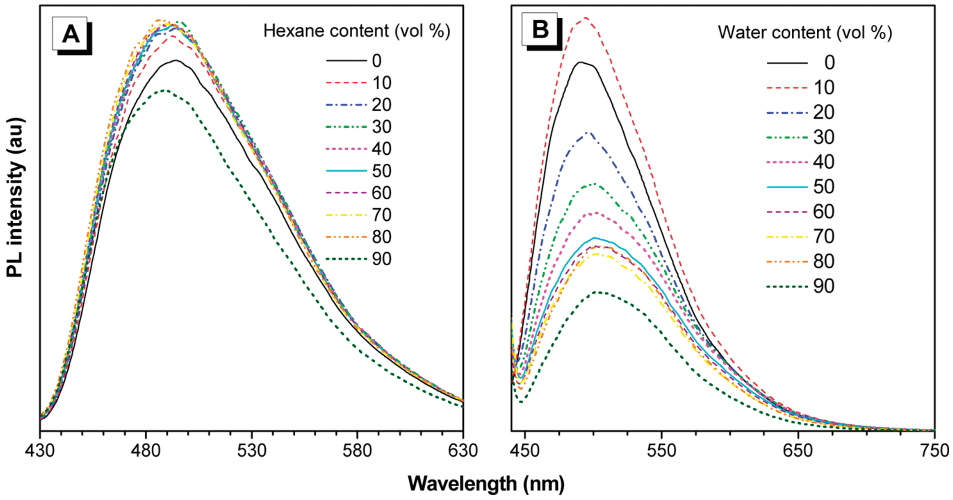


Figure 12. PL spectra of **P1** in (A) THF/hexane and (B) THF/water mixtures with different hexane and water fractions. Concentration: 10 μM; excitation wavelength: 424 nm.

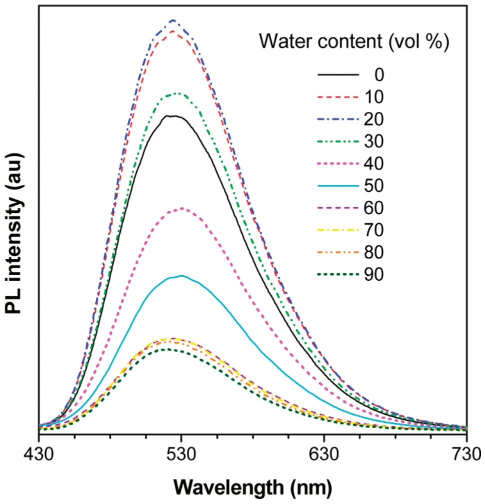


Figure 13. PL spectra of **P2** in THF and THF/water mixtures with different water fractions. Concentration: 10 μM; excitation wavelength: 400 nm.

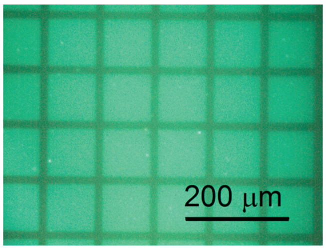


Figure 14. Two-dimensional fluorescent photopattern generated by photooxidation of **P1**. The photograph was taken under a fluorescence optical microscope.

9.79% (Figure 13). Addition of small amount of water (<40%) into its THF solution has enhanced its light emission. Further increment of the water content has, however, decreased the PL, with the intensity at 90% water content being one-third of that in pure THF. Such result demonstrates that the PL technique is a more sensitive tool than the CD spectroscopy for detecting aggregate formation in the polymer.

Photopatterning. Since **P1** and **P2** are emissive in the solid state, we explored their potential use as PL imaging materials.[27] UV irradiation of a thin film of **P1** through a mask bleaches the exposed regions, while the unexposed regions remain emissive. A photopattern is thus generated without performing the development process (Figure 14).

■ CONCLUSION

In this work, diphenylacetylenes bearing stereogenic (−)-menthyl groups are synthesized and polymerized by WCl_6−Ph_4Sn, furnishing poly(diphenylacetylene)s with high molecular weights in moderate yields. All the polymers are soluble in common organic solvents and are thermally stable ($T_d \geq 250$ °C). They show large specific optical rotations and strong CD signals in the absorption region of the polyene backbone in the solution and aggregate states, suggesting that their main chains are helically rotating in a preferred screw sense by the chiral pendants. Strong green lights are observed when their solutions and nanoaggregates in poor solvents are photoexcited. UV irradiation of their films photooxidizes the exposed parts, generating two-dimensional fluorescent photopatterns.

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