Helical Disubstituted Polyacetylenes: Synthesis and Chiroptical Properties of Poly(phenylpropiolate)s

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ABSTRACT: Disubstituted polyacetylenes with helical chirality have been rarely prepared due to the involved synthetic difficulty, and we here report a facile polymerization system for the synthesis of such polymers. Two groups of chiral acetylenes, i.e., $C_6H_5C{\equiv}CCO_2R^*$ {R* = [(1*S*)-*endo*]-(−)-borneyl (**1**), (1*R*,2*S*,5*R*)-(−)-menthyl (**5**), cholesteryl (**6**)} and $C_6H_5C{\equiv}CCO_2C_6H_4CO_2R^*$ [R* = borneyl (**2**), menthyl (**3**), cholesteryl (**4**)], are prepared by esterifications of phenylpropiolic acids with borneol, menthol, and cholesterol. Polymerizations of **1**−**4** are effected by WCl_6−Ph_4Sn, giving poly(phenylpropiolate)s P**1**−P**4** with high molecular weights in moderate yields. The structures and properties of the polymers are characterized and evaluated by IR, UV, NMR, CD, TGA, and SEM analyses. All the polymers are stable: neither decreases in their molecular weights nor changes in their spectra are detected after the polymers have been stored on shelf for ∼3 years, and no weight losses are recorded when the polymers are heated to ∼300 °C. Although the polymers do not possess regioregular *Z* or *E* conformations, the polyacetylene backbones are induced to helically rotate by the chiral pendants, as verified by the strong Cotton effects in the backbone absorption region of the polymers (molar ellipticity up to 102 300 deg cm^2 dmol^{-1}). The polymers exhibit helical thermochromism, with their chain helicity being continuously and reversibly tunable by temperature change. The helical polymers are capable of self-assembling, as demonstrated by the formation of twisted ribbons upon diffusing a THF solution of P**3** into hexane.

Introduction

Almost all natural polymers (protein, sugar, DNA, etc.) possess molecular chirality;[1] in contrast, most synthetic polymers (polyethylene, polypropylene, polystyrene, etc.) are optically inactive. Synthesis of chiral polymers is of great interest because it can generate artificial macromolecules with biomimetic helical conformations, which may serve as simple models to help advance our understanding on the complex biomacromolecular systems.[2] 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, light polarization, photonic switching, chiral separation, and so forth.[2,3] Polyacetylenes are a group of such optically and electronically active macromolecules, whose conjugated backbones can be induced to helically rotate when the surrounding environments exert chiral forces on the polymer chains[4] or when the chiral pendants perturb the polymer chains in an asymmetric fashion.[5−12]

In the early days, the catalysts for acetylene polymerizations had little tolerance to functional groups, which had significantly obstructed the progress in the development of helical polyacetylenes. Indeed, up to the end of 1980s, only two research groups led by Ciardelli[5] and Tang[6] had worked on the synthesis of helical polyacetylenes from nonpolar monosubstituted acetylenes. It was not until the discovery of the functionality-tolerant organorhodium catalysts[7d,13] that the interest and activity in the area of helical polyacetylenes had surged. Various chiral groups have now been successfully incorporated into monosubstituted poly(1-alkyne)s and poly(arylacetylene)s through different functional bridges. For example, in our group alone, more than 50 kinds of monosubstituted polyacetylenes bearing chiral moieties of naturally occurring species such as amino acids, saccharides, nucleosides, lipids, and sterols have been designed and synthesized.[9,10,12,14]

It is known that monosubstituted polyacetylenes without functional bridges and/or bulky groups such as poly(1-octyne) $-[HC{=}C(C_6H_{13})]_n-$ and poly(phenylacetylene) $-[HC{=}C(C_6H_5)]_n-$ are unstable.[15,16] The steric and electronic effects of the functional and/or bulky pendants can, however, help stabilize the polymers. Poly(1-octyne), for example, starts to lose its weight when heated to ∼150 °C,[15] and 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 refrigerator under nitrogen and in the dark".[5] Introduction of a bulky naphthylphenylmethylsilyl [(−)-NpPhMeSi*] group into poly(1-octyne) enhances its stability: the chiral polymer can be handled in normal laboratory conditions and do not lose any weights when heated to ∼250 °C.[6] The weight loss temperature for poly(phenylacetylene) is ∼225 °C,[15] while that for its derivative carrying a mesogenic group, e.g., $-\{HC{=}C[C_6H_4\text{-}p\text{-}CO_2(CH_2)_6O\text{-Biph-CN}]\}_n-$, is as high as ∼400 °C due to the protective jacket effect of the functional side chains.[17] Poly(propyne) $\{-[HC{=}C(CH_3)]_n-\}$ is so unstable that it readily decomposes under ambient conditions, but its congener $-\{HC{=}C[CH_2\text{-}NHCO_2\text{-}(S)\text{-}CH_2C^*H(CH_3)C_2H_5]\}_n-$ shows higher stability in solution, thanks to the stabilization effect of the intramolecular hydrogen bonds between the carbamate moieties of the pendant groups.[11h]

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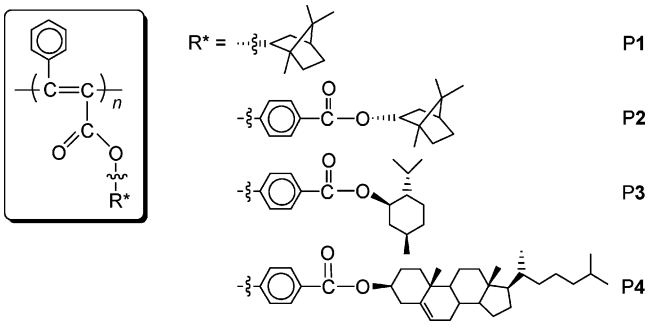
In addition to the "pendant approach" discussed above, "dual substitution" is another way to boost the stability of polyacetylenes. A polyacetylene with two substituents in its repeat unit (or a disubstituted polyacetylene) is generally more stable than its monosubstituted counterpart, due to the obvious steric effect. For example, poly(1-chloro-2-phenylacetylene) {−[ClC═C(C_6H_5)]$_n$−}, a disubstituted derivative of poly(phenylacetylene), is so stable that it does not suffer from any decrease in its molecular weight when heated at 200 °C in air for 20 h.[15] It is envisioned that chiral disubstituted polyacetylenes should be thermally stable, which may enable them to find useful practical applications, for instance, as chiral stationary phases in the chromatographic drug enantioseparation.[18] The synthesis of chiral disubstituted polyacetylenes has, however, been difficult, due to the lack of effective polymerization systems for functional disubstituted acetylenes. So far, only a few optically active disubstituted polyacetylenes have been prepared. The chiral groups are incorporated into the disubstituted polyacetylenes through multistep silicon chemistry,[19] possibly because of the need to avoid the use of polar functional groups, which are poisoning to the tantalum and niobium chloride catalysts. If the chiral groups can be incorporated into the polyacetylene structures via "normal" functional groups such as ester, it will greatly facilitate the molecular design and polymer synthesis and significantly widen the scope of research on chiral disubstituted polyacetylenes because a vast variety of chiral building blocks possesses the ester-forming hydroxyl (e.g., sterols) and carboxyl groups (e.g., amino acids).[20]

The objective of this work is to develop effective polymerization systems for the synthesis of chiral disubstituted polyacetylenes. We have recently succeeded in polymerizing substituted propiolates (RC≡CCO_2R'), a group of disubstituted acetylenes containing ester functionality, using molybdenum chlorides as catalysts.[21] In this work, we try to extend the utility of the propiolate polymerization to the synthesis of chiral disubstituted polyacetylenes. Using naturally occurring species as starting materials, we designed and synthesized a series of chiral phenylpropiolates. Surprisingly, though the molybdenum chlorides worked well as catalysts for the polymerizations of the achiral phenylpropiolates,[21] they failed to initiate the polymerizations of their chiral congeners. Delightfully, however, we found that the WCl_6−Ph_4Sn mixture could polymerize the chiral phenylpropiolates. The tungsten catalyst normally produces polyacetylenes with irregular or random stereostructures, but it is generally believed that "stereoregular cis geometrical structure is indispensable for helix induction to acetylenic polymers".[11e,h] The few known examples of chiral disubstituted polyacetylenes all show small Cotton effects in the backbone absorption spectral region with molar ellipticities ([θ]) smaller than 35 000 deg cm^2 dmol^{-1}.[19] Our chiral poly(phenylpropiolate)s (P**1**−P**4**; Chart 1), however, exhibit high Cotton effects in the similar spectral region ([θ] up to ∼102 300 deg cm^2 dmol^{-1}), though they are prepared from the polymerizations initiated by the sterically nonspecific tungsten catalyst.

Results and Discussion

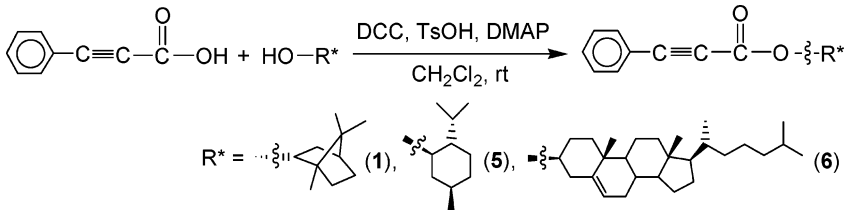
Monomer and Polymer Syntheses. Phenylpropiolate monomers **1**, **5**, and **6** are prepared by one-pot, single-step esterification reactions of phenylpropiolic acid, a commercial reagent, with chiral alcohols [(1*S*)-*endo*]-(−)-borneol, (1*R*,2*S*,5*R*)-(−)-menthol, and cholesterol, respectively, in the presence of 1,3-dicyclohexylcarbodiimine (DCC), *p*-toluenesulfonic acid (TsOH), and 4-(dimethylamino)pyridine (DMAP) (Scheme 1). Three derivatives of **1**, **5**, and **6**, namely, aryl phenylpropiolates **2**−**4**, are designed, in which the chiral groups are attached to the acetylene triple bond through a benzoate functional bridge (Scheme 2). The aryl phenylpropiolates are prepared by first etherizing ethyl 4-hydroxybenzoate with benzyl bromide. The ester bond in the resultant product (**7**) is then hydrolyzed in an ethanolic solution of potassium hydroxide, followed by neutralization with a dilute acid. The benzoic acid derivative (**8**) is esterified with the chiral alcohols, giving chiral esters **9**. Cleavage of the ether bond in **9** is effected by palladium-catalyzed hydrogenation, and esterification of the obtained alcohols (**10**) with phenylpropiolic acid produces the final desirable disubstituted acetylene monomers (**2**−**4**). All the reactions proceeded smoothly and the expected products were isolated in good to excellent yields (34−92%). Whereas **5** and **3** are yellow liquids, other monomers are white solids. The products are characterized by spectroscopic methods, and all the monomers give satisfactory analytic data corresponding to their expected molecular structures (see Experimental Section for detailed spectroscopic data).

Chart 1



We first tried to polymerize **1** by [Rh(nbd)Cl]$_2$ and $MoOCl_4$, which are effective catalysts for the polymerizations of chiral monosubstituted propiolates (HC≡CCO_2R^*).[22] Reactions of **1** catalyzed by these catalysts, however, give no polymeric products (Table 1, nos. 1 and 2). The $MoCl_5$−Ph_4Sn mixture also fails to polymerize the monomer, which is somewhat surprising, because the Mo mixture is a good catalyst for the polymerization of achiral phenylpropiolates.[21] Although no successful examples can be found in the literature on using tungsten halides as catalysts for polymerizations of propiolates,[22,23] we tried to use tungsten chlorides to initiate the polymerization of **1**. $WOCl_4$−Ph_4Sn fails to serve as a catalyst for the propiolate polymerization, which is expected in some sense. Unexpectedly, however, **1** is converted by WCl_6−Ph_4Sn at room temperature to a red powdery polymeric product, albeit in a low yield. Raising the temperature to 60 °C does not change the M_w of the polymer much but increases its yield by ∼3-fold (Table 1, no. 6). The reaction at 80 °C, however, produces only trace amount of polymeric product, indicating that the polymerization has a narrow temperature window. Encouraged by the results of the WCl_6-catalyzed polymerization of **1**, we tried to convert its congeners **5** and **6** to their corresponding polymers by the same catalyst but failed to obtain any polymeric products. Changing cocatalyst, solvent, and temperature

Scheme 1



Scheme 2

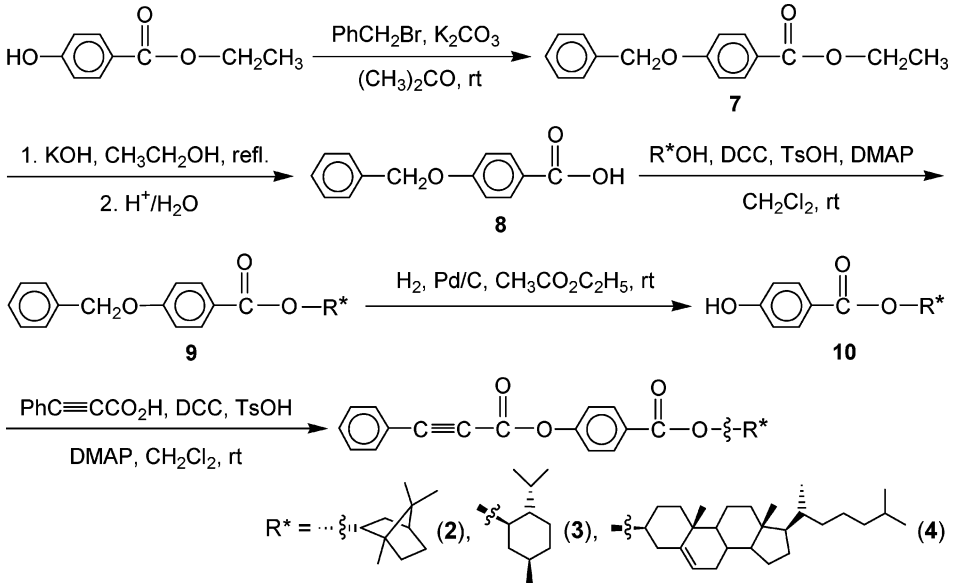
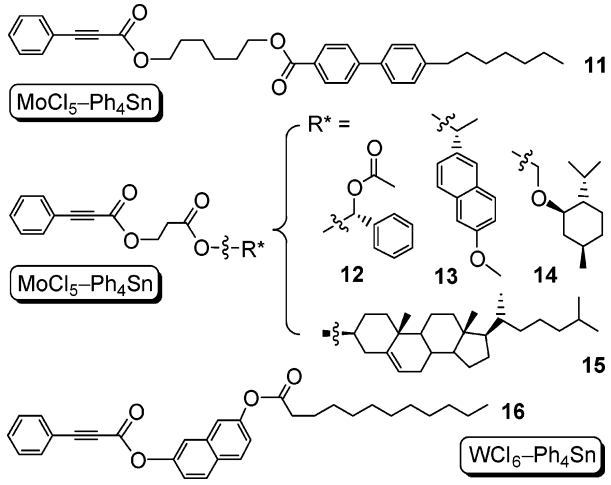


Table 1. Polymerization of [(1*S*)-*endo*]-(−)-Borneyl Phenylpropiolate (1)[a]

no.	catalyst[b]	solvent	temp[c] (°C)	yield (%)	M_w[d]	M_w/M_n[d]
1	$[Rh(nbd)Cl]_2$	CH_3CN	40	0		
2	$MoOCl_4-Ph_4Sn$	toluene	60	0		
3	$MoCl_5-Ph_4Sn$	toluene	60	0		
4	$WOCl_4-Ph_4Sn$	toluene	60	0		
5	WCl_6-Ph_4Sn	toluene	rt	7.7	17 600	1.8
6	WCl_6-Ph_4Sn	toluene	60	22.6	13 000	1.8
7	WCl_6-Ph_4Sn	toluene	80	*e*		

[a] Carried out under nitrogen for 24 h; $[M]_0 = 0.2$ M, [cat.] = [cocat.] = 10 mM (for $[Rh(nbd)Cl]_2$, [cat.] = 0.2 mM). [b] Abbreviation: nbd = 2,5-norbornadiene. [c] rt = room temperature. [d] Determined by SEC in THF on the basis of a polystyrene calibration. [e] Trace.

Chart 2



did not help, and all the attempted polymerizations were ended up with dismay. Clearly the W catalyst is substrate-sensitive.

We are intrigued by our observation that the Mo catalyst works well for the polymerization of achiral phenylpropiolates such as **11** (Chart 2) but completely fails to initiate the polymerization of its chiral counterpart such as **1**. Is this due to the monomer chirality or something else? We scrutinized the polymerization results of some achiral and chiral phenylpropiolates. As can be seen from Chart 2, the Mo catalyst can effect the polymerizations of not only achiral (**11**) but also chiral phenylpropiolates (**12**−**15**).[24] On the other hand, the polymerization of the achiral aryl phenylpropiolates such as **16** cannot be initiated by the Mo catalyst but can be effected by its W counterpart.[25] These results suggest that the catalytic activity is not defined by the molecular chirality of the monomers but by their steric effects. The Mo catalyst is active toward the phenylpropiolates with linear alkyl chains attached to the propiolate ester bond (**11**−**15**), whereas the W catalyst is good for the monomers with bulky aliphatic (**1**) and aromatic rings (**16**). The failure of the W catalyst in initiating the polymerization of **5** and **6** is probably because their cyclic pendants are too sterically demanding.

It is rationalized that if the bulky chiral cyclic groups are separated from the propiolate ester bond by sterically less demanding phenyl rings, the resultant monomers may be polymerized by the W catalyst. This is indeed the case, as proven by the polymerization results of the chiral aryl phenylpropiolates (**2**−**4**) shown in Table 2. Monomer **2** behaves much like its conger **1**: the Rh and Mo catalysts again fail to polymerize **2**, but WCl_6-Ph_4Sn gives a polymer with a high molecular

Table 2. Polymerizations of Aryl Phenylpropiolates (2−4)[a]

no.	catalyst[b]	solvent	temp (°C)	yield (%)	M_w[c]	M_w/M_n[c]
	4-{[(1*S*)-*endo*]-(−)-Borneyloxycarbonyl}phenyl Phenylpropiolate (**2**)					
1	$[Rh(nbd)Cl]_2$	CH_3CN	40	0		
2	$MoOCl_4-Ph_4Sn$	toluene	60	0		
3	$MoCl_5-Ph_4Sn$	toluene	60	*e*		
4	$WOCl_4-Ph_4Sn$	toluene	60	*e*		
5	WCl_6-Ph_4Sn	toluene	60	19.5	14 600	1.4
6	WCl_6-Ph_4Sn	toluene	80	71.4	32 800	1.8
	4-[(1*R*,2*S*,5*R*)-(−)-Menthoxycarbonyl]phenyl Phenylpropiolate (**3**)					
7	WCl_6-Ph_4Sn	toluene	60	32.8	19 500	1.6
8	WCl_6-Ph_4Sn	toluene	80	37.9	29 600	1.9
	4-[(3-Cholesteryl)oxycarbonyl]phenyl Phenylpropiolate (**4**)					
9	WCl_6-Ph_4Sn	toluene	60	43.0	43 300	2.2
10	WCl_6-Ph_4Sn	toluene	80	49.3	*d*	

[a] Carried out under nitrogen for 24 h; $[M]_0 = 0.2$ M, [cat.] = [cocat.] = 10 mM (for $[Rh(nbd)Cl]_2$, [cat.] = 0.2 mM). [b] Abbreviation: nbd = 2,5-norbornadiene. [c] Determined by SEC in THF on the basis of a polystyrene calibration. [d] Insoluble. [e] Trace.

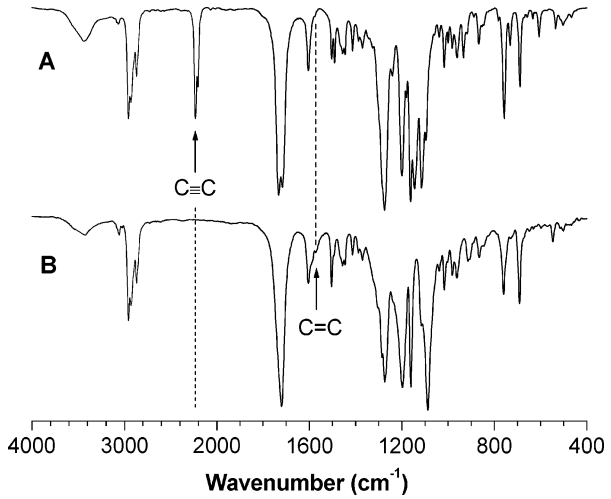


Figure 1. IR spectra of (A) monomer **3** and (B) its polymer P**3** (sample taken from Table 2, no. 7).

weight (M_w 32 800) in high yield (71.4%) under optimal polymerization conditions. Different from its congener **1**, monomer **2** can be polymerized better at a higher temperature (cf. Table 2, nos. 5 and 6 vs Table 1, nos. 5−7). Similarly, the chiral aryl phenylpropiolates carrying the bulky menthol (**3**) and cholesterol groups (**4**) cannot be polymerized at all by the Rh and Mo catalysts but can be better polymerized by the W catalyst at the higher temperature (80 °C) in terms of yield and/or M_w, although the polymer obtained from **4** at the high temperature is insoluble.

Structural Characterization by Spectroscopy. The purified products are carefully characterized by spectroscopic methods, and all the polymers give satisfactory analysis data (see Experimental Section). An example of the IR spectrum of P**3** is shown in Figure 1 (the spectrum of **3** is also given in the same figure for the purpose of comparison). Monomer **3** exhibits very strong C≡C stretching doublets at 2233 and 2205 cm^{-1} (Figure 1A). The strong absorption is due to the electronic conjugation of the propiolate carbonyloxy group with the acetylene triple bond,[21] and the doublet vibrations are possibly associated with the orientation of the bulky substituent relative to the triple bond because the

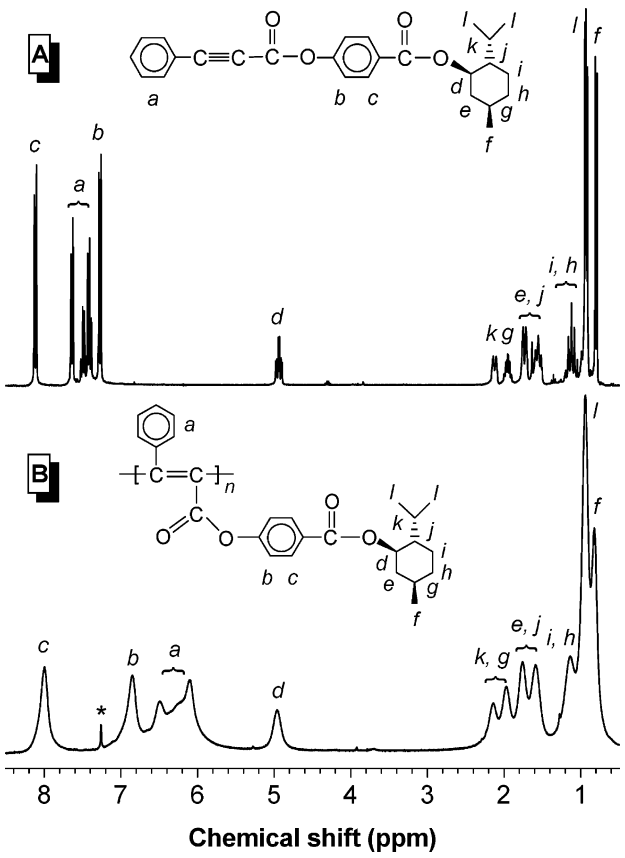


Figure 2. ^1H NMR spectra of chloroform solutions of (A) monomer **3** and (B) its polymer P**3** (sample from Table 2, no. 7) at room temperature (∼23 °C). The solvent peak is marked with an asterisk (∗).

phenylpropiolates with linear alkyl chains attached to the propiolate ester bond (**11**−**15**) show only singlet peaks at ∼2230 cm^{-1}.[21,25] However, polymer P**3** does not show any C≡C stretching band at ∼2230 cm^{-1} (Figure 1B). On the other hand, a new band associated with C=C stretching is observed at 1574 cm^{-1}, suggesting that the triple bond of the monomer has been transformed by the W-catalyzed polymerization to the double bond of the polymer.

The molecular structure of P**3** is further confirmed by the NMR analyses. The protons of the phenyl group linked to the acetylene triple bond of monomer **3** resonate at δ 7.65 and 7.43, which are not observed in the spectrum of polymer P**3** (Figure 2). Two new broad resonance peaks are observed at δ 6.49 and 6.10. Since the resonance of the aromatic protons of styrene ($H_2C=CC_6H_5$) occurs upfield from that of phenylacetylene ($HC\equiv CC_6H_5$),[25] the peaks at δ 6.49 and 6.10 are thus not really new but due to upfield shift of the resonance of the phenyl protons caused by the conversion of the triple bond of **3** to the double bond of P**3**. The peaks are broad because the aromatic ring is directly attached to a rigid polymer backbone.[26] The broad resonance peaks also suggest that the polymer possesses an irregular *Z*/*E* stereostructure.[13d,15a,17,26] No unexpected signals are observed in the spectrum of P**3**, verifying the high purity of its molecular structure.

Figure 3 shows the ^{13}C NMR spectrum of P**3** along with that of its monomer (**3**) in chloroform. The monomer exhibits two resonance peaks of acetylene carbons at δ 89.2 and 80.0, which completely disappear in the spectrum of its polymer. Two new resonance peaks

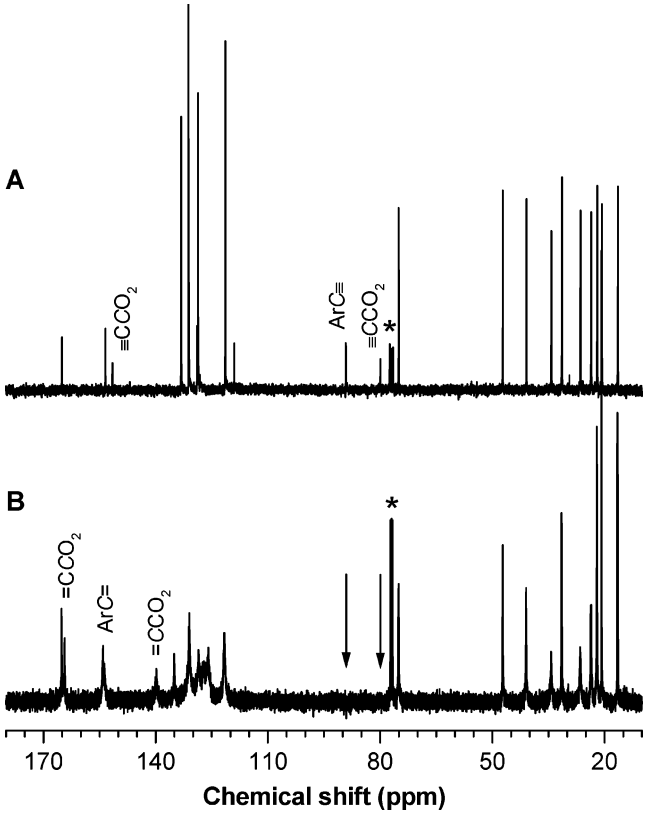


Figure 3. ^{13}C NMR spectra of chloroform solutions of (A) monomer **3** and (B) its polymer P**3** (sample from Table 2, no. 7) at room temperature. The solvent peaks are marked with asterisks (*).

appear in the spectrum of P**3** at δ 153.6 and 140.0. The resonance peaks of the backbone carbons of poly(phenylacetylene) have been reported to locate at δ 142.8 and 131.7[27,28] and those of poly(methylpropiolate) $\{-[HC{=}C(CO_2CH_3)]_n-\}$ at δ 134 and 128.[29] We have found that the backbone carbons of an achiral poly(phenylpropiolate) such as P**11** absorb at δ 131.8 and 129.8.[21] It thus seems reasonable to assign the peaks at δ 153.6 and 140.0 to the backbone carbon resonance of P**3**. The resonance peak of the carbonyl carbon of the monomer at δ 151.6 downfield shifts to δ 163.6 after polymerization.

Thermal Stability and Electronic Absorption. As mentioned in the Introduction section, the chiral monosubstituted poly(1-alkyne)s with small branched alkyl side chains are sensitive to oxygen, light, and heat and readily decompose upon exposing to the environmental surrounding.[5] Our disubstituted poly(phenylpropiolate)s can, however, be handled with ease and stored on the shelf under ambient conditions. Polymer P**1**, for example, shows practically no decrease in its molecular weight after stored on the shelf in our laboratory for ~3 years [e.g., for an as-prepared sample, $M_w = 13\,000$ and $M_w/M_n = 1.8$ (cf. Table 1, no. 6); for the sample after ~3 year storage, $M_w = 12\,970$ and $M_w/M_n = 1.6$]. Moreover, as shown in Figure 4, all the polymers (P**1**−P**4**) are thermally very stable and virtually do not lose any weights when heated to a temperature as high as ~300 °C, irrespective of the kinds of the chiral pendants. The high thermal stability of the chiral disubstituted polyacetylenes is due to the steric and electronic effects of the pendant groups. In every one of the repeat units of the polymers, there exist two bulky substituents, which form "seamless" jackets wrapping around the

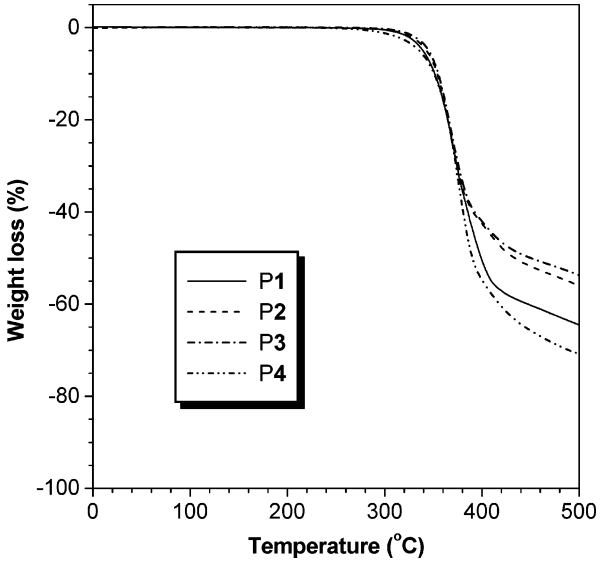


Figure 4. TGA thermograms of P**1**−P**4** (samples taken from Table 1, no. 6 and Table 2, nos. 5, 7, and 9) recorded under nitrogen at a heating rate of 20 °C/min.

polyacetylene backbones and protect them from the attacks of thermolytic species.[15] The aromatic rings and the ester bonds may form resonance structures with the polyene backbones to stabilize or deactivate the radical species, if formed, and hence enhance the resistance of the polymers against thermal degradation.

The chloroform solution of P**1** absorbs in the visible with a band edge of >500 nm (Figure 5A). Since its monomer (**1**) does not absorb at $\lambda > 300$ nm, the absorption of P**1** in the long wavelength region thus must be due to the electronic transition of its double-bond backbone. Polymer P**2** shows two absorption maxima at ~338 and ~401 nm, probably due to its different chain configurations or conformations. Polymers P**3** and P**4** show similar spectral profiles, with their molar absorptivities being comparable to or somewhat lower than those of P**2**. In our previous studies on the chiral monosubstituted polyacetylenes, we have found that the electronic transitions of their solutions are very sensitive to solvents and show very large solvatochromism.[9,10,12] A poly(phenylacetylene) bearing D-glucose pendants, for example, displays an absorption peak at ~440 nm in chloroform, which completely disappears in toluene. This is, however, not the case for the chiral disubstituted poly(phenylpropiolate)s: little changes in the absorption spectra of P**1**−P**4** are observed when their solvents are changed from chloroform to toluene (cf. panels A and B of Figures 5). Their THF solutions also show similar absorption spectra (Figure s1; Supporting Information). This is probably due to the high rigidity of the backbones of the disubstituted polyacetylenes. The steric effect of two bulky substituents effectively stiffens the polyene backbones, making their chain conformations more resistant to the perturbations by solvents.

Chain Helicity and Solvent Effect. The stereoregular chiral poly(phenylacetylene)s prepared from the rhodium catalysts take helical conformations, whose ellipticities vary in magnitude and reverse in sign when their solvents are changed.[9−12] Will the chiral poly(phenylpropiolate)s (P**1**−P**4**) with irregular stereostructures prepared from the tungsten catalyst also take helical conformations and, if so, will their chain helicity change with solvent? To answer these questions, we

Table 3. Specific Optical Rotations of Polymers P1−P4 in Different Solvents[a]

	$[\alpha]^{20}_D$, deg (*c*, g/dL)			
solvent	P**1**	P**2**	P**3**	P**4**
THF	−545.7 (0.042)	+85.6 (0.035)	+697.9 (0.038)	+49.7 (0.037)
chloroform	−396.6 (0.047)	+73.5 (0.049)	+641.3 (0.046)	+34.0 (0.050)
toluene	−387.6 (0.045)	+168.6 (0.049)	+736.9 (0.051)	+89.6 (0.054)

[a] Specific optical rotations ($[\alpha]^{20}_D$, deg) of THF solutions (*c*, g/dL) of the corresponding monomers: **1**, −19.6 (0.044); **2**, −16.2 (0.047); **3**, −49.7 (0.085); and **4**, +6.6 (0.111).

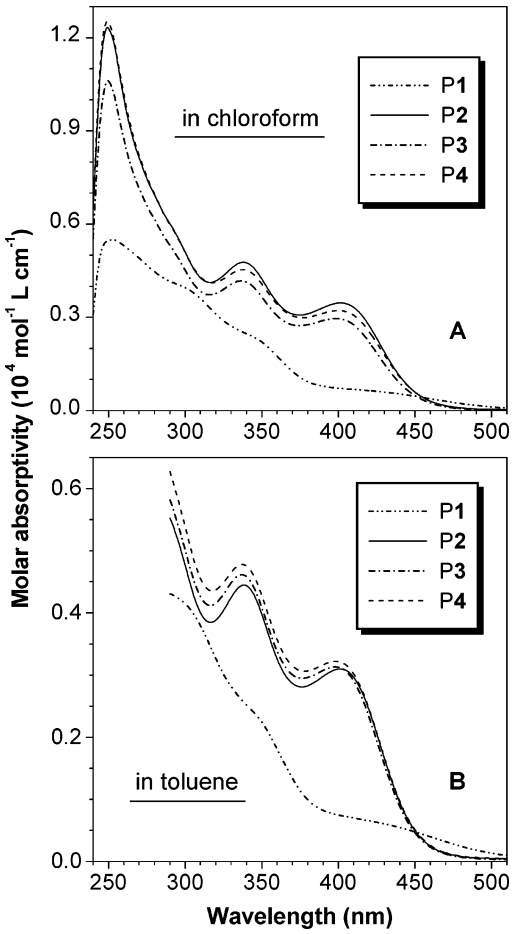


Figure 5. UV spectra of P**1**−P**4** (samples taken from Table 1, no. 6 and Table 2, nos. 5, 7, and 9) in (A) chloroform and (B) toluene at room temperature. The spectra of the polymers in toluene below 290 nm were not taken to avoid the interference of the solvent absorption (the shortest wavelength usable is 290 nm when toluene is used as solvent for UV analysis).

measured their specific optical rotations ($[\alpha]^{20}_D$). As can be seen from Table 3, the $[\alpha]^{20}_D$ values of the polymers (−545.7° to +736.9°) are much higher than those of their corresponding monomers (−49.7° to +6.6°), implying that the polyacetylene backbones have been induced by the chiral pendants to helically rotate in a one-handed screw sense. The $[\alpha]^{20}_D$ values of the polymers change with solvents, but the directions of their optical rotations remain unchanged, in contrast to our previous observations that the $[\alpha]^{20}_D$'s of the solutions of the chiral monosubstituted poly(phenylacetylene)s reverse their signs even when the polarity of their solvents are similar.[9,12] Interestingly, however, although both P**1** and P**2** possess the same kind of chiral moiety [i.e., (−)-borneyl], the $[\alpha]^{20}_D$ of the former is up to 6.4-fold larger than that of the latter in magnitude and opposite to that of the latter in sign, demonstrating that the chiroptical properties of the polymers can be tuned to a great extent by changing their molecular structures.

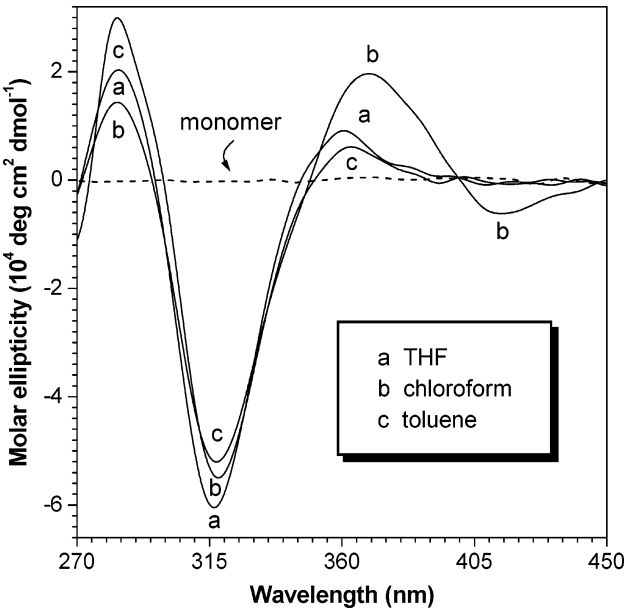


Figure 6. CD spectra of monomer **1** in THF and polymer P**1** (Table 1, no. 6) in different solvents at room temperature. Polymer concentration: 1.56−1.67 mM.

To confirm whether the macromolecular chains are really spiraling in a helical sense, we measured the circular dichroism (CD) spectra of the polymer solutions. As shown in Figure 6, in THF, P**1** exhibits a strong peak at ∼317 nm with a large molar ellipticity ($[\theta]$ ∼60 500 deg cm^2 dmol^{-1}), whereas its monomer (**1**) is CD-inactive at wavelengths longer than 250 nm, giving an almost flat line up to the visible spectral region. The Cotton effect at ∼317 nm thus must be due to the absorption of the polyacetylene backbone, unambiguously confirming that the main chain of the polymer is helically rotating with an excess in one handedness. Clearly the stereoirregular polyacetylene prepared from the tungsten catalyst can spiral in a screw sense, although it is generally believed that the polyacetylenes with irregular *Z*/*E* stereostructures can hardly be induced to take helical conformations.[11] When the solvent of the polymer solution is changed from THF to chloroform, the CD pattern remains unchanged but the peak intensity varies, suggesting that some parts of the helical chain segments have changed their handedness or helicity accompanying the solvent change. A similar phenomenon is observed when the solvent is changed to toluene. The small solvent effects on the chain helicity of P**1** are probably due to the backbone rigidity of the disubstituted polyacetylene, which imparts a high stability to the helical chain conformation, thwarting its conversion from one handedness to another.

The backbone CD absorption is observed not only in P**1** but also in its congeners P**2**−P**4**. As shown in Figure 7A, the first Cotton effect of P**2** associated with its backbone helicity appears at 354 nm, though its chiral substituent is located far from the backbone. Similarly,

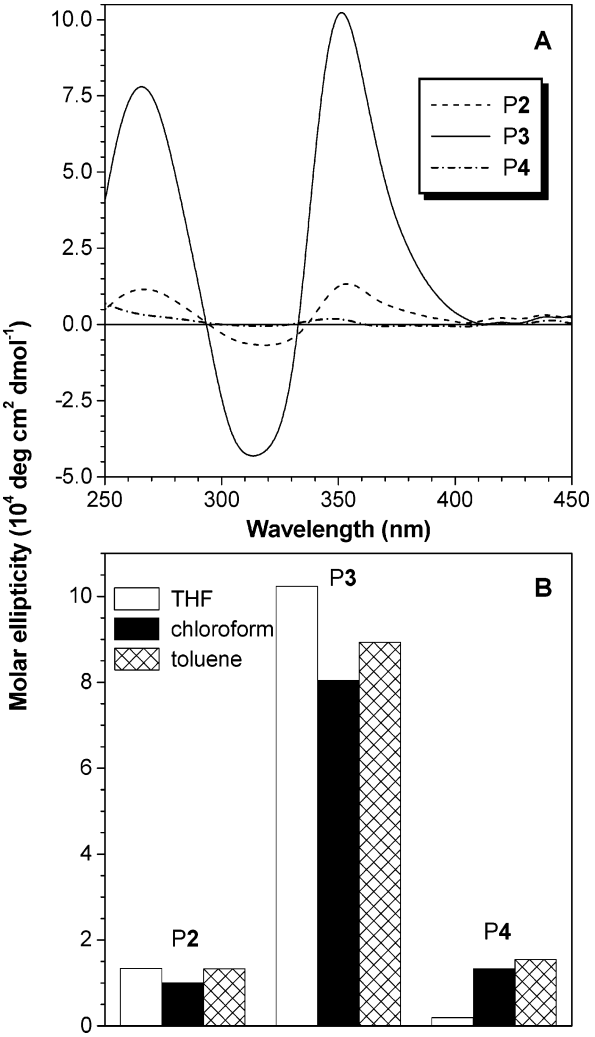


Figure 7. (A) CD spectra of P**2**−P**4** (samples taken from Table 2, nos. 5, 7, and 9) in THF at room temperature. (B) Variations of the first Cotton effects of P**2**−P**4** with solvents. Polymer concentration: 0.74−1.26 mM.

the CD spectrum of P**3** reveals that the polymer chain spirals in one preferred direction. The spectral profile of P**3** is similar to that of P**2**, but CD peaks of the former are much stronger than those of the latter. The molar ellipticity of P**3** at 351 nm is 102 300 deg cm^2 dmol^{-1}, ~3-fold higher than the highest value previously reported for the chiral disubstituted polyacetylenes in the similar spectral region ($[\theta]_{max}$ = 34 500 deg cm^2 dmol^{-1}).[19b] The main chain absorptions of P**4** in THF are rather weak. This is probably because its chain segments with left- and right-handedness are similarly populated with no one handedness being dominated in this solvent. The changes of the first Cotton effects at 356 nm with solvents for P**2**−P**4** are summarized in Figure 7B. When the solvent of P**2** is changed from THF to chloroform and to toluene, its first Cotton effect varies to a small extent with its sign remains unchanged (+). Similarly, the first Cotton effects of P**3** and P**4** experience small variations in magnitude and no reversals in sign when their solvents are changed. Like in the case of P**1** discussed above, the spectral stability of P**2**−P**4** against the solvent perturbations is probably again associated with the rigidity of their backbones.

Helical Thermochromism and Biomimetic Self-Assembly. Molar ellipticity of a helical polymer often changes with temperature, in many cases decreases with a temperature increase, due to thermally induced conformational randomization or helical unwinding.[5,7] This kind of helical thermochromism is useful and has found applications in temperature sensing, optical display, information storage, and so forth.[30,31] The chain helicity of chiral monosubstituted polyacetylenes is temperature-sensitive, but their helical thermochromism often suffers from such disadvantages as narrow range of working temperatures and poor reversibility of CD spectra due to the thermal instability of the polymers.[15,16] For example, the first Cotton effect of a poly(*N*-propargylalkylamide) at ~390 nm quickly diminishes (from ca. −10 000 deg cm^2 dmol^{-1} to almost zero) when the temperature is increased by merely 20 °C (from 20 to 40 °C).[32] As discussed above (cf. Figure 4), all of our chiral disubstituted poly(phenylpropiolate)s are thermally stable. We thus examined whether their chain helicity can be reversibly tuned in a wider temperature range.

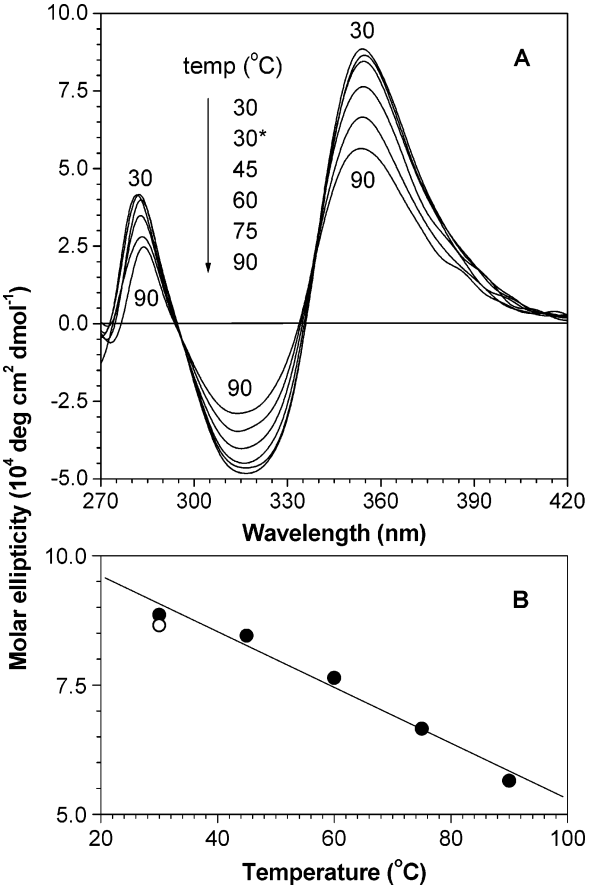


Figure 8. (A) CD spectra of P**3** (Table 2, no. 7) in toluene (1.13 mM) at different temperatures and (B) temperature effect on its molar ellipticity at 354 nm. The spectral data marked with asterisk (∗) and represented by open circle (○) are for the polymer solution returned to 30 °C after heating to 90 °C.

Figure 8A shows the CD spectra of a toluene solution of P**3** measured at various temperatures: from around room temperature (30 °C) to slightly below the boiling point of the solvent (90 °C). When the temperature is increased from 30 to 45 °C, the CD signals decrease in intensity. The CD spectrum progressively weakens when the temperature is gradually increased to 90 °C. As can be seen from the plot shown in Figure 8B, the first Cotton effect of P**3** at 354 nm monotonically deceases with an increase in temperature. When the polymer solution is naturally cooled from 90 to 30 °C, its CD spectrum recovers, nearly overlapping with the

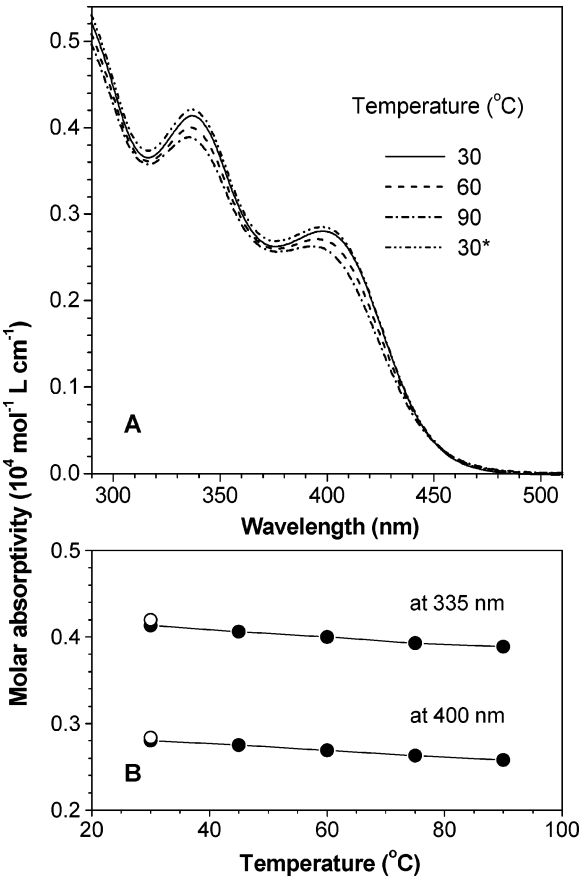


Figure 9. (A) UV spectra of P**3** (sample from Table 2, no. 7) in toluene at different temperatures and (B) variation of the molar absorptivity of P**3** at 335 and 400 nm with temperature. The spectral data marked with asterisk (∗) and represented by open circle (○) are for the polymer solutions returned to 30 °C after heating to 90 °C.

spectrum taken in the prepperturbation state. This suggests that the thermally "denatured" chain segments have folded back to the natural state during the cooling process and reveals that the chain helicity of P**3** can be continuously and reversibly manipulated by temperature.

Although the disubstituted polyacetylenes are thermally stable in the solid state (as verified by the TGA analyses), it is still a concern whether the polymers are stable in the solutions, as many people have reported that certain monosubstituted polyacetylenes decompose more rapidly in the solution state than in the solid state.[16] To address this concern, we measured the molecular weights of the polymers after their solutions had been progressively heated to 90 °C in air. The M_w and M_w/M_n of a thermally treated P**1**, for example, are 13 020 and 1.7, respectively, which are essentially the same as those of the starting material (M_w = 13 000, M_w/M_n = 1.8). The molecular weight change for P**3** is also small ($\Delta M_w = -1.3\%$). We measured the UV spectra of the polymer solutions at different temperatures, examples of which are given in Figure 9. The UV spectrum changes little even when the temperature is raised to 90 °C. When the solution is cooled back to 30 °C, the spectrum completely reinstalls (within experimental error). The M_w and UV data thus confirm that the polymers have not suffered from thermal degradation during the heating process and suggest that the helical thermochromism is caused by the reversible conformational changes of the chain segments, which

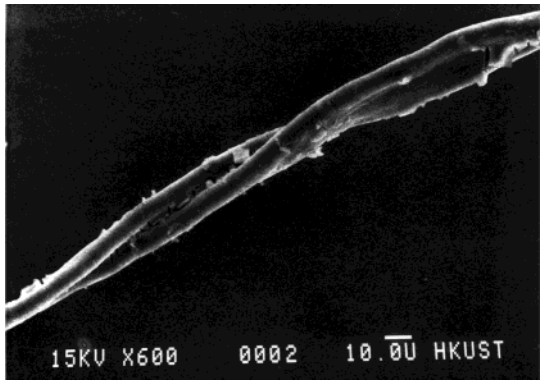


Figure 10. SEM photomicrograph of a twisted fiber formed upon diffusing a THF solution (3.5 mM) of P**3** (sample from Table 2, no. 5) into hexane. Scale bar: 10 μm.

practically do not affect the effective conjugation lengths of the polymer backbones. The severe steric hindrance of the two bulky substituents in each monomer repeat unit would hamper the chiral pendants from rotating to the opposite directions, and the decrease in the chain helicity is thus likely caused by the denature processes of helix untwining and pitch lengthening induced by the thermal perturbation.

It has become clear that the chirality of the pendant groups can be transcribed to the helicity of the polymer chains, although the poly(phenylpropiolate)s do not possess regular stereostructures. Can the helical chains be further organized into higher-order biomimetic structures through self-assembling? In our previous studies on the helical amphiphilic poly(phenylacetylene)s containing naturally occurring building blocks such as amino acids, sugars, nucleosides, and lipids, we have found that the polymers reproducibly self-organize into biomimetic hierarchical structures including micelles, vesicles, tubules, helical filaments, honeycomb patterns, mollusk shapes, and so forth.[9,10,12] We checked whether the chiral disubstituted poly(phenylpropiolate)s can also undergo similar self-assembling processes. Figure 10 shows a partial view of a long helical fiber of P**3** obtained upon diffusing its THF solution into hexane. The fiber consists of left- and right-handed strands, somewhat resembling the double helix of DNA. Each strand is ribbonlike in shape, suggesting that the morphological structure is assembled through side-by-side association of helical sheets. This demonstrates that the chain helicity of the chiral poly(phenylpropiolate) can be amplified to the macroscopic twist through self-organization. Detailed investigations on the self-assembling behaviors and mechanisms of the polymers are in progress in collaboration with our physicist colleagues and will be published in a separate paper in due course.

Concluding Remarks

In this work, we have successfully expanded the scope of applicability of our previously developed propiolate polymerization system[21] to the synthesis of chiral disubstituted polyacetylenes. By modifying the polymerization conditions or, more specifically, by replacing the molybdenum chlorides with the WCl_6-Ph_4Sn mixture, we succeeded in polymerizing the chiral phenylpropiolate monomers (**1**−**4**) into high molecular weight polymers in reasonable yields. The chiral poly(phenylpropiolate)s (P**1**−P**4**) exhibit a range of unique properties including thermal stability, electronic conjugation, optical activity, helical thermochromism, and self-as-

sembling capability. These attributes make the polyacetylenes promising candidates for specialty materials and may enable them to find practical applications in the high-tech industries.

The poly(phenylpropiolate)s are the first examples of helical disubstituted polyacetylenes containing "normal" and "ubiquitous" ester functional groups. In this regard, the success of our work is of far-reaching implications and opens a new avenue in the development of new disubstituted polyacetylenes with helical chirality and thermal stability. Our work offers a versatile tool for the ready creation of a large variety of new functional disubstituted polyacetylenes through simple couplings of propiolic acids with alcohols (sugars, sterols, lipids, etc.) or propargyl alcohols with acids (amino acids, fatty acids, fruit acids, etc.). In fact, the concept developed in this study has enabled us to quickly generate a series of new chiral disubstituted poly(phenylpropiolate)s such as P**12**−P**15**.[24] These polyacetylenes also possess irregular geometric (*Z*/*E*) configurations but exhibit very strong Cotton effects in the polyene backbone absorption region ([θ] up to ∼1 141 500 deg cm^2 dmol^{-1}), once again demonstrating that stereoregularity is not a necessary condition for the disubstituted polyacetylenes to be induced to helically rotate in a one-handed screw sense. This thus brings the acetylenic polymers into line with the vinyl polymers: amorphous vinyl polymers with irregular stereostructures are known to be induced to exhibit chain helicity by bulky substituents.[3,33−35]

Experimental Section

Materials and Instrumentation. Toluene (BDH) was predried over molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. Dichloromethane and acetonitrile (Lab-Scan) were dried over molecular sieves and distilled over calcium hydride. Except for molybdenum(V) chloride (Acros), all other reagents and solvents were purchased from Aldrich and used as received without further purification.

The IR spectra were measured on a Perkin-Elmer 16 PC FT-IR spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS; $\delta = 0$) or chloroform (7.26) as internal reference. The UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer, and the molar absorptivities (ϵ) of the polymers were calculated on the basis of their monomer repeat units. The mass spectra were recorded on a Finnigan TSQ 7000 triple quadrupole mass spectrometer operating in a chemical ionization (CI) mode using methane as carrier gas. The molecular weights of the polymers were estimated by a Waters Associates size-exclusion chromatograph (SEC) system. Degassed THF was used as eluent at a flow rate of 1.0 mL/min. A set of monodisperse polystyrenes covering molecular weight range 10^3−10^7 was used as calibration standards.

The thermal stability of the polymers was evaluated on a Perkin-Elmer TGA 7 under dry nitrogen at a heating rate of 20 °C/min. The specific optical rotations ($[\alpha]_D^{20}$) were measured on a Perkin-Elmer 241 polarimeter at 20 °C using a beam of plane-polarized light of the D line of a sodium lamp (589.3 nm) as monochromatic source. The CD spectra were recorded on a Jasco J-720 spectropolarimeter in 1 mm quartz curettes using a step resolution of 0.2 nm, a scan speed of 50 nm/min, a sensitivity of 0.1°, and a response time of 0.5 s. Each spectrum was the average of 5−10 scans. The SEM micrographs were taken on a JEOL JSM-35 CF scanning electron microscope operating at 15 kV after sputtering a thin layer (∼10−15 Å) of gold on the samples using a denton sputtering unit.

Monomer Synthesis. The phenylpropiolates containing [(1*S*)-*endo*]-(−)-borneyl (**1**), (1*R*,2*S*,5*R*)-(−)-menthyl (**5**), and cholesteryl groups (**6**) were synthesized by esterifications of phenylpropiolic acid with the corresponding chiral alcohols in the presence of DCC, TsOH, and DMAP (cf. Scheme 1). The aryl phenylpropiolates (**2**−**4**), in which the chiral groups are linked to the acetylene triple bonds via benzoate functional bridges, were prepared according to the reactions shown in Scheme 2. Typical experimental procedures for the synthesis of the phenylpropiolate monomers (**1**−**6**) are given below.

[(1*S*)-*endo*]-(−)-Borneyl Phenylpropiolate (1). In a typical run, [(1*S*)-*endo*]-(−)-borneol (1.6 g, 10.4 mmol), DCC (3.2 g, 15.5 mmol), TsOH (0.4 g, 2.0 mmol), and DMAP (0.25 g, 2.0 mmol) were dissolved in 250 mL of dry dichloromethane in a 500 mL, two-necked flask in an atmosphere of dry nitrogen. The solution was cooled to 0−5 °C with an ice−water bath, to which 1.5 g of phenylpropiolic acid (10.3 mmol) dissolved in 50 mL of dichloromethane was added under stirring through a dropping funnel. The reaction mixture was stirred overnight. After filtering out the formed urea solid, the solution was concentrated by a rotary evaporator. The product was purified by a silica gel column using chloroform/hexane (2:1 by volume) as eluent. White solid of **1** was isolated in 62.0% yield. IR (KBr), ν (cm^{-1}): 2223 and 2208 (vs, C≡C), 1703 and 1690 (vs, C═O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.61 (m, 2H, Ar−H ortho to C≡C), 7.39 (m, 3H, Ar−H para and meta to C≡C), 5.04 (m, 1H, OCH), 2.42 (m, 1H), 2.04 (m, 1H), 1.78 (m, 1H), 1.72 (m, 1H), 1.34 (m, 2H), 1.11 (m, 1H), 0.91 [m, 9H, $(CH_3)_3$]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 154.4 (CO_2), 132.8 (aromatic carbons ortho to C≡C), 130.3 (aromatic carbon para to C≡C), 128.4 (aromatic carbons meta to C≡C), 119.7 (aromatic carbon linked with C≡C), 85.6 (Ar*C*≡), 81.9 (OCH), 81.0 (≡*C*CO_2), 48.8, 47.8, 44.7, 36.4, 27.8, 26.9, 19.6, 18.7, 13.4. MS (CI): *m*/*e* 282.1 (M$^+$, calcd 282.1).

(1*R*,2*S*,5*R*)-(−)-Menthyl Phenylpropiolate (5). The synthetic procedure for this compound is similar to that for **1**. Pale yellow liquid; yield 56.1%. IR (neat), ν (cm^{-1}): 2228 and 2214 (vs, C≡C), 1706 (vs, C═O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.60 (m, 2H, Ar−H ortho to C≡C), 7.38 (m, 3H, Ar−H para and meta to C≡C), 4.85 (ddd, 1H, OCH), 2.14 (d, 1H), 1.95 (m, 1H), 1.75 (d, 1H), 1.51 (m, 2H), 1.13 (m, 4H), 0.92 [m, 6H, $(CH_3)_2$], 0.79 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 153.6 (CO_2), 132.8 (aromatic carbons ortho to C≡C), 130.4 (aromatic carbon para to C≡C), 128.4 (aromatic carbons meta to C≡C), 119.7 (aromatic carbon linked with C≡C), 85.7 (Ar*C*≡), 81.0 (≡*C*CO_2), 76.2 (OCH), 46.8, 40.6, 34.0, 31.4, 26.1, 23.3, 21.9, 20.6, 16.2. MS (CI): *m*/*e* 284.2 (M$^+$, calcd 284.2).

Cholesteryl Phenylpropiolate (6). Its synthetic procedure is similar to that for **1**. White solid; yield 34.1%. IR (KBr), ν (cm^{-1}): 2223 (vs, C≡C), 1706 (vs, C═O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.56 (m, 2H, Ar−H ortho to C≡C), 7.39 (m, 3H, Ar−H para and meta to C≡C), 5.40 (d, 1H, ═CH), 4.77 (m, 1H, OCH), 2.44 (t, 2H), 1.99−0.68 (m, 41H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 153.4 (CO_2), 139.2 (*C*═CH), 132.9 (aromatic carbons ortho to C≡C), 130.4 (aromatic carbon para to C≡C), 128.5 (aromatic carbons meta to C≡C), 123.0 (═CH), 119.7 (aromatic carbon linked with C≡C), 85.7 (Ar*C*≡), 81.0 (≡*C*CO_2), 76.0 (OCH), 56.6, 56.1, 50.0, 42.2, 39.7, 39.5, 37.8, 36.9, 36.5, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.6, 24.2, 23.8, 22.8, 22.5, 21.0, 19.2, 18.7, 11.8. MS (CI): *m*/*e* 515.5 [(M + 1)$^+$, calcd 515.5].

Ethyl 4-Benzyloxybenzoate (7). In a 500 mL round-bottom flask, 5.0 g (31.0 mmol) of ethyl 4-hydroxybenzoate and 6.0 g (43.0 mmol) of potassium carbonate were dissolved in 200 mL of acetone under gentle stirring. To the solution was added 6.9 g (40.0 mmol) of benzyl bromide, and the resulting mixture was stirred at room temperature for 48 h. The reaction was poured into 300 mL of water acidified with 30 mL of 37% hydrochloric acid. The solid was collected by suction filtration and purified by a silica gel column using chloroform as eluent. The white solid **7** was isolated in 97.0% yield.

4-Benzyloxybenzoic Acid (8). In a 500 mL round-bottom flask equipped with a condenser were placed 7.9 g (31.0 mmol) of **7** and 250 mL of 4% (w/v) ethanol solution of potassium hydroxide. The contents were refluxed for 4 h. The mixture was then poured into 300 mL of 1 M hydrochloric acid. The

product was collected by suction filtration and dried under vacuum. The white solid **8** was isolated in 93.0% yield.

Alkyl 4-Benzyloxybenzoates (9). [(1*S*)-*endo*]-(−)-Borneyl 4-benzyloxybenzoate was prepared by esterification of 4-benzyloxybenzoic acid (**8**) with [(1*S*)-*endo*]-(−)-borneol using DCC as dehydrating agent. Purification of the product was achieved by a silica gel column using chloroform/hexane (2:1 by volume) as eluent, giving a white solid in 69.4% yield. (1*R*,2*S*,5*R*)-(−)-Menthyl and cholesteryl 4-benzyloxybenzoates were prepared by similar procedures by esterifications of **8** with (1*R*,2*S*,5*R*)-(−)-menthol and cholesterol and obtained as white solids in 72.5 and 95.7% yields, respectively.

Alkyl 4-Hydroxybenzoate (10). [(1*S*)-*endo*]-(−)-Borneyl 4-hydroxybenzoate was prepared by the following procedures: a solution of 4.0 g (11.0 mmol) of **9** in 100 mL of ethyl acetate was hydrogenated at atmospheric pressure in the presence of 500 mg of 10% palladium/carbon. Hydrogen was allowed to be absorbed in 2 h, and the reaction was then stopped. The mixture was filtered via a filter paper, and the solvent was then evaporated. The product was isolated as white solid in 96.8% yield. (1*R*,2*S*,5*R*)-(−)-Menthyl and cholesteryl 4-hydroxybenzoates were prepared by similar procedures by hydrogenations of (1*R*,2*S*,5*R*)-(−)-menthyl and cholesteryl 4-benzyloxybenzoates and obtained as white solids in 91.3 and 69.6% yields, respectively.

4-{[(1*S*)-*endo*]-(−)-Borneyloxycarbonyl}phenyl Phenylpropiolate (2). The monomer was prepared by esterification of phenylpropiolic acid with [(1*S*)-*endo*]-(−)-borneyl 4-hydroxybenzoate by a procedure similar to that for the preparation of **1**. White solid; yield 68.2%. IR (KBr), ν (cm^{-1}): 2228 and 2202 (vs, C≡C), 1730 and 1710 (vs, C=O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.13 (d, 2H, Ar−H ortho to CO_2), 7.65 (m, 2H, Ar−H ortho to C≡C), 7.44 (m, 3H, Ar−H para and meta to C≡C), 7.28 (d, 2H, Ar−H meta to CO_2), 5.12 (m, 1H, OCH), 2.48 (m, 1H), 2.11 (m, 1H), 1.82 (m, 1H), 1.76 (m, 1H), 1.32 (m, 2H), 1.14 (m, 1H), 0.92 [m, 9H, $(CH_3)_3$]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 165.7 (Ar*C*O_2), 153.4 (aromatic carbon linked with OCO), 151.6 (≡C*C*O_2), 133.2 (aromatic carbons ortho to C≡C), 131.1 (aromatic carbons ortho to CO_2 and para to C≡C), 128.9 (aromatic carbon linked with CO_2), 128.6 (aromatic carbons meta to C≡C), 121.4 (aromatic carbons meta to CO_2), 118.9 (aromatic carbon linked with C≡C), 89.2 (Ar*C*≡), 80.7 (OCH), 79.9 (≡*C*CO_2), 49.0, 47.8, 44.9, 36.8, 28.0, 27.3, 19.7, 18.8, 13.5. MS (CI): *m/e* 403.1 [(M + 1)$^+$, calcd 403.1].

4-[(1*R*,2*S*,5*R*)-(−)-Menthoxycarbonyl]phenyl Phenylpropiolate (3). It was prepared by a procedure similar to that for the preparation of **5**. Yellow liquid; yield 91.7%. IR (neat), ν (cm^{-1}): 2233 and 2205 (vs, C≡C), 1732 and 1716 (vs, C=O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.11 (d, 2H, Ar−H ortho to CO_2), 7.65 (m, 2H, Ar−H ortho to C≡C), 7.43 (m, 3H, Ar−H para and meta to C≡C), 7.27 (d, 2H, Ar−H meta to CO_2), 4.93 (ddd, 1H, OCH), 2.14 (d, 1H), 1.95 (m, 1H), 1.75 (d, 1H), 1.51 (m, 2H), 1.13 (m, 4H), 0.92 [m, 6H, $(CH_3)_2$], 0.79 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 165.1 (Ar*C*O_2), 153.4 (aromatic carbon linked with OCO), 151.6 (≡C*C*O_2), 133.2 (aromatic carbons ortho to C≡C), 131.21 (aromatic carbons ortho to CO_2), 131.15 (aromatic carbons para to C≡C), 128.9 (aromatic carbon linked with CO_2), 128.7 (aromatic carbons meta to C≡C), 121.4 (aromatic carbons meta to CO_2), 119.0 (aromatic carbon linked with C≡C), 89.2 (Ar*C*≡), 80.0 (≡*C*CO_2), 75.0 (OCH), 47.2, 40.9, 34.2, 31.4, 26.5, 23.6, 22.0, 20.7, 16.5. MS (CI): *m/e* 405.2 [(M + 1)$^+$, calcd 405.2].

4-(Cholesteryloxycarbonyl)phenyl Phenylpropiolate (4). Its preparation procedure was similar to that for **6**. White solid; 53.7%. IR (KBr), ν (cm^{-1}): 2232 and 2206 (vs, C≡C), 1720 (vs, C=O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.10 (aromatic carbons ortho to CO_2), 7.62 (m, 2H, Ar−H ortho to C≡C), 7.43 (m, 3H, Ar−H para and meta to C≡C), 7.26 (aromatic carbons meta to CO_2), 5.43 (d, 1H, =CH), 4.86 (m, 1H, OCH), 2.46 (t, 2H), 1.99−0.68 (m, 41H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 165.0 (ArCO_2), 153.4 (aromatic carbon linked with OCO), 151.6 (≡C*C*O_2), 139.5 (*C*=CH), 133.2 (aromatic carbons ortho to C≡C), 131.20 (aromatic carbons ortho to CO_2), 131.16 (aromatic carbon para to C≡C), 128.9 (aromatic carbon linked with CO_2), 128.8 (aromatic carbons meta to C≡C), 122.9 (=CH), 121.3 (aromatic carbons meta to CO_2), 119.0 (aromatic carbon linked with C≡C), 89.1 (Ar*C*≡), 8.0 (≡*C*CO_2), 74.8 (OCH), 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.3, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8. MS (CI): *m/e* 635.5 [(M + 1)$^+$, calcd 635.5].

Polymerization Reactions. All the polymerization reactions and manipulations were carried out under dry nitrogen using Schlenk techniques in a vacuum line system or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purifications of the polymers, which were conducted in an open atmosphere. A typical experimental procedure for the polymerization of **1** is given below:

Into a baked 20 mL Schlenk tube with a stopcock in the sidearm was added 226.0 mg (0.80 mmol) of monomer **1**. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. Freshly distilled toluene (1.5 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 15.9 mg of tungsten(VI) chloride and 17.2 mg of tetraphenyltin in 1.5 mL of toluene. The two tubes were aged at 60 °C for 15 min, and the monomer solution was transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at 60 °C under nitrogen for 24 h. The solution was then cooled to room temperature, diluted with 5 mL of chloroform, and added dropwise to 500 mL of acetone through a cotton filter under stirring. The precipitate was allowed to stand overnight and was then filtered with a Gooch crucible. The polymer was washed with acetone and dried in a vacuum oven to a constant weight.

Characterization Data. P**1**: Red powdery solid; yield 22.6%. M_w 17 600; M_w/M_n 1.8 (SEC; Table 1, no. 5). IR (KBr), ν (cm^{-1}): 1709 (vs, C=O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.74 (Ar−H ortho to C=C), 6.38 (Ar−H para and meta to C=C), 5.35 (OCH), 1.99, 1.56, 0.94. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 164.0 (=C*C*O_2), 143.0 (Ar*C*=C), 138.0 (=*C*CO_2), 134.0 (aromatic carbons ortho to C=C), 131.0 (aromatic carbon para to C=C), 125.0 (aromatic carbons meta to and linked with C=C), 81.9 (OCH), 49.8, 78.3, 44.6, 34.7, 25.6, 19.8, 18.8, 14.5. UV (THF, 78 μM), λ (nm)/ϵ (10^4 mol^{-1} L cm^{-1}): 305/0.33, 355/0.17.

P**2**: Orange powdery solid; yield 19.5%. M_w 14 600; M_w/M_n 1.4 (SEC, Table 2, no. 5). IR (KBr), ν (cm^{-1}): 1722 (vs, C=O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.04 (Ar−H ortho to CO_2), 6.88 (Ar−H meta to CO_2), 6.55 (Ar−H ortho to C=C), 6.15 (Ar−H para and meta to C=C), 5.15 (m, 1H, OCH), 2.30, 2.13, 1.80, 1.35, 0.97. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 165.7 (ArCO_2), 164.1 (=C*C*O_2), 154.0 (aromatic carbon linked with OCO), 153.5 (Ar*C*=), 139.6 (=*C*CO_2), 134.9 (aromatic carbons ortho to C=C), 130.9 (aromatic carbons ortho to CO_2 and para to C=C), 128.4 (aromatic carbons linked with CO_2 and meta to C=C), 126.1 (aromatic carbon linked with C=C), 121.6 (aromatic carbons meta to CO_2), 80.6 (OCH), 49.1, 48.0, 45.0, 37.0, 28.2, 19.9, 19.1, 13.8. UV (THF, 64 μM), λ (nm)/ϵ (10^4 mol^{-1} L cm^{-1}): 234/1.91, 335/0.47, 400/0.35.

P**3**: Orange powdery solid; yield 32.8%. M_w 19 500; M_w/M_n 1.6 (SEC, Table 2, no. 7). IR (KBr), ν (cm^{-1}): 1720 (vs, C=O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.00 (Ar−H ortho to CO_2), 6.85 (Ar−H meta to CO_2), 6.49 (Ar−H ortho to C=C), 6.10 (Ar−H para and meta to C=C), 4.96 (OCH), 2.14, 1.97, 1.76, 1.59, 1.14, 0.94, 0.82. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 164.6 (ArCO_2), 163.8 (=C*C*O_2), 153.6 (aromatic carbon linked with OCO), 153.2 (Ar*C*=), 139.3 (=*C*CO_2), 134.5 (aromatic carbons ortho to C=C), 130.9 (aromatic carbons ortho to CO_2 and para to C=C), 128.1 (aromatic carbon linked with CO_2 and meta to C=C), 125.5 (aromatic carbon linked with C=C), 121.2 (aromatic carbons meta to CO_2), 74.7 (OCH), 47.3, 40.7, 34.2, 31.2, 26.5, 23.4, 21.8, 20.6, 16.3. UV (THF, 85 μM), λ (nm)/ϵ (10^4 mol^{-1} L cm^{-1}): 234/1.81, 335/0.44, 400/0.30.

P**4**: Orange powdery solid; yield 43.0%. M_w 43 300; M_w/M_n 2.2 (SEC, Table 2, no. 9). IR (KBr), ν (cm^{-1}): 1722 (vs, C=O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.98 (aromatic carbons ortho to CO_2), 6.82 (Ar−H meta to CO_2), 6.46 (Ar−H ortho to C=C), 6.07 (Ar−H para and meta to C=C), 5.44

(=CH), 4.86 (m, 1H, OCH), 2.49, 2.01, 1.51, 1.28, 1.10, 0.9, 0.73. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 164.9 ($ArCO_2$), 164.3 (=CCO_2), 154.0 (aromatic carbon linked with OCO and Ar*C*=), 139.3 (=CCO_2 and *C*=CH), 135.0 (aromatic carbons ortho to C=C), 131.0 (aromatic carbons ortho to CO_2 and para to C=C), 128.3 (aromatic carbon linked with CO_2 and meta to C=C), 122.7 (=CH), 121.6 (aromatic carbons meta to CO_2), 74.8 (OCH), 56.7, 56.1, 50.1, 42.4, 39.6, 38.2, 37.1, 36.8, 36.3, 35.9, 32.0, 28.4, 28.2, 24.5, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.1. UV (THF, 71 μM), λ (nm)/ϵ (10^4 mol^{-1} L cm^{-1}): 234/1.44, 335/0.44, 400/0.32.

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Supporting Information Available: UV spectra of THF solutions of P**1**−P**4** at room temperature (Figure s1). This material is available free of charge via the Internet at http://pubs.acs.org.

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