Helical Conjugated Polymers: Synthesis, Stability, and Chiroptical Properties of Poly(alkyl phenylpropiolate)s Bearing Stereogenic Pendants

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ABSTRACT: Chiral poly(alkyl phenylpropiolate)s $-\{(C_6H_5)C{=}C[CO_2(CH_2)_2OCOR^*]\}_n-$ with R* = (*S*)-(+)-[1-(6-methoxy-2-naphthyl)ethyl (P**1**), (1*R*,2*S*,5*R*)-(−)-menthoxymethyl (P**2**), (*S*)-(+)-(α-acetoxy)benzyl (P**3**), and cholesteryloxy (P**4**) were synthesized, and their structures and properties were investigated. The monomers [$C_6H_5C{\equiv}CCO_2(CH_2)_2OCOR^*$; **1**−**4**] were prepared by esterifications of stereogenic acids **8**−**10** or chloroformate (**11**) with 3-hydroxyethyl phenylpropiolate (**7**) in high yields. Polymerizations of **1**−**4** were effected by $MoCl_5-Ph_4Sn$ at 60 or 80 °C, and polymers with high molecular weights (M_w up to $\sim 100 \times 10^3$) were obtained in moderate yields. The polymers were characterized by IR, NMR, TGA, UV, and CD analyses. All of the polymers are stable, losing little of their weights when heated to ≥300 °C and undergoing no chain scissions when annealed in air at ≥150 °C. The macromolecular chains take helical conformations with preferred handedness, and their helical chirality can be reversibly tuned by solvent or temperature to varying extents.

Introduction

Polyacetylene is the best-known conjugated polymer, whose doped form shows high conductivity that stands comparison with that of copper.[1] Its notorious intractability and instability have, however, greatly detracted from its potential for technological applications. Attachments of appropriate pendants to the polyacetylene backbone can not only help improve the processability and stability but also generate new polyacetylene derivatives with functional properties that are absent in the parent form.[2,3] An example in this regard is the incorporation of stereogenic groups into polyacetylene chains. Enthusiastic synthetic effort in the area has resulted in the creation of a large variety of helical substituted polyacetylenes, most of which are soluble, some of which are stable, and all of which are optically active, although the optical activity varies considerably from one polymer to another.[4−6]

Most of the optically active polyacetylenes bear *one substituent* in each of their monomer repeat units (and are hence *monosubstituted*), with an overwhelming majority of them being poly(phenylacetylene) and polypropargyl derivatives.[4−6] While the monosubstituted polyacetylenes are more stable than their unsubstituted polyacetylene parent, their stabilities are still of concern for many practical applications.[7,8] One way to further enhance the polymer stability is to add *one more substituent* into the repeat unit to make a *disubstituted* polyacetylene, which is generally more stable than its monosubstituted homologue.[3a,9] For example, poly(1-chloro-2-phenylacetylene), an achiral disubstituted polyacetylene, does not degrade when heated in air at 120 °C for 20 h, whereas poly(phenylacetylene) readily decomposes when treated under the same conditions.[9] It is envisioned that the chiral substituted polyacetylenes will behave in a similar manner; that is, a helical disubstituted polyacetylene will be more stable than its monosubstituted counterpart.

Helical disubstituted polyacetylenes have, however, been seldom prepared.[10] The rareness of such polymers is mainly due to the synthetic difficulty originating from the lack of efficient polymerization systems for disubstituted acetylenes containing functional groups. While $TaCl_5$ and $NbCl_5$ are the most widely used catalysts for the polymerizations of nonfunctional or nonpolar disubstituted acetylenes such as 1-phenyl-1-alkynes,[2] they are intolerant of functional groups. Indeed, the transition-metal halides are so incompatible to polar moieties that they fail to initiate the polymerization of a disubstituted acetylene containing even an ester unit, a functional group often found in common organic molecules.[3a,11,12]

In our previous work, we succeeded in polymerizing a group of chiral disubstituted acetylenes bearing ester functionality, i.e., phenylpropiolates ($C_6H_5C{\equiv}CCO_2R^*$), using an inexpensive WCl_6-Ph_4Sn mixture, a "classic" metathesis catalyst.[11,13,14] Our success may offer access to a potentially large family of helical disubstituted polyacetylenes because a great number of stereogenic propiolates can be facilely prepared by simple esterification reactions of propiolic acid, a commercially available compound, with chiral alcohols, which are synthetically ubiquitous and naturally abundant. Indeed, with ease, we have already prepared two groups of propiolates by attaching naturally occurring sterols to phenylpropiolate directly (Scheme 1, eq 1) or via an aromatic ring (eq 2) and effected their polymerizations using the W catalyst in our previous studies.[11,15]

To further demonstrate the versatility of the propiolate system and to explore its utility potential in the synthesis of helical disubstituted polyacetylenes, in this work, we attached stereogenic units to phenyl-propiolate via a short aliphatic chain. Although the alkyl phenylpropiolates can be prepared through the route shown

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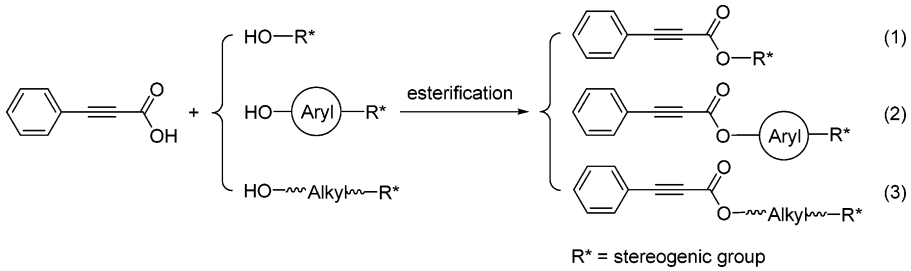
Scheme 1



Scheme 2

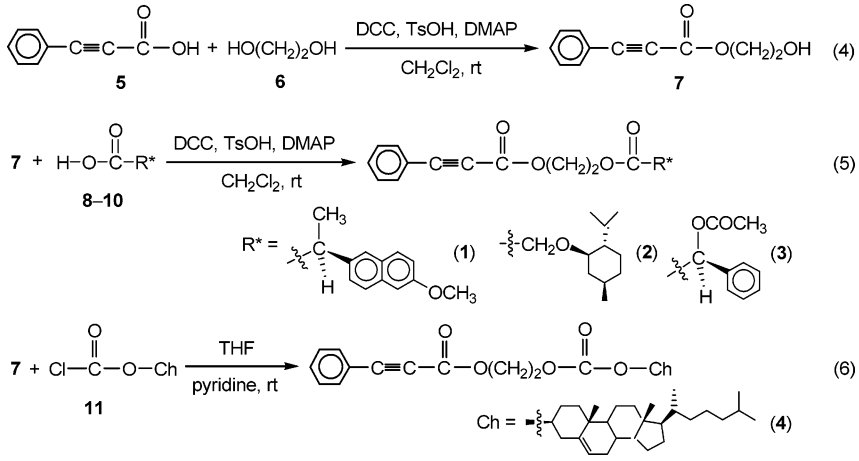
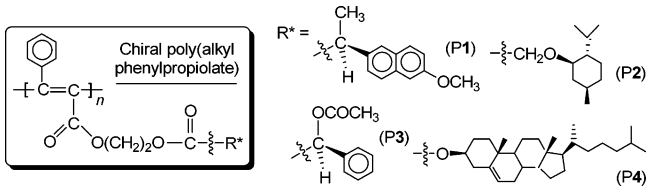


Chart 1



in eq 3 (Scheme 1), we took a different synthetic approach, as given in eqs 4−6 (Scheme 2). This synthetic path is more "economic" because it subjects the more expensive chiral compounds to just single steps of reactions. The syntheses were straightforward, and the products **1**−**4** were obtained in high yields. The monomers were, however, not polymerizable by the W catalyst, indicating that the catalytic process is substrate-sensitive. In this report we tell how the new monomers can be polymerized and what properties of the resultant poly(alkyl phenylpropiolate)s (P**1**−P**4**; Chart 1) exhibit.

Results and Discussion

Polymer Synthesis. The stereogenic alkyl phenylpropiolates **1**−**4** are, as discussed above, prepared by the molecularly economic synthetic routes shown in Scheme 2. Monomers **1**−**3** are synthesized by esterification of phenylpropiolic acid (**5**) with ethylene glycol (**6**) in dichloromethane (DCM) at room temperature (eq 4) followed by a successive esterification of 2-hydroxyethyl phenylpropiolate (**7**) with stereogenic acids **8**−**10** in the presence of 1,3-dicyclohexylcarbodiimine (DCC), *p*-toluenesulfonic acid (TsOH), and 4-(dimethylamino)-pyridine (DMAP). Taking advantage of the commercial availability of cholesteryl chloroformate (**11**), monomer **4** is prepared by esterification of **11** with **7** in the presence of pyridine (eq 6). The reactions went smoothly, and the desirable monomers were isolated in high yields (∼84−97%) after column purifications. While **1** and **4** are white solids, **2** and **3** are pale yellow liquids. All of the monomers were characterized by spectroscopic methods, from which satisfactory analysis data were obtained (see Experimental Section for details).

Table 1. Polymerization of 2-{(*S*)-(+)-[1-(6-Methoxy-2-naphthyl)ethyl]carbonyloxy}ethyl Phenylpropiolate (1)[a]

no.	catalyst	solvent	temp (°C)	yield (%)	M_w[b]	M_w/M_n[b]
1	$[Rh(nbd)Cl]_2$[c]	CH_3CN	40	0		
2	WCl_6-Ph_4Sn	toluene	60	0		
3	$MoCl_5-Ph_4Sn$	toluene	rt[d]	0		
4	$MoCl_5-Ph_4Sn$	toluene	60	57.6	74 200	2.7
5	$MoCl_5-Ph_4Sn$	toluene	80	trace		

[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] Determined by GPC in THF on the basis of a polystyrene calibration. [c] nbd = 2,5-norborndiene. [d] Room temperature (∼23 °C).

To polymerize the monomers, we tried different catalyst systems. We first attempted to polymerize **1** using $[Rh(nbd)Cl]_2$, a good catalyst for polymerization of monosubstituted propiolates ($HC{\equiv}CCO_2R$).[16] Stirring a mixture of $[Rh(nbd)Cl]_2$ and **1** in acetonitrile at 40 °C for 24 h, however, yielded no polymeric product (Table 1, no. 1). Clearly the rhodium complex is incapable of initiating the polymerization of **1**, a disubstituted propiolate. WCl_6-Ph_4Sn could not polymerize **1** either, which is striking because the W mixture can effectively initiate polymerizations of aryl phenylpropiolates.[11] $MoCl_5-Ph_4Sn$, delightfully, polymerized **1** at 60 °C into a polymer with a high molecular weight (∼74×10^3) in a good yield (∼58%; Table 1, no. 4). No or trace amount of polymer product was obtained when the reaction was carried out at a lower (rt) or higher temperature (80 °C; Table 1, nos. 3 and 5), indicative of thermally sensitive nature of the propiolate polymerization.

We then tried to polymerize monomers **2**−**4**, and the results are summarized in Table 2. None of the mono-

Chart 2

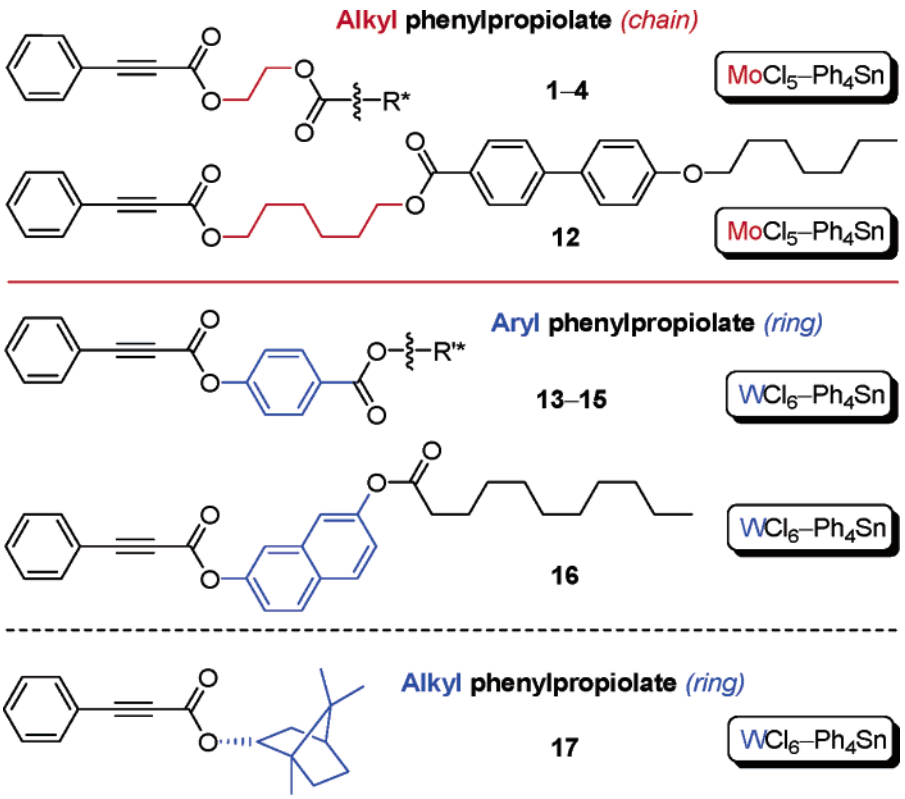


Table 2. Polymerizations of Ethyl Phenylpropiolates (2−4)[a]

no.	catalyst	temp (°C)	yield (%)	M_w[b]	M_w/M_n[b]
	2-[(1*R*,2*S*,5*R*)-(−)-Menthoxymethylcarbonyloxy]ethyl Phenylpropiolate (**2**)				
1	WCl_6-Ph_4Sn	60	trace		
2	$MoCl_5-Ph_4Sn$	60	trace		
3	$MoCl_5-Ph_4Sn$	80	17.8	60 900	2.0
	2-{(*S*)-(+)-[(α-Acetoxy)benzyl]carbonyloxy}ethyl Phenylpropiolate (**3**)				
4	WCl_6-Ph_4Sn	80	0		
5	$MoCl_5-Ph_4Sn$	60	trace		
6	$MoCl_5-Ph_4Sn$	80	34.3	15 400[c]	1.5
	2-(Cholesteryloxycarbonyl)ethyl Phenylpropiolate (**4**)				
7	WCl_6-Ph_4Sn	80	trace		
8	$MoCl_5-Ph_4Sn$	80	6.2	96 400	3.2

[a] Carried out under nitrogen in toluene for 24 h; $[M]_0 = 0.2$ M, [cat.] = [cocat.] = 10 mM. [b] Determined by GPC in THF on the basis of a polystyrene calibration. [c] Soluble fraction (completely soluble in chloroform but only partially soluble in THF).

mers could be polymerized by WCl_6-Ph_4Sn. The polymerizations of **2**−**4** catalyzed by $MoCl_5-Ph_4Sn$ were again temperature-sensitive, but the best results for the polymerizations of these monomers were obtained at the highest temperature we examined, that is, 80 °C. The polymers of **2** and **4** as well as **1** are completely soluble in THF, but that of **3** is only partially soluble in THF, though it is completely soluble in halogenated solvents such as chloroform and DCM. The characterization of this polymer was thus conducted in the halogenated solvents.

It becomes clear that WCl_6-Ph_4Sn is ineffective in polymerizing the alkyl phenylpropiolates **1**−**4**. In our previous work, however, we have found that this mixture works well for the polymerizations of the aryl phenylpropiolates containing similar chiral units R* (**13**−**15**).[11] As can be easily recognized from Chart 2, the main structural difference between these two sets of monomers are the groups attached to the propiolate oxygen atoms (marked in color): ethyl chains in **1**−**4** vs phenyl rings in **13**−**15**. It is amazing that such a small structural difference has caused such a big difference in the polymerizability of the monomers by the different catalysts. Is this due to steric or electronic effects? To get a clue to the question, we compared the polymerizabilities of some propiolate monomers with similar molecular structures. Monomer **12**, which possesses a hexyl chain, is polymerizable by the Mo catalyst, whereas monomer **16**, which possesses a naphthyl ring, is polymerizable by the W catalyst.[17] This set of data further proves the general trend that the Mo and W mixtures are effective catalysts for the alkyl and aryl phenylpropiolates, respectively, but still does not provide a clear answer to the question raised above.

Monomer **17**, however, can be polymerized by the W catalyst[18] but not the Mo mixture. Since the borneyl group of **17** is an aliphatic but not aromatic ring, the electronic effect can thus be excluded. The major structural difference between monomer **17** and monomers **1**−**4** as well as **12** is the bulkiness of the alkyl groups. It can thus be concluded that the steric effect has played an important role in determining the polymerizabilities of the phenylpropiolate monomers. In other words, the Mo and W mixtures are capable of polymerizing the sterically less (**1**−**4** and **12**) and more demanding phenylpropiolates **13**−**17**, respectively. It is noteworthy that the former catalyst cannot polymerize the latter monomers, and vice versa, revealing the stereospecific nature of the phenylpropiolate polymerizations.

Structural Characterization. The polymeric products were characterized by spectroscopic methods, and all the polymers gave satisfactory analysis data corresponding to their expected molecular structures (see

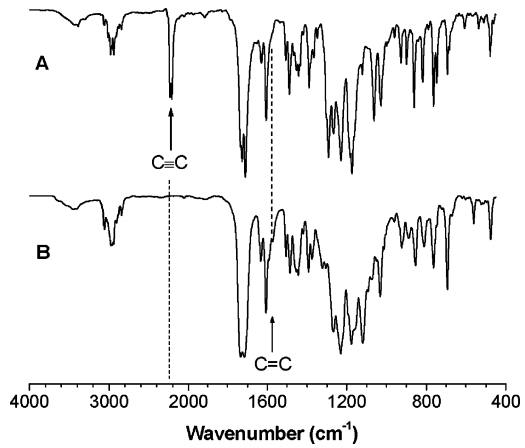


Figure 1. IR spectra of (A) monomer **1** and (B) its polymer P**1**.

Experimental Section for details). An example of the IR spectrum of P**1** is shown in Figure 1, the spectrum of whose monomer (**1**) is also given in the same figure for comparison. The monomer shows absorption bands at 2232 and 2209 cm^{-1} associated with C≡C stretching. The vibration bands are strong due to the electronic communication between the propiolate ester group and the acetylene triple bond.[19] No C≡C stretching bands are observed in the spectrum of P**1**. On the other hand, a new band associated with C=C stretching of the polyene backbone appears at 1573 cm^{-1}, proving that P**1** is formed by the conversion of the acetylenic triple bonds to the olefinic double bonds.

Figure 2 shows the ^{1}H NMR spectra of polymer P**1** and its monomer **1** in chloroform. The protons of the phenyl ring linked to the acetylene triple bond of **1** resonate at δ 7.43 and 7.37 (*a*; Figure 2A), which disappear in the spectrum of P**1** (Figure 2B). The transformation of the acetylenic triple bond to the olefinic double bond upfield shifts the absorptions of the phenyl protons, whose resonance now occurs at δ 6.76 (*a*; Figure 2B).[19] Interestingly, the resonance peaks of the ethyl protons (*b*, *c*, *e*, and *d*) also upfield shift upon polymerization, whereas those of the naphthyl (*f*) and methoxy protons (*g*) slightly downfield shift. No unexpected signals are observed in the spectrum of the polymer, and all the peaks can be readily assigned to the resonance of appropriate protons as marked in Figure 2B. The NMR analyses thus confirm that the triple bonds have been consumed by the acetylene polymerization and that the molecular structure of the polymer is indeed P**1**, as shown in Chart 1.

Figure 3 shows the ^{13}C NMR spectrum of P**1** along with that of its monomer **1**. While the acetylene carbon atoms of **1** resonate at δ 86.7 and 80.1, these peaks are completely absent in the spectrum of its polymer (P**1**). Instead, two new peaks appear at δ 150.8 and 140.4. The olefinic carbons of poly(methyl propiolate) $\{-[HC{=}C(CO_2CH_3)]_n-\}$ is known to resonate at δ 134 and 128.[16] Since P**1** can be viewed as a disubstituted congener of poly(methyl propiolate), the new peaks at δ 150.8 and 140.4 can thus be assigned to the resonance of polyene carbons of P**1**. This once again proves that the propiolate polymerization is realized through the transformation of the triple bonds to the double bonds. Similar to what observed in the polymerizations of aryl propiolates **13**−**15**,[11] the polymerization of **1** also causes a downfield shift of the resonance peak of the carbonyl carbon

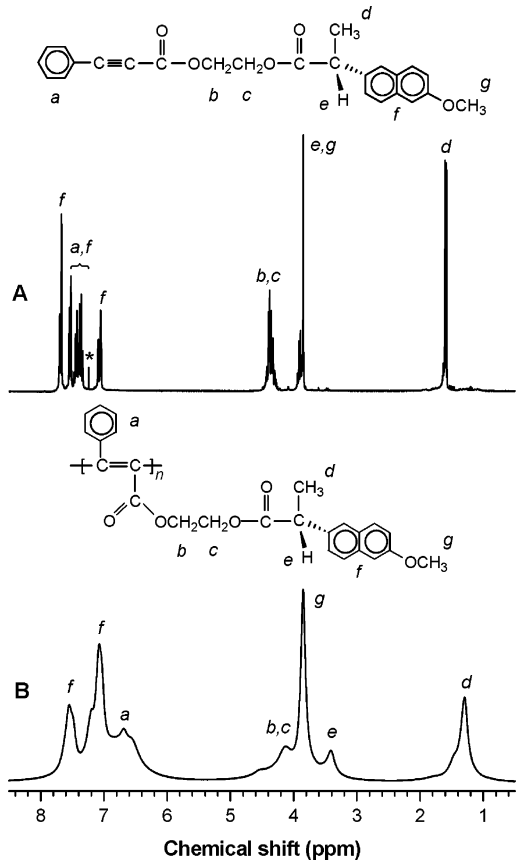


Figure 2. ^{1}H NMR spectra of chloroform solutions of (A) **1** and (B) its polymer P**1**. The solvent peak is marked with an asterisk (*).

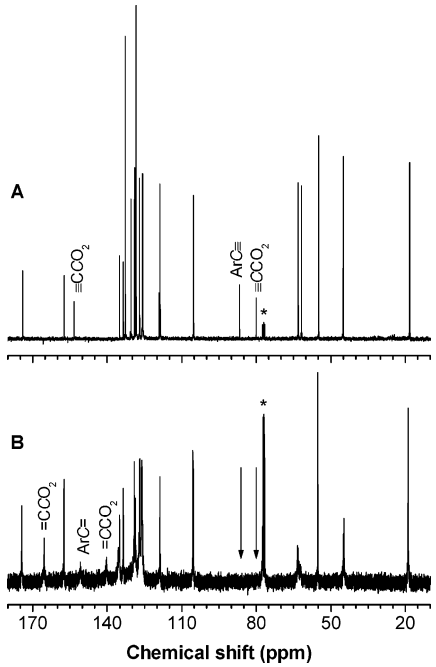


Figure 3. ^{13}C NMR spectra of chloroform solutions of (A) **1** and (B) its polymer P**1**. The solvent peaks are marked with asterisks (*).

directly linked to the acetylene triple bond (from δ 153.3 to 165.5).[16]

Thermal Stability. (Unsubstituted) polyacetylene readily decomposes upon exposure to air at room temperature because of its high reactivity with oxygenic species.[1−3] Polymers P**1**−P**4** are polyacetylene deriva-

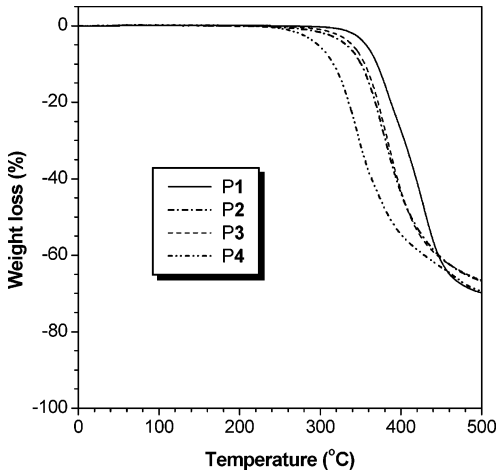


Figure 4. TGA thermograms of polymers P**1**−P**4** recorded under nitrogen at a heating rate of 20 °C/min.

Table 3. Thermolysis Resistance of Poly(2-{(*S*)-(+)-[1-(6-Methoxy-2-naphthyl)ethyl]carbonyloxy}ethyl Phenylpropiolate) (P1)[a]

no.	temp (°C)	M_w[b]	M_w/M_n[b]
1[c]	∼23[d]	74 200	2.7
2	80	78 000	2.3
3	100	74 000	2.4
4	150	78 700	2.5
5	200	insoluble	

[a] Annealed in air at a given temperature for 2 h. [b] Determined by GPC in THF on the basis of a polystyrene calibration. [c] Starting material. [d] Room temperature.

tives, and it is of interest to learn how stable they are. GPC analyses of the polymer samples stored under ambient conditions (in air) for >2 years find no decrease in their molecular weights, revealing that the polymers are stable at room temperature. TGA analyses of the polymers indicate that they are also stable at elevate temperatures. As can be seen from Figure 4, P**1** loses merely 5% of its weight when heated to a temperature as high as 357 °C (T_5). The T_5's of P**2**, P**3**, and P**4** are 333, 340, and 297 °C, respectively, which are well comparable to that of polystyrene (330 °C),[20] a stable commodity polymer.

To further examine the stability of the polymers, we annealed P**1** at different temperatures in air for 2 h. Table 3 lists the molecular weight changes of the polymer after the thermal treatment. Little change in M_w is observed when P**1** is annealed at temperature up to 150 °C, while further heating to 200 °C leads to gel formation. This confirms that the polymer is resistant to thermal degradation caused by oxidative chain scission. The high stability of the polymer is possibly due to the jacket effect of its pendant groups as well as the electron-withdrawing effect of the ester groups in the immediate vicinity of the polyene backbone. The former effect sterically shields the polyene backbone from the attack of the thermolytic species, and the latter effect reduces the reactivity of the polymer through the electronic interaction of the ester groups with the polyene backbone.

Electronic Transition. The UV spectra of the chloroform solutions of the polymers are shown in Figure 5. The polymers exhibit absorption maxima (λ_{max}) in the wavelength regions of ∼320−330 and ∼370−390 nm with varying molar absorptivities (ϵ_{max}). These absorption peaks must be due to the polyene backbones

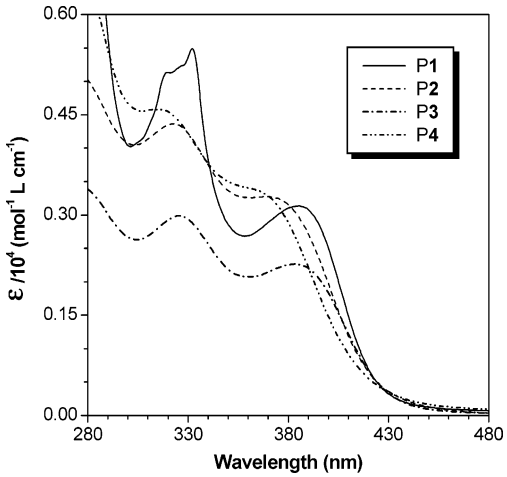


Figure 5. UV spectra of poly(alkyl phenylpropiolate)s P**1**−P**4** in chloroform at room temperature.

of P**1**−P**4** because none of their monomers possesses a chromophoric group that absorbs at wavelengths longer than ∼300 nm.[11,19] The λ_{max} and ϵ_{max} values of the backbone absorptions of the polymers suggest that their effective conjugation lengths are short, being just a few monomer repeat units, due to the steric effects of their pendant groups (there exist two substituents in one monomer repeat unit). This offers a circumstantial evidence for their low reactivity and high resistance to thermolytic and oxidative decompositions.

Chiroptical Properties. All of the poly(phenylpropiolate)s (P**1**−P**4**) are optically active. The specific optical rotations ($[\alpha]^{20}_D$) of P**1**−P**3** (−544° to +511°) are almost 1 order of magnitude higher than those of their monomers (−60.0° to +52.1°) in the same solvents, suggestive of chirality contribution from the polyene backbones. In other words, the stereogenic pendants have induced the polyacetylene chains to helically rotate with an excess of one preferred handedness. The $[\alpha]^{20}_D$ values of P**4** are lower than those of P**1**−P**3**, but the change in its $[\alpha]^{20}_D$ with solvent is bigger, indicating that the chain helicity of P**4** is more susceptible to the environmental change. It is, however, noteworthy that, though the magnitudes of the $[\alpha]^{20}_D$'s of the polymers vary with solvent, their signs (+ or −) remain unchanged. This is in contrast to what observed in the helical monosubstituted polyacetylene systems, where not only the magnitudes of their $[\alpha]^{20}_D$'s change vigorously but also their signs reverse with a change in solvent.[4−7] For example, the $[\alpha]^{20}_D$ values of a poly(phenylacetylene) bearing l-alanine pendants are +440.0° and −953.2° in THF and chloroform, respectively (noting the sign inversion).[21] A disubstituted polyacetylene chain is generally more rigid than a monosubstituted one,[22] and it is believed that the chain stiffness of P**1**−P**4** has helped keep their helical-sense preference unaltered by the solvent perturbation.

Acetylene polymerizations initiated by Mo- and W-based catalysts are known to yield stereoirregular polymers.[13] Many research groups have found that stereoregularity is a prerequisite for monosubstituted polyacetylenes to take helical chain conformations.[2,5,23] The stereoirregular poly(aryl phenylpropiolate)s bearing stereogenic pendants (P**13**−P**15**) prepared in our previous work using WCl_6−Ph_4Sn as catalyst were chiroptically active,[11] suggesting that the conformational regularity is not necessarily a requirement for a disubstituted polyacetylene chain to rotate in a helical

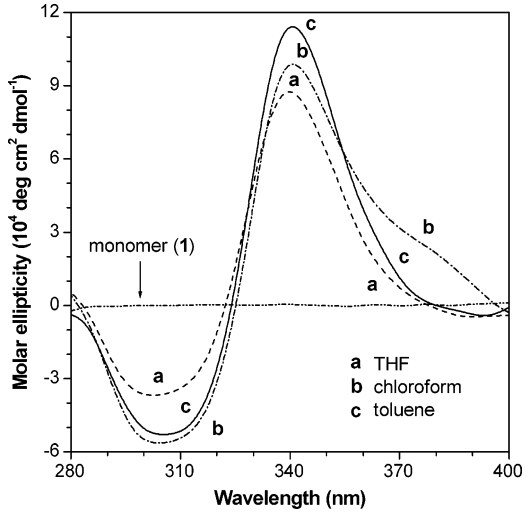


Figure 6. Circular dichroism spectra of monomer **1** in THF and its polymer P**1** in different solvents. Concentration: 1.04−1.44 mM.

fashion. Will the stereoirregular poly(alkyl phenylpropiolate)s take helical chain conformations? To answer this question, we investigated the chiroptical properties of P**1**−P**4** using circular dichroism (CD) spectroscopy.

Figure 6 shows the CD spectra of P**1** in different solvents as well as that of it monomer **1** in THF. The THF solution of the polymer exhibits strong Cotton effects at 303 and 340 nm with molar ellipticities ([θ]) of −36 800 and +87 500 deg cm^2 dmol^{-1}, respectively. Since the THF solution of **1** is CD-inactive at wavelengths longer than ∼285 nm, the CD bands at 303 and 340 nm must be due to the absorptions of the segments of the polyene backbone of P**1**, thus unambiguously confirming that its polyene chain possesses a helical conformation with an excess of one-handedness. The spectral pattern of P**1** remains the same when its solvent is changed from THF to chloroform or toluene, indicating that the same screw sense dominates in the chloroform or toluene solution. The Cotton effects of the polymer are, however, intensified, suggesting that the preferred handedness of its helical chain further prevails over the opposite one in the chloroform or toluene solution.

The CD spectral analyses of P**2**−P**4** verify that all the polymers, like their cousin P**1**, possess helical conformations. The chloroform solution of P**2** exhibits a [θ] value of −48 300 deg cm^2 dmol^{-1} at 340 nm (Figure 7A). This value is 7.5-fold higher (in absolute term) than that (+6400) of poly[(1*R*,2*S*,5*R*)-(−)-menthyl propiolate] (−{HC═C[CO$_2$-(−)-Men]}$_n$−; P**18**), a monosubstituted polyacetylene bearing the same (−)-Men pendant and prepared by a similar Mo catalyst.[23] Stereoirregular P**2** is prepared by a Mo catalyst, but its absolute [θ] value is even higher than that of a stereoregular P**18** prepared by a Rh catalyst (+9100).[23] Taking into account that the main structural difference between P**2** and P**18** is their substitution mode (di- vs monosubstitution), it can be concluded that it is the molecular structure rather than the chain stereoregularity that dictates the helical chirality of the polypropiolates. Polymer P**3** exhibits even stronger Cotton effects with opposite signs, suggesting that more chain segments of P**3** take the preferred helical conformation with a screw sense opposite to that of P**2**. The CD activity of P**4** is, however, weak, suggesting that only a small statistic excess of its chain segments is spiraling in the preferred helical sense in the chloroform solution. The reason for this is unclear at present but may be associated with the relative flexibility of the carbonate group in the pendant, which makes the chirality transcription from the stereogenic pendant to the polyene backbone a less efficient process.[6e]

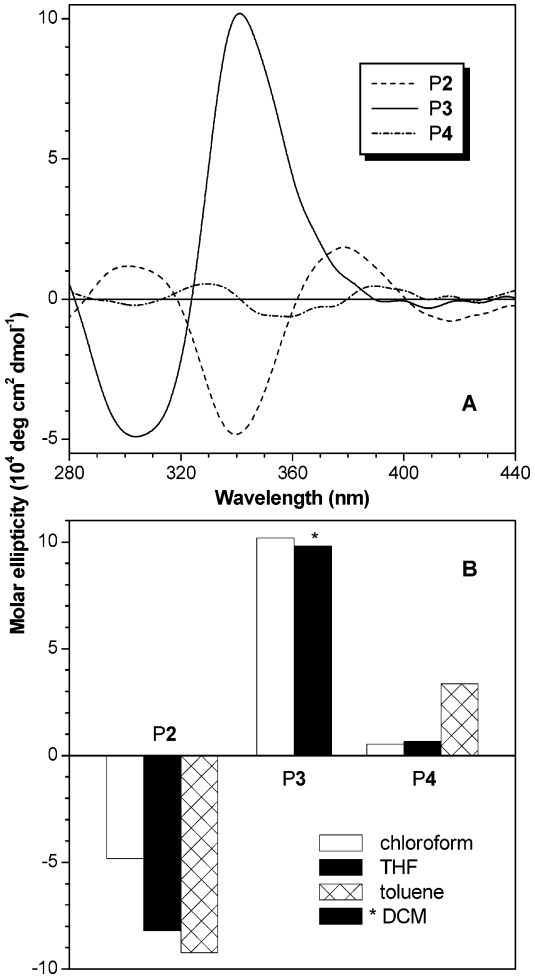


Figure 7. (A) Circular dichroism spectra of P**2**−P**4** in chloroform and (B) solvent dependence of Cotton effects of P**2** at 340 nm, P**3** at 340 nm, and P**4** at 333 nm. Polymer concentration: 0.76−1.47 mM.

The molar ellipticities of P**2**−P**4** also change with solvent, as depicted in Figure 7B. The variations in [θ] with solvent for the polymers share some similarities with those in $[\alpha]^{20}_D$ (cf. Table 4). The orders of the [θ] values of P**2** and P**4** ($|[\theta]_{chloroform}| < |[\theta]_{THF}| < |[\theta]_{toluene}|$) are the same as those of the $[\alpha]^{20}_D$ values in the same solvents ($|[\alpha]_D{}^{20}{}_{chloroform}| < |[\alpha]_D{}^{20}{}_{THF}| < |[\alpha]_D{}^{20}{}_{toluene}|$). The extent of variation is the biggest for **P4**, with its [θ] in toluene (+33 500) being 6.25-fold higher than that in chloroform. However, in this case again, none of the polymers (including P**1**; cf. Figure 6) changes its signs of Cotton effects with solvent. A similar phenomenon has been observed in the helical disubstituted poly(aryl phenylpropiolate) (P**13**−P**15**) system.[11] The steric crowdedness caused by the existence of two substituent groups in one monomer repeat unit of a disubstituted polyacetylene imposes an energy barrier, which is high enough to endow the polymer with a resistance to the solvent-induced inversion in the helical-sense preference.

Table 4. Specific Optical Rotations of Poly(alkyl phenylpropiolate)s P1−P4 in Different Solvents[a]

	$[\alpha]^{20}_D$ (*c*, g/dL)			
solvent	P**1**	P**2**	P**3**	P**4**
THF	+511.0 (0.042)	−544.0 (0.050)	*b*	+17.9 (0.058)
$CHCl_3$	+625.0 (0.052)	−294.8 (0.046)	+871.3 (0.048)[c]	+12.6 (0.046)
toluene	+592.1 (0.048)	−565.1 (0.047)	*d*	+114.1 (0.051)

[a] $[\alpha]^{20}_D$ values of THF solutions of monomers (concentration given in the parentheses): for **1**: +22.4° (0.058 g/dL); for **2**: −60.0° (0.061 g/dL); for **3**: +52.1° (0.043 g/dL), for **4**: −8.6° (0.051 g/dL). [b] Partially soluble. [c] $[\alpha]^{20}_D$ in DCM: +883.0° (0.054 g/dL). [d] Insoluble.

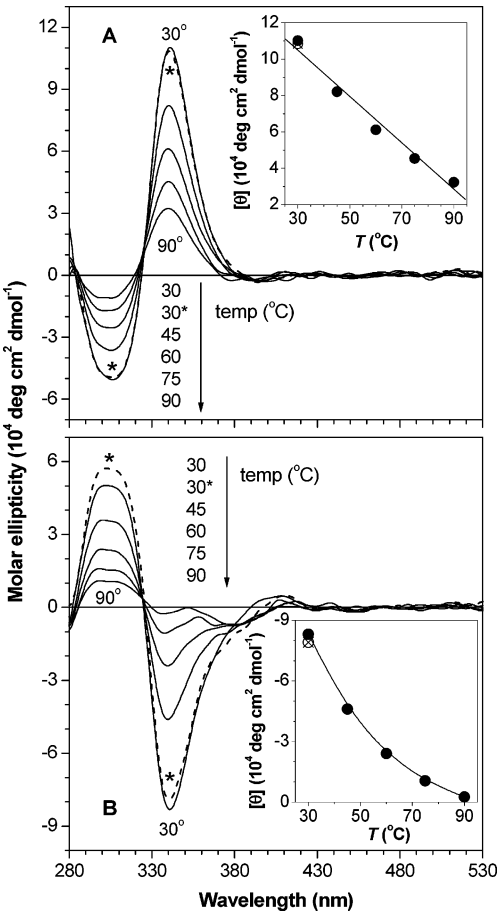


Figure 8. Circular dichroism spectra of toluene solutions of (A) P**1** and (B) P**2** at different temperatures. Polymer concentration: 1.22 (P**1**) and 1.16 (P**2**) mM. The CD spectra of the polymers heated to 90 °C and then cooled to 30 °C are shown in dotted lines and marked with start (*) symbols. Insets: variations of the molar ellipticity at 340 nm with temperature in toluene solutions of (A) P**1** and (B) P**2**.

Helicity Tuning by Temperature. The preference of the helical sense of the polypropiolates cannot be changed by temperature either. However, the magnitudes of their molar ellipticities can be tuned to large extents reversibly by the thermal stimulus. When the temperature of a toluene solution[24] of P**1** is increased from 30 to 40 °C, the intensity of its first Cotton effect at 340 nm is decreased from +110 200 to +82 100 deg cm^2 $dmol^{-1}$ (Figure 8A). The molar ellipticity of P**1** continuously decreases with a further increase in temperature, probably because a higher temperature causes more chain segments to undergo conformational randomization, like what happens in the thermally induced denaturing or unfolding processes of proteins.[6d] However, even when the temperature is raised to 90 °C, the spectral pattern of P**1** remains unvaried, and its Cotton effect is still strong (+32 300), indicating that the polymer chain is not randomized even when it is heated to the temperature close to the boiling point of the solvent.[24,25] When the solution is cooled to room temperature, the original CD spectrum of the polymer is completely reinstalled, demonstrating that the tuning of the helical chirality by temperature is fully reversible.

Similarly, the molar ellipticity of P**2** can be thermally manipulated in a reversible fashion (Figure 8B). Remarkably, although the Cotton effect of this polymer drops to nearly zero or its chain conformation is almost randomized when the solution is heated to 90 °C, its CD spectrum returns to the original shape with similar peak intensities when the solution is cooled to room temperature. The helicity reversibility or "memory" capability is thus a general property for all the helical polypropiolates including the poly(alkyl phenylpropiolate)s synthesized in this work as well as their aryl congeners prepared in our previous study.[11] Careful scrutiny of the temperature effects, however, reveals some difference between the two groups of polypropiolates. The first Cotton effect of the poly(aryl phenylpropiolate) bearing (1*R*,2*S*,5*R*)-(−)-menthyl pendant (−{$(C_6H_5)C{=}C[CO_2{-}C_6H_4$-*p*-OCO-(−)-Men]}$_n$−; P**14**) at 354 nm is decreased from +88 550 to +56 460 deg cm^2 $dmol^{-1}$ (with a $|\Delta[\theta]|$ of 32 090) when its toluene solution is heated from 30 to 90 °C.[11] For the same extent of temperature change, P**2** shows a 2.5-fold higher ellipticity change ($|\Delta[\theta]| = 80\,500$), noting that this polymer bears the same chiral pendant of (−)-Men. The structural difference between P**2** and P**14** is that the former has an alkyl (ethyl) spacer while the latter has an aromatic (phenyl) ring between the two ester groups. The internal plasticizing effect of the soft alkyl spacer makes the polymer chain of P**2** somewhat less stiff and hence more responsive to the thermal stimulus. On the other hand, the rigid aromatic ring stiffens the polymer chain of P**14**, making it more resistant to the thermal agitation. The chain stiffening effect of rigid aromatic rings is further evidenced by a recent work on helical polycarbodiimides. The disubstituted polycarbodiimides with rigid, bulky anthryl pendants possess extremely stable helical conformations, whose chiroptical activities remain constant even after the polymers have been annealed in toluene at 80 °C for >34 h.[26]

Concluding Remarks

Functional disubstituted acetylenes have been difficult to polymerize.[2,3] The polymerizations of the alkyl phenylpropiolates **1**−**4** were not easy, but through catalyst selection and process optimization, we eventually succeeded in converting the stereogenic monomers into high molecular weight polymers (P**1**−P**4**), adding a group of new members to the short list of functional disubstituted polyacetylene family.

Unlike their monosubstituted counterparts, the disubstituted poly(alkyl phenylpropiolate)s are stable. The polymers are thermolysis- and oxidation-resistant, losing little of their weights when heated to ≥300 °C under nitrogen and suffering from no decrease in their mo-

lecular weights when annealed in air at ≥150 °C. Compared to the helical monosubstituted poly(phenylacetylene)s, the disubstituted poly(alkyl phenylpropiolate)s are conformationally more stable, whose preference of helical sense is not alterable by such external perturbations as solvent and temperature.

The bulkiness of the group linked to the propiolate oxygen atom (marked in red or blue color in Chart 2) is found to dramatically affect polymerization behavior of the monomer and chiroptical property of the polymer. Thus, the monomers with sterically less (**1**−**4** and **12**) and more demanding groups (**13**−**17**) can *only* be polymerized by one of the Mo and W catalysts, while the optical activity of the polymers with sterically less (P**1**−P**4**) and more demanding groups (P**13**−P**15**) can be tuned by external stimuli to larger and smaller extents, respectively. Inspired by the insights gained in this study, we are currently working on the design and synthesis of chiral poly(phenylpropiolate)s with longer chains (e.g., octyl) and bulkier rings (e.g., anthryl) in an effort to develop helical disubstituted polyacetylenes with opposite attributes, that is, higher stimuli responsiveness and stronger perturbation resistance, respectively.

Experimental Section

General Information. Toluene (BDH) was predried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. DCM 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.

The IR spectra were measured on a Perkin-Elmer 16 PC FT-IR spectrophotometer. The NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer using chloroform-*d* as the solvent and tetramethylsilane ($\delta = 0$) or chloroform (7.26) as the 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 the carrier gas. The molecular weights of the polymers were estimated by a Waters Associates GPC system. Degassed THF was used as the eluent at a flow rate of 1.0 mL/min. A set of monodisperse polystyrene standards covering the molecular weight range of 10^3−10^7 was used for molecular weight calibration.

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 CD spectra were measured 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 molar concentrations of the polymer solutions were calculated on the basis of the repeat units of the polymers.

Monomer Syntheses. The alkyl phenylpropiolates **1**−**3** were prepared by the esterification of phenylpropiolic acid (**5**) with ethylene glycol (**6**) (Scheme 2, eq 4) followed by another esterification of 2-hydroxyethyl phenylpropiolate (**7**) with stereogenic acids **8**−**10** (eq 5) using DCC as the dehydrating agent. The cholesterol-containing phenylpropiolate **4** was prepared by the esterification of **7** with cholesteryl chloroformate (**11**) in the presence of pyridine. Typical experimental procedures for the syntheses of the monomers are given below.

2-Hydroxyethyl Phenylpropiolate (7). In a 500 mL two-necked flask under nitrogen were dissolved 4.5 g (72.5 mmol) of **6**, 4.0 g (19.5 mmol) of DCC, 0.5 g (2.5 mmol) of TsOH, and 0.3 g (2.5 mmol) of DMAP in 200 mL of dry DCM. The solution was cooled to 0−5 °C with an ice−water bath, to which 2.0 g (13.7 mmol) of **5** dissolved in 50 mL of DCM was added under stirring via 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/acetone (10:1 by volume) as the eluent. Colorless liquid of **7** was isolated in 50.8% yield.

2-{(*S*)-(+)-[1-(6-Methoxy-2-naphthyl)ethyl]carbonyloxy}-ethyl Phenylpropiolate (1). This monomer was prepared by esterification of **7** with (*S*)-(+)-6-methoxy-α-methyl-2-naphthaleneacetic acid (**8**). The synthetic procedure is similar to that described above for the preparation of **7**. White solid of **1** was isolated in 88.1% yield. IR (KBr), ν (cm^{-1}): 2232 and 2209 (vs, C≡C), 1726 and 1711 (vs, C═O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.54 [m, 3H, Ar−H meta to OCH_3 and meta and ortho to $CH(CH_3)$], 7.43 (m, 2H, Ar−H ortho to C≡C), 7.37 [m, 4H, Ar−H para and meta to C≡C and ortho to $CH(CH_3)$], 7.05 (m, Ar−H ortho to OCH_3), 4.35 [m, 4H, $(OCH_2)_2$], 3.85 [m, 1H, C*H*(CH_3)], 3.76 (s, 3H, OCH_3), 1.53 [d, 3H, CH(C*H*$_3$)]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 174.0 [*C*O_2CH(CH_3)], 157.4 (aromatic carbon linked with OCH_3), 153.3 (≡C*C*O_2), 135.1, 133.5, 132.7 (aromatic carbons ortho to C≡C), 130.5 (aromatic carbon para to C≡C), 129.1, 128.7, 128.3 (aromatic carbons meta to C≡C), 127.0, 125.9, 125.7, 119.1 (aromatic carbon linked with C≡C), 118.7, 105.3, 86.7 (Ar*C*≡), 80.1 (≡CCO_2), 63.1 [*C*H_2OCOCH(CH_3)], 61.8 (≡CCO_2*C*H_2), 54.7 (OCH_3), 45.0 [*C*H(CH_3)], 18.2 [CH(*C*H$_3$)]. MS (CI): *m*/*e* 403.1 [$(M + 1)^+$, calcd 403.1].

2-[(1*R*,2*S*,5*R*)-(−)-Menthoxymethylcarbonyloxy]ethyl Phenylpropiolate (2). Its preparation was similar to that of **1**, but (−)-menthoxyacetic acid (**9**), instead of **8**, was used. Pale yellow liquid of **2** was isolated in 96.8% yield. IR (KBr), ν (cm^{-1}): 2222 (vs, C≡C), 1764 and 1715 (vs, C═O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.60 (m, 2H, Ar−H ortho to C≡C), 7.38 (m, 3H, Ar−H para and meta to C≡C), 4.45 (m, 4H, OCH_2), 4.17 (m, 2H, $OCOCH_2O$), 3.18 (ddd, 1H, OCH), 2.30 (m, 1H), 2.04 (m, 1H), 1.60 (m, 3H), 1.30 (m, 3H), 0.98−0.79 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 170.6 (*O*C*O*CH_2O), 153.6 (≡C*C*O_2), 133.0 (aromatic carbons ortho to C≡C), 130.8 (aromatic carbon para to C≡C), 128.6 (aromatic carbons meta to C≡C), 119.4 (aromatic carbon linked with C≡C), 87.2 (Ar*C*≡), 80.3 (≡C*C*O_2), 80.2 (OCO*C*H_2O), 65.8 (OCH), 63.3 (*C*H_2OCO), 62.0 (≡CCO_2*C*H_2), 48.1, 39.9, 34.4, 31.5, 25.5, 23.3, 22.2, 20.9, 16.2. MS (CI): *m*/*e* 387.1 [$(M + 1)^+$, calcd 387.1].

2-{(*S*)-(+)-[(α-Acetoxy)benzyl]carbonyloxy}ethyl Phenylpropiolate (3). It was prepared by the esterification of **7** with (*S*)-(+)-*O*-acetylmandelic acid (**10**) using a procedure similar to that described above for the preparation of **7**. Pale yellow liquid of **3** was isolated in 96.7% yield. IR (KBr), ν (cm^{-1}): 2218 (vs, C≡C), 1747 and 1713 (vs, C═O). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.61 (m, 2H, Ar−H ortho to C≡C), 7.50−7.36 (m, 8H, Ar−H), 5.97 (s, 1H, CH), 4.37 (m, 4H, OCH_2), 2.20 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 170.2 (CH_2*O*C*O*CH), 168.5 (*O*C*O*CH_3), 153.4 (≡C*C*O_2), 133.4 (aromatic carbon linked with CH), 133.0 (aromatic carbons ortho to C≡C), 130.8 (aromatic carbon para to C≡C), 129.2 (aromatic carbons ortho to CHOCOCH_3), 128.8 (aromatic carbons meta to CH), 128.6 (aromatic carbons meta to C≡C), 127.5 (aromatic carbon para to CH), 119.3 (aromatic carbon linked with C≡C), 87.0 (ArC≡), 80.1 (≡CCO_2), 74.3 (CH), 62.9 (*C*H_2OCO), 62.6 (≡CCO_2CH_2), 20.7 (CH_3). MS (CI): *m*/*e* 367.1 [$(M + 1)^+$, calcd 367.1].

2-(Cholesteryloxycarbonyl)ethyl Phenylpropiolate (4). In a 250 mL two-necked flask under nitrogen was dissolved 5.7 g (12.8 mmol) of cholesteryl chloroformate (**11**) in 100 mL of dry DCM. The solution was cooled to 0−5 °C with an ice−water bath, to which 2.5 g (13.2 mmol) of **7** and 1.4 g (17.2 mmol) of pyridine in 25 mL of DCM was injected through a syringe. The mixture was slowly warmed to room temperature and stirred overnight. DCM was evaporated using a rotary evaporator. The solid residue in the flask was dissolved in 50 mL of chloroform, and the solution was washed with water and dried over anhydrous magnesium sulfate. The crude

product was purified on a silica gel column using chloroform as the eluent. Recrystallization from ethanol/water mixture (4:1 by volume) gave 5.6 g of white powdery product of **4** (yield 84.4%). IR (KBr), ν (cm^{-1}): 2221 (vs, C≡C), 1750 and 1720 (vs, C=O). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.58 (m, 2H, Ar−H ortho to C≡C), 7.35 (m, 3H, Ar−H para and meta to C≡C), 5.39 (d, 1H, =CH), 4.41 (m, 4H, OCH_2), 2.34 (t, 2H), 1.99−0.67 (m, 41H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 154.2 (≡CCO_2), 153.6 (OCO_2), 139.2 (*C*=CH), 133.0 (aromatic carbons ortho to C≡C), 130.7 (aromatic carbon para to C≡C), 128.5 (aromatic carbons meta to C≡C), 123.0 (C=*C*H), 119.4 (aromatic carbon linked with C≡C), 87.1 (Ar*C*≡), 80.2 (≡CCO_2), 78.3 (OCH), 64.7, 63.3, 56.6, 56.1, 49.9, 39.7, 39.5, 37.9, 36.8, 36.5, 36.1, 35.7, 31.84, 31.78, 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* 603.6 [$(M + 1)^+$, calcd 603.6].

Polymerization Reactions. All the polymerization reactions and manipulations were carried out under nitrogen using Schlenk techniques in a vacuum line system or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purification of the polymers, which was done 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 322.0 mg (0.80 mmol) of **1**. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. Freshly distilled toluene (2 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 10.9 mg of molybdenum(V) chloride and 17.2 mg of tetraphenyltin in 2 mL of toluene. The catalyst solution was aged at 60 °C for 15 min, into which the monomer solution was added 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, which was then filtered with a Gooch crucible. Polymer P**1** was washed with acetone and dried in a vacuum oven to a constant weight.

Characterization Data. P**1**: Yellow powdery solid; yield 57.6%. M_w: 74 200; M_w/M_n: 2.7 (GPC, Table 1, no. 4). IR (KBr), ν (cm^{-1}): 1734 and 1716 (vs, C=O). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.63 [Ar−H meta to OCH_3 and meta and ortho to $CH(CH_3)$], 7.15 (Ar−H ortho to OCH_3), 6.76 (Ar−H ortho, para, and ortho to C=C), 4.12 (OCH_2), 3.93 (OCH_3), 3.41 [C*H*(CH3)], 1.37 [CH(C*H*$_3$)]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 174.5 [$CO_2CH(CH_3)$], 165.5 (=CCO_2), 157.3 (aromatic carbon linked with OCH_3), 150.8 (Ar*C*=), 140.4 (=CCO_2), 135.6, 135.0, 133.5, 129.1, 128.6, 126.9, 126.2, 125.9, 118.8, 105.5, 63.3 (OCH_2), 55.2 (OCH_3), 44.8 [*C*H(CH$_3$)], 18.8 [CH(*C*H$_3$)]. UV ($CHCl_3$, 2.98×10^{-4} mol/L), λ_{max}: 332 nm; ϵ_{max}: 0.55×10^4 mol^{-1} L cm^{-1}.

P**2**: Yellow powdery solid; yield 17.8%. M_w: 60 900; M_w/M_n: 2.0 (GPC, Table 2, no. 3). IR (KBr), ν (cm^{-1}): 1763 and 1714 (vs, C=O). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.54 (Ar−H ortho, para, and meta to C=C), 4.15 (OCH_2), 3.80 ($OCOCH_2O$), 3.10 (OCH), 2.28, 1.94, 1.64, 1.28, 0.83. ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 170.3 ($OCOCH_2O$), 165.3 (=CCO_2), 133.6 (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), 79.8 (OCO*C*H$_2$O), 65.7 (OCH), 63.1 (*C*H$_2$OCOCH$_2$ and =CCO_2*C*H$_2$), 47.8, 39.8, 34.3, 31.4, 25.4, 23.3, 22.1, 20.7, 16.5. UV ($CHCl_3$, 2.9×10^{-4} mol/L), λ_{max}: 320 nm; ϵ_{max}: 0.43×10^4 mol^{-1} L cm^{-1}.

P**3**: Yellow powdery solid; yield 34.3%. M_w: 15 400; M_w/M_n: 1.5 (GPC, Table 2, no. 6). IR (KBr), ν (cm^{-1}): 1746 and 1714 (vs, C=O). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.21 (Ar−H), 6.62−6.47 (Ar−H ortho, para, and meta to C=C), 5.68 (CH), 4.12 (OCH_2), 2.10 (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 169.8 (CH_2OCO), 168.6 ($OCOCH_3$), 165.6 (=CCO_2), 150.6 (Ar*C*=), 140.2 (=*C*CO2), 135.4, 133.2, 129.1, 128.7, 127.7, 126.8, 125.8, 74.3 (CH), 63.5 (*C*H$_2$OCO), 62.2 (=CCO_2*C*H$_2$), 20.6 (CH_3). UV ($CHCl_3$, 2.4×10^{-4} mol/L), λ_{max}: 325 nm; ϵ_{max}: 0.30×10^4 mol^{-1} L cm^{-1}.

P**4**: Yellow powdery solid; yield 6.2%. M_w: 96 400; M_w/M_n: 3.2 (GPC, Table 2, no. 8). IR (KBr), ν (cm^{-1}): 1746 and 1717 (vs, C=O). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.63 (Ar−H ortho, para, and meta to C=C), 5.38 (=CH), 4.39 (OCH_2), 2.29, 1.53, 1.11, 0.96, 0.86, 0.78, 0.69. ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 164.2 (=CCO_2), 154.2 (Ar*C*=), 139.1 (=*C*CO_2 and *C*=CH), 126.5 (aromatic carbons ortho, para, meta, and linked to C=C), 122.8 (C=*C*H), 77.9 (OCH), 64.5, 56.8, 56.3, 50.1, 42.4, 39.7, 38.1, 36.6, 36.4, 36.0, 32.1, 28.1, 24.5, 24.2, 23.1, 23.0, 22.8, 22.7, 21.3, 19.5, 18.9, 12.1. UV ($CHCl_3$, 1.6×10^{-4} mol/L), λ_{max}: 315 nm; ϵ_{max}: 0.46×10^4 mol^{-1} L cm^{-1}.

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