Synthesis and Properties of Stereoregular Polyacetylenes Containing Cyano Groups, Poly[[4-[[[*n*-[(4′-cyano-4-biphenylyl)oxy]alkyl]oxy]carbonyl]phenyl]acetylenes]

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ABSTRACT: We have succeeded in synthesizing soluble, stereoregular, and high molecular weight polyacetylenes containing polar cyano functional groups in high yields. Two new cyanoalkyne monomers, [4-[[[*n*-[(4′-cyano-4-biphenylyl)oxy]alkyl]oxy]carbonyl]phenyl]acetylenes (**1**; *n* = 6, 12), are synthesized via multistep reactions. $[Rh(nbd)Cl]_2$ effects the polymerization of **1**, producing polymers (**2**) with high molecular weights (M_w up to 158 000) in high yields (up to 71%). Spectroscopic analysis reveals that the polymers possess alternating-double-bond backbones with high stereoregularity. The electronic and thermal transitions in **2** are sensitive to their stereostructures: The polymer with higher stereoregularity absorbs at longer wavelength and melts at higher temperature. The polymers prepared in DMF-based solvents are completely soluble in DMF, THF, and chloroform, although the dissolution takes quite a long time (up to a week) due to the high stereoregularity of the polyacetylene backbones and the strong electronic interaction among the push−pull mesogenic pendant groups. The polymers are thermally very stable (temperature for 5% weight loss: ca. 400 °C) and can be melt-processed in a moderate temperature range (ca. 100−150 °C).

Introduction

Polyacetylene is the best-known conducting polymer, whose doped form exhibits metallic conductivity.[1] Its intractability and instability, however, have significantly limited the scope of its applications. Synthesis of substituted polyacetylenes has attracted much interest among polymer scientists because polyacetylenes with suitable substituents not only will have better processibility and stability but also may possess novel properties that are not found in the parent form. Many substituted polyacetylenes have been synthesized, some of which are soluble in common organic solvents and stable in air even at elevated temperatures.[2,3] Some pendant groups have endowed polyacetylenes with novel properties such as chirality (optical activity), (enantio)-permselectivity, radiolysis susceptibility, photoconductivity, magnetism, and liquid crystallinity.[4] Most substituted polyacetylenes prepared so far, however, bear nonpolar alkyl and/or aryl groups.[2] Introduction of polar functional pendant groups into the polyacetylene structure would further advance the polyacetylene science and open up new avenues in developing polyacetylene-based specialty materials. Many groups have attempted to polymerize acetylene monomers with polar groups, but such efforts have met with only limited success.[2] For example, polymerizations of functional acetylene monomers containing cyano (−CN), amino ($-NH_2$), hydroxy (−OH), and carboxy ($-CO_2H$) groups gave either oligomers or insoluble products, normally in low yields.[5] Because many possible side reactions could be induced by the "toxic" interaction between the functional groups and organometallic catalysts, synthesis of polyacetylenes with polar substituents remains largely a challenge.

We have recently succeeded in developing rhodium-based catalysts for polymerizing phenylacetylene and (*p*-methylphenyl)acetylene in water under an atmosphere of air.[6] Encouraged by the extraordinary tolerance of the catalysts to the polar media, we decided to explore the possibility of developing polymerization systems for acetylene monomers containing polar functional groups. We first focused our efforts on synthesizing cyano-containing polyacetylenes because the poly(cyanoalkynes) may possess unique materials properties. The polymers, for example, might be electrical-field responsive because of the large dipole moment of the cyano group. When the molecular structure of the pendant group is so designed as to link a donor and the cyano acceptor together via an aromatic ring, the polymer side chains may exhibit second-order optical nonlinearity induced by the push−pull donor−acceptor interaction. Polyacetylenes are third-order nonlinear-optically active because of the conjugation along the alternating-double-bond backbones.[7] Thus, a suitably designed cyano-containing polyacetylene may be both $\chi^{(2)}$- and $\chi^{(3)}$-active and exhibits intriguing nonlinear optical properties. Such a polyacetylene might also be both conductive and liquid crystalline, offering attractive possibilities for developing novel "molecular electronics" materials.[8] The cyano group is rich in the variety of chemical reactions (e.g., reduction, hydrolysis, and nucleophilic addition by Grignard reagents),[9] and thus the cyano-containing polyacetylenes may also serve as versatile precursor polymers, being easily converted, via suitable polymer reactions, to other functional polyacetylenes containing amino ($-NH_2$), carboxy ($-CO_2H$), and carbamoyl ($-CONH_2$) groups.

Realization of all the attractive potential applications requires the development of versatile polymerization systems for synthesizing the polymers. It is obvious that the exploration of the materials properties of the polymers could not be started without creating the

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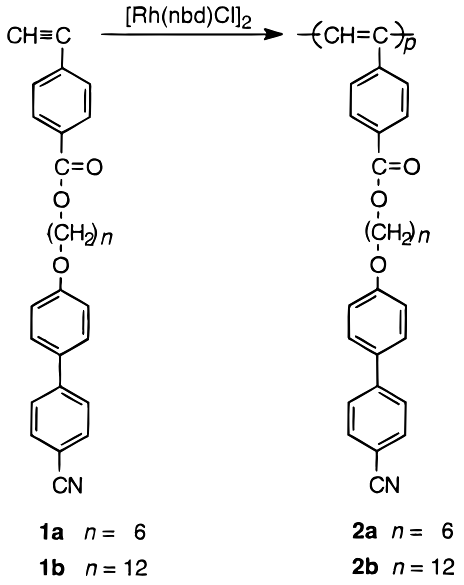
Scheme 1



polymeric materials first. The polymerization of cyanoalkynes, however, has been quite difficult. Many different kinds of initiators (e.g., anionic, Ziegler–Natta, and photochemical initiation systems) have been tried, most of which failed to produce soluble high-molecular-weight polymers.[2d,e,5a–f] Metathesis catalysts such as $MoCl_5$–R_4Sn have also proven ineffective. The polymerization of cyanoacetylene or propiolonitrile (HC≡CCN) catalyzed by $MoCl_5$–Ph_4Sn gave only a 3% insoluble black powdery substance after a very long polymerization time (92 h),[5a] while the polymerization of 5-cyano-1-pentyne [$HC{\equiv}C(CH_2)_3CN$] initiated by $MoCl_5$–Me_4Sn yielded polymers with molecular weights of only a few thousand.[5f]

We here report our work on developing polymerization systems for synthesizing high molecular weight polyacetylenes containing cyano functional groups. We synthesized two new cyanoalkynes containing push–pull cyanoalkoxybiphenyl mesogens with different spacer length, [4-[[[*n*-[(4′-cyano-4-biphenylyl)oxy]alkyl]oxy]carbonyl]phenyl]acetylene (**1**, *n* = 6, 12). While the "classical" metathesis catalysts of WCl_6– and $MoCl_5$–Ph_4Sn were ineffective, $[Rh(nbd)Cl]_2$ initiated polymerizations of **1**, producing stereoregular polymers (**2**) with high molecular weights in high yields (Scheme 1).

Experimental Section

Materials. Dioxane, THF, and toluene were purchased from Aldrich, dried over 4A molecular sieves, and distilled from sodium benzophenone ketyl immediately prior to use. Triethylamine and DMF (both from Aldrich) were dried over molecular sieves and distilled from calcium hydride under normal and reduced pressure, respectively. Phenylacetylene (PA) was purchased from Farchan, distilled from calcium hydride, and stored in sealed ampules in a dark, cold place. 4-Bromotoluene, bis(triphenylphosphine)palladium(II) chloride, copper(I) iodide, potassium iodide, (trimethylsilyl)acetylene, 6-bromo-1-hexanol, 12-bromo-1-dodecanol, 4′-hydroxy-4-biphenylcarbonitrile, and thionyl chloride were all purchased from Aldrich, while potassium permanganate and pyridine were both from Nacalai Tesque. Norbornadienerhodium(I) chloride dimer [$[Rh(nbd)Cl]_2$], tungsten(VI) chloride, tetraphenyltin (all from Aldrich), and molybdenum(V) chloride (Acros) were used as received without further purification. Technical-grade methanol was used to precipitate the polymer products.

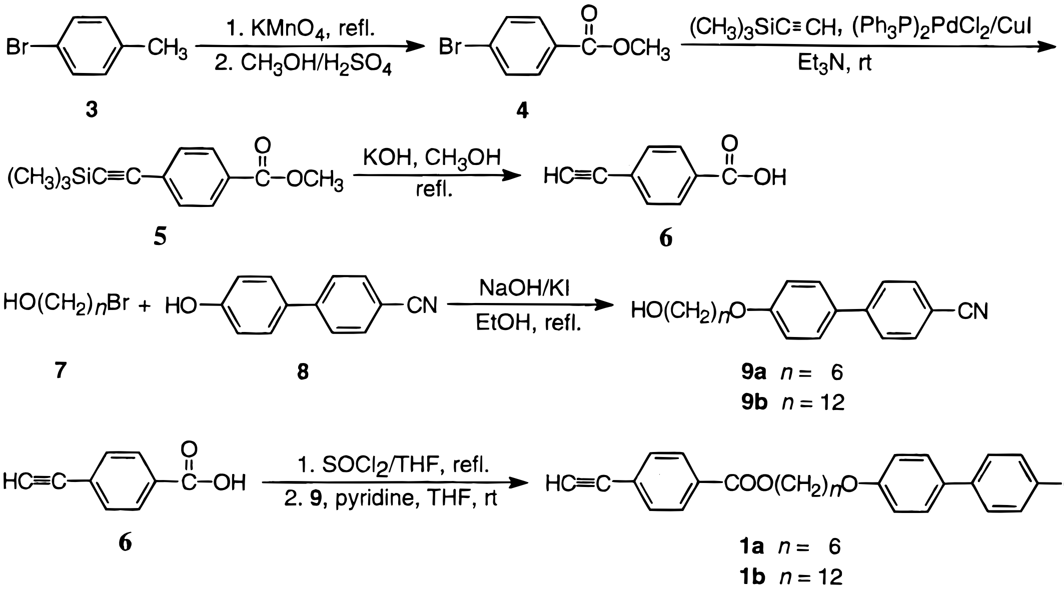
Instruments. Infrared spectra were recorded on a Perkin Elmer 16 PC FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer using chloroform-*d* or THF-d_8 as solvent. Tetramethylsilane (TMS), chloroform-*d*, or THF-d_8 was used as the internal reference for the NMR analysis. UV spectra were recorded on a Milton Roy Spectronic 3000 Array spectrophotometer, and molar absorptivities (ϵ) of the polymers were calculated on the basis of their repeat units. Mass spectra were recorded on a Finnigan TSQ 7000 triple quadrupole mass spectrometer operating in a chemical ionization (CI) mode using ammonia as the carrier gas. Molecular weights of the polymers were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a Waters 510 HPLC pump, a Rheodyne 7725i injector with a stand kit, a set of Styragel columns (HT3, HT4, and HT6; molecular weight range 10^2–10^7), a column temperature controller, a Waters 486 wavelength-tunable UV–vis detector, a Waters 410 differential refractometer, and a system DMM/scanner with an 8-channel scanner option. All the polymer solutions were prepared in THF (ca. 2 mg/mL) and filtered through 0.45-μm PTFE syringe-type filters before being injected into the GPC system. THF was used as the eluent at a flow rate of 1.0 mL/min. The column temperature was maintained at 40 °C, and the working wavelength of the UV–vis detector was set at 254 nm. A set of monodisperse polystyrene standards (Waters) were used for calibration purposes. Thermogravimetric analysis (TGA) of the polymers was performed on a Perkin Elmer TGA 7 under dinitrogen at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) thermograms of the polymers were recorded on a Setaram DSC 92 under dinitrogen at a heating or cooling rate of 10 °C/min. An Olympus BX 60 polarized optical microscope (POM) equipped with a Linkam TMS 92 hot stage was used in cross-polarized mode for the visual observation of thermal behavior of the polymers.

Monomer Synthesis. We designed a multistep synthetic route (Scheme 2) to two cyano-containing phenylacetylene derivatives, [4-[[[*n*-[(4′-cyano-4-biphenylyl)oxy]alkyl]oxy]carbonyl]phenyl]acetylenes (**1**, *n* = 6, 12), both of which are new compounds. (Note that compounds **1** should be named as esters, i.e., *n*-[(4′-cyano-4-biphenylyl)oxy]alkyl 4-ethynylbenzoates, according to the IUPAC systematic nomenclature rules. Taking into account that (i) the compounds **1** serve as acetylene monomers in this study and (ii) their polymers **2** are polyacetylenes rather than polyesters, we give the priority to the triple bond over the ester bond in our nomenclature.) Typical experimental procedures for preparing the new acetylene monomers are given below.

Methyl [4-(Trimethylsilyl)ethynyl]benzoate (5). Methyl 4-bromobenzoate (**4**) was obtained by oxidation of 4-bromotoluene with $KMnO_4$ followed by acid-catalyzed esterification of the resulting acid with MeOH, using standard experimental procedures.[9] The ester **4** was converted to **5** by a coupling reaction with (trimethylsilyl)acetylene according to a published procedure[10] with some modifications: To a 100-mL, two-necked flask were added 140 mg (0.2 mmol) of $PdCl_2(PPh_3)_2$, 10 mg (0.05 mmol) of CuI, and 40 mL of a triethylamine solution of **4** (2.15 g, 10 mmol) under an atmosphere of dry dinitrogen. After all the catalysts were dissolved, (trimethylsilyl)acetylene (1.7 mL, 12 mmol) was injected into the flask and the mixture was stirred at room temperature for 8 h. The triethylamine solvent was then evaporated by a rotary evaporator. The residue in the flask was extracted with 100 mL of benzene, and the crude product was purified on a silica-gel column using a hexane/benzene mixture as the eluent. Recrystallization in 70% aqueous ethanol gave 2.1 g of **5** (yield: 90%). IR (KBr), υ (cm^{-1}): 2160 (s, C≡C), 1720 (s, CO_2CH_3). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.0 (m, 2H, aromatic protons), 7.5 (m, 2H, aromatic protons), 3.9 (s, 3H, OCH_3), 0.3 (s, 9H, $(CH_3)_3Si$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 166.5 (CO_2), 131.9, 129.7, 129.4, 127.8 (aromatic carbons), 104.0, 97.7 (C≡C), 52.2 (OCH_3), −0.2 ($(CH_3)_3Si$).

4-Ethynylbenzoic Acid (6). In a 100-mL flask were placed 1.25 g of **5** and 50 mL of a 4% (w/v) ethanol solution of KOH, and the contents were refluxed for 4 h. The mixture was then poured into 100 mL of 1 M HCl, and the color of the precipitate quickly changed from colorless to brick red. The isolated product was dried in a vacuum oven at room temperature. Yield: 0.66 g (84%). IR (KBr), υ (cm^{-1}): 3272 (s, C≡C), 1686 (s, CO_2H). ^1H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 13.1

Scheme 2



(br, 1H, CO_2H), 7.9 (m, 2H, aromatic protons), 7.6 (m, 2H, aromatic protons), 4.4 (s, 1H, $\equiv$CH).

4′-[(1-Hydroxy-6-hexyl)oxy]-4-biphenylcarbonitrile (9a). In a 250-mL Erlenmeyer flask equipped with a condenser, 3.9 g (20 mmol) of 4′-hydroxy-4-biphenylcarbonitrile (**8**) and 0.8 g (20 mmol) of NaOH were dissolved in 100 mL of 96% ethanol under gentle heating with stirring. To the homogeneous solution were added 3.98 g (24 mmol) of 6-bromo-1-hexanol and a catalytic amount of potassium iodide, and the resulting mixture was then refluxed for 12 h. Ethanol was distilled off by a rotary evaporator. The solid residue in the flask was dissolved in 50 mL of chloroform, which was then washed with 30 mL of water. The aqueous phase was extracted with 50 mL of chloroform, and the combined organic parts were dried over 10 g of sodium sulfate. The crude product was purified on a silica-gel column using ether as the eluent. Recrystallization from 96% ethanol gave 4.2 g of product (yield: 71%). IR (KBr), ν (cm^{-1}): 3252 (br, OH), 2224 (s, $C\equiv N$), 1252 (s, ArOR). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.7−7.5 (m, 6H, aromatic protons), 7.0 (m, 2H, aromatic protons), 4.0 (t, 2H, CH_2OAr), 3.7 (m, 2H, CH_2OH), 1.9−1.3 (m, 8H, $(CH_2)_4$).

4′-[(1-Hydroxy-12-dodecyl)oxy]-4-biphenylcarbonitrile (9b). This compound was prepared by the reaction of 12-bromo-1-dodecanol with **8** using an experimental procedure similar to that detailed above. Because the silica-gel column failed to separate the product from the reactant **8**, the product was purified by an alumina column and recrystallized from 96% ethanol. Yield: 68.3%. IR (KBr), ν (cm^{-1}): 3298 (br, OH), 2234 (s, $C\equiv N$), 1252 (s, ArOR). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.7−7.5 (m, 6H, aromatic protons), 7.0 (m, 2H, aromatic protons), 4.0 (t, 2H, CH_2OAr), 3.7 (t, 2H, CH_2OH), 1.9−1.2 (m, 20H, $(CH_2)_{10}$).

[4-[[[6-[(4′-Cyano-4-biphenylyl)oxy]hexyl]oxy]carboxyl]phenyl]acetylene (1a). Into a 50-mL, two-necked, round-bottomed flask were added 0.44 g (3 mmol) of **6** and 10 mL of $SOCl_2$. After refluxing for 2 h, the excess $SOCl_2$ was distilled off under reduced pressure. The solid content left in the flask was dissolved in 10 mL of THF and cooled down using an ice bath. A solution of **9a** (0.89 g, 3 mmol) and pyridine (1 mL) in 10 mL of THF was injected into the flask, and the mixture was slowly warmed up to room temperature and stirred overnight. THF was then distilled off using a rotary evaporator. The solid residue in the flask was dissolved in 50 mL of benzene, and the resulting benzene solution was washed with water and dried over sodium sulfate. The crude product was purified on a silica-gel column using benzene and then a chloroform/benzene (v/v = 1/5) mixture as eluents. Recrystallization from 96% ethanol gave 0.71 g of product (yield: 56%). IR (KBr), ν (cm^{-1}): 3240 ($\equiv$CH), 2226 ($C\equiv N$, $C\equiv CH$), 1714 (CO_2R). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.0 (m, 2H, aromatic protons), 7.7−7.5 (m, 8H, aromatic protons), 7.0 (m, 2H, aromatic protons), 4.3 (t, CO_2CH_2), 4.0 (t, 2H, CH_2OAr), 3.2 (s, 1H, $\equiv$CH), 1.9−1.5 (m, 8H, $(CH_2)_4$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 82.8 ($\equiv$CAr), 80.0 ($\equiv$CH), 67.9 (CH_2OAr), 65.1 (CO_2CH_2). MS (CI; NH_3): *m/z* 441.3 [$(M + NH_4)^+$, calcd 441.2].

[4-[[[12-[(4′-Cyano-4-biphenylyl)oxy]dodecyl]oxy]carboxyl]phenyl]acetylene (1b). Into a 50-mL flask were added 0.73 g (5 mmol) of **6**, 2 mL of $SOCl_2$, and 5 mL of chloroform. After refluxing for 2 h, the excess amount of $SOCl_2$ reactant and the chloroform solvent were distilled off under reduced pressure. The solid content left in the flask was dissolved in 10 mL of THF and cooled down using an ice bath. A solution of **9b** (1.9 g, 5 mmol) and pyridine (1 mL) in 10 mL of THF was injected into the flask, and the mixture was slowly warmed up to room temperature and stirred overnight. The product was purified similarly as detailed above. Yield: 1.44 g (56.7%). IR (KBr), ν (cm^{-1}): 3236 ($\equiv$CH), 2226 ($C\equiv N$, $C\equiv CH$), 1722 (CO_2R). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.0 (m, 2H, aromatic protons), 7.7−7.5 (m, 8H, aromatic protons), 7.0 (m, 2H, aromatic protons), 4.3 (t, CO_2CH_2), 4.0 (t, 2H, CH_2OAr), 3.2 (s, 1H, $\equiv$CH), 1.9−1.3 (m, 20H, $(CH_2)_{10}$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 82.8 ($\equiv$CAr), 79.9 ($\equiv$CH), 68.2 (CH_2OAr), 65.3(CO_2CH_2). MS (CI; NH_3): *m/z* 525.4 [$(M + NH_4)^+$, calcd 525.3].

Polymerization. All the polymerization reactions and manipulations were carried out under an atmosphere of prepurified dinitrogen using Schlenk techniques either in vacuum-line systems or in an inert-atmosphere glovebox (Vacuum Atmospheres) except for the purification of the resulting polymers, which was done in an open atmosphere. Typical experimental procedures for polymerizing **1** using $[Rh(nbd)Cl]_2$ catalyst are given below.

Poly[[4-[[[6-[(4′-cyano-4-biphenylyl)oxy]hexyl]oxy]carboxyl]phenyl]acetylene] (2a). Into a baked 20-mL Schlenk tube with a side arm was added 169.4 mg (0.4 mmol) of **1a**. The tube was evacuated under vacuum and then flushed with dry dinitrogen three times through the side arm. One milliliter of a DMF/Et_3N mixture (4:1 by volume) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 9.2 mg (0.02 mmol) of $[Rh(nbd)Cl]_2$ in 1 mL of the DMF/Et_3N mixture, which was transferred to the monomer solution using a hypodermic syringe. The reaction mixture was stirred at room temperature under dinitrogen for 24 h. The mixture was then diluted with 5 mL of THF and added dropwise to 100 mL of methanol under stirring. The precipitate was centrifuged and dried in a vacuum oven at room temperature to a constant weight. Precipitate: yellowish brown powder. Yield: 71%. M_w: 26 900, M_w/M_n: 3.8 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3038 (w, =CH), 2224 (s, $C\equiv N$), 1716 (s, CO_2R). ^1H NMR (300 MHz, THF-d_8), δ (TMS, ppm): 7.7−7.5 (aromatic protons), 7.0

Table 1. Polymerization of [4-[[[*n*-[(4′-Cyano-4-biphenylyl)-oxy]alkyl]oxy]carbonyl]phenyl]acetylenes (1)[a]

no.	catalyst	solvent	polymer (**2**) yield (%)	polymer (**2**) M_w[b]	polymer (**2**) M_w/M_n[b]
		Monomer **1a** ($n = 6$)			
1	WCl_6-Ph_4Sn	dioxane	0		
2	WCl_6-Ph_4Sn	THF	0		
3	$MoCl_5-Ph_4Sn$	toluene	0		
4	$[Rh(nbd)Cl]_2$	THF/Et_3N[c]	40[d]	18 600[e]	2.9[e]
5	$[Rh(nbd)Cl]_2$	DMF/Et_3N[c]	71	26 900	3.8
		Monomer **1b** ($n = 12$)			
6	WCl_6-Ph_4Sn	dioxane	0		
7	WCl_6-Ph_4Sn	toluene	29	5 400	1.5
8	$MoCl_5-Ph_4Sn$	toluene	0		
9	$[Rh(nbd)Cl]_2$	THF/Et_3N[c]	59[d]	20 300[e]	4.1[e]
10	$[Rh(nbd)Cl]_2$	DMF	70	158 000	4.0

[a] Polymerized under dinitrogen at room temperature for 24 h. $[M]_0 = 0.2$ M. For the W and Mo catalyst systems, [cat.] = [cocat.] = 20 mM; for the Rh catalyst system, [cat.] = 10 mM. [b] Determined by GPC in THF on the basis of a polystyrene calibration. [c] Volume ratio of THF or DMF to Et_3N: 4:1. [d] Partially soluble in THF. [e] For the THF-soluble fraction.

(*trans* olefin proton), 6.9 (aromatic protons), 6.8 (*trans* olefin proton), 5.9 (*cis* olefin proton), 4.2 (CO_2CH_2), 3.9 (CH_2OAr), 1.8−1.3 ($(CH_2)_4$). UV (THF, 1.5×10^{-5} mol/L), λ_{max} (nm)/ϵ_{max} (mol^{-1} L cm^{-1}): 273/1.8×10^4 (sh), 295/2.7×10^4 , 424/1.8×10^3 (sh).

Poly[[4-[[[12-[(4′-cyano-4-biphenylyl)oxy]dodecyl]oxy]-carboxyl]phenyl]acetylene] (2b). The monomer solution was prepared by dissolving 203.1 mg of **1b** in 1 mL of DMF in a 20-mL baked Schlenk tube, into which was injected a pre-prepared catalyst solution (9.2 mg of $[Rh(nbd)Cl]_2$ in 1 mL of DMF). The mixture was stirred under dinitrogen at room temperature for 24 h. The polymer product was precipitated in methanol, centrifuged, and dried in a vacuum oven. Product: golden yellow powder. Yield: 70%. M_w: 158 000, M_w/M_n: 4.0 (GPC, polystyrene calibration). IR (KBr), υ (cm^{-1}): 3040 (w, =CH), 2224 (s, C≡N), 1716 (s, CO_2R). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.6−6.9 (aromatic protons), 6.7 (*trans* olefin proton), 5.7 (*cis* olefin proton), 4.3 (CO_2CH_2), 3.9 (CH_2OAr), 1.8−1.2 ($(CH_2)_{10}$). UV (THF, 2.7×10^{-5} mol/L), λ_{max} (nm)/ϵ_{max} (mol^{-1} L cm^{-1}): 272/2.0×10^4 (sh), 295/3.2×10^4, 426/3.1×10^3 (sh).

Results and Discussion

Polymerization Behavior. We designed two cyano-containing acetylene monomers (**1**) by attaching cyanoalkoxybiphenyl groups of different methylene spacer length to the phenyl ring in phenylacetylene (PA) at the *para* position via an ester bond. The designed synthetic route to **1** involved multistep reactions (cf. Scheme 2). All the reactions proceeded smoothly, and the expected products were isolated in high yields. Since the monomers are new compounds, we fully characterized **1** using spectroscopic methods and obtained satisfactory analysis data.

We first attempted to polymerize **1** using the classical metathesis catalysts. When **1a** was mixed with WCl_6-Ph_4Sn in dioxane, no polymeric product was isolated after 24 h of reaction (Table 1, no. 1). The result is rather surprising because Moigne et al. found that WCl_6 was an effective catalyst for the polymerizations of $HC{\equiv}CC_6H_4$-*p*-CO_2R (R = alkyl, Ph) in dioxane.[11] The noticeable structural difference from Moigne's monomers is that there is a cyano group in **1**. It thus became clear that the polar cyano group in **1a** is toxic to the W catalyst system. Further attempts by using different solvents (THF, toluene) and catalyst ($MoCl_5-Ph_4Sn$) all ended up with failure.

We recently discovered that the $[Rh(nbd)Cl]_2$ complex effects polymerizations of PAs ($HC{\equiv}CC_6H_4$-*p*-R; R = H, CH_3) in water, a very polar solvent.[6] Unfortunately, however, the polymers were insoluble. Because of the remarkable tolerance of the catalyst toward the polar environment, we tried to polymerize **1a** by $[Rh(nbd)Cl]_2$. Since **1a** is not soluble in water, we used a THF/Et_3N mixture (4:1 by volume) as the polymerization solvent. Although the concentration of the Rh catalyst (10 mM) was only half of that of the W catalyst, a yellowish brown polymer was isolated in 40% yield after 24 h of polymerization (Table 1, no. 4). The isolated polymer, however, was only partially soluble. GPC analysis of the soluble fraction of the polymer gave a polystyrene-calibrated M_w of 18 600. The Rh complex often produces polymers with relatively high polydispersity indexes or wide molecular weight distributions (M_w/M_n up to 5.5).[6,12] This was also the case in the polymerization of **1a**: the M_w/M_n value (2.9) of the resulting polymer was somewhat higher than that for the most probable distribution (2.0). When we changed the solvent from THF/Et_3N to DMF/Et_3N, a polymer with a higher molecular weight was obtained in a higher yield (Table 1, no. 5). Most importantly, the polymer was completely soluble in such common organic solvents as DMF, THF, and chloroform, although the dissolution took several days. Thus, the polymer yield and solubility could be fine "tuned" by simply changing the polymerization solvent.

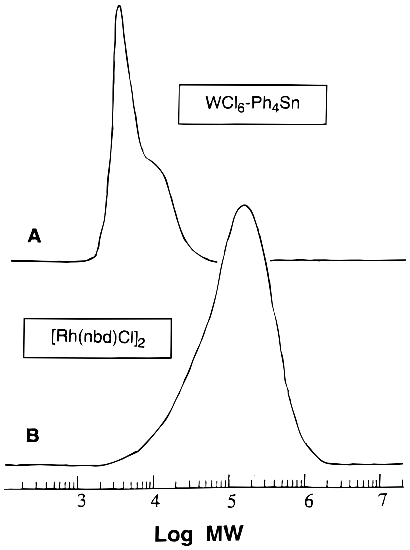


Figure 1. Gel permeation chromatograms of reaction products of **1b** catalyzed by (A) WCl_6-Ph_4Sn (sample from Table 1, no. 7) and (B) $[Rh(nbd)Cl]_2$ (sample from Table 1, no. 10).

Polymerization behavior of **1b**, which possesses a longer methylene spacer ($n = 12$), was similar to that of **1a**. No polymer was obtained when WCl_6-Ph_4Sn was used in dioxane, while an oligomer with an M_w of 5400 was obtained in a low yield when toluene was used as the solvent (Table 1, no. 7). $MoCl_5-Ph_4Sn$ in toluene, however, failed to give any isolable polymeric product. $[Rh(nbd)Cl]_2$ effected the polymerization of **1b**. In this case again, DMF was found to be a better solvent than the THF/Et_3N mixture, producing a completely soluble polymer with a high molecular weight (M_w 158 000) in high yield (70%).

Figure 1 shows GPC traces of the reaction products of **1b** isolated from the W and Rh catalyst systems. The product isolated from the WCl_6-Ph_4Sn/toluene system exhibited a sharp peak in the low molecular weight region along with a shoulder in the somewhat higher molecular weight region (Figure 1A). Although the polystyrene calibration prevented us from obtaining

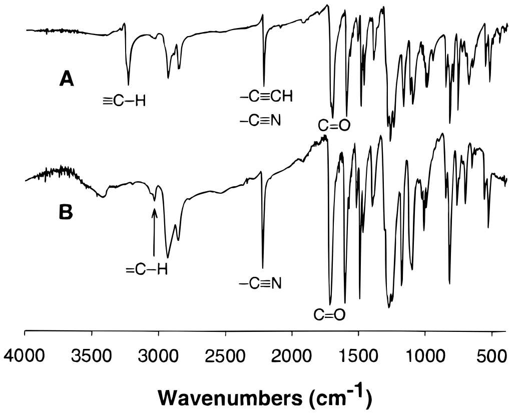


Figure 2. IR spectra of (A) monomer **1a** and (B) its polymer **2a** (KBr; sample from Table 1, no. 5).

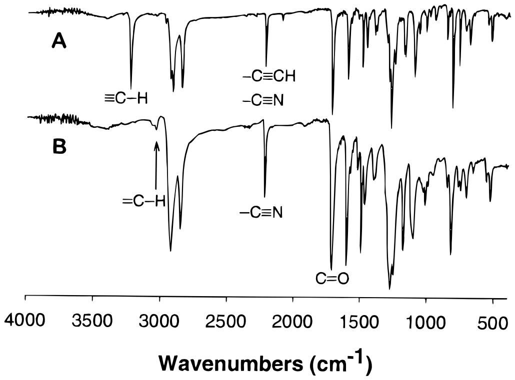


Figure 3. IR spectra of (A) monomer **1b** and (B) its polymer **2b** (KBr; sample from Table 1, no. 10).

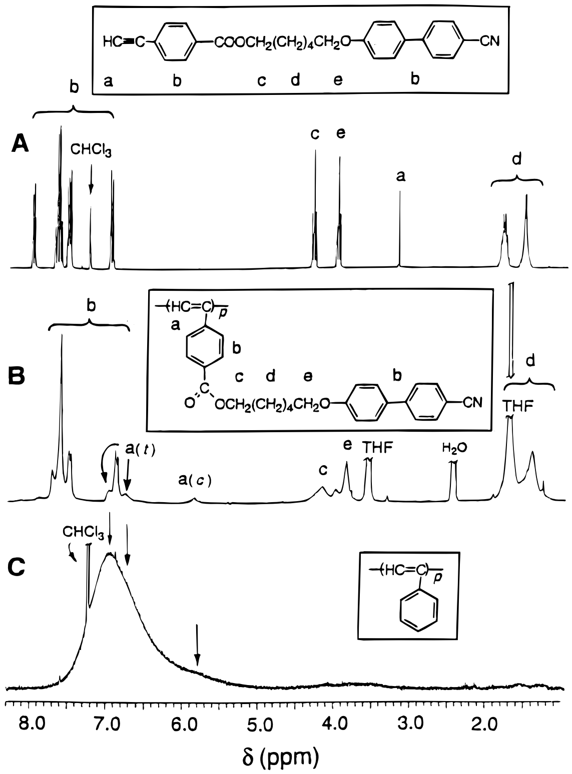


Figure 4. ^{1}H NMR spectra of (A) monomer **1a** (in chloroform-*d*) and (B) its polymer **2a** (in THF-d_8; sample from Table 1, no. 5). The spectrum for (C) poly(phenylacetylene) prepared from WCl_6–Ph_4Sn is shown for comparison.

absolute molecular weights of the product, we suspect that the sharp peak and the neighboring shoulder might be respectively from trimers and oligomers of **1b**. In contrast, the product obtained from the $[Rh(nbd)Cl]_2$/DMF system showed only one peak in the high molecular weight region, suggesting that the Rh-catalyzed polymerization proceeded without many complications of other side reactions, if any.

Although the polymers of **1** produced in the DMF-based solvents were completely soluble, the dissolution took quite a long time (up to a week). In a control experiment, PA, the parent form of **1**, was polymerized by $[Rh(nbd)Cl]_2$ in DMF or DMF/Et_3N under identical conditions. The resulting poly(phenylacetylene)s (PPAs) were only partially soluble, and the soluble fractions were perfectly stereoregular (*cis* content: 100%). The long dissolution time of the polymeric products of **1** might also be due to their high stereoregularity, and we thus used spectroscopic methods to characterize the molecular structures of the polymers.

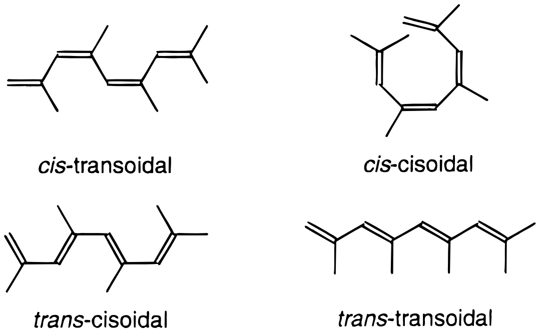
Structural Characterization. Figure 2 shows IR spectra of monomer **1a** and its polymer. As can be seen from Figure 2A, **1a** clearly exhibited a strong absorption band at 3240 cm^{-1}, due to the ≡CH stretching vibration in the monosubstituted acetylene. The aromatic rings showed a weak =CH stretching band at 3038 cm^{-1}, and the stretching bands of C≡C and C≡N groups overlapped at 2226 cm^{-1}. Because of the high sensitivity of the C=O stretching vibration in IR analysis, the ester group in **1a** absorbed strongly at 1714 cm^{-1}.

The strong ≡CH stretching band, however, was absent in the IR spectrum of the polymer (Figure 2B). The relative intensity of the stretching band at 3038 cm^{-1} (vs CH_2 absorption band at 2936 cm^{-1}) increased and a new absorption band appeared at ca. 3061 cm^{-1} as a shoulder, suggesting that the triple bond in the monomer has changed to a double bond in the polymer and confirming that the Rh catalyst has initiated the acetylene polymerization. The C≡N absorption band at 2226 cm^{-1} was still strong, although its relative intensity vs the CH_2 stretching band decreased. The relative intensity of the C=O stretching band remained unchanged. The IR data indicate that the cyano and ester functional groups in **1a** have survived from the Rh-catalyzed acetylene polymerization and confirm that the resulting polymer possesses a polyacetylene-type molecular structure (**2a**), as shown in Scheme 1.

The polymer obtained from **1b** exhibited similar spectral characteristics. The ≡CH stretching band was absent, the relative intensity of =CH absorption increased, and the C≡N and C=O bands were clearly seen (Figure 3B). Thus, the Rh catalyst is tolerant of the polar cyano and ester groups: It selectively effects the acetylene polymerization without attacking other functional groups coexisting in the monomer structure.

The polyacetylene structure of **2a** was further confirmed by NMR analysis. The absorption peak of the acetylene proton in **1a** appeared at δ 3.2 as a singlet, which, however, completely disappeared in the NMR spectrum of **2a** (Figure 4). Alternatively, **2a** showed three new peaks at δ 7.0, 6.8, and 5.9. Simionescu and Percec observed that the *cis* olefin proton in the *cis*-transoidal PPA absorbed at δ 5.82, while the *trans* olefin proton in the *trans*-cisoidal PPA absorbed at δ 6.85.[13] Because **2a** is basically a PPA derivative, it seems reasonable to assign the peak at δ 5.9 to the *cis* proton absorption in the *cis*-transoidal **2a** (Chart 1).[6,14] Since *cis*-cisoidal **2a** with a tight helix conformation would not be soluble, the absorption peaks at δ 7.0 and 6.8 might be from the *trans* olefin protons in **2a**, although we are unable to unambiguously assign which peak belongs to the *trans*-cisoidal or *trans*-transoidal structure at the present time. We have noticed that the peak at δ 7.0

Chart 1



has not been detected so far because it overlaps with the absorption peaks of the aromatic protons in PPA.[13] The peak at δ 7.0 is clearly observable in the spectrum of **2a** because of (i) the strong deshielding effect of the electron-withdrawing cyano and ester groups which induced a large downfield shift of the absorption peaks of some of the aromatic protons and (ii) the stereoregularity of the polymer backbone which gave well-resolved absorption peaks, as opposed to those of the PPA prepared by the classical metathesis catalysts.

When a polymer takes a random chain conformation, it normally gives an unresolved spectrum,[15] as shown in Figure 4C for a random PPA prepared from the WCl_6−Ph_4Sn catalyst system. Because of the random distribution of all four possible types of the stereoisomeric configuration along the polymer main chain, the olefinic and aromatic absorption peaks became an averaged sum of the stereosegments of different configuration, merging into one broad, structureless peak spreading over a spectral range as wide as ca. 3 ppm. The *cis* proton absorption "peak" at ca. δ 5.8 degenerated into a long tail, whereas the *trans* proton absorption "peaks" were not distinguishable any more, completely submerged under the overwhelming absorption peak(s) of the aromatic protons. The relatively sharp NMR peaks of **2a** suggest that the stereoregularity of the polymer is fairly high.[15] The high stereoregularity of **2a** may be due to (i) the strong stereoregulating power of the Rh catalyst and (ii) the alignment induced by the electronic interaction among the mesogenic pendant groups, which may provide an ordered environment for the monomer to undergo stereospecific polymerizations, as observed in other synthetic and biological polymerization systems.[15,16]

The ^{1}H NMR spectrum of **2b** (Figure 5B) was similar to that of **2a**. No acetylene proton absorption was observed at δ 3.2. Instead two new peaks appeared at δ 6.7 and 5.7, which are assignable respectively to the absorption of *trans* and *cis* protons in **2b**, according to the discussion detailed above. The peak at ca. δ 7.0 responsible for the absorption of one kind of *trans* proton diminished to a hardly-distinguishable bump. Thus, **2b** practically consisted of only two kinds of stereosegments, whereas **1b** had three kinds of stereostructures. The NMR peaks of **2b** were sharper and better-resolved than those of **2a**, suggesting that **2b** has higher stereoregularity than **2a**. In the liquid crystal (LC) research, it has been found that the long methylene spacer units enhance the ordering of some side-chain LC polymers.[17] When the alkyl spacer unit is long enough, it undergoes self-crystallization, thus imposing better ordering on the LC systems. Because the length of the methylene spacer units in **1b** (12) is longer than that in **1a** (6), the mesogenic groups in **1b** may be better aligned, thus providing a well-ordered environment for **1b** to undergo the Rh-catalyzed stereospecific polymerization.[6]

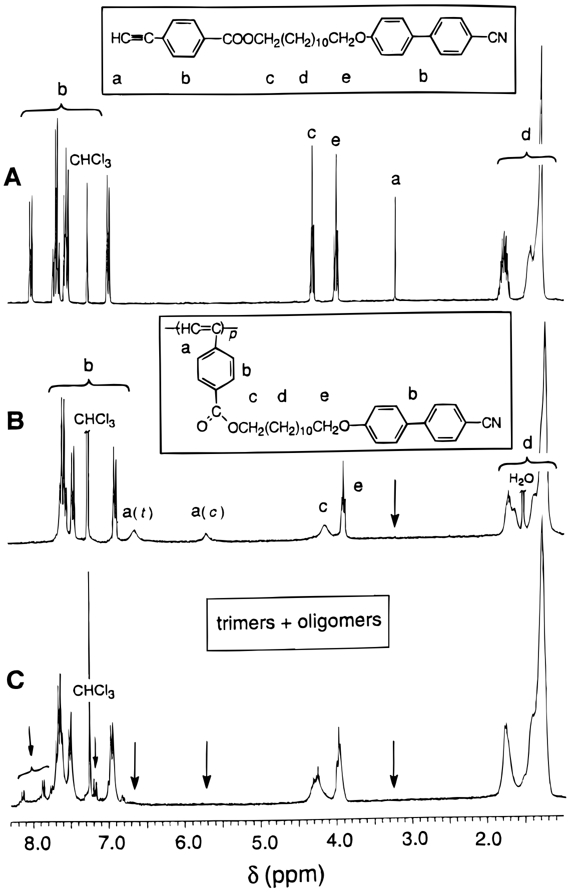


Figure 5. ^{1}H NMR spectra of (A) monomer **1b** and its reaction productions catalyzed by (B) $[Rh(nbd)Cl]_2$ (sample from Table 1, no. 10) and (C) WCl_6−Ph_4Sn (sample from Table 1, no. 7). All the spectra were measured in chloroform-*d* at room temperature.

The reaction products of **1b** from the WCl_6−Ph_4Sn catalyst exhibited absorption peaks of neither acetylene nor olefin protons (Figure 5C). Thus **1b** had undergone some kind of W-catalyzed reaction (no triple bond left), but the products were not polyacetylenes (no olefin bond formed). The products showed a few new peaks in the aromatic proton absorption region. It is known that 1,2,4-triphenylbenzene, a cyclotrimerization product of PA, absorbs at δ 7.13, while the 1,3,5-trimer absorbs at δ 7.61.[18] Thus, the peak at δ 7.2 in Figure 5C might be assignable to the 1,2,4-trimer of **1b**. A 1,3,5-trimer is normally produced together with a 1,2,4-isomer during the cyclotrimerization of a substituted acetylene.[19] The 1,3,5-trimer of **1b** might have also formed in the W-catalyzed reaction. Its absorption peak at δ 7.6, however, was difficult to distinguish because of its overlapping with the overwhelming aromatic absorption peaks located in the same spectral region. Cianciusi et al. observed absorption peaks in the range of δ 7.2−8.1 for their thermally treated PA oligomers,[18] and Simionescu and Percec identified that the peaks in the range of δ 7.6−8.2 were from polyphenylene rings in their thermal isomerization products of PPA.[13] It thus seems reasonable to assume that the peaks in the range of δ 7.7−8.2 in Figure 5C are from the cyclic oligomers of **1b**. The NMR data suggest that WCl_6−Ph_4Sn catalyst effected the cyclotrimerization and cyclooligomerization of **1b**, which is consistent with the GPC data presented in Figure 1A. The W catalyst can polymerize $HC{\equiv}CC_6H_4$-*p*-CO_2R to high molecular weight poly-

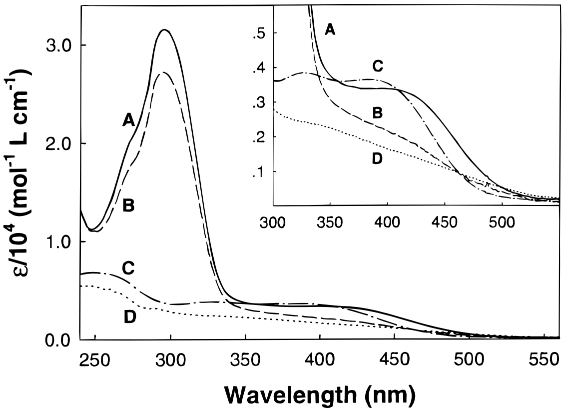


Figure 6. UV spectra of polymers (A) **2b** (sample from Table 1, no. 10) and (B) **2a** (sample from Table 1, no. 5). The spectra for poly(phenylacetylene)s prepared from (C) [Rh(cod)(tos)-(H_2O) (*cis* content: 99.5%; sample from Table 3, no. 5 in ref 6) and (D) WCl_6-Ph_4Sn (sample from Figure 4C) are shown for comparison. All the spectra were measured in THF at room temperature.

mers,[11] but the cyano group in **1b** completely changed the reaction path: that is, from polymerization to cyclization.

The electronic absorption spectra of the cyano-containing polyacetylenes were quite informative. Polymer **2b** absorbed strongly at 295 nm (λ_{max}) with an ϵ_{max} as high as 3.2×10^4 (Figure 6A). The strong absorption peak is assignable to the *K*-band of the cyanoalkoxybiphenyl mesogen in **2b**, because PPA, the parent form of **2b** without the biphenyl chromophore, exhibited no absorption peak at around 295 nm. The *K*-band of an alcohol solution of biphenyl locates at 246 nm with an ϵ_{max} of 2.0×10^4.[14] The large red-shift in λ_{max} (49 nm) and the big increase in ϵ_{max} (1.6 times) in the *K*-band of **2b** suggest that the cyanoalkoxybiphenyl mesogen is well-polarized by the push−pull interaction between the donor (−OR) and acceptor (−CN) groups. Similarly, **2a** exhibited a strong *K*-band of the push−pull cyanoalkoxybiphenyl mesogen at 295 nm. Thus, both **2a** and **2b** might be $\chi^{(2)}$-active.[7]

While the cyanoalkoxybiphenyl mesogens absorbed in the short-wavelength region, the conjugated polyacetylene backbone should absorb at longer wavelengths. As shown in the inset of Figure 6, **2b** exhibited a shoulder peak at 426 nm with an ϵ_{max} of 3.1×10^3. Compared with **2b**, **2a** absorbed at a shorter wavelength (424 nm) with a lower absorptivity (1.8×10^3). It is well-known that a steric effect causes chromic shift. As revealed by the NMR analysis, **2a** has lower stereoregularity or is less ordered than **2b**. Thus, the shorter λ_{max} and lower ϵ_{max} of **2a** may arise from its lower stereoregularity because a structurally less regular polyacetylene may consist of more such segments whose neighboring double bonds are out of coplanarity. To further check the steric effect on the electronic transitions in polyacetylenes, we measured UV spectra of two PPAs with different stereoregularity.[6] While the stereoregular PPA with a *cis* content of ca. 100% exhibited two absorption peaks at 327 (ϵ_{max} 3.8×10^3) and 389 nm (ϵ_{max} 3.6×10^3) (Figure 6C), the absorption spectrum of the random PPA in the same wavelength range was basically a structureless tail with low absorptivity. The UV data of the PPAs thus confirm that the electronic transitions in polyacetylenes are sensitive to their backbone stereoregularity. IR and NMR analyses have been powerful tools for estimating the stereoregularity of polyacetylenes,[2,6,13,20] and we here demonstrate that the UV analysis can also be used for studying stereostructures of substituted polyacetylenes.

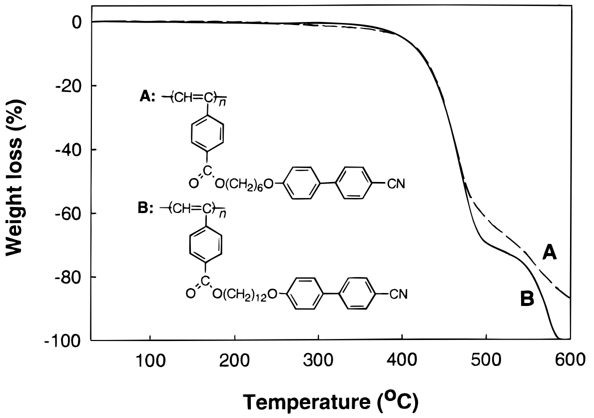


Figure 7. TGA thermograms of polymers (A) **2a** (sample from Table 1, no. 5) and (B) **2b** (sample from Table 1, no. 10) measured under dinitrogen at a heating rate of 20 °C/min.

Polymer Properties. The cyano-containing polyacetylenes **2** exhibited very high thermal stability. The temperature for 5% weight loss in **2a** was 398 °C (Figure 7A), much higher than that in PPA (225 °C).[3b] Moigne's polymers—$[CH{=}C(C_6H_4\text{-}p\text{-}CO_2\text{-alkyl})]_n$—lose ca. 30−70% weight at ca. 425 °C,[11] while at the same temperature, **2a** maintained most of its weight (weight loss: ca. 10%), suggesting that the biphenyl groups have contributed to the high thermal stability of the polymer. The rigid biphenyl groups may have formed a protective "jacket"[21] via the strong electronic interaction among the polarized cyanoalkoxybiphenyl mesogens, shielding the alkyl spacer and the polyacetylene backbone from thermal attack. When temperature increases to such a point at which the protective jacket breaks, the polymer would undergo catastrophic degradation. This was actually the case for the thermal degradation of **2a**, as evidenced by the sharp slope of its TGA thermogram in the high-temperature range. The thermal stability of **2b** was similar to that of **2a**, indicating that the jacket effect was so overwhelming that the thermal stability of the polymers became insensitive to the length of their methylene spacers.

It has often been the case that the high thermal stability of a polymer is at the expense of its processibility. Many substituted polyacetylenes degrade before melt;[2,3b] that is, they cannot be processed by the conventional plastic processing technologies such as molding, extruding, blowing, and compressing, which significantly limits the scope of their applications. Without a doubt, development of melt-processable polyacetylenes is of practical importance. Polymers **2** are thermally very stable because of the rigid and polarized biphenyl mesogens. The rigid biphenyl jacket may prevent the polymers from melting; on the other hand, the long methylene spacer may melt at a moderate temperature which then "dissolve" the rigid polyacetylene main chain and the biphenyl side jacket. It is of interest to check how the polymers behave, and we thus used DSC to study their thermal transitions.

The first cooling scan in the DSC analysis of **2b** detected a sharp exothermic peak centered at 123.0 °C (ΔH = 4.1 kJ/mol), while the second heating scan recorded an endothermic peak of similar size (ΔH = 3.5 kJ/mol) at 131.1 °C (Figure 8). The second cooling scan gave results identical with those obtained in the first cooling scan within experimental error, indicating that the thermal transition was reversible with excellent reproducibility and that the polymer had not undergone

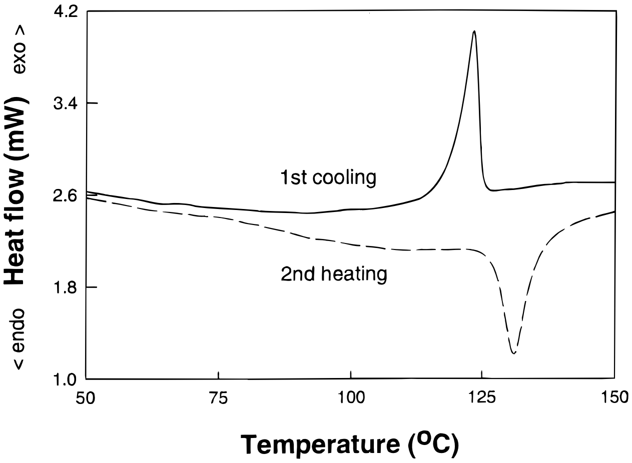
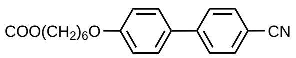
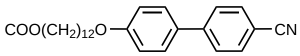


Figure 8. DSC thermograms of polymer **2b** (sample from Table 1, no. 10) measured under dinitrogen at a heating or cooling rate of 10 °C/min.

Table 2. Melting Transitions (T_m) of Poly(phenylacetylene) Derivatives[a]

		T_m (°C)[b]	
no.	$-[CH{=}C(C_6H_4\text{-}p\text{-}R)]_n-$	heating[c]	cooling[d]
1[e]	H (random)	283.0 (dec.)	
2[f]	H (stereoregular, 100% *cis*)	>350.0	
3[g]	$COO(CH_2)_7CH_3$	75	
4[g]	$COO(CH_2)_{15}CH_3$	26	
5[h]		107.7 (115.5)	99.0 (103.2)
6[i]		131.1 (138.5)	123.0 (133.0)

[a] Measured on DSC under dinitrogen at a heating or cooling rate of 10 °C/min. [b] Data in parentheses are obtained from polarized optical microscopic (POM) observation. [c] The first (nos. 1 and 2) or second (nos. 3–6) heating scan. [d] The first cooling scan. [e] Sample from Figure 4C. [f] Sample from Table 2, no. 6, in ref 6. [g] Data from ref 11. [h] Sample from Table 1, no. 5. [i] Sample from Table 1, no. 10.

any thermal degradation during the scan circles. To check the origin of the DSC peak, we conducted POM measurements of the polymer sample. When we warmed up **2b** in the POM hot stage, we found that the solid powders completely melted at 138.5 °C. When the sample was cooled down, the liquid started to solidify at 133.0 °C. The POM observation thus confirms that the DSC peaks correspond to the melting process in **2b**.

Table 2 compares thermal properties of several PPA derivatives. We first measured DSC thermograms of the parent PPAs as a control. The PPA with a random conformation showed no melting transition peak below 200 °C. It started to decompose from 200 °C and exhibited a big endothermic decomposition peak centered at 283.0 °C. Thus, like many other substituted polyacetylenes,[2,3b] the PPA is not melt-processable. Interestingly, the stereoregular PPA was thermally much more stable, starting to decompose at a much higher temperature (283.3 °C) with no decomposition peak being observed even at 350 °C. Thermal properties (e.g., glass transition, melting point, and decomposition temperature) of many polymers are dependent on the stereoregularity of their molecular structures,[22] but this is the first example for a polyacetylene in which the thermal stability of a PPA is affected by its stereoregularity to a great extent.

Moigne et al.[11] have observed that poly[[4-[[(8-octyl)oxy]carbonyl]phenyl]acetylene] exhibits a broad endothermic melting peak centered at 75 °C (Table 2, no. 3). When the length of the alkyl tail increases to 16, the melting point (T_m) decreases to 26 °C. The transition peak is again very broad, over a temperature range (ΔT) of more than 60 °C. Compared with Moigne's polymers, the T_m of **2a** was higher (107.7 °C; Table 2, no. 5) and its transition temperature range was narrower [ΔT: 22.7 °C (1st cooling); 29.9 °C (2nd heating)]. In contrast to the trend observed by Moigne et al. for their polymers, when the spacer length increased from 6 methylene units in **2a** to 12 in **2b**, the T_m increased and the ΔT became even narrower [15.2 °C (1st cooling); 17.7 °C (2nd heating)].

The poly[[4-[[(*n*-alkyl)oxy]carbonyl]phenyl]acetylenes] prepared by Moigne et al. using the WCl_6 catalyst are structurally "impure", containing cyclohexadiene sequences in the polyacetylene backbones.[11] The cyclic structural defects certainly perturb the stereoregularity of the polymer backbones. When the main-chain double bonds are out of coplanarity, the pendant groups would have difficulty aligning together. Furthermore, the alkyl pendant groups in Moigne's polymers are not really mesogenic or at most poorly mesogenic, and thus the driving force for them to align together could be quite small. When the long hexadecyl tails are poorly aligned, they would act as plasticizers, thus significantly lowering the T_m of the polymer. In our system, the polyacetylene main chains are stereoregular and the cyanoalkoxybiphenyl side chains are mesogenic. The backbone stereoregularity would allow the pendant groups to locate in the same planes, and the electronic interaction among the polarized push–pull mesogens would induce ordered alignment of the pendant groups. Indeed, the dissolution of **2b** in THF or DMF was very slow (taking about a week), probably because of the alignment or even self-crystallization of the pendant groups. T_i's of some side-chain LC polymers have been found to increase with an increase in the spacer length because of the better ordering or the self-crystallization of the longer methylene spacers.[23] As revealed by the spectroscopic analysis detailed above, **2b** was more stereoregular than **2a**. The higher stereoregularity and the longer spacer length would induce better ordering in **2b**, thus increasing, instead of decreasing, its T_m.

Conclusion

Many groups have attempted to polymerize cyanoalkynes, most of which, however, have ended up with disappointments. We have for the first time succeeded in polymerizing a group of new cyano-containing acetylene monomers (**1**) to soluble, stereoregular, and high molecular weight polymers (**2**). Electronic and thermal transitions of **2** are sensitive to their stereoregularity, which may find potential applications in the development of novel electrooptical and thermochromic devices. In addition to their high thermal stability and solution-castability, the polymers are melt-processable, offering processing advantages over many other substituted polyacetylenes. The molecular structure of **2** is unique in that a conjugated polyacetylene backbone and the push–pull mesogenic pendant groups are coexisting in one polymer chain, and thus **2** may possess intriguing electronic and optical properties. The polymerization system we developed here paves the way for polymer scientists to exercise "molecular engineering" endeavors to fine-"tune" the molecular structure of the polymers, which may eventually lead to the development of polyacetylenes with such novel materials properties as being both $\chi^{(2)}$- and $\chi^{(3)}$-active and both conductive and liquid crystalline. We are currently working on exploring the novel materials properties of the polymers with the aim of developing polyacetylene-based specialty materials.

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