# Synthesis, Mesomorphism, Isomerization, and Aromatization of Stereoregular Poly{[4-({[6-({[4′-(heptyl)oxy-4-biphenylyl]carbonyl}oxy)-hexyl]oxy}carbonyl)phenyl]acetylene}

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ABSTRACT: The polymerizations of a functional phenylacetylene derivative, [4-({[6-({[4′-(heptyl)oxy-4-biphenylyl]carbonyl}oxy)hexyl]oxy}carbonyl)phenyl]acetylene (**1**), are effected by molybdenum and tungsten halides and rhodium−diene complexes. The rhodium-initiated polymerizations produce polymers (**2**) of high molecular weights ($M_n$ up to $1.2 \times 10^5$) in high yields (up to 93%). IR, UV, and NMR analyses confirm that **2** possesses a stereoregular alternating-double-bond backbone with a predominant cis conformation. DSC, POM, and XRD measurements reveal that **2** is liquid crystalline: it shows smectic A mesophase in the temperature range 135−146 °C. The *cis*-rich **2** undergoes active isomerization to the trans conformation at 170 °C. Intrachain cyclization followed by chain scission at ca. 200 °C releases 1,3,5-trisubstituted benzene as the sole aromatization product, proving that the repeat units of the polymer chains are linked in a regular head-to-tail fashion.

## Introduction

Polymerizations of phenylacetylene and its derivatives have been well studied,[1−3] and the resulting poly(phenylacetylene)s have been found to exhibit novel materials properties such as photoconductivity,[4] optical nonlinearity,[5] photoluminescence,[6] $\gamma$-radiolysis susceptibility,[7] permselectivity,[8] and chiral recognizability.[9] Obviously, the microstructures of the polymers affect their physical and chemical properties; for example, whether the monomer (repeat) units are linked in a head-to-tail or head-to-head mode affects the conformation and then the packing arrangements of the polymer chains,[10] which in turn affects the transport pathways in the photoconduction and enantiopermeation or chiral separation processes of the polymer materials.[4,11] Notwithstanding the vast variety of the poly(phenylacetylene)s prepared, the linkage modes of the monomer units have not been well understood. While it is generally believed that metathesis mechanisms are involved in the phenylacetylene polymerizations initiated by transition-metal catalysts,[1] Hirao et al. have recently demonstrated that the phenylacetylene polymerization initiated by an organorhodium complex, i.e., Rh(C≡CPh)(nbd)$(PPh_3)_2$ (nbd = 2,5-norbornadiene),[12] propagates in an insertion mechanism.[13] In the propagation reaction, there are theoretically several addition modes: the polymer chains can grow with the monomers adding to the active centers in head-to-tail, head-to-head, and tail-to-tail fashions.[10] On the basis of the theoretical consideration of steric and electronic (resonance) effects, many groups have "automatically" assumed that their acetylene polymerizations propagate in a head-to-tail mode. Experimental substantiation of such assumption, however, remains yet to be done. Occasionally, head-to-head and tail-to-tail linkages of the repeat units in some polyacetylene systems have also been advocated.[14]

NMR analysis is a powerful tool in elucidating microstructures of macromolecules.[15] The assignments of absorption peaks of the poly(phenylacetylene)s, however, have been sometimes quite difficult and confusing, because the double-bond backbones and the aromatic pendant groups absorb in the similar chemical shift ($\delta$) region. The situation becomes even worse when the polymers are synthesized by the "classical" $MoCl_5$- and $WCl_6$-based metathesis catalysts: The exceedingly broad peaks simply make it impossible to differentiate the absorptions by the main chains and by the pendant groups.[2a,d] The polymers synthesized from organorhodium catalysts show much sharper NMR peaks, but the correct peak assignments are still at times quite challenging. For example, in our previous paper,[2a] we mistakenly assigned the peaks at $\delta$ 6.7−6.8 to the absorption by the trans olefin protons in the polyacetylene main chains.[2b] In this work, we synthesized a new poly(phenylacetylene) derivative (**2**; Chart 1) using Mo-, W-, and Rh-based catalysts and thoroughly characterized the molecular structure of the polymer using NMR spectroscopy. We evaluated the substituent constants ($Z$)[16] for the quantitative calculation of the $\delta$ values of poly(phenylacetylene)s, with the aim of facilitating the assignments of the absorption peaks and the estimation of the polymer microstructures.

Simionescu and Percec have found that thermal treatment of cis poly(phenylacetylene) induces cyclization and releases triphenylbenzenes as decomposition products.[17] The thermal degradation may follow the mechanism shown in Scheme 1. Upon heating, the cis segment of **5** isomerizes to **6**. The *cis*-hexatriene moiety of **6** then undergoes the thermally allowed pericyclic reaction of [x6d] electrocyclization,[18,19] giving the cyclohexadiene species **7**. Chain scission of the sterically crowded **7** generates two resonance-stabilized radicals **8** and **9**,[20,21] and subsequent aromatization of the cyclohexadiene moiety in **9** produces the trisubstituted benzene **12**. We rationalize that, by analyzing the aromatization products, we may gain insights into the addition modes in the polymerization reactions. Thus, (i) if the aromatization gives only 1,3,5-substituted benzene, the monomer repeat units must be linked or

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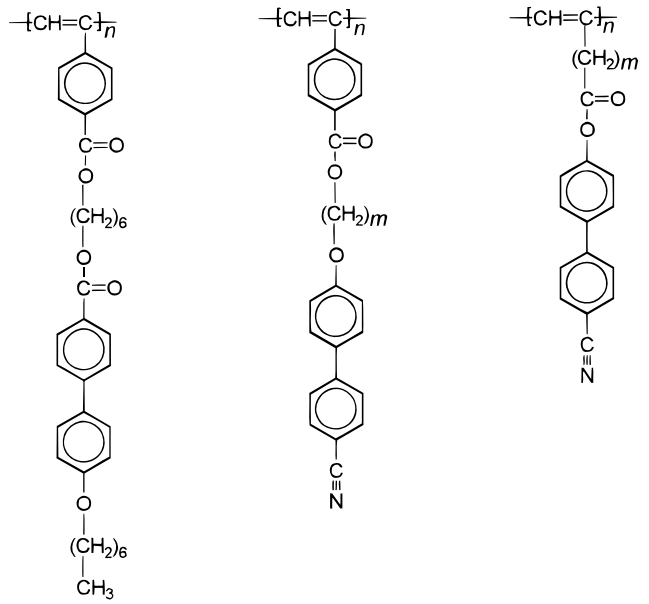
**Chart 1**



**2** **3** **4**

the polymerization must have propagated in a head-to-tail mode; (ii) if the substitution is at the 1,2,4-position, the chain growth must be via head-to-head (or tail-to-tail) addition; and (iii) if a mixture of 1,3,5- and 1,2,4-substituted benzenes is produced, the polymerization would have proceeded in a nonstereospecific manner. In this study, we investigated the thermally induced isomerization of **2** and found that the aromatization reaction produced exclusively 1,3,5-substituted benzene, thus experimentally proving that the polymer chain possesses a regular head-to-tail microstructure.

We are interested in the development of side-chain liquid-crystalline polyacetylenes and have previously synthesized a group of mesogen-containing poly(phenylacetylene)s of general structure of **3** (Chart 1).[2a] Unfortunately, however, the polymers exhibit no liquid-crystalline properties.[22] The nonmesomorphism of **3** may stem from (i) the high rigidity of the poly(phenylacetylene) backbone and (ii) the strong electronic interaction of the polarized [(cyano)biphenylyl]oxy pendants. In our previous work, we tackled the problem (i): we fine-tuned the backbone rigidity by replacing the phenyl group of the *phenyl*acetylene unit with alkyl chains and successfully developed a large variety (more than 20 different kinds) of liquid-crystalline polyalkynes of general structure of $-\{HC{=}C[(CH_2)_m-\text{mesogen}]\}_n-$ (e.g., **4** in Chart 1).[22,23] Some of the polymers show unique mesomorphic properties originating from the relatively rigid polyalkyne backbone such as rotation-induced high strength disclinations, shear-induced inversion walls, and solidification-induced banded textures.[23] In this work, we tackled the problem (ii); that is, we tried to tune the electronic interaction of the mesogenic pendants. It is well-known that strong electronic interaction promotes direct crystallization from isotropic liquid, and replacing the highly polar cyano group with a less polar alkoxy group[24,25] may allow the liquid-crystalline mesophases to form. We have previously found that polymers **3** show novel swelling-induced optical anisotropy in organic solvents,[2a] and it is expected that the long heptoxy tail in **2** may also act as internal plasticizer to enable the mesogenic groups to move together and to align along specific direction. In this report, we demonstrate that this approach does work and that **2**, albeit with a rigid poly(phenylacetylene) backbone, shows mesomorphic properties.

## Experimental Section

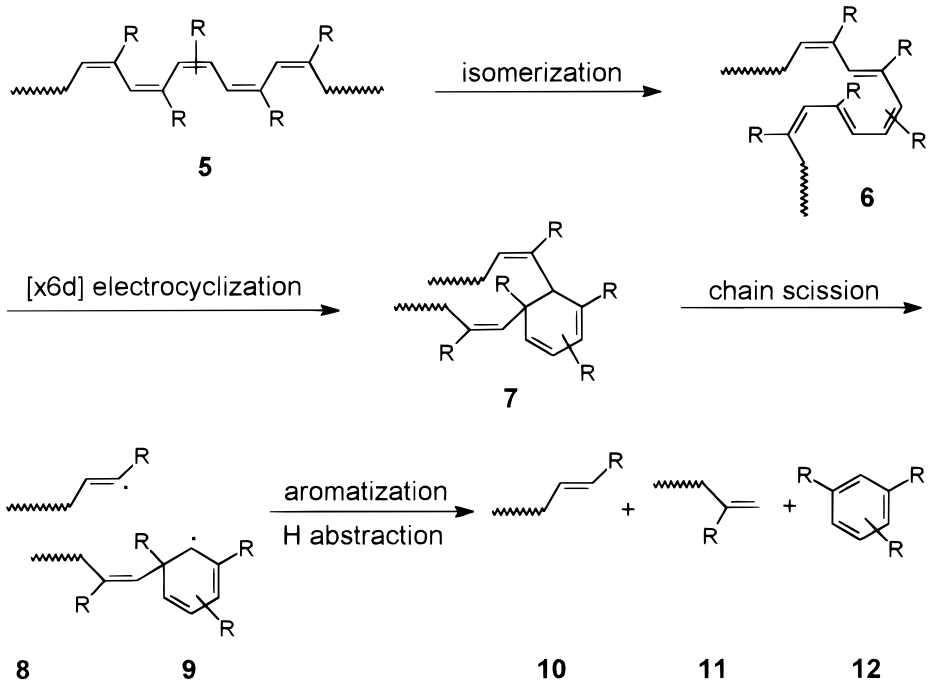
**Materials.** Dioxane (Aldrich), THF (Lab-Scan), and toluene (BDH) were predried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. Triethylamine (Aldrich) was also predried but purified from calcium hydride by simple distillation. 4′-Hydroxy-4-biphenylcarboxylic acid (**13**), 1,3-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), and *p*-toluenesulfonic acid (TsOH) were all purchased from Aldrich. The rhodium complexes $[Rh(nbd)Cl]_2$, $Rh(nbd)(tos)(H_2O)$, $[Rh(nbd)(PMe_3)_3]PF_6$, $[Rh(cod)Cl]_2$, $Rh(cod)(tos)(H_2O)$, $Rh(cod)(NH_3)Cl$, and Rh(cod)(pip)Cl [where nbd = 2,5-norbornadiene, cod = 1,5-cyclooctadiene, tos = *p*-toluenesulfonate (or TsO), pip = piperidine] were synthesized according to published procedures.[2d,26] 4-Ethynylbenzoic acid was synthesized as reported in our previous paper.[2a] All other commercial reagents including the metal halide catalysts were purchased from Aldrich and used as received without further purification. Technical grade acetone was used to precipitate the polymeric products.

**Instrumentation.** Infrared (IR) spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were measured on a Bruker ARX 300 NMR spectrometer using chloroform-*d* or dichloromethane-$d_2$ as solvent. Tetramethylsilane ($\delta = 0$), chloroform ($\delta = 7.26$), and/or dichloromethane ($\delta = 5.38$) were used as internal references for the NMR analysis. UV−vis spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer, and molar absorptivity ($\epsilon$) of **2** was calculated on the basis of its repeat unit. Mass spectra (MS) were recorded on a Finnigan TSQ 7000 triple quadrupole mass spectrometer operating in a chemical ionization (CI) mode using methane as carrier gas. Elemental analysis was performed by a commercial analytical company, M-H-W Laboratories. Molecular weights of the polymers were estimated by a Waters Associates gel permeation chromatography (GPC) using 12 monodisperse polystyrenes (molecular weight range $10^2-10^7$) as calibration standards. Differential scanning calorimetry (DSC) analysis was carried out on a Setaram DSC 92 under nitrogen at a scanning 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 mesomorphic textures. X-ray diffraction (XRD) patterns were recorded on a Philips PW 1830 powder diffractometer at room temperature using the monochromatized X-ray beam from the nickel-filtered Cu Kα radiation with a wavelength of 1.5406 Å (scan rate 0.01°/s; scan range 2−30°). The samples for the XRD experiments were prepared by quickly quenching by liquid nitrogen the polymers annealed at their liquid-crystalline states.[22,23]

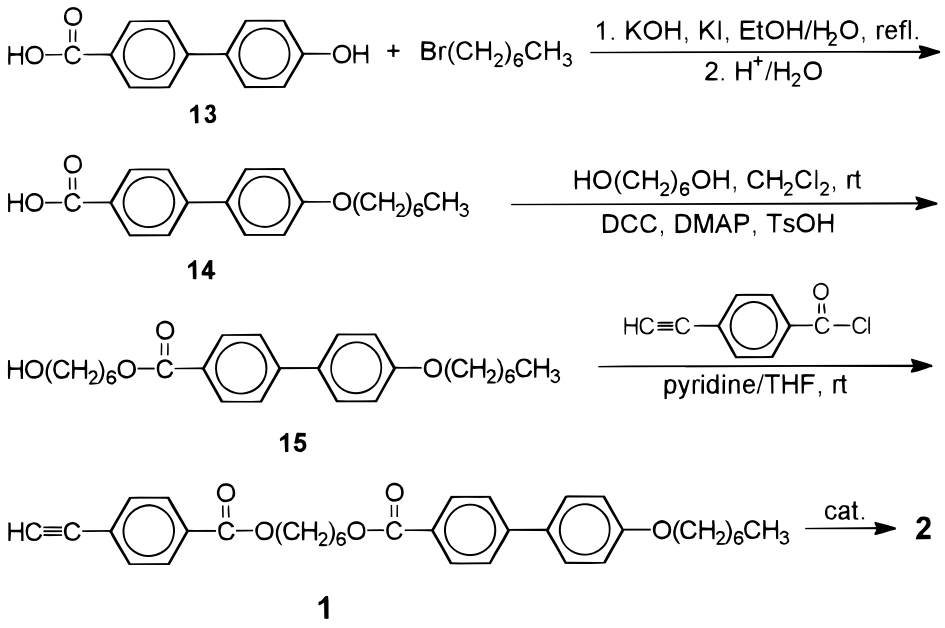
**Monomer Synthesis.** The phenylacetylene derivative **1** was synthesized by the multiple-step reactions shown in Scheme 2. Detailed experimental procedures and characterization data are given below.

**4′-(Heptyl)oxy-4-biphenylylcarboxylic Acid (14).** In a 1000 mL round-bottom flask equipped with a condenser, 10 g (46.7 mmol) of **13**, 5.23 g of KOH (93.5 mmol), and a catalytic amount of KI were dissolved in 500 mL of ethanol/water mixture (6:1 by volume) under gentle heating and stirring. To the solution was added 12 g (67 mmol) of 1-bromoheptane, and the resulting mixture was refluxed for 30 h. The reaction mixture was poured into 300 mL of water acidified with 20 mL of 37% hydrochloric acid. The solid was collected by suction filtration. Recrystallization in glacial acetic acid gave 9 g of white crystalline product (yield 61.7%). IR (KBr), $\nu$ ($cm^{-1}$): 3200−2300 (br, $CO_2H$), 1684 (s, C=O). $^1H$ NMR (300 MHz, DMSO-$d_6$), $\delta$ (ppm): 12.95 (s, $CO_2H$), 8.09 (d, 2H, Ar−H ortho to $CO_2H$), 7.83 (m, 4H, Ar−H), 7.14 (d, 2H, Ar−H ortho to $OC_7H_{15}$), 4.11 (t, 2H, $OCH_2$), 1.83 (m, 2H, $OCH_2CH_2$), 1.48 [m, 8H, $(CH_2)_4$], 0.97 (t, 3H, $CH_3$). $^{13}C$ NMR (75 MHz, DMSO-$d_6$),

**Scheme 1**




**Scheme 2**




$\delta$ (ppm): 167.41 (C═O), 159.20 (aromatic carbon linked with $OC_7H_{15}$), 144.15 (aromatic carbon para to $CO_2H$), 131.28 (aromatic carbon para to $OC_7H_{15}$), 130.15 (aromatic carbons ortho to $CO_2H$), 128.91 (aromatic carbon linked with $CO_2H$), 128.32 (aromatic carbons meta to $CO_2H$), 126.28 (aromatic carbons meta to $OC_7H_{15}$), 115.21 (aromatic carbons ortho to $OC_7H_{15}$), 67.77 ($OCH_2$), 31.45 ($CH_2C_3H_7$), 28.87 ($CH_2C_2H_5$), 28.64 ($OCH_2CH_2$), 25.68 ($OC_2H_4CH_2$), 22.26 ($CH_2CH_3$), 14.16 ($CH_3$).

**6-Hydroxy-1-hexyl [4-(Heptyl)oxy-4-biphenylyl]carboxylate (15).** 4′-(Heptyl)oxy-4-biphenylylcarboxylic acid (**14**; 1.7 g, 5.44 mmol), 1,6-hexanediol (1.3 g, 11 mmol), TsOH (0.2 g, 1.16 mmol), and DMAP (0.1 g, 0.82 mmol) were dissolved in 400 mL of dry $CH_2Cl_2$ in a 500 mL two-necked flask under nitrogen. The solution was cooled to 0−5 °C with an ice bath, to which 1.8 g of DCC (7.5 mmol) in 50 mL of dichloromethane was added under stirring via a dropping funnel with a pressure-equalization arm. The mixture was stirred at room temperature overnight. After filtering out the formed insoluble urea crystals, the filtrate was concentrated by a rotary evaporator. The crude product was purified by a silica gel column using $CHCl_3$/acetone mixture (10:1 by volume) as eluent. After recrystallization from ethanol/water (3:1 by volume), 1.6 g of white crystalline product was obtained (yield 71.3%). IR (KBr), $\nu$ ($cm^{-1}$): 3316 (br, OH), 1714 (s, C═O). $^1$H NMR (300 MHz, $CDCl_3$), $\delta$ (ppm): 8.35 (d, 2H, Ar−H ortho to $CO_2R$), 7.58 (m, 4H, Ar−H), 7.00 (d, 2H, Ar−H ortho to $OC_7H_{15}$), 4.34 (t, 2H, $CH_2OCO$), 4.00 (t, 2H, $OCH_2$), 3.67 (t, 2H, $HOCH_2$), 1.81 (m, 4H, $CH_2CH_2OCO$, $OCH_2CH_2$), 1.61−1.35 [m, 14H, $(CH_2)_7$], 0.90 (t, 3H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$ (ppm): 166.64 (C═O), 159.45 (aromatic carbon linked with $OC_7H_{15}$), 145.24 (aromatic carbon para to $CO_2R$), 131.91 (aromatic carbon para to $OC_7H_{15}$), 130.03 (aromatic carbons ortho to $CO_2R$), 128.51 (aromatic carbon linked with $CO_2R$), 128.29 (aromatic carbons meta to $OC_7H_{15}$), 126.40 (aromatic carbons meta to $CO_2R$), 114.96 (aromatic carbons

**Table 1. Polymerization of [4-({[6-({[4′-(Heptyl)oxy-4-biphenylyl]carbonyl}oxy)hexyl]oxy}carbonyl)phenyl]acetylene**[a]

| no. | catalyst[b] | solvent | yield (%) | $M_n$[c] | $M_w/M_n$[c] | cis %[d] |
|---|---|---|---|---|---|---|
| 1 | $WCl_6-Ph_4Sn$ | dioxane | 0 | | | |
| 2 | $WCl_6-Ph_4Sn$ | toluene | 7.2 | 28 200 | 2.04 | |
| 3 | $MoCl_5-Ph_4Sn$ | dioxane | 0 | | | |
| 4 | $MoCl_5-Ph_4Sn$ | toluene | 10.2 | 14 200 | 2.33 | |
| 5 | $[Rh(nbd)Cl]_2$ | $Et_3N$/THF[e] | 93.0 | 122 000 | 5.23 | 92 |
| 6 | $Rh(nbd)(tos)(H_2O)$ | THF | 0 | | | |
| 7 | $[Rh(nbd)(PMe_3)_3]PF_6$ | THF | 5.7 | 79 200 | 9.64 | 73 |
| 8 | $[Rh(cod)Cl]_2$ | $Et_3N$/THF[e] | 85.7 | 83 800 | 4.60 | 91 |
| 9 | $Rh(cod)(tos)(H_2O)$ | THF | 73.5 | 26 800 | 3.93 | 85 |
| 10 | $Rh(cod)(NH_3)Cl$ | THF | 93.1 | 62 600 | 6.38 | 92 |
| 11 | Rh(cod)(pip)Cl | THF | 92.8 | 72 400 | 5.33 | 91 |

[a] At room temperature under nitrogen for 24 h; $[M]_0 = 0.2$ M, [cat.] = ([cocat.] =) 10 mM. [b] Abbreviation: nbd = 2,5-norborndiene, tos = *p*-toluenesulfonate, cod = 1,5-cyclooctadiene, pip = piperidine. [c] Determined by GPC in THF on the basis of a polystrene calibration. [d] Determined by $^1$H NMR spectra according to eq 1. [e] Volume ratio of $Et_3N$ to THF: 1:4.

ortho to $OC_7H_{15}$), 68.17 ($PhOCH_2$), 64.85 ($CH_2OCOPh$), 62.83 ($HOCH_2$), 32.64 ($HOCH_2-CH_2$), 31.77 ($CH_2C_3H_7$), 29.26 ($CH_2$-$CH_2OCOPh$), 29.04 ($CH_2C_2H_5$), 28.94 ($PhOCH_2CH_2$), 26.00 [$HO(CH_2)_2CH_2$], 25.87 [$HO(CH_2)_3CH_2$], 25.43 ($PhOC_2H_4CH_2$), 22.59 ($CH_2CH_3$), 14.05 ($CH_3$).

**[4-({[6-({[4′-(Heptyl)oxy-4-biphenylyl]carbonyl}oxy)-hexyl]oxy}carbonyl)phenyl]acetylene (1).** Into a 50 mL two-necked round-bottom flask were added 0.8 g (5.5 mmol) of 4-ethynylbenzoic acid, 2 mL of thionyl chloride, and 15 mL of THF. After refluxing for 2 h, the solvent and excess $SOCl_2$ were distilled off under reduced pressure. The solid left in the flask was dissolved in 15 mL of THF and cooled to 0−5 °C using an ice bath. A solution of **15** (2.2 g, 5.3 mmol) and pyridine (0.6 mL) in 25 mL of THF was injected into the flask, and the mixture was slowly warmed to room temperature and stirred overnight. THF 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 dichloromethane as eluent. Recrystallization from absolute ethanol gave 1.2 g of white crystalline product (yield 45%). IR (KBr), $\nu$ ($cm^{-1}$): 3312 (s, HC≡), 1714 (s, C=O), 648 (s, ≡C−H). $^1$H NMR (300 MHz, $CDCl_3$), $\delta$ (ppm): 8.06 (d, 2H, Biph−H; Biph = biphenyl), 8.00 (d, 2H, Ph−H meta to HC≡C), 7.57 (m, 6H, Ph−H ortho to HC≡C), 7.00 (d, 2H, Biph−H ortho to $OC_7H_{15}$), 4.35 (m, 4H, $CH_2OCO$, $CO_2CH_2$), 4.00 (t, 2H, $OCH_2$), 3.22 (s, 1H, HC≡), 1.81 (m, 6H, $CH_2CH_2OCO$, $CO_2CH_2CH_2$, $OCH_2CH_2$), 1.55−1.29 [m, 12H, $(CH_2)_6$], 0.90 (t, 3H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$), $\delta$ (ppm): 166.60 (C=O), 165.90 (C=O), 159.40 (aromatic carbon linked with $OC_7H_{15}$), 145.20 (aromatic carbon linked with $PhOC_7H_{15}$), 132.20 (aromatic carbons ortho to HC≡C), 132.00 (aromatic carbon para to $OC_7H_{15}$), 130.40 (aromatic carbons meta to HC≡C), 130.00 (aromatic carbon para to HC≡C), 129.40 (aromatic carbons meta to $PhOC_7H_{15}$), 128.40 (aromatic carbon para to $PhOC_7H_5$), 128.30 (aromatic carbons ortho to $PhOC_7H_{15}$), 126.70 (aromatic carbon linked with HC≡C), 126.40 (aromatic carbons meta to $OC_7H_{15}$), 114.90 (aromatic carbons ortho to $OC_7H_{15}$), 82.80 (≡C), 79.90 (HC≡), 68.10 ($PhOCH_2$), 65.10 (≡$CPhCO_2CH_2$), 64.80 ($CH_2OCOBiph$), 31.80 ($CH_2C_3H_7$), 29.20 ($CH_2CH_2OCOBiph$), 29.00 (≡$CPhCO_2CH_2$-$CH_2$), 28.70 ($CH_2C_2H_5$), 28.60 ($OCH_2CH_2$), 26.00(≡$CPhCO_2$-$C_2H_4CH_2$), 25.79 ($CH_2C_2H_4OCOBiph$), 25.77 [$BiphO(CH_2)_2CH_2$], 22.60 ($CH_2CH_3$), 14.00 ($CH_3$). MS (CI; $CH_4$): *m/e* 540.7 [$M^+$, calcd 540.3]. Anal. Calcd for $C_{35}H_{40}O_5$: C, 77.78; H, 7.41. Found: C, 75.35; H 7.39.

**Polymerization.** All the polymerization reactions and manipulations were carried out under a nitrogen atmosphere using an inert-atmosphere glovebox (Vacuum Atmospheres) or Schlenk techniques in a vacuum line system, except for the purification of the polymers, which was done in an open atmosphere. A typical procedure for the polymerization of **1** catalyzed by $[Rh(nbd)Cl]_2$ is given below: Into a baked 20 mL Schlenk tube with a three-way stopcock on the sidearm was added 227.0 mg of **1**. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. One milliliter of THF/$Et_3N$ 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 mg of $[Rh(nbd)Cl]_2$ in 1 mL of THF/$Et_3N$ mixture (4:1 by volume). The monomer solution was then transferred to the catalyst solution using a hypodermic syringe. The polymerization mixture was stirred under nitrogen at room temperature for 24 h. The mixture was then diluted with 5 mL of THF and added dropwise to 500 mL of acetone under stirring through a cotton filter. The precipitate was allowed to stand overnight, which was then filtered by a Gooch crucible, washed with acetone, and dried in a vacuum oven to a constant weight. A yellow powdery polymer was obtained in 93.0% yield. $M_w$ = 637 500, $M_w/M_n$ = 5.23 (GPC, polystyrene calibration). IR (KBr), $\nu$ ($cm^{-1}$): 3036 (w, =C−H), 1716 (s, C=O). $^1$H NMR (300 MHz, $CD_2Cl_2$), $\delta$ (ppm): 7.91 (Biph−H), 7.58 (Ph−H meta to backbone), 7.45 (Biph−H), 6.84 (Ph−H meta to backbone), 6.68 (Ar−H), 5.76 (cis =C−H), 4.16 ($CH_2OCO$), 3.86 ($OCH_2$), 1.68 ($OCH_2CH_2$), 1.38−1.25 [$O(CH_2)_2(CH_2)_2$, $(CH_2)_4CH_3$], 0.84 ($CH_3$). $^{13}$C NMR (75 MHz, $CD_2Cl_2$), $\delta$ (ppm): 166.52 (C=O), 165.97 (C=O), 159.85 (aromatic carbon linked with $OC_7H_{15}$), 146.45 (=C−), 145.23 (aromatic carbon linked with $PhOC_7H_{15}$), 139.57 (aromatic carbon linked with backbone), 132.18 (aromatic carbon para to $OC_7H_{15}$), 130.28 (aromatic carbon meta to $PhOC_7H_{15}$), 129.70 (H−C=, aromatic carbons meta and para to backbone), 128.92 (aromatic carbon para to $PhOC_7H_{15}$), 128.51 (aromatic carbon ortho to $PhOC_7H_{15}$), 127.66 (aromatic carbon ortho to backbone), 126.54 (aromatic carbon meta to $OC_7H_{15}$), 115.17 (aromatic carbons ortho to $OC_7H_{15}$), 68.46 ($PhOCH_2$), 65.14 (≡$CPhCO_2CH_2$, $CH_2OCOBiph$), 32.19 ($CH_2C_3H_7$), 29.67 ($CH_2CH_2OCOBiph$), 29.48 (≡$CPhCO_2$-$CH_2CH_2$), 29.04 ($CH_2C_2H_5$), 26.37 ($CH_2C_2H_4OCOBiph$), 26.08 [$PhO(CH_2)_2-CH_2$], 23.01 ($CH_2CH_3$), 14.25 ($CH_3$). UV (THF, $8.52 \times 10^{-5}$ mol/L), $\lambda_{max}$ (nm)/$\epsilon_{max}$ ($mol^{-1}$ L $cm^{-1}$): 295/29 × $10^3$, 426/3.1 × $10^3$ (sh).

## Results and Discussion

**Polymer Synthesis.** A multiple-step reaction scheme is designed to synthesize the acetylene monomer **1** (cf. Scheme 2). All the reactions proceed smoothly, and the expected products are isolated in high yields. All the intermediates and the final product are carefully characterized using standard spectroscopic methods, and satisfactory analysis data are obtained (see Experimental Section).

It is known that metathesis catalysts such as $WCl_6$ and $MoCl_5$ can polymerize substituted acetylenes.[1] We thus attempted to polymerize **1** using the $WCl_6$- and $MoCl_5$-based catalysts. It is found, however, that the tungsten and molybdenum halides are ineffective or poor catalysts for the polymerization of **1** (Table 1, nos. 1−4).

In contrast, Rh−nbd complexes work well for the polymerization of **1**. For example, when $[Rh(nbd)Cl]_2$ is used to initiate the polymerization of **1** in a mixture of

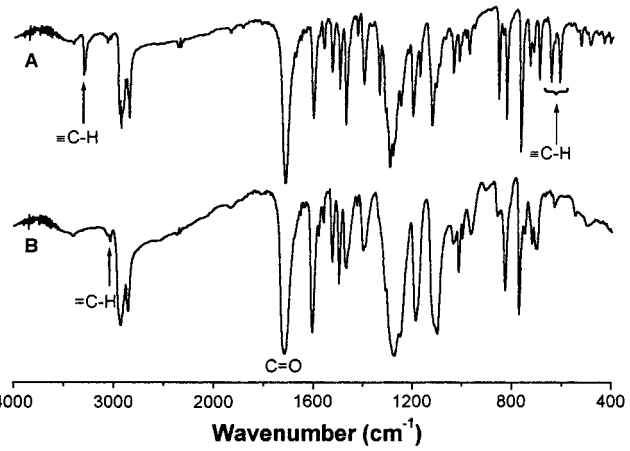



**Figure 1.** IR spectra of (A) monomer **1** and (B) polymer **2** (KBr; sample from Table 1, no.5 ).

THF and triethylamine, an orange polymer is obtained in high yield (93.0%) after 24 h polymerization (Table 1, no. 5). The polymer has a high molecular weight ($M_n$ = 1.22 × $10^5$) and possesses high stereoregularity (cis content 92%). Although Rh(nbd)(tos)($H_2O$) can polymerize phenylacetylene in water,[2d] it fails to polymerize **1**. [Rh(nbd)($PMe_3$)$_3$]$PF_6$ can polymerize **1**, but the yield is rather low (5.7%). The polymerization of **1** seems quite sensitive to the type of ligands in the Rh−nbd complexes.

Different from the Rh−nbd counterparts, all the Rh−cod complexes effectively polymerize **1**. Tabata[3a] and Furlani[3c] have found that basic additives such as $Et_3N$ and NaOH accelerate Rh-catalyzed phenylacetylene polymerizations. The nitrogen-containing organorhodium complexes of Rh(cod)($NH_3$)Cl and Rh(cod)(pip)Cl give high molecular weight polymers with high stereoregularity in high yields in THF *only* (Table 1, nos. 10 and 11). Thus, the incorporation of the basic ligands into the Rh−cod complexes can obviate the need of using large amount of the basic additives.

**Structure Characterization.** Figure 1 shows the IR spectra of **1** and its polymer **2**. As can be seen from Figure 1A, **1** exhibits three absorption bands at 3312, 648, and 614 $cm^{-1}$ due to the ≡C−H stretching and bending vibrations. All these absorption bands disappear in the spectrum of **2** (Figure 1B). A small absorption band appears at 3036 $cm^{-1}$ due to the =C−H vibration in the polymer chain. Thus, the IR spectra confirm that **2** is formed via the polymerization of the acetylene triple bond.

The molecular structure of **2** is further characterized by NMR spectroscopy. The absorption peak of the acetylene proton in **1** appears at $\delta$ 3.22 as a singlet, which, however, completely disappears in the spectra of **2** (Figure 2). Alternatively, **2** shows three new peaks at $\delta$ 7.58, 6.68, and 5.76. The peak at $\delta$ 5.76 can be readily assigned beyond doubt to the absorption by the cis olefin proton in the *cis*-transoidal **2**.[2,3,9,17] The absorption of the aromatic protons of styrene ($H_2C$=$CHC_6H_5$) is upfield from that of phenylacetylene (HC≡$CC_6H_5$).[27] The acetylene polymerization converts the trip bond in **1** to the double bond in **2**, and the peaks at $\delta$ 7.58 and 6.68 are thus not really "new" but due to the upfield shift of the absorption of the phenyl protons c and b, respectively. The peaks are relatively broad, because the aromatic ring is directly attached to the stiff polyacetylene backbone. This is in contrast to the well-resolved, sharp absorption peaks of the biphenyl protons (i−l), whose motion is decoupled from the polymer main chain by the flexible hexamethylene spacer.

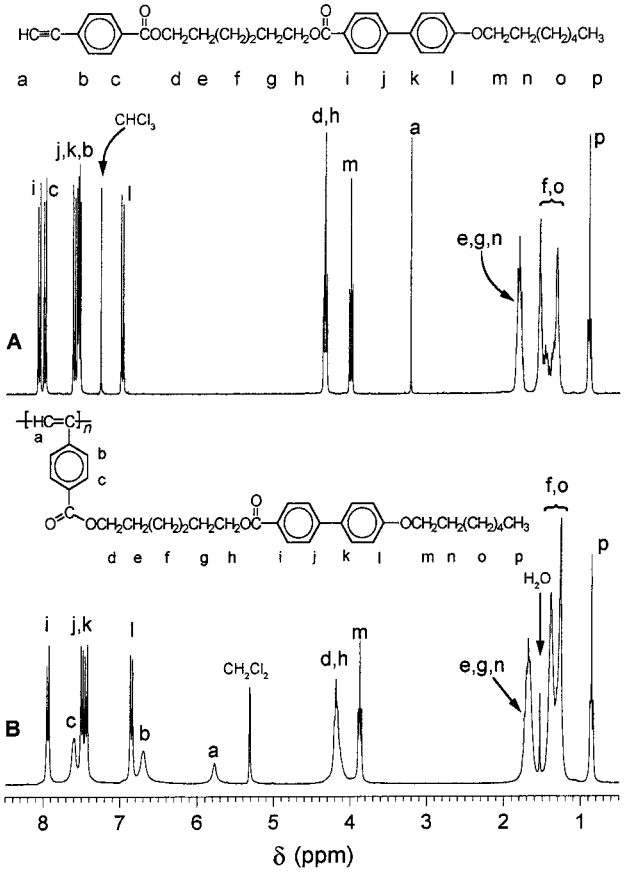
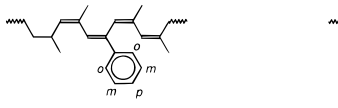



**Figure 2.** $^1H$ NMR spectra of (A) monomer **1** in $CDCl_3$ and (B) polymer **2** (sample from Table 1, no. 5) in $CD_2Cl_2$.

**Table 2. Substituent Constants (*Z*) of Poly(phenylacetylene) (PPA) and Chemical Shifts ($\delta$) of 2[a]**




| | $Z_o$ | $Z_m$ | $Z_p$ | | $\delta_o$[c] | $\delta_m$[c] |
|---|---|---|---|---|---|---|
| **PPA** | -0.63 | -0.32 | -0.32 | **2** | 6.74 (6.68) | 7.65 (7.58) |

[a] Estimated by $Z_{PPA} = \delta_{PPA} - 7.26$ and $\delta_2 = 7.26 + Z_{PPA} + Z_{CO_2CH_3}$ with the $\delta_{PPA}$ and $Z_{CO_2CH_3}$ data taken respectively from refs 2d and 27. [b] R = $(CH_2)_6OCO-Biph-OC_7H_{15}$. [c] Cacld (found).

To further prove the correct assignments of the peaks at $\delta$ 7.58 and 6.68, we calculated the substituent constants (*Z*) according to the well-known "additivity principle"[16]

$$\delta = 7.26 + \sum Z \qquad (1)$$

using the $\delta$ values of a 100% *cis*-poly(phenylacetylene).[2d] The *Z* values obtained are all negative (Table 2), indicating that the poly(phenylacetylene) backbone donates electrons to the phenyl ring. Adding to eq 1 the *Z* values of poly(phenylacetylene) backbone and methoxycarbonyl group,[27] it is estimated that the phenyl protons ortho and meta to the backbone absorb respectively at $\delta$ 6.74 and 7.65, in good agreement with the experimental results.

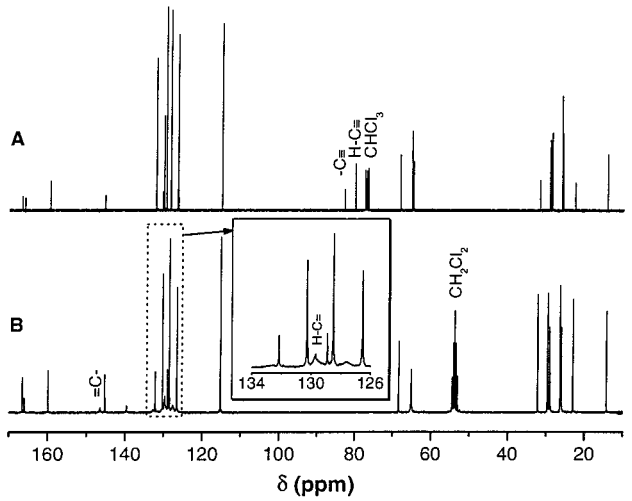



**Figure 3.** $^{13}C$ NMR spectra of (A) monomer **1** in $CDCl_3$ and (B) polymer **2** (sample from Table 1, no. 5) in $CD_2Cl_2$.

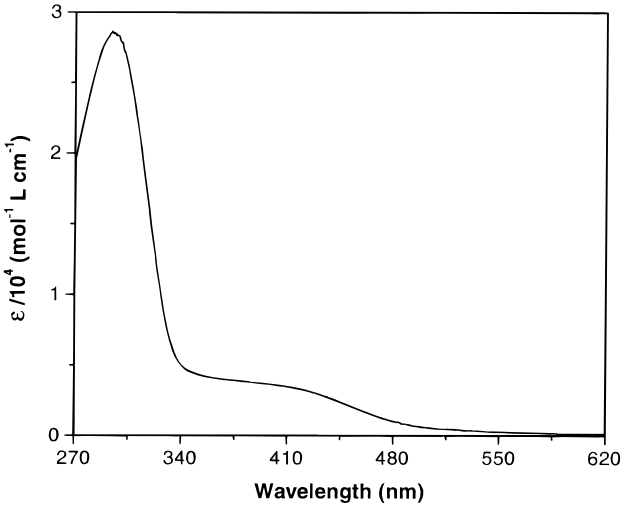



**Figure 4.** UV spectra of **2** (sample from table 1, no. 5) in THF.

Having assigned the $^1H$ NMR spectrum, we can now estimate the cis content of **2** using the following equation[2,22]

$$\text{cis } \% = [A_{5.76}/(A_{\text{total}}/13)] \times 100\% \qquad (2)$$

where $A_{5.76}$ is the area of the absorption peak at $\delta$ 5.76 and $A_{\text{total}} = A_{7.91} + A_{7.58} + A_{7.45} + A_{6.84} + A_{6.68} + A_{5.76}$. It is found that all the polymers synthesized from the organorhodium catalysts possess predominant cis conformation (cf. Table 1).

Figure 3 shows the $^{13}C$ NMR spectra of monomer **1** and its polymer **2**. The monomer shows absorption peaks of acetylene carbons at $\delta$ 82.8 and 79.9. The spectrum of **2** can be divided into two chemical shift regions: one for the aliphatic carbons in the upfield of $\delta$ 10−70 and another one for the unsaturated carbons in the downfield of $\delta$ 110−170. The peaks in the higher field are assigned to the absorption of the carbons of the alkyl spacer and tail, and those in the lower field are assigned to the absorption of the carbons of the main chain and the aromatic rings except the peaks at $\delta$ 166.52 and 165.97, which are due to the absorption of the carbonyl carbons. (See Experimental Section for detailed peak assignments.) No absorption peaks of acetylene carbons are observed in the spectrum of **2**. Percec and Rinaldi[28] and Furlani and Feast[29] have reported that the backbone carbons in the *cis*-poly(phenylacetylene) absorbs at $\delta$ 142.8(1) and 131.7(1). The peak at $\delta$ 146.45 in Figure 3B thus can be assigned to the absorption of the quaternary carbon (HC═*C*) and that at $\delta$ 129.70 to the tertiary carbon (H*C*═C) in the main chain of **2**.

The polymer shows a broad electronic absorption spectrum well extending to visible spectral region with an absorption maximum at 295 nm ($\epsilon_{\max} = 29 \times 10^3$ mol$^{-1}$ L cm$^{-1}$) and a shoulder peak at 426 nm ($\epsilon_{\max} = 3.1 \times 10^3$ mol$^{-1}$ L cm$^{-1}$; Figure 4). The strong absorption at 295 nm can be assigned to the K band of the biphenyl mesogen of **2**. The intensity of the K band is weaker than that ($\epsilon_{\max} = 32 \times 10^3$ mol$^{-1}$ L cm$^{-1}$) of the polymer **3** with 12 aliphatic carbon atoms at the same wavelength.[2a] The hypochromic effect of 3000 mol$^{-1}$ L cm$^{-1}$ suggests that the biphenyl mesogen of **2** is less polarized. The broad peak in the visible region is from the absorption of the polyacetylene backbone of **2**. The backbone of the polymer **3** absorbs at the same wavelength (426 nm) with the same molar absorptivity (3.1 $\times 10^3$ mol$^{-1}$ L cm$^{-1}$),[2a] indicating that the backbones of the two polymers, i.e., **2** and **3**, have the same conjugation lengths.

In our previous work, we found that the backbone of a stereoregular poly(phenylacetylene) {−[HC═C-($C_6H_5$)]$_n$−} with a cis content of ca. 100% absorbed at 389 nm.[2a] Thus, compared to that of the parent form, the backbone of **2** absorbs at longer wavelength with a bathochromic shift of 37 nm. It has often been reported that the absorption peak of a poly(phenylacetylene) derivative shifts to longer wavelength as the size of its substituent increases. For example, Masuda and Higashimura[30] have found that poly[(*o*-methylphenyl)-acetylene] absorbs at 440 nm, while poly{[*o*-(trimethylsilyl)phenyl]acetylene}, which possesses a bulkier trimethylsilyl substituent, absorbs at 520 nm. Okamoto et al.[31] have also observed that their poly(phenylacetylene) derivatives with bulkier substituents at the para position absorb at longer wavelengths. Grubbs and coworkers[1b] have proposed that the steric requirements of the substituents impose a planar conformation on the polymer backbone. The large substituent of **2** may have prevented the polyacetylene backbone from bending and forced the main chain or the segment of the backbone to take a straightened conformation. The effective conjugation length along a straight chain or segment would be longer than that in a bent coil. Thus, while the parent poly(phenylacetylene) absorbs in the near-UV region, the absorption of **2** well locates in the visible region.

**Mesomorphic Property.** It is clear that, compared to the polymer **3**, **2** possesses the same length of the backbone conjugation but contains less polarized mesogenic pendants. To check whether the less polarized mesogens with a long heptoxy tail would enable the formation of liquid-crystalline mesophases, we investigated the mesomorphic properties of **2**.

Figure 5 shows the DSC thermogram of **2** measured under nitrogen at a heating rate of 10 °C/min. The baseline unevenly drifts upward but drops down at 135.5 °C. The polymer **3** with a similar number of aliphatic carbon atoms melts at 131.1 °C (by DSC) or 138.5 °C (by POM).[2a] Thus, **2** may undergo melting transition at 135.5 °C. The endothermic peak accompanying the melting process, however, is not well developed, because of the subsequent exothermic isomerization of **2** at higher temperature (vide post).

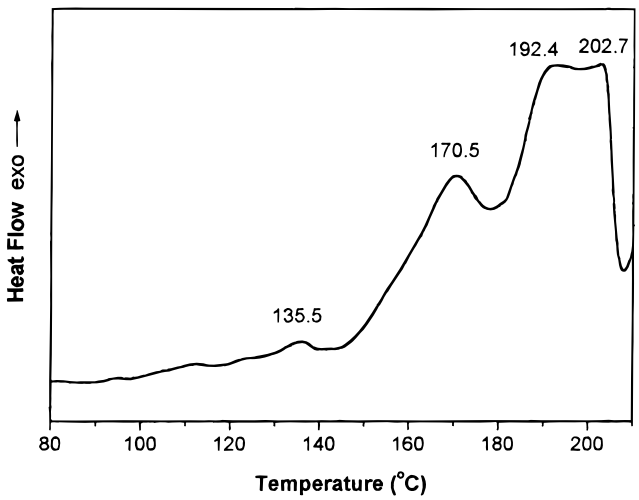



**Figure 5.** DSC thermogram of **2** (sample from Table 1, no. 11) measured under nitrogen at a heating rate of 10 °C/min.

Figure 6 shows the POM microphotograph taken after a melted sample of **2** was cooled to and annealed at 133.6 °C. Clearly, many small bâtonnets have emerged from the homeotropic dark background. Closer inspection of the texture reveals the existence of tiny bands, whose directors are perpendicular to the long axes of the bâtonnets. Such in-domain bands have often been observed during the formation of focal-conic textures of liquid-crystalline polyacetylenes,[22,23] suggesting that the mesophase of **2** is smectic A in nature. We tried to grow the bâtonnets to bigger focal-conic domains but failed. Because of the rigidity of the poly(phenylacetylene) backbone, the viscosity of the system sharply increases when the temperature is lowered, preventing the texture from further developing. The system partially solidifies when the temperature drops a few degrees to 130.6 °C.

To verify the mesophase assignment and to learn more about the molecular packing arrangements, we carried out XRD measurements of **2** employing the quenching technique we previously developed.[22,23] A sample of **2** rapidly quenched by liquid nitrogen from 140 °C exhibits a Bragg reflection at $2\theta = 2.4°$. The layer thickness derived from the Bragg angle is 36.78 Å. This corresponds well to the molecular length (37.54 Å) of the repeat unit of **2** at its most extended conformation, confirming the smecticity of the mesophase. On the other hand, the samples quenched from 130 and 115 °C show no peaks at $2\theta = 2.4°$ but display sharp Bragg reflection at $2\theta = 4.9°$ ($d = 18.02$ Å), probably due to the crystallization of the ({[(heptyl)oxy]biphenylyl}-carbonyl)oxy group[22] in the solidifying **2** below its melting point (135.5 °C).

**Isomerization and Aromatization.** When **2** is further heated to higher temperature, it shows three exothermic peaks at 170.5, 192.4, and 202.7 °C (Figure 5). Kakuchi and co-workers[32] have found that a deuterated poly(phenylacetylene) undergoes isomerization and aromatization respectively at 177 and 212 °C. The peak at 170.5 °C thus may be correlated to the cis−trans isomerization of **2** (cf. Scheme 1). Indeed, **2** is orange in color at room temperature but darkens to tangerine after the treatment at around 170 °C, in accordance with the previous finding that *trans*-polyacetylenes have longer conjugation length than their cis counterparts.[1] The big and broad peaks at ca. 200 °C may be associated with the aromatization accompanied by the chain scission reaction.

Figure 7 shows the GPC curves of the thermally treated **2**. The molecular weight of the polymer remains constant below 120 °C. After heating at 150 °C for 5 min, the polymer shows a small peak with a polystyrene-calibrated molecular weight of 2560. The major peak of the polymer shifts from $4.54 \times 10^5$ to $1.75 \times 10^5$, indicating that the polymer had undergone chain scission reaction. Increasing the temperature increases the height of the minor peak at the molecular weight of 2560 and shifts the major peak to low molecular weight region. The minor peak is monodisperse and should be, in all probability, the aromatization product released from the chain scission reaction.

The thermally treated **2** is further characterized by $^1$H NMR spectroscopy. No spectral change is observed after the polymer has been treated at 120 °C (Figure

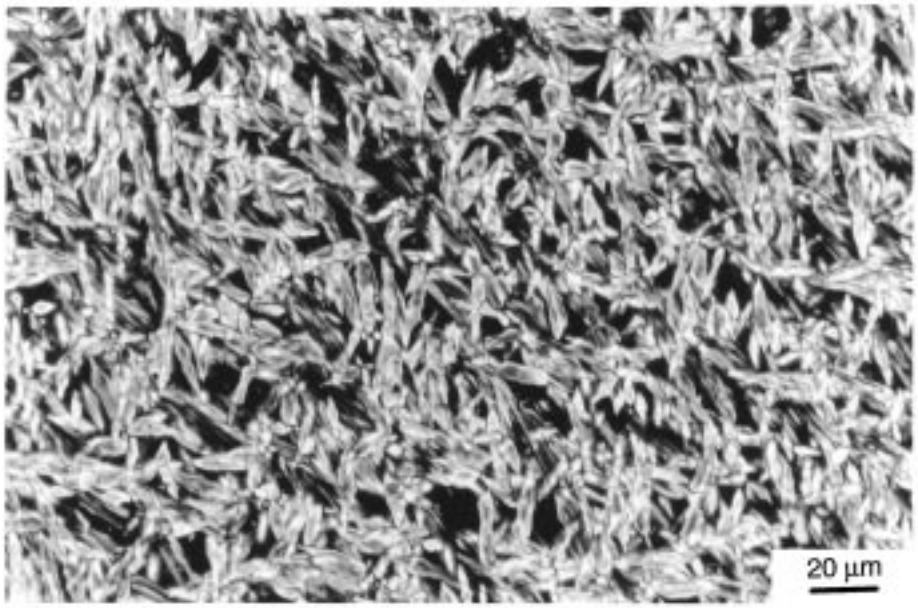



**Figure 6.** Texture observed under POM (magnification 400×) after a melted **2** (sample from Table 1, no. 5) was cooled to and annealed at 133.6 °C for 15 min.

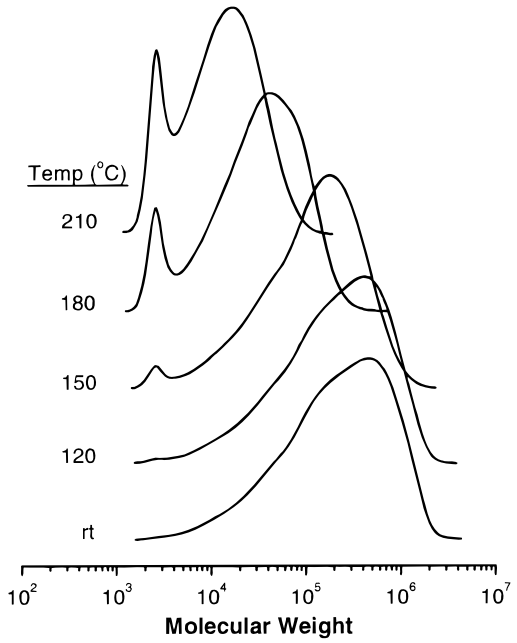



**Figure 7.** Gel permeation chromatograms of **2** (sample from Table 1, no. 11) thermally treated under nitrogen at different temperatures for 5 min.

8), consistent with the above-discussed GPC data. Only a few noiselike spiky "peaks" appear in the spectrum of **2** treated at 150 °C, indicating that the change, if any, in the molecular structure of **2** after the thermal treatment is negligibly small. Big structural change, however, occurs if **2** is further treated at higher temperature. Thus, when **2** is heating at ⩾180 °C, the absorption peak of the *cis*-olefin proton at $\delta$ 5.76 disappears, with the phenyl and biphenyl signals merging into broad peaks. Clearly, the thermally induced isomerization has converted the cis-transoidal **2** to the trans forms with different variation in conformation. According to Furnali and co-workers,[33] 1,3,5-triphenylbenzene absorbs at $\delta$ 7.83, while the absorption of its 1,2,4-cousin appears at $\delta$ 7.14. The polymer treated at the high temperatures exhibits a sharp singlet at $\delta$ 7.83 but no peaks in the region of $\delta$ 7.1−7.4 (excluding the solvent peak at $\delta$ 7.26), indicating that the isomerization releases 1,3,5-trisubstituted benzene as the sole aromatization product. This is further confirmed by the well-resolved, sharp absorption peaks of the three substituents: six doublets in the aromatic region, one multiplet at $\delta$ 4.25, and one triplet at $\delta$ 3.91. If the aromatization had produced both the 1,3,5- and 1,2,4-trisubstituted benzenes, the absorption peaks would have been more complicated and less resolved. The polymer reaction is so clean that it may serve as an environmentally benign tool for generating useful organics from used polyacetylenes.

## Conclusion

In summary, in this study, we designed and synthesized a high-molecular-weight cis-rich stereoregular poly(phenylacetylene) derivative (**2**) using the organorhodium complexes. We evaluated the substituent constants ($Z$) of the *cis*-poly(phenylacetylene) backbone, which should facilitate correct characterization of molecular structures of poly(phenylacetylene) derivatives by NMR spectroscopy. Utilizing the thermal isomerization process of **2**, we identified 1,3,5-trisubstituted benzene as its sole aromatization product, thus providing the first unambiguous experimental evidence for head-to-tail linkage of the repeat units in the poly(phenylacetylene) chains. We endowed **2** with liquid crystallinity through molecular engineering endeavor by fine-tuning the polarity of the mesogenic pendants, presenting the first example of a liquid-crystalline polyacetylene with a highly rigid poly(phenylacetylene) backbone. We further revealed that **2** is photoconductive,[4e] details of which will be published in a separate paper in due course.

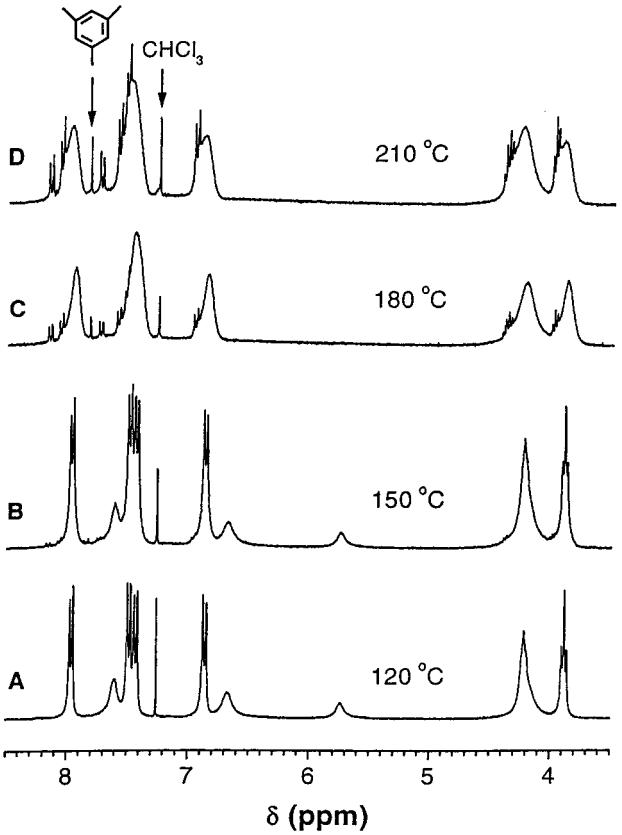



**Figure 8.** $^1$H NMR spectra of **2** (sample from Table 1, no. 11) thermally treated under nitrogen at different temperatures for 5 min.

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