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PART • A

**Monomers by
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The image shows a chemical structure of a monomer with a vinyl group and a hydroxyl group, and two 3D ball-and-stick models of molecular structures.

Polymer Chemistry

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Synthesis and Liquid Crystalline Properties of Poly(1-alkyne)s Carrying Triphenylene Discogens

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ABSTRACT: Triphenylene-containing 1-decyne)s with different alkyl chain lengths and their mesomorphic properties are investigated. The monomers [HC=C(CH₂)_mCO₂C₁₈H₆ (OC_mH_{2m+1})₅; *m* = 4–9] are prepared by consecutive etherization, coupling, and esterification reactions. The monomers form columnar phases at room temperature. The polymerizations of the monomers are effected by [Rh(nbd)Cl]₂, producing soluble polymers in high yields (up to 84%). The structures and properties of the polymers are characterized and evaluated by IR, NMR, TGA, DSC, POM, and XRD analyses. All the polymers are thermally stable, losing little of their weights when heated to 300 °C. The isotropization temperature of the polymers increases initially with the length of alkyl chain but decreases on further extension. Although the polymers with shorter and longer alkyl chain lengths adopt a homogeneous hexagonal columnar structure, those with intermediate ones form mesophases with mixed structures.

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Keywords: conjugated polymers; discotic liquid crystals; liquid-crystalline polymers (LCP); polyacetylenes; triphenylene

INTRODUCTION

Discotic liquid crystals (DLCs) have attracted great attention among researchers since they are first discovered by Chandrasekhar et al. in 1977.¹ DLCs are an interesting class of liquid crystals. As their discs are stacked one on top of another to form columns,^{2–4} they possess unique optoelectronic properties, allowing them to find an array of potential applications in one-dimensional conductors, photoconductors, photovoltaic

solar cells, field effect transistors, and so forth.^{5–9}

Research activity in the field of DLCs has grown rapidly and to date many discogens have been developed, including hexaalkanoate-substituted benzene,¹ hexaalkynyl-substituted benzene,¹⁰ triphenylene derivatives,^{11–14} (thio)truxene derivatives,^{15–17} naphthalene derivatives,¹⁸ and octa-substituted metallophthalocyanine. Among them, triphenylene derivatives are particularly promising because their chemistry is readily accessible. They are also thermally and chemically stable and show a variety of mesophases.

Much effort has been devoted to the molecular modification of triphenylene. A number of triphenylene-containing dimers and oligomers have been prepared, which are composed of two

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or several mesogenic groups linked via flexible, or rarely rigid, spacers.^{13,14} Synthesis of liquid crystalline polymers is of great interest owing to their self-organizing characteristics, which give rise to enhanced processability and mechanical and thermal stabilities over conventional polymeric materials. Whereas mesomorphic polymers containing rod-like mesogens have been extensively investigated,^{19–37} research in discotic liquid crystalline polymers has been less well explored because only a few discogens are available from which polymers can be derived. To date, the most widely prepared polymers are those with triphenylene moieties, which either utilize as main building blocks or side chains attached to the backbones of polysiloxanes and poly(meth)acrylates.^{38–48}

Our group has prepared a variety of liquid crystalline polyacetylenes carrying different flexible spacers, functional bridges, mesogenic cores, and functional tails.^{49–57} We have discovered that the polymers exhibit some unique mesomorphic structures originating from the synergistic interactions between the polymers and the mesogenic appendages, including rotation-induced high strength disclinations and shear-induced inversion walls.⁵⁴ They are luminescent and photoconductive^{56,58–60} and their luminescence and photoconductivity can be modulated by electric field and thermal perturbation. Incorporation of discogens into the polyacetylene structures are expected to give new materials capable of enhancing existing or creating new, novel electronic and optical properties. The polymers may show high charge carrier mobility due to long-range ordering along the columns of the discotic liquid crystalline phases.^{8,61} The electron-rich nature of the triphenylene discs may make the polymers suitable for doping with electron acceptors, resulting in the formation of *p*-type organic semiconductors. In this article, we report for the first time the synthesis of discotic liquid crystalline polyacetylenes containing triphenylene mesogens with different lengths (*m*) of alkyl chains [P1(*m*); Chart 1].

EXPERIMENTAL

Materials

Dioxane (Nacal; Tesque), THF (Lab-Scan), and toluene (BDH) were predried over 4 Å molecular sieves and distilled from sodium benzophenone

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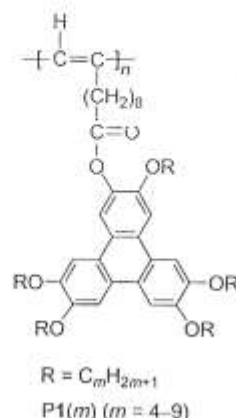


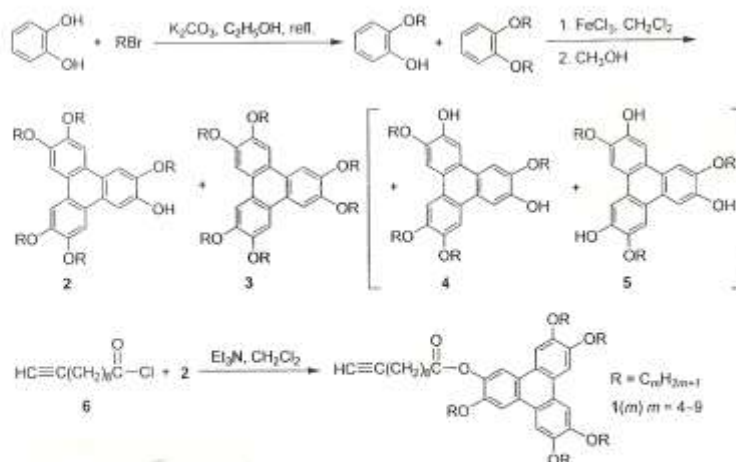
Chart 1. Chemical structures of triphenylene-containing poly(1-decyne)s.

ketyl under nitrogen immediately prior to use. Dichloromethane (DCM) and dimethylformamide (DMF) were purchased from Lab-Scan, dried over molecular sieves, and distilled over calcium hydride under nitrogen. Triethylamine (Et₃N) was distilled under normal pressure and dried over KOH. All other reagents were purchased from Aldrich and used without further purification.

Instrumentation

IR spectra were recorded on a Perkin Elmer 16 PC FTIR spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker ARX 300 NMR spectrometer using chloroform-*d* as solvent and tetramethylsilane ($\delta = 0$) or chloroform ($\delta = 7.26$) as internal references. The mass spectra were recorded on a Finnigan TSQ 7000 triple quadrupole mass spectrometer operating in a chemical ionization (CI) mode using methane as carrier gas. Elemental analysis was performed on a Carlo Erba 1106 microanalysis instrument. The molecular weights of the polymers were estimated by a Waters Associates GPC system. Degassed THF was used as eluent at a flow rate of 1.0 mL/min. A set of monodisperse polystyrene standards covering the molecular weight range of 10³–10⁷ was used for the 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. A TA DSC Q-100 was used to measure the phase tran-



Scheme 1. Synthesis of triphenylene-containing 1-decyne.

sition thermograms. Enthalpies of the phase transitions were obtained from the peak integrals multiplied by the molecular weights of the monomers or the monomer repeat units of the polymers. Divide the enthalpy values by the peak maxima gave the corresponding entropy changes. An Olympus BX 60 POM equipped with a Linkam TMS 92 hot stage was used to observe the anisotropic optical textures. The XRD patterns were recorded on a Philips PW1830 powder diffractometer with a graphite monochromator using 1.5406 Å Cu K α wavelength at room temperature (scanning rate: 0.05°/s, scan range 2–30°). The polymer samples for the XRD measurements were prepared by freezing the molecular arrangements in the liquid crystalline states by liquid nitrogen as previously reported.^{52,55}

Monomer Synthesis

The triphenylene-containing monomers 1(4)–1(9) were prepared according to Scheme 1. Typical procedures are shown below.

2-Hexyloxyphenol and 1,2-di(hexyloxy)benzene

Into a 1 L round-bottom flask were dissolved 30 g (0.273 mol) of 1,2-dihydroxybenzene, 59 g (0.358 mol) of 1-bromohexane, and 150 g (1.1 mol) of K_2CO_3 in 500 mL of ethanol. The solution was heated under reflux for 24 h. After

cooled to room temperature, the solution was filtered. The solvent was removed under vacuum and the residue was washed with diluted hydrochloric acid and brine, and dried over $MgSO_4$. The crude product was purified by silica-gel column chromatography using DCM as eluent, producing 17.3 g of 2-hexyloxyphenol and 41.7 g of 1,2-di(hexyloxy)benzene.

Characterization data: 2-hexyloxyphenol: 1H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.91 (m, 1H, Ar-H), 6.82 (m, 3H, Ar-H), 5.73 (s, 1H, OH), 3.98 (t, 2H, OCH_2), 1.77 (m, 2H, OCH_2CH_2), 1.45 [m, 2H, $O(CH_2)_2CH_2$], 1.33 [m, 4H, $O(CH_2)_2(CH_2)_2$], 0.9 (t, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 145.9, 145.7, 121.2, 120.0, 114.4, 111.5, 68.8, 31.5, 29.1, 25.6, 22.5, 13.9. MS (CI): m/e 195.13 [(M+H) $^+$, calcd 195.13]. Characterization data: 1,2-di(hexyloxy)benzene: 1H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.88 (s, 4H, Ar-H), 3.98 (t, 4H, OCH_2), 1.81 (m, 4H, OCH_2CH_2), 1.44 [m, 4H, $O(CH_2)_2CH_2$], 1.34 [m, 8H, $O(CH_2)_2(CH_2)_2$], 0.9 (t, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 149.2, 120.9, 114.0, 69.2, 31.6, 29.3, 25.7, 22.6, 13.6. MS (CI): m/e 278.22 (M $^+$, calcd 278.22).

2-Hydroxy-3,6,7,10,11-penta(hexyloxy)triphenylene (2)

Into another round-bottom flask were dissolved 30 g of 2-hexyloxyphenol and 72.4 g of 1,2-di(hexyloxy)benzene in 300 mL of dry DCM. The

flask was cooled with an ice-water bath and 233 g of anhydrous FeCl_3 was added in portion in 30 min under vigorous stirring. The solution was stirred at room temperature for 30 min and cooled to 0 °C again. About 100 mL of cold methanol was then slowly added. After stirring for 30 min, 500 mL of water was added and the mixture was extracted with 500 mL of DCM three times. The organic phase was collected and dried with MgSO_4 . After solvent evaporation, the crude products were purified by silica-gel column chromatography, using petroleum ether/DCM mixture (1:15 v/v) as eluent. Eleven grams of 2-hydroxyl-3,6,7,10,11-penta(hexyloxy)triphenylene was obtained as white crystals.

Characterization data: ^1H NMR (300 MHz, CDCl_3), δ (ppm): 7.95 (s, 1H, Ar-H), 7.81 (m, 4H, Ar-H), 7.75 (s, 1H, Ar-H), 5.91 (s, 1H, OH), 4.23 (m, 10H, OCH_2), 1.93 (m, 10H, OCH_2CH_2), 1.58 [m, 10H, $\text{O}(\text{CH}_2)_2\text{CH}_2$], 1.39 [m, 20H, $\text{O}(\text{CH}_2)_2(\text{CH}_2)_2$], 0.93 (t, 15H, CH_3). ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 149.1, 149.0, 148.8, 148.7, 145.8, 145.2, 123.9, 123.7, 123.6, 123.5, 123.2, 122.9, 107.6, 107.4, 107.3, 107.2, 106.4, 104.3, 69.90, 69.85, 69.1, 31.7, 31.64, 31.61, 29.5, 29.4, 29.29, 29.25, 25.85, 25.81, 22.65, 22.61, 14.0. MS (CI): *m/e* 744.63 (M^+ , calcd 744.53).

10-Undecynoyl Chloride (6)

Into a two-necked round-bottom flask equipped with a condenser were added 7.1 g (0.01 mol) of 10-undecynoic acid and 7 g (0.059 mol) of thionyl chloride. The solution was heated under reflux for 3 h. After removal of excess thionyl chloride, 10-undecynoyl chloride was obtained by vacuum distillation at 140 °C/15 mmHg. Yield: 6 g (75.8%).

10-(9-decynylcarbonyloxy)-3,6,7,10,11-penta(octyloxy)triphenylene [1(8)]

In a two-necked round-bottom flask under nitrogen were dissolved 1 g (1 mmol) of 2-hydroxy-3,6,7,10,11-penta(octyloxy)triphenylene and 0.2 g (2 mmol) of dry triethylamine in 20 mL of dry DCM. A solution of 10-undecynoyl chloride (100 mg, 1.2 mmol) in 2 mL of dry DCM was then injected. After stirring at room temperature for 2 h, diluted hydrochloric acid was added and the solution was extracted with DCM. The organic layer was dried over MgSO_4 and filtered. After solvent evaporation, the residue was purified by

silica-gel chromatography using petroleum ether/ethyl acetate mixture (30:1 v/v) as eluent. Recrystallization from ethanol twice gave a brown sticky solid in 83.2% yield (1.08 g).

IR (KBr), ν (cm^{-1}): 3253 (=C-H stretching), 1757, 1613, 719 (=C-H bending). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.03 (s, 1H, Ar-H), 7.77 (m, 5H, Ar-H), 4.21 (m, 10H, OCH_2), 2.68 (t, 2H, COCH_2), 2.21 (td, 2H, = CCH_2), 2.00–1.80 [m, 13H, HC= and $(\text{CH}_2)_4$], 1.65–1.33 [m, 60H, $(\text{CH}_2)_{10}$], 0.94 (t, 15H, CH_3). ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 172.0 (C=O), 149.6, 149.3, 149.1, 148.8, 148.6, 139.7, 127.8, 124.5, 123.4, 123.1, 123.0, 116.6, 107.9, 107.1, 106.7, 106.4, 105.8, 84.7 (=C- CH_2), 69.8, 69.6 (HC=), 69.4, 69.1, 68.7, 68.1, 34.1, 31.8, 29.5, 29.4, 29.3, 29.2, 29.0, 28.7, 28.4, 26.2, 26.15, 26.12, 25.1, 22.7, 18.4 (=C- CH_2), 14.1 (CH_3). MS (CI): *m/e* 1049.76 [(M+H) $^+$, calcd 1049.76]. Anal. Calcd for $\text{C}_{69}\text{H}_{108}\text{O}_{17}$: C, 79.01; H, 10.31. Found: C, 78.61; H, 10.12.

Other monomers were prepared by similar procedures and their characterization data were shown below.

I(4). Brown sticky solid; yield 90.2%. IR (KBr), ν (cm^{-1}): 3249 (=C-H stretching), 1756, 1616, 697 (=C-H bending). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 7.98 (s, 1H, Ar-H), 7.71 (m, 5H, Ar-H), 4.21 (m, 10H, OCH_2), 2.66 (t, 2H, COCH_2), 2.19 (td, 2H, =C- CH_2), 1.95–1.83 [m, 13H, =CH and $(\text{CH}_2)_6$], 1.65–1.39 [m, 20H, $(\text{CH}_2)_{10}$], 1.05 (t, 15H, CH_3). ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 172.0 (C=O), 149.5, 149.2, 149.0, 148.7, 148.5, 139.6, 127.7, 124.4, 123.3, 123.0, 122.8, 116.5, 107.7, 107.0, 106.6, 106.3, 105.7, 84.6 (=C- CH_2), 69.3, 69.2 (HC=), 68.9, 68.7, 68.3, 63.1, 34.1, 31.4, 29.15, 29.12, 28.9, 28.6, 28.4, 25.0, 22.1, 18.3 (=C- CH_2), 13.9 (CH_3). MS (CI): *m/e* 769.07 [(M+H) $^+$, calcd 769.07]. Anal. Calcd for $\text{C}_{48}\text{H}_{68}\text{O}_7$: C, 76.56; H, 8.85. Found: C, 76.30; H, 9.00.

I(5). Grey sticky solid; yield 90.9%. IR (KBr), ν (cm^{-1}): 3257 (=C-H stretching), 1751, 1613, 699 (=C-H bending). ^1H NMR (300 MHz, CDCl_3), δ (ppm): 7.99 (s, 1H, Ar-H), 7.73 (m, 5H, Ar-H), 4.21 (m, 10H, OCH_2), 2.67 (t, 2H, COCH_2), 2.20 (td, 2H, =C- CH_2), 1.95–1.85 [m, 13H, =CH and $(\text{CH}_2)_6$], 1.57–1.40 [m, 30H, $(\text{CH}_2)_{12}$], 0.98 (t, 15H, CH_3). ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 172.0 (C=O), 149.5, 149.2, 149.0, 148.7, 148.6, 139.6, 127.8, 124.4, 123.3, 123.0, 122.9, 122.8, 107.8, 107.0, 106.6, 106.3,

105.8, 84.6 (=C-CH₂), 69.7, 69.6 (HC=), 69.3, 69.1, 68.6, 68.1, 34.1, 31.7, 29.16, 29.1, 29.0, 28.9, 28.7, 28.4, 28.3, 28.2, 25.0, 22.7, 22.53, 22.50, 18.3 (=C-CH₂), 14.1 (CH₃). MS (CI): *m/e* 839.13 [(M+H)⁺], calcd 839.131. Anal. Calcd for C₅₄H₇₈O₇: C, 77.33; H, 9.31. Found: C, 76.08; H, 8.98.

I(6). Brown sticky solid; yield 89.0%. IR (KBr), ν (cm⁻¹): 3286 (=C-H stretching), 2112 (C=C stretching), 1752, 1615, 721 (=C-H bending). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.05 (s, 1H, Ar-H), 7.81 (m, 5H, Ar-H), 4.21 (m, 10H, OCH₂), 2.67 (t, 2H, COCH₂), 2.20 (td, 2H, =C-CH₂), 1.96-1.85 [m, 13H, HC= and (CH₂)₆], 1.59-1.38 [m, 40H, (CH₂)₂₀], 0.96 (t, 15H, CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 172.0 (C=O), 149.7, 149.4, 148.9, 148.8, 139.8, 127.9, 124.6, 123.5, 123.1, 123.0, 116.7, 107.9, 107.2, 106.9, 106.5, 105.9, 84.5 (=C-CH₂), 69.9, 69.8 (HC=), 69.5, 69.2, 68.8, 68.1, 34.1, 31.7, 29.41, 29.37, 29.32, 29.21, 29.0, 28.7, 28.5, 25.83, 25.77, 25.1, 22.6, 18.4 (=C-CH₂), 14.0 (CH₃). MS (CI): *m/e* 909.24 [(M+H)⁺], calcd 909.24. Anal. Calcd for C₅₉H₉₈O₇: C, 77.97; H, 9.69. Found: C, 77.50; H, 9.40.

I(7). Brown sticky solid; yield 90.2%. IR (KBr), ν (cm⁻¹): 3251 (=C-H stretching), 1743, 1628, 719 (=C-H bending). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.03 (s, 1H, Ar-H), 7.78 (m, 5H, Ar-H), 4.20 (m, 10H, OCH₂), 2.67 (t, 2H, COCH₂), 2.20 (td, 2H, =C-CH₂), 1.94-1.85 [m, 13H, HC= and (CH₂)₆], 1.63-1.36 [m, 50H, (CH₂)₂₅], 0.92 (t, 15H, CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 172.0 (C=O), 149.6, 149.4, 149.1, 148.8, 148.7, 139.7, 127.8, 124.6, 123.4, 123.1, 123.0, 116.6, 107.9, 107.2, 106.8, 106.5, 105.9, 84.6 (=C-CH₂), 69.8, 69.4 (HC=), 69.2, 68.8, 68.1, 68.1, 34.1, 31.8, 29.46, 29.42, 29.38, 29.2, 29.0, 28.7, 28.4, 26.13, 26.06, 22.6, 18.4 (=C-CH₂), 14.1 (CH₃). MS (CI): *m/e* 979.45 [(M+H)⁺], calcd 979.45. Anal. Calcd for C₆₄H₉₈O₇: C, 78.53; H, 10.02. Found: C, 78.10; H, 9.80.

I(9). Brown sticky solid; yield 88.5%. IR (KBr), ν (cm⁻¹): 3257 (=C-H stretching), 1751, 1607, 713 (=C-H bending). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.06 (s, 1H, Ar-H), 7.81 (m, 5H, Ar-H), 4.21 (m, 10H, OCH₂), 2.67 (t, 2H, COCH₂), 2.20 (td, 2H, =C-CH₂), 1.96-1.83 [m, 13H, HC= and (CH₂)₆], 1.80-1.38 [m, 70H,

(CH₂)₃₅], 0.96 (t, 15H, CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 172.0 (C=O), 149.7, 149.3, 149.2, 148.9, 148.8, 139.8, 127.9, 124.6, 123.5, 123.2, 123.1, 116.6, 108.0, 107.3, 106.9, 106.6, 105.9, 84.5 (=C-CH₂), 69.9, 69.8 (HC=), 69.5, 69.2, 68.8, 68.1, 34.1, 31.9, 29.6, 29.5, 29.43, 29.41, 29.3, 29.2, 29.0, 28.7, 28.5, 26.2, 26.1, 25.1, 21.7, 18.4 (=C-CH₂), 14.0 (CH₃). MS (CI): *m/e* 1119.84 [(M+H)⁺], calcd 1119.84. Anal. Calcd for C₇₄H₁₁₈O₇: C, 79.43; H, 10.55. Found: C, 79.26; H, 10.11.

Polymerization

The polymerization reactions and manipulations were carried out under nitrogen using an inert-atmosphere glovebox (for tungsten catalyst) or at room temperature in air (for Rh complex). Typical procedures for the polymerization of **I(8)** by [Rh(nbd)Cl]₂ are given below.

Into a 20 mL test tube were added 210 mg of **I(8)** and 5 mg of [Rh(nbd)Cl]₂. Freshly distilled mixture solvent (2 mL) of THF/Et₃N (3:1 v/v) was then injected. After stirring in air for 24 h at room temperature, the solution was diluted with 5 mL of chloroform and added dropwise to 500 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and was filtered with a Gooch crucible. The polymer was washed with acetone and dried in a vacuum oven to a constant weight.

Characterization

PI(8). Brown solid; yield 70.1%. *M_w* 16,000, *M_w*/*M_n* 2.0 (GPC, Table 1, no. 3). IR (KBr), ν (cm⁻¹): 1755, 1613. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.05, 7.55, 7.23 (Ar-H), 6.08 (Z proton), 4.19, 3.97, 2.64, 1.84-1.69 [(CH₂)₆], 1.62-1.38 [(CH₂)₃₀], 0.93 (CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 171.7 (C=O), 149.1, 148.6, 147.8, 139.5, 127.9, 123.8, 122.7, 122.1, 116.4, 107.5, 106.5, 106.6, 105.8, 69.8, 69.5, 68.9, 34.1, 31.8, 29.5, 29.3, 29.0, 26.2, 25.1, 22.6, 14.4.

PI(4). Brown solid; yield 60.5%. *M_w* 20,700, *M_w*/*M_n* 2.0. IR (KBr), ν (cm⁻¹): 1758, 1618. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.06, 7.68, 7.23 (Ar-H), 6.08 (Z proton), 4.21, 3.98, 2.68, 1.85-1.68 [(CH₂)₆], 1.65-1.35 [(CH₂)₁₀], 0.96 (CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 171.9 (C=O), 148.8, 148.5, 147.7, 139.4, 127.9, 123.7, 122.6, 122.4, 116.2, 109.1, 106.7, 106.2, 105.6,

Table 1. Thermal Transitions and Corresponding Thermodynamic Parameters of *PI(n)*^a

Monomer	<i>T_c</i> [Δ <i>H</i> , kJ/mol; Δ <i>S</i> , J/mol K]	
	Cooling	Heating
1(4)	i 81.6 (-5.00; -14.10) Col	Col 81.9 (4.97; 14.01) i
1(5)	i 106.5 (-7.69; -20.30) Col	Col 106.3 (7.65; 20.23) i
1(6)	i 110.3 (-8.14; -21.21) Col -26.4 (-2.83; -9.45) k	k -32.2 (3.92; 12.84) Col 110.1 (8.15; 21.27) i
1(7)	i 117.0 (-7.62; -19.54) Col	Col 116.6 (7.78; 19.97) i
1(8)	i 111.8 (-5.92; -15.38) Col -31.7 (-5.22; -17.13) k	k 20.8 (33.07; 112.56) Col 105.5 (4.40; 11.62) i
1(9)	i 113.5 (-6.06; -15.68) Col -21.9 (-16.68; -56.56) k	k 19.8 (33.13; 113.15) Col 110.7 (5.85; 15.25) i

k, crystalline state; Col, columnar phase; i, isotropic liquid.

^a Data taken from the DSC thermograms recorded under nitrogen during the first cooling and second heating scans.

69.6, 69.3, 68.5, 34.1, 31.4, 29.1, 28.6, 25.1, 19.1, 13.9.

PI(5). Brown solid; yield 61.6%. M_w 20,400, M_w/M_n 2.0. IR (KBr), ν (cm⁻¹): 1752, 1615. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.05, 7.65, 7.21 (Ar-H), 6.12 (Z proton), 4.19, 3.97, 2.67, 1.86–1.65 [(CH₂)₆], 1.61–1.31 [(CH₂)₁₅], 0.98 (CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 171.7 (C=O), 148.6, 148.5, 147.9, 139.6, 127.9, 123.7, 122.8, 122.4, 116.5, 109.2, 106.8, 106.4, 105.8, 69.7, 69.3, 68.7, 34.2, 28.3, 26.6, 25.0, 24.2, 22.6, 14.1.

PI(6). Brown solid; yield 63.2%. M_w 19,800, M_w/M_n 2.8 (GPC, Table 1, no. 8). IR (KBr), ν (cm⁻¹): 1753, 1618. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.01, 7.72, 7.19 (Ar-H), 6.09 (Z proton), 4.19, 3.94, 2.64, 1.84–1.69 [(CH₂)₆], 1.62–1.25 [(CH₂)₂₀], 0.93 (CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 171.6 (C=O), 148.7, 148.5, 148.0, 139.6, 127.9, 123.8, 122.9, 122.3, 116.6, 106.5, 105.9, 69.7, 69.3, 68.8, 34.2, 31.7, 30.1, 29.4, 25.9, 25.4, 25.2, 22.6, 14.1.

PI(7). Brown solid; yield 59.3%. M_w 16,700, M_w/M_n 2.2. IR (KBr), ν (cm⁻¹): 1752, 1615. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.05, 7.65, 7.21 (Ar-H), 6.12 (Z proton), 4.19, 3.97, 2.67, 1.86–1.65 [(CH₂)₆], 1.61–1.31 [(CH₂)₂₅], 0.98 (CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 171.7 (C=O), 148.6, 148.5, 147.9, 139.6, 127.9, 123.8, 122.8, 122.3, 116.6, 107.9, 106.9, 105.8, 69.7, 69.3, 68.8, 34.2, 31.9, 29.5, 29.3, 28.7, 28.5, 26.1, 25.4, 25.2, 22.6, 14.1.

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PI(9). Brown solid; yield 82.2%. M_w 16,400, M_w/M_n 2.0. IR (KBr), ν (cm⁻¹): 1751, 1610. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.05, 7.63, 7.23 (Ar-H), 6.08 (Z proton), 4.19, 3.94, 2.64, 1.84–1.69 [(CH₂)₆], 1.62–1.38 [(CH₂)₃₅], 0.93 (CH₃). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 171.7 (C=O), 149.6, 149.3, 148.8, 139.7, 127.9, 123.5, 122.6, 122.3, 116.5, 107.9, 106.9, 105.8, 69.9, 69.2, 68.1, 34.1, 31.9, 29.6, 29.3, 28.9, 28.5, 26.2, 26.1, 24.9, 14.8.

RESULTS AND DISCUSSION

Monomer Synthesis

To enrich the research field of discotic liquid crystalline polymers, we synthesized a group of triphenylene-containing acetylenes with different lengths of alkyl chains according to Scheme 1. 2-Hydroxy-3,6,7,10,11-penta(alkoxy)triphenylenes (**2**) are the key intermediates for the synthesis of the monomers. Synthetic procedures for these compounds are based on the trimerization of the dialkylbenzenes,⁶² terphenyl intermediates,⁶¹ or the biphenyl routes.^{46,64–67} The biphenyl route enjoys high product yields but involves multistep reaction procedures. To simplify the synthetic procedure, we prepared compound **2** with different alkoxy chains by a two-step reaction. Herein, etherization of 1,2-dihydroxybenzene with alkyl bromide gives mono and disubstituted products, which undergo trimerization in the presence of FeCl₃ to form triphenylenes. Theoretically, four compounds can be obtained but we cannot isolate or even detect the presence of **4** and **5** by thin-layer chromatogra-

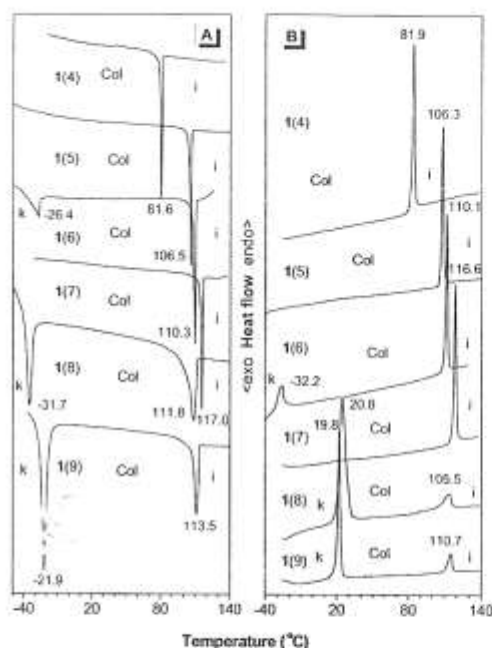


Figure 1. DSC thermograms of monomers **1**(*m*) (*m* = 4–9) recorded under nitrogen during the (A) first cooling and (B) second heating cycles at a scan rate of 10 °C/min.

phy. Compound **2** is isolated from the mixture by column chromatography, which furnishes the desirable products [**1**(*m*)] in high yields upon reaction with 10-undecynoyl chloride (**6**). All the new monomers are characterized by standard spectroscopic methods as well as elemental analysis (see Experimental section for details).

Mesomorphism

The acetylene monomers are sticky solids and exhibit liquid crystallinity at room temperature. The mesomorphic transitions of the monomers are investigated by differential scanning calorimetry (DSC) combined with polarized optical microscopy (POM). The DSC thermograms of the monomers are shown in Figure 1, and the mesomorphic textures of **1**(4) and **1**(7) are depicted in Figure 2 as examples. The first cooling scan of **1**(4) detects a sharp peak at 81.6 °C [Fig. 1(A)]. The DSC thermogram recorded in the second heating cycle also exhibits a single transition at 81.9 °C. POM observation reveals that upon cooling the isotropic liquid to 50 °C, a

pseudo focal-conic fan texture corresponding to columnar phase emerges [Fig. 2(A)].¹⁸ The monomer with five methylene units shows a exothermic peak at 106.5 °C during the first cooling scan. Cooling **1**(5) from the isotropic liquid state to 80 °C results in the formation of pseudo focal-conic fan texture of columnar phase. The mesomorphism is enantiotropic and a peak associated with Col–i transition is detected in the second heating scan.

The DSC thermogram of **1**(6) shows two transition peaks at 110.3 and –26.4 °C in the first cooling cycle. With the aid of POM, the peak at 110.3 °C is assigned to the transition from the isotropic state to the columnar phase because typical pseudo focal-conic fan texture is observed when the monomer is cooled to below this transition temperature. The columnar texture can be observed during both heating and cooling scans, indicating that the liquid crystalline tran-



Figure 2. Polarized optical micrographs observed on cooling (A) **1**(4) to 50 °C and (B) **1**(7) to 110 °C from their isotropic states at a cooling rate of 1 °C/min.

Table 2. Polymerizations of Triphenylene-Containing Acetylenes 1(a)–(i)

No.	Monomer	Catalyst	Solvent ^a	Yield (%)	M_n^c	M_w/M_n^c
1	1(8)	WCl ₆ -Ph ₃ Sn	Toluene	Trace		
2	1(8)	WCl ₆ -Ph ₃ Sn	Dioxane	Trace		
3	1(8)	[Rh(nbd)Cl] ₂	THF/Et ₃ N	70.1	16,000	2.0
4	1(4)	[Rh(nbd)Cl] ₂	THF/Et ₃ N	60.5	20,700	2.0
5	1(5)	[Rh(nbd)Cl] ₂	THF/Et ₃ N	61.6	20,400	2.0
6	1(7)	[Rh(nbd)Cl] ₂	THF/Et ₃ N	59.3	16,700	2.2
7	1(9)	[Rh(nbd)Cl] ₂	THF/Et ₃ N	82.2	16,400	2.0
8	1(6)	[Rh(nbd)Cl] ₂	THF/Et ₃ N	63.2	19,800	2.8
9	1(6)	[Rh(nbd)Cl] ₂	Toluene/Et ₃ N	71.8	21,100	2.4
10	1(6)	[Rh(nbd)Cl] ₂	DCM/Et ₃ N	83.9	18,900	2.3
11	1(6)	[Rh(nbd)Cl] ₂	DMF/Et ₃ N	53.1	19,900	2.5

nbd, 2,5-norbornadiene; DCM, dichloromethane; DMF, dimethylformamide.

^a Carried out under nitrogen (nos. 1 and 2) or air (nos. 3–11) at 60 °C (nos. 1 and 2) or room temperature (nos. 3–11) for 24 h; [M]₀ = 0.1 M, [cat] = [cocat] = 5 mM; for Rh catalyst, [cat] = 2 mM.

^b For the mixtures of THF, toluene or DCM with Et₃N, volume ratio = 3:1.

^c Estimated by GPC in THF on the basis of a polystyrene calibration.

sition is enantiotropic in nature. A sharp peak is detected at 117.0 °C by the DSC analysis of 1(7) in the cooling cycle. The mesophase in this temperature is identified to be columnar by the POM observation [Fig. 2(B)]. The thermogram recorded in the second heating cycle is the mirror image to that of the cooling scan and the associated transition from columnar phase to isotropic state occurs at 116.6 °C.

In the first cooling of 1(8), two peaks corresponding to i-Col and Col-k transitions appear at 111.8 and -31.7 °C. The heating scan detects two peaks at 20.8 and 105.5 °C, which are associated with k-Col and Col-i transitions, respectively. Monomer 1(9) behaves mesomorphically similar to 1(8). During the first cooling cycle, 1(9) shows two peaks at 113.5 and -21.9 °C. When the isotropic liquid is cooled to 110 °C, pseudo focal-conic columnar texture is observed. In the second heating cycle, two transition peaks appear at 19.8 and 110.7 °C, which are respectively identified as k-Col and Col-i transitions by the POM observations.

Table 1 summarizes the thermodynamic parameters associated with the discotic transitions of the monomers. All the mesomorphic transitions are characterized by large enthalpy (ΔH) and entropy changes (ΔS), thus ruling out the possibility of nematicity to the mesophases of the acetylene liquid crystals because of the poorer ordering packing in the nematic phase. Although all the monomers form the same mesophase, the isotropization temperature (T_i) varies with the length of alkyl chain. The T_i increases

progressively from 81.9 °C in 1(4) to 116.6 °C in 1(7). Further increment of the alkyl chain length to nine methylene units in 1(9), however, drops the value to 110.7 °C. Extension of the chain length may enhance the packing arrangements, as suggested by the better developed mesomorphic texture observed in 1(7) than in 1(4). On the other hand, internal plasticization by the alkyl chain may have played a role in decreasing the T_i . The competition between the two antagonistic effects may have led to such a two-step T_i change with the alkyl chain length.

Polymerization Reactions

Mo- and W-based catalysts are the most widely used "classical" initiators for acetylene polymerizations.^{69–75} In our previous work, we found that WCl₆-Ph₃Sn performs better than MoCl₅-Ph₃Sn for the polymerizations of biphenyl-containing 1-alkynes with ester functionalities.²² We thus first attempted to polymerize 1(8), using WCl₆-Ph₃Sn as catalyst. Polymerization conducted at 60 °C in toluene, however, gives only trace amount of polymeric product (Table 2, no. 1). Changing the solvent to dioxane also ends up in disappointment. The catalyst may be poisoned by the ester and ether moieties in the monomer, leading to the failure in the polymerization reaction.

Although the results obtained from WCl₆-Ph₃Sn are poor, we do not give up. Since complexes of late transition metals such as Rh are

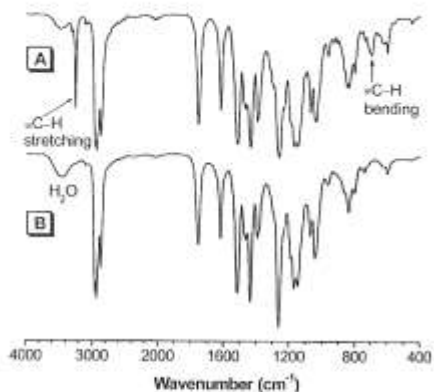


Figure 3. IR spectra of (A) 1(4) and (B) its polymer P1(4).

known to be more tolerant of functional groups,^{35,76–90} we tried to polymerize the monomer by $[\text{Rh}(\text{nbd})\text{Cl}]_2$. Stirring 1(8) in THF/ Et_3N with a catalytic amount of $[\text{Rh}(\text{nbd})\text{Cl}]_2$ at room temperature for 24 h, delightfully, produces a brown solid in 70% yield. Analysis of the sample by GPC gives an M_w value of 1.6×10^4 , confirming its polymeric nature. Under the same conditions, all the monomers are converted into polymers in satisfactory yields with molecular weights of $\sim 2 \times 10^4$. Solvent seems to affect little the molecular weight but yield of the polymers. While polymerization of 1(6) in THF/ Et_3N gives a polymer in 63% yield, the yield raises to 72% in toluene/ Et_3N . Changing the solvent to DCM/ Et_3N further increases the value to 84%. The yield, however, drops to 53% when the reaction is carried in DMF/ Et_3N .

Structural Characterization

All the purified polymerization products are characterized by IR and NMR spectroscopies and give satisfactory data corresponding to their expected molecular structures. An example of the IR spectrum of P1(4) is shown in Figure 3; for comparison, the spectrum of its monomer 1(4) is also given. The monomer absorbs at 3286 and 721 cm^{-1} , due to $=\text{C}-\text{H}$ stretching and bending vibrations, respectively. All these absorption bands, however, disappear in the spectrum of the polymer, indicating that all the triple bonds of the monomer have been consumed by the polymerization reaction.

Figure 4 shows the ^1H NMR spectra of 1(6) and its polymer P1(6) in chloroform-*d*. The spectrum of P1(6) shows no acetylene proton resonance of 1(6) at $\delta \sim 2.0$. The methylene proton next to the triple bond at $\delta \sim 2.2$ also disappears after polymerization owing to its transformation to the allylic proton in the polymer. Instead, a new broad peak appears in the olefin absorption region (δ , 6.4–5.5). Masuda and Higashimura reported the *Z* olefin proton of a poly(1-alkyne), poly(3,3-dimethyl-1-pentyne), resonates at δ 6.05.⁹¹ Thus, the peak at δ 6.09 should be related to the resonance of the *Z* olefin proton of the polyacetylene backbone. Using an equation developed by us and other groups,^{52,85,92,93} the *Z* content of P1(6) is estimated to be 34.1% (or 65.9% *E*). The polymer thus consists of a mixture of *Z* and *E* structures, as evidenced by its relatively broad resonance peaks.

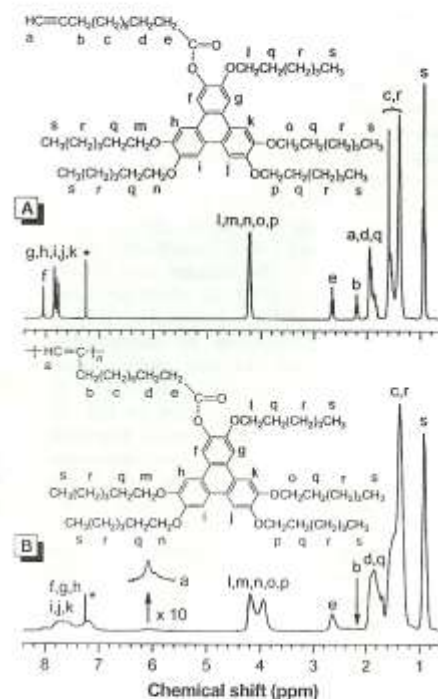


Figure 4. ^1H NMR spectra of chloroform solutions of (A) 1(6) and (B) its polymer P1(6) (sample taken from Table 2, no. 8). The solvent peaks are marked with asterisks.

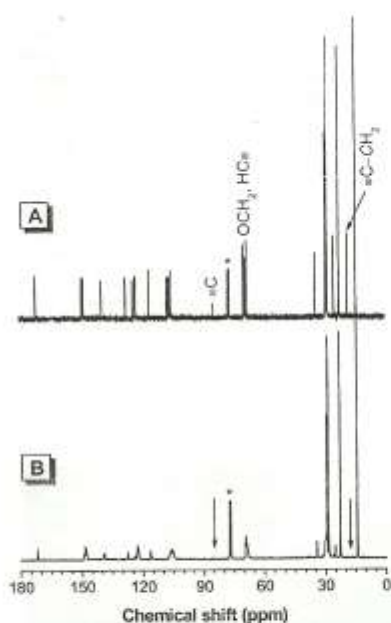


Figure 5. ^{13}C NMR spectra of (A) 1(6) and (B) its polymer PI(6) (sample taken from Table 2, no. 8) in chloroform-*d*. The solvent peaks are marked with asterisks.

The ^{13}C NMR analysis also offers detailed information on the molecular structure of PI(6). The acetylene carbon atoms of 1(6) resonate at δ 84.5 and 69.6, which are absent in the spectrum of the polymer (Fig. 5). The resonance peak of the propargyl carbon ($=\text{C}-\text{CH}_2$) of 1(6) is also absent because it has been transformed into an allylic structure ($=\text{C}-\text{CH}_2$) in PI(6) by the acetylene polymerization. The resonance peaks of the olefin carbon atoms of the polymer main chain, however, cannot be identified because of their overlapping with the peaks of the carbon atoms of the triphenylene pendants.

Thermal Stability

Since the formation of mesophases of thermotropic liquid crystals are realized by the application of heat, the thermal stability of the polymers is thus of primary concern. Unsubstituted poly(1-alkyne)s such as poly(1-butyn) and

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poly(1-hexyne) $[-\text{HC}=\text{C}-\text{C}_m\text{H}_{2m+1}]_n-$; $m = 2, 4$) are very unstable and cannot even be isolated at room temperature from their polymerization mixtures without degradation.^{34,36} Our polymers, however, enjoy high thermal stability and start to lose their weights at temperatures as high as 300 °C (Fig. 6). Thus, the incorporation of the triphenylene discs as side chains into the poly(1-decyn) structure has dramatically enhanced the resistance of the polymers to thermolysis. The mesogenic appendages may have well wrapped the polyene backbones and thus protect them from the perturbations by heat and/or attacks by the degradative species.^{32,35}

Closer analysis of the TGA thermograms reveals that the decomposition temperature (T_d) is high for polymers with longer tail lengths. The polymers may have not decomposed by the pyrolytic cleavage of the allylic bond as such degradation route would give the same T_d values for all the polymers. The decomposition of the polymers is probably via an ester bond breakage mechanism, which cuts off the linkage between the triphenylene appendages with different lengths of peripheral alkoxy chains and the polyacetylene backbone.

Mesomorphic Properties

After confirming the thermal stability of the polymers, we investigated their mesomorphic prop-

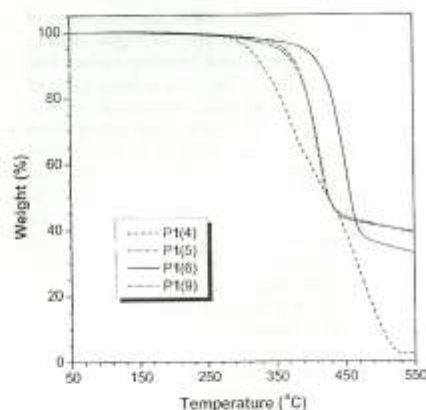


Figure 6. TGA thermograms of PI(4), PI(5), PI(6) (sample from Table 2, no. 8), and PI(9) measured under nitrogen at a heating rate of 20 °C/min.

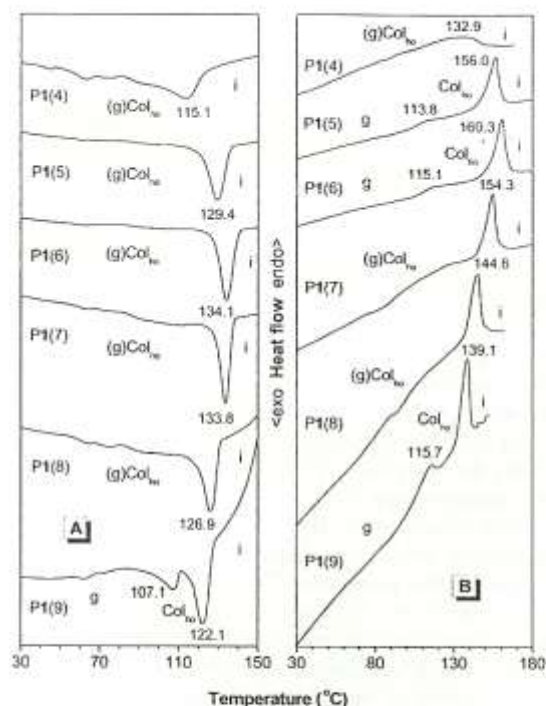


Figure 7. DSC thermograms of mesomorphic polyacetylenes P1(4), P1(5), P1(6) (sample from Table 2, no. 8), P1(7), P1(8) (Table 2, no. 3), and P1(9) recorded under nitrogen during the (A) first cooling and (B) second heating scans at a scan rate of 10 °C/min.

erties. Figure 7 shows the DSC thermograms of the polymers recorded under nitrogen during the first cooling and second heating cycles. The thermogram recorded in the first cooling cycle of P1(4) displays a broad peak associated with *i*-Col transition at 115 °C. The corresponding Col-*i* transition is detected at ~133 °C in the second heating cycle. No glass transition (T_g) is detected in both cycles. When the alkyl chain length is increased, the transition peaks become sharper and the T_g becomes readily detectable in the heating and/or cooling cycles on other polymers. Clearly, the longer chains have offered more freedom for the polymer segments and the mesogenic pendants to act separately.

Figure 8 shows the POM microphotographs of the mesomorphic textures of P1(4) and P1(9). When P1(4) is cooled from its isotropic state, small anisotropic entities and thread-like structures emerge from the dark background of the isotropic liquid [Fig. 8(A)]. The fine textures cannot grow to large monodomains even after

annealed for 2 h. The polyacetylene backbone interferes the packing of the mesogenic pendants and distorts the growth of the ordered domains, which cannot be offset by the plasticization effect of the short alkyl chains. When the alkyl chain length is increased to nine methylene units, the anisotropic entities grow bigger but the exact nature of the mesophase is difficult to identify. Even if we repeatedly grow the liquid crystals with care, we still failed to obtain any readily characteristic textures. Poorly defined optical texture is also observed by Imir and coworkers⁴⁶ for their triphenylene-containing poly(methyl methacrylate). Grubbs and coworkers³⁸ compared the mesomorphic behaviors of poly(norbornadiene), poly(butadiene), and poly(ethylene) carrying triphenylene pendant; and found that their X-ray patterns were sim-

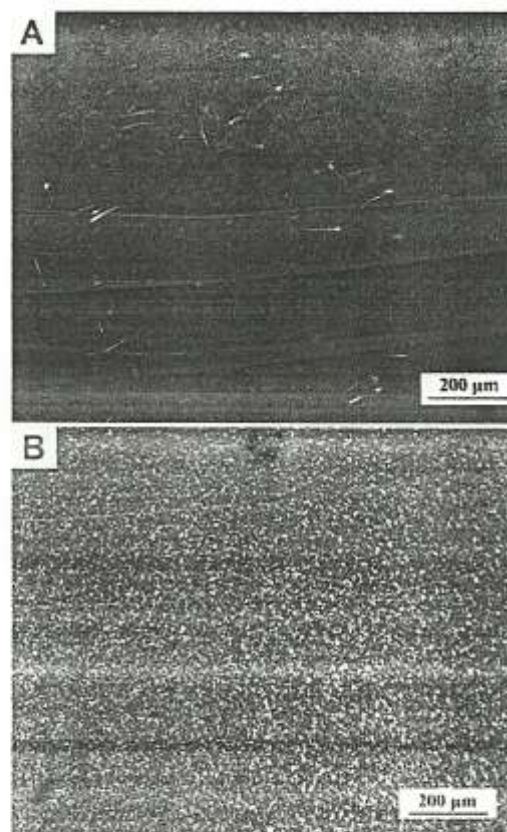


Figure 8. POM textures observed on cooling (A) P1(4) and (B) P1(9) to 100 °C from their isotropic states at a cooling rate of 1 °C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 3. Thermal Transitions and Corresponding Thermodynamic Parameters of Discotic Liquid Crystalline Polymers P1(*m*)^a

Polymer	<i>T_i</i> (Δ <i>H</i> , kJ/mol; Δ <i>S</i> , J/mol K)	
	Cooling	Heating
P1(4)	i 115.1 (-1.01; -2.60) Col _h (g)	(g)Col _h , 132.9 (1.40; 3.45) i
P1(5)	i 129.4 (-4.64; -11.53) Col _h (g)	g 113.8 (-) Col _h , 156.0 (5.08; 11.84) i
P1(6)	i 134.1 (-4.34; -10.66) Col _h (g)	g 115.1 (-) Col _h , 160.3 (5.02; 11.59) i
P1(7)	i 133.8 (-2.36; -5.80) Col _h (g)	(g)Col _h , 154.3 (2.45; 5.73) i
P1(8)	i 126.9 (-1.70; -4.25) Col _h (g)	(g)Col _h , 144.6 (1.52; 3.60) i
P1(9)	i 122.1 Col _h , 107.1 (-) g (-3.29; -8.40) ^b	g 115.7 (-) Col _h , 139.1 (3.18; 7.62) i

g, glassy state; Col_h, ordered hexagonal columnar phase; i, isotropic liquid.

^a Data taken from the DSC thermograms recorded under nitrogen during the first cooling and second heating scans.

^b Sum of overlapping transitions.

lar. These results suggest that the backbone rigidity does not play an important role in the liquid crystalline properties of triphenylene-containing polymers.

The thermal transitions and the corresponding enthalpy and entropy changes of P1(*m*) are summarized in Table 3. The large Δ*H* and Δ*S* changes involved in the mesomorphic transitions of the polymers again support the assignment of columnar phases to the mesophases of the polyacetylene liquid crystals. The *T_i* of the polymers increases initially with alkyl chain length but decreases on further extension, due to the competition between the constructive (packing) and destructive (plasticization) effects.

We carried out powder XRD experiments in order to collect more information concerning the molecular arrangements, mode of packing, and types of order in the mesophases of the polyacetylene liquid crystals. The polymer with an alkyl chain length of four methylene units shows an XRD pattern consisting of one low-angle peak and two high-angle reflections (Fig. 9). The diffuse halo at $2\theta = 20.3$ is characteristic for a liquid-like order of the alkoxy chains; while the broad peak at 25.9 indicates an ordered stacking of the triphenylene discs. The *d* spacing derived from the peak at $2\theta \sim 6.0$ is 14.72 Å, which supports the assignment of columnar phase to the mesophase of the polymer (Table 4). Since rectangular or oblique columnar phases show two peaks with similar intensity at low-angle region, the appearance of a single reflection at $2\theta \sim 6.0$ implies that the texture observed in Figure 8(A) is associated with an ordered hexagonal columnar phase. The packing of the columns is, however, not well-ordered, as evidenced by the width of the low-angle peak.

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This may account for the difficulty of the anisotropic entities to grow into large-size monodomain texture.

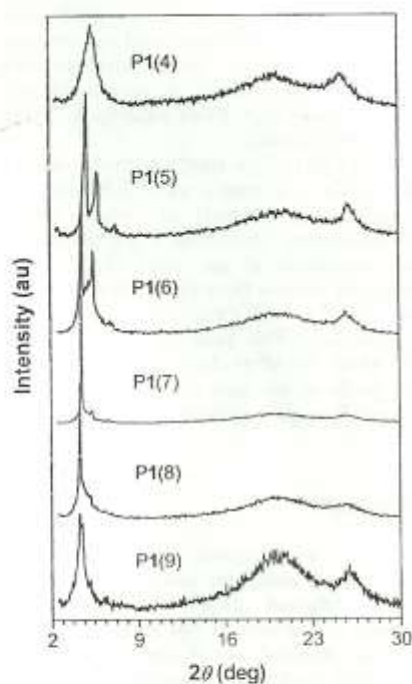


Figure 9. X-ray diffraction patterns of mesomorphic polyacetylenes quenched from their liquid crystalline states: (A) P1(4) at 100 °C, (B) P1(5) at 110 °C, (C) P1(6) at 130 °C (sample from Table 2, no. 8), (D) P1(7) at 128 °C, (E) P1(8) at 125 °C (Table 2, no. 3), and (F) P1(9) at 110 °C.

Table 4. X-ray Diffraction Analysis Data of P1(*m*)^a

Polymer	<i>T</i> (°C)	<i>d</i> ₁ (Å)	<i>d</i> ₂ (Å)	<i>d</i> ₃ (Å)	<i>d</i> ₄ (Å)
P1(4)	100	16.20		4.45	3.51
P1(5)	110	17.48	15.10	4.29	3.40
P1(6)	130	19.19	16.06	4.43	3.46
P1(7)	128	19.62	16.66	4.41	3.46
P1(8)	125	20.30		4.46	3.46
P1(9)	110	20.53		4.41	3.44

^a The mesophases in the liquid crystalline states at the given temperatures were frozen by the rapid quenching with liquid nitrogen.

Similarly, the XRD diffractogram of P1(5) displays Bragg reflections at low and high angles, from which *d* spacings corresponding to the assignment of ordered hexagonal columnar phase can be derived. However, different from P1(4), in this case, we observed two peaks at $2\theta = 4.88^\circ$ and 5.85° associated with the intercolumnar spacing. The mesophase of P1(5) may thus involve mixed columnar packing arrangements. The peaks are much stronger and sharper than those in P1(4), in agreement with the DSC analysis that P1(5) exhibits a higher transition temperature.

When the alkyl chain length is increased to 6 and then 7, the reflection peak at 5.85° progressively weakens in intensity to such an extent that its maximum cannot be easily identified. Further, increment of the alkyl chain length completely eliminates the signal and now all the columns of P1(8) and P1(9) are packed in the single structure. The peak at 4.88° becomes broader. Thus, the alkyl chain length affects not only the packing but also the structure of the liquid crystalline polyacetylenes.

CONCLUSIONS

In this work, we designed and synthesized a group of discotic acetylene monomers and polymers with different alkyl chain lengths and investigated the effects of the structural variations on the chemical and physical properties of the (macro)molecules. Our results can be summarized as follows:

1. The monomers are prepared by a multistep reaction route. They are all liquid crystalline and form columnar phases at room temperature.

2. $\text{WCl}_6\text{-Ph}_4\text{Sn}$ is the most widely used catalyst for the polymerizations of mesogenic 1-alkynes but fails to polymerize 1(*m*). $[\text{Rh}(\text{nbd})\text{Cl}]_2$, on the other hand, initiates the polymerizations of the monomers, furnishing soluble polymers in high yields.
3. All the polymers are thermally stable, losing little of their weights when heated to 300°C . Whereas polymers with short and long alkyl chain lengths possess a homogeneous hexagonal columnar structure, those with intermediate ones form mesophases with mixed structures.

Thus, the structural change in the alkyl chain length has affected the structure and packing of the mesomorphic polymers. The structure-property relationship gained in this study is expected to help guide future structural design endeavor in the development of discotic liquid crystalline polyacetylenes with desirable properties.

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