Diacetylenes for Novel Molecular Composites[†]

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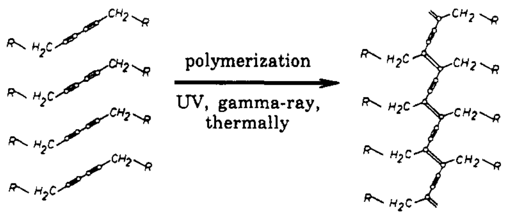
Received February 1, 1994. Revised Manuscript Received May 25, 1994[⊗]

We have taken a new approach to obtain homogeneous molecular composites from diacetylene monomers containing mesogenic groups and flexible substituents. The model systems presented are diacetylenes with biphenol mesogenic groups and alkyl spacers, labeled "*m*-*n*DABP" monomers, $H(CH_2)_mC{\equiv}CC{\equiv}C(CH_2)_nCOOPhPhOCO(CH_2)_nC{\equiv}CC{\equiv}C(CH_2)_mH$, where m and n are the numbers of the outer and inner methylene spacers. It is expected that their polymers will have the properties of molecular composites which have the extended polydiacetylene chains as the rigid molecular fibers and a mesogenic group with flexible spacers as the liquid-crystalline (LC) matrix. The synthesis and characterization of *m*-*n*DABP monomers (with $n = 8$, $m = 3$ and 8) and their polymers by differential calorimetry (DSC), optical microscopy, X-ray diffraction, and Raman spectroscopy are reported. Both monomers are readily polymerized by radiation (γ-ray, electrons, X-ray, or UV). The 8-8DABP monomer showed unusual behavior. It can be polymerized by red laser beam (λ = 750.7 nm). The monomers are liquid crystalline at elevated temperatures. We have found that 8-8DABP can be polymerized in highly ordered smectic states.

Introduction

Molecular composites (MCs) are materials with rigid molecular "fibers" dispersed in a flexible or semiflexible matrix which interacts with the molecular fibers.[1-3] The enhancement of the mechanical properties, as compared to conventional fiber-reinforced composites, is expected because of the large aspect ratio of the molecular fibers and the maximizing interaction between the fibers and the matrix on a molecular level.[1-3] However, there is one problem associated with MC systems, phase separation between the molecular fibers and their matrix.[2-4,6] In rigid-rod/flexible MCs the homogeneous phase can be obtained only at a concentration of the molecular rods lower than the critical concentration (usually about 2–4%).[3,4] At higher concentrations the aggregation of the rod molecules occurs, as predicted by Flory's theory.[5] This heterogeneity deteriorates the mechanical performance of MCs down to the level of macroscopic composites.[6] One way to remedy the above problem is to prepare single-component MCs in which rod molecules and the polymer matrix are chemically connected. Block copolymers[3b,7,8] and graft copolymers[9-11] have been employed to achieve homogeneous MCs with a wider range of fiber content. Here we will introduce another approach to obtain single-component MCs from liquid-crystalline diacetylene monomers containing mesogenic groups and flexible substituents.



Upon polymerization , rigid extended chain molecular fiber can be created along the polymer chain.

Figure 1. Topochemical polymerization of diacetylenes.

It is well-known that diacetylene monomers can undergo topochemical polymerization in the solid state initiated by radiation, heat or stress[12-14] (Figure 1), and many polydiacetylene (PDA)s can be obtained as nearly defect-free, single crystals.[12-16] PDA single crystals showed very high measured tensile strengths and moduli. For example, an ultimate tensile modulus of 45 GPa was found for poly[1,6-diolbis(phenylurethane)hexa-2,4-diyne], $(=C(R)C{\equiv}CC(R)=)_n$ where $R = -CH_2OCONHC_6H_5$, and

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[†] Abstract published in Bulletin of the American Physical Society (Meeting Abstract), March 1994, 39(1), 700.

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

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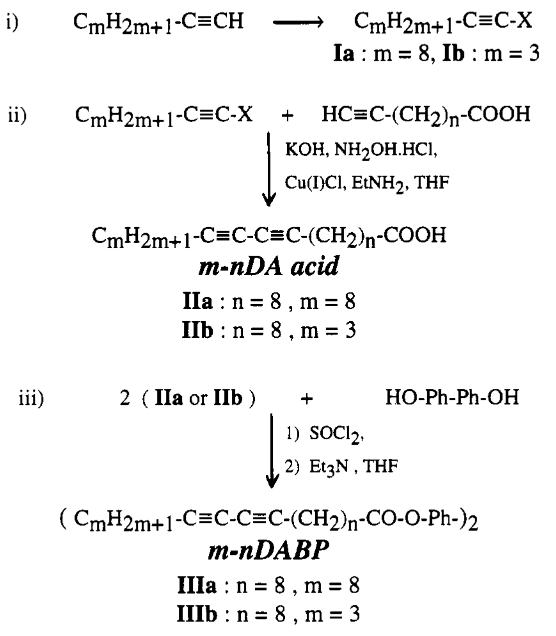
Scheme 1. Synthesis of *m-n*DABP



of 62 GPa for poly[1,6-diolbis(ethylurethane)hexa-2,4-diyne], where $R = -CH_2OCONHC_2H_5$.[14,16]

Thus, the topochemically polymerized material from diacetylene compounds could provide a novel type of MC in which the PDA chains act as the rigid molecular fibers and the substituents act as the matrix. The choices of substituent groups can be tailored to provide the desired properties for MC systems.

As model systems, we have studied the diacetylene monomers called "*m-n*DABP", $H(CH_2)_mC{\equiv}CC{\equiv}C(CH_2)_nCOOPhPhOCO(CH_2)_nC{\equiv}CC{\equiv}C(CH_2)_mH$, where *m* and *n* are the number of outer and inner methylene units, BP stands for biphenyl (the type of mesogenic group used), and DA stands for the diacetylene group.

We expect that the incorporated mesogenic group and the methylene spacers should provide sufficient molecular-packing order to allow the diacetylene groups to undergo (topochemical) polymerization in liquid-crystalline states.

In this paper we report the synthesis and characterization of the *m-n*DABP monomers and polymers (with *n* = 8, *m* = 8 and 3).

Experimental Section

Materials. 1-Decyne, ethylmagnesium bromide, iodine, 1-pentyne, bromine, copper(I) chloride, 70% ethylamine (in water), hydroxylamine hydrochloride, and 4,4′-dihydroxybiphenyl were obtained from Aldrich and used as received. 10-Undecynoic acid (Lancaster Synthesis) was used as received. Dried diethyl ether and dried tetrahydrofuran (THF) were prepared by refluxing the solvent over lithium aluminum hydride overnight and freshly distilled before use. Triethylamine was dried over $LiAlH_4$, redistilled, and kept over 4A molecular sieves. Thionyl chloride was distilled twice prior use. All the other reagents were used as received, unless otherwise specified.

Monomer Synthesis. The synthesis of *m-n*DABP monomers was carried out according to Scheme 1. First the 1-haloalkyne (**I**) was prepared from the 1-alkyne which has *m* methylene units. Then **I** was coupled unsymmetrically with the acetylenic acid (with *n* methylene units) by the Cadiot–Chodkiewicz coupling reaction[17] to get the intermediate product, *m-n*DA acid, **II**. The acid **II** was coupled with 4,4′-dihydroxybiphenyl in the presence of triethylamine to obtain the *m-n*DABP monomer, **III**. The halogen (X) in **I** can be either iodide or bromide. To satisfy the necessary unsymmetric coupling conditions, bromide has been chosen for the short outer spacers (*m*, i.e., *m* = 3, X = Br) and iodide for the longer spacers (i.e., *m* = 8, X = I). Iodo derivatives were prepared via Gridnard reaction,[18] and bromo derivatives were prepared by the modified Strauss's reaction.[19]

1-Iododecyne, Ia. A solution of 1-decyne (25.00 g, 0.181 mol) in 50 mL of dried diethyl ether was added dropwise under an argon atmosphere at ca. 0 °C over an ethylmagnesium bromide solution (0.30 mol in 100 mL of diethyl ether). The mixture was stirred at 35 °C for 1 h. The resulting solution was cooled to ca. 15 °C, and pulverized iodine (80.0 g, 0.315 mol) was slowly added from a solid additional funnel over a period of 1.5 h. The mixture was stirred at 30 °C for another 1.5 h. Meanwhile, three 50-mL portions of dried diethyl ether was occasionally added to reduce the viscosity built up during the reaction. The resulting solution was cooled to room temperature, diluted with 30 mL of diethyl ether, and hydrolyzed by diluted acetic acid (pH ≈ 2, by slowly pouring the content into the diluted acid solution). The organic phase was extracted with diethyl ether, washed several times with 10% $Na_2S_2O_3$ solution (to remove the unreacted iodine), washed several times with water, and dried over $MgSO_4$. The solvent (ether) was removed in the rotary evaporator at 30 °C. Note that *care must be taken in this step, not to heat the solution above 40 °C since iododecyne **Ia** can couple with the remained 1-decyne or with itself to get* $C_8H_{15}C{\equiv}CC{\equiv}CC_8H_{15}$ *at high temperature.* The resulting oily crude product was purified by silica gel column chromatography (eluted with hexane) to give 43.0 g of 1-iododecyne, **Ia**, as a pale yellow oil. The yield was about 90% based on 1-decyne used. ^1H NMR ($CDCl_3$, TMS) δ (ppm) = 0.88 (t, 3H, $-CH_3$), 1.0–1.5 (m, 12H, internal $-CH_2-$), and 2.35 (t, 2H, $-CH_2C{\equiv}CI$).

1-Bromopentyne, Ib. Potassium hypobromite (KOBr) solution was prepared by slowly adding liquid bromine (60 mL, 1.16 mol) into a cold solution of KOH (200 g in 800 mL of ice water). Then a solution of 1-pentyne (27.25 g, 0.40 mol) in 30 mL of ethanol was added dropwise over the KOBr solution at ice temperature. The mixture was stirred at room temperature for 14 h. The organic phase was extracted by diethyl ether, washed with water, and dried over $MgSO_4$. Solvent and most of the starting material (1-pentyne) were vacuum evaporated at 30–35 °C to get a crude pale yellow oil. Crude product was further purified by silica gel column chromatography (hexane) to obtain 24.0 g (40–45% yield) of 1-bromopentyne, **Ib**, as a colorless oil. ^1H NMR ($CDCl_3$, TMS) δ (ppm) = 0.98 (t, 3H, CH_3), 1.52 (sextet, 2H, $-CH_2CH_2CH_3$), and 2.18 (t, 2H, $-CH_2C{\equiv}CBr$).

Heneicosa-10,12-diynoic Acid, 8-8DA Acid, IIa. A procedure described in the literature[17] was followed with some modification. A solution of 10-undecynoic acid (5.490 g, 0.03 mol) in 20 mL of 10% KOH was treated under argon with 400 mg of hydroxylamine hydrochloride and a Cu^ICl solution (400 mg of Cu^ICl in 6.0 g of 70% ethylamine). The contents were cooled to ca. 15 °C and a solution of **Ia** (8.03 g, 0.03 mol) in 15 mL of THF was added dropwise over 0.5 h. The reaction mixture was stirred at 20 °C for 30 min and then acidified with 2 N H_2SO_4 to pH = 2. The organic phase was extracted by diethyl ether. The combined ether phase was washed with diluted H_2SO_4 (pH = 2), washed with plain water, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by silica gel column chromatography (hexane/diethyl ether, 80:20). The desired product, 8-8DA acid **IIa** was recrystallized from petroleum ether (40–60 °C) to give 4.0 g (41% yield) of white crystals, mp 49.5–50.0 °C. ^1H NMR ($CDCl_3$, TMS) δ (ppm) = 0.88 (t, 3H, CH_3), 1.25–1.65 (m, 24H, internal $-CH_2-$), 2.24 (t, 4H, $-CH_2C{\equiv}C-C{\equiv}CCH_2-$), and 2.35 (t, 2H, $-CH_2COOH$). FTIR (KBr pellet): ν (cm^{-1}) 3000–3400 (m, br, COO*H*), 2949.8 (vs), 2866.5 (s), 2170.9 and 2153.0 (vw, –C≡C– str), 1652.9 (vs, C═O str), 1451.5 (s),

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Table 1. Polymerization and Thermochromic Transitions of *m*-*n*DABP Monomers

m-*n*DABP monomers	monomer color	polymerization by UV (245 nm) or γ-ray	polymerization by red laser (750.7 nm)	thermochromic transitions T_{rm} ↔ (50–60 °C) ↔ 120 °C
8-8DABP	colorless	→ blue → purple → brown → reddish gold	→ blue → dark purple	blue ↔ orange ↔ yellowish gold
3-8DABP	light beige	→ pink → red	→ (no color change)	pink ↔ orange ↔ yellowish gold

Table 2. Thermal Data of the 8-8DABP Monomer

DSC scans (15 °C/min)	transition temp (°C)[a]	ΔH (kcal/mol)[b]	ΔS (kcal/mol K)
first cooling	$T_1 = 46.3$	−1.45	−4.54
	$T_2 = 62.7$	−2.00	−5.96
	$T_i = 81.9$	−15.16	−4.27
second heating	$T_1 = 50.6$	1.14	3.52
	$T_2 = 71.7$	1.28	3.71
	$T_i = 89.7$	14.87	41.00

[a] T_1 is the lowest transition temperature, T_2 is the higher transition temperature, and T_i is the istropization (LC to isotropic) temperature. [b] Fomular weight of 8-8DABP is 786 g/mol.

1429.4 (m), 1317.0 (w), 1298.0 (w), 1255.0 (m), 1036.4 (2), 931.85 (w), and 696.9 (m).

Hexadeca-10,12-diynoic Acid, 3-8DA Acid, IIb. The procedure described above was followed by the bromoalkyne **Ib** (4.42 g, 0.03 mol). 3-8DA acid, **IIb**, was obtained as a colorless powder, mp 49 °C. The yield was 35–40%. ^{1}H NMR ($CDCl_3$, TMS) δ (ppm) = 0.88 (t, 3H, CH_3), 1.2–1.6 (m, 14H, internal $-CH_2-$), 2.24 (overlapped triplet, 4H, $-CH_2C{\equiv}CC{\equiv}CCH_2-$), and 2.35 (t, 2H, $-CH_2COOH$).

4,4′-Bis(heneicosadiynoate)biphenyl, 8-8DABP, IIIa. In a dried, round-bottom flask the diacetylenic acid **IIa** (1.92 g, 0.006 mol) was treated with an excess amount of thionyl chloride (19.3 g, 0.162 mol), functioning as both the solvent and the reagent, at ca. 0 °C. The solution was slowly heated to 40 °C and stirred at that temperature for 5 h, and then the excess amount of thionyl chloride was removed by vacuum evaporation. The reddish brown precipitate of the corresponding acid chloride was dissolved in 10 mL of dry THF and injected into another dried, three-neck round-bottom flask. A solution of 4,4′-dihydroxybiphenyl (0.500 g, 0.0027 mol) in 25 mL of dry THF and 5 mL of triethylamine was added dropwise at ca. 0 °C and the mixture was stirred at 25 °C for 5 h. The organic content was extracted a few times with diethyl ether. The combined ether phase was washed several times with a saturated solution of $NaHCO_3$ (to remove the remaining acid and acid chloride), washed with water, and dried over $MgSO_4$. The solvent was evaporated, and the crude product was purified by silica gel column chromatography (hexane/diethyl ether, 50:50) 8-8DABP **IIIa**, 0.8 g, 38% yield, based on the biphenol used) was obtained as a white powder. **IIIa** shows liquid crystalline phases at elevated temperatures with the isotropic transition temperature at 89.7 °C (DSC, second heating scan, 15 °C/min, see Table 2). HPLC (THF solvent): purity >99%. ^{1}H NMR ($CDCl_3$, TMS) δ(ppm) = 7.56 (d, 4H, *H*Ph, ortho to COO−gr), 7.15 (d, 4H, *H*Ph, meta to COO−gr), 2.58 (t, 4H, CH_2COOPh), 2.24 (t, 8H, $CH_2C{\equiv}CC{\equiv}CCH_2$), 1.73 (pentet, 4H, CH_2CH_2-COOPh), 1.2–1.5 (m, 44H, internal CH_2), and 0.86 (t, 6H, CH_2). FTIR (KBr pellet) ν (cm^{-1}) 3440 (vw, overtone of C=O str), 2948 (m), 2928 (s), 2879 (s), 2166.2 and 2130.6 (vw, −C≡C− str), 1717.5 (vs, C=O str), 1611.5 (vw), 1479.6 (m), 1465 (m), 1434 (w), 1373 (w), 1238 (m), 1228 (s, C–O), 1125.2 (m), 858.8 (m), and 738.7 (w).

4,4′-Bis(hexadeca-10,12-diynoate)biphenyl, 3-8DABP, IIIb. Using the same procedure as described above with the acetylenic acid **IIb** (1.49 g, 0.006 mol), 3-8DABP, **IIIb**, was obtained as a light beige powder. The isotropization temperature was 99.6 °C (DSC, second heating scan, 10 °C/min). The yield was ca. 45%. HPLC (THF solvent): purity > 98%. ^{1}H NMR ($CDCl_3$, TMS) δ (ppm) = 7.56 (d, 4H, *H*Ph, ortho to COO− gr), 7.15 (d, 4H, *H*Ph, meta to COO− gr), 2.58 (t, 4H, CH_2COOPh), 2.24 (overlapped triplet, 8H, $CH_2C{\equiv}CC{\equiv}CCH_2$), 1.73 (pentet, 4H, CH_2CH_2-COOPh), 1.2–1.5 (m, 24H, internal CH_2), and 0.86 (t, 6H, CH_3).

Polymerization of the Monomers. The solid monomer films were used for polymerization by a UV lamp (λ = 254 nm) to get partially polymerized samples and to observe the color changes (chromic transitions) upon polymerization. The solid films were prepared by casting a monomer solution on glass or quartz substrates, evaporating the solvent and drying in a vacuum desiccator at room temperature for a few hours. Polymer powder samples used in this study were obtained by polymerizing monomer powder with 20 Mrad of ^{60}Co γ-radiation at room temperature (dose rate of ca. 26.8 krad/h). The residual monomer and oligomers in the polymer sample were washed away with chloroform and the sample was dried in a vacuum desiccator overnight prior to use.

Characterization Techniques. The 200 MHz ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer in a solution of $CDCl_3$ with tetramethylsilane (TMS) as an internal standard.

FTIR spectra were recorded with a Digi-Lab FTS-60 FTIR spectrometer. The samples were dispersed in KBr pellets and 256 scans were used for each spectrum.

High-pressure liquid chromatography (HPLC), a Perkin-Elmer Series 10 LC, equipped with a PL gel column, was used to check the purity of the products. The measurement was performed by using a UV detector and THF as the solvent.

Differential scanning calorimetry (DSC) experiments were performed on a DuPont Instrument 912 DSC, Thermal Analysis 200.

Optical microscopy was carried out with a Carl-Zeiss polarizing optical microscope equipped with a Metter FP-82 hot stage, controlled by a Metter FP-800 central processor, and a 35 mm camera.

Wide-angle X-ray diffraction (WAXD) powder patterns of 8-8DABP monomer were obtained from a Rigaku Rotaflex X-ray spectrometer (40 kW of rotating anode with a current of 150 mA, λ = 1.5418 Å) equipped with a temperature controller. The 2θ range recorded was from 2° to 50°.

WAXD powder patterns of polymerized 8-8DABP were obtained from a Phillips XRG 3100 X-ray spectrometer (12-kW rotating anode with a current of 30 mA, λ = 1.5418 Å).

Raman spectra were recorded on a Dilor Raman spectrometer. The laser source was an argon ion pumped laser with a tunable titanium sapphire laser. The output laser wavelength used was 750.7 nm and the slit width used was 200 μm. A macroscopic chamber was used to obtain the solution spectra and a microscope was used to obtained the powder spectra.

Results and Discussion

Synthesis of the Monomers. The diacetylenic acid **II** can be synthesized by an unsymmetric coupling reaction in which Cu$^+$ ion acts as the catalyst and hydroxylamine hydrochloride acts as the reducing agent to maintain the existing of Cu$^+$ in the reaction. For 8-8DA acid, **IIa**, the iodoalkyne **Ia** was used since iodide is a good leaving group and can give a fast coupling rate. The Gridnard reagent was chosen to synthesize **Ia** with high yield (typically 90% or more). For the short chain alkynes, the iodo derivative is too reactive and it tends to give the self-coupling product of $(C_mH_{2m+1})C{\equiv}CC{\equiv}C(C_mH_{2m+1})$ in the coupling reaction. For 3-8DA acid, **IIb**, the bromoalkyne was thus used. **Ib** was conveniently synthesized from the reaction of 1-alkyne with hypobromite ion (OBr$^-$) in an aqueous phase with alcohol (methanol or ethanol) as the cosolvent. We have synthesized the series of *m*-*n*DA acids for *n* = 8 and *m* = 3–16 and found that the bromo derivatives are suitable for short-chain alkynes (*m* = 3, 4, and 5) and the iodo derivatives are used with longer chain length (*m* = 6–16) as shown in Scheme 2. The acid **II** was transformed to its acid chloride to increase reactivity and reacted with

Scheme 2. Synthesis of $C_mH_{2m+1}C{\equiv}CX$

$$C_mH_{2m+1}\text{-}C{\equiv}CH \xrightarrow[2)\ I_2,\ H_3O^+]{1)\ \text{EtMgBr / dry ether}} C_mH_{2m+1}\text{-}C{\equiv}C\text{-}I$$

For m = 6 to 16

$$C_mH_{2m+1}\text{-}C{\equiv}CH \xrightarrow{\text{KOBr}} C_mH_{2m+1}\text{-}C{\equiv}C\text{-}I$$

For m = 3, 4, 5

the biphenol to obtain the ester product, *m*-*n*DABP monomers, **III.**

^{1}H NMR spectra of the monomers (e.g., in Figure 2A, for 8-8DABP) showed the downfield shift of the protons connected to the carbonyl group from $\delta = 2.35$ ppm for the carboxylic acid **II** to 2.58 ppm for the phenyl ester (–COOPh) group. FTIR spectra (e.g., in Figure 2B) also confirmed the absence of a broad carboxylic hydroxyl-(OH) stretching mode (around 2800–3500 cm^{-1}) and the presence of an ester stretching vibration at ca. 1720 cm^{-1} compared to that of the acid at ca. 1650 cm^{-1}. NMR spectra also showed two characteristic doublets at $\delta = 7.15$ and 7.56 ppm for the protons on para-disubstituted biphenyl rings.

The monomers are very soluble in chloroform, methylene chloride, carbon tetrachloride, THF, and acetone. They are soluble in diethyl ether and partially soluble in methanol and ethanol. The crystallized monomers can be polymerized easily by radiation. They need to be stored in chloroform solution and recrystallized (with hexane/CH_2Cl_2, 50:50) before use.

Thermal and Liquid-Crystalline Properties. As described, the LC properties of *m*-*n*DABP monomers should have sufficiently ordered molecular packing for the diacetylene polymerization. Both 8-8DABP and 3-8DABP showed thermotropic LC properties. They were characterized by DSC, polarized optical microscopy, and X-ray diffraction techniques.

Three transitions observed from DSC scans of 8-8DABP monomer (Figure 6A and Table 1) showed the existence of multiphases in this material. At the isotropization temperature T_i, a large enthalpy change ($\Delta H \approx 15$ kcal/mol or 79.1 J/g) was observed, indicating a transition between an isotropic phase and an ordered phase. Under the optical microscope, the phase between T_i and T_2 showed a spherulitic, crystallike texture after the first cooling scan. However, this phase flowed under a shearing force, which indicates that it is a highly ordered smectic phase. Figure 7A shows the clear existence of a smectic texture after annealing the sample at 83 °C for 2.5 h. Moreover, after slow cooling from the melt (1–2 °C/min) the lancet-like texture, which is characteristic of the smectic B phase,[20] was observed.

Upon further cooling from the first smectic phase, a mosaic texture was obtained. The optical micrograph in Figure 7B shows the mosaic texture at 55 °C which may correspond to another highly ordered smectic phase. The ΔH value of 1–2 kcal/mol at the second transition ($T_2 = 62.7$ °C) is close to values of transitions to three-dimensional ordered smectic phases occurring in many liquid crystals.[20] This phase may be smectic G or smectic H. The lowest temperature phase (at temperatures < T_1) is a crystalline phase whose WAXD pattern and unit-cell parameters indicate a three-dimensional crystalline order.

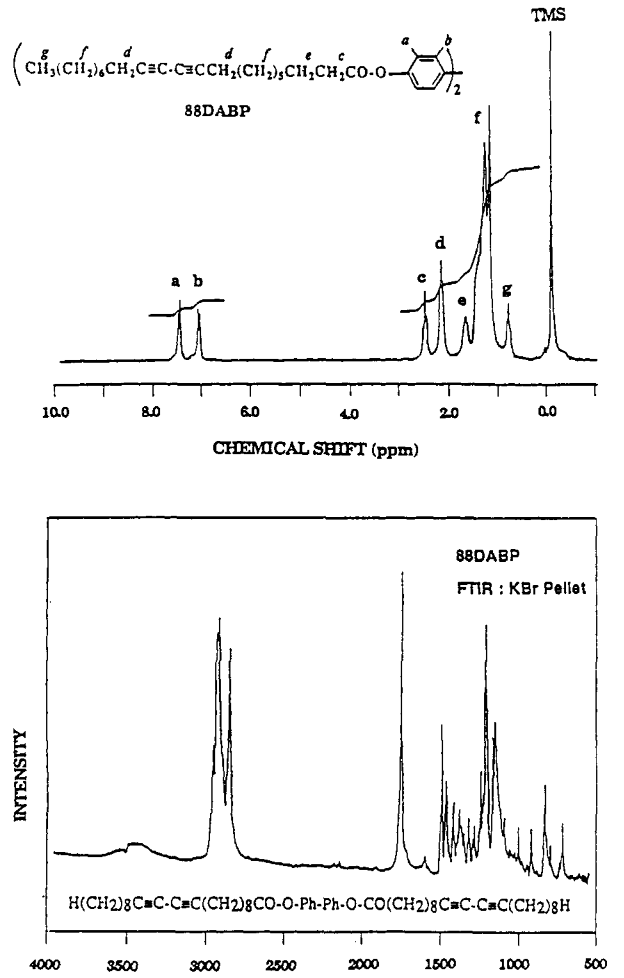

Figure 2. (A) ^{1}H NMR ($CDCl_3$). (B) FTIR spectra of the 8-8DABP monomer.

A DSC thermogram of 3-8DABP is shown in Figure 6B. Both the heating and cooling scans showed a large peak ($\Delta H = 72.8$ J/g or 10.4 kcal/mol) which corresponds to the gradual transition between the isotropic and crystalline phase. The soulder of this transition contains a nematic phase which can be observed after slowly cooling from the isotropic phase. Its domain texture is presented in Figure 7C.

WAXD of 8-8DABP Monomer. Powder WAXD patterns of 8-8DABP monomer at different temperatures are shown in Figure 8. Prior to each data collection, the monomer powder was annealed at the desired temperature for 1 h. Three temperatures, 75 °C, 55 °C, and room temperature (ca. 20 °C), were selected in accord with the DSC thermograms. The WAXD patterns revealed different structural organization in each phase. The *d* spacings indexed as d_{100}, d_{010}, and d_{001} are listed in Table 3.

The pattern at room temperature showed several sharp peaks at large 2θ value ($2\theta > 15°$), indicating a crystalline phase. The two phases at elevated temperatures showed the characteristics of LC (smectic) patterns which usually consist of two reflection regions, the low 2θ angle reflections corresponding to the smectic layer thickness, and the higher angle reflections ($2\theta > 15°$) corresponding to the order within the layers. The reflection at $2\theta \approx 5°$ (*d* spacing

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Table 3. *d* Spacings in 8-8DABP Calculated from WAXD Patterns in Figures 8 and 9

temp (°C)	calculated *d* spacings (Å)[a] d_{100}	d_{010}	d_{001}	tiled angle (deg)[b]
polymer				
room temp[c]	50.04	9.25	4.90	28.2
monomer				
room temp	53.04	8.54	9.97	31.6
55	53.04	8.56	9.91	31.6
75	50.52		8.97	35.8

[a] The *c*-axis direction is parallel to the extended chain direction of PDA. [b] The molecular length of 8-8DABP monomer calculated assuming an all-trans conformation is approximately 62.3 Å. That of 8-8DABP polymer is approximately 56.75 Å. [c] Room temperature was ca. 20 °C.

≈ 17.0–17.5 Å indexed as 300) gives a smectic layer thickness (d_{100}) of about 53 Å at a temperature 55 °C and 50.5 Å at 75 °C. Since the calculated molecular length of 8-8DABP monomer in a fully extended conformation is approximately 62.3 Å, the monomer molecule in the smectic layers must be tilted 31.6° and 35.8° at 55 and 75 °C, respectively. The WAXD pattern of smectic phases at 75 °C can be fitted with a pseudohexagonal unit cell where the [100] direction is maintained and the [001] direction relates to the hexagonal axes occurring within the layers. This supports the optical microscopic observation that this phase could be the smectic B (tilted phase) which has a pseudohexagonal arrangement within the layers.[21,22] The WAXD at 55 °C can be roughly fitted with either a pseudohexagonal unit cell (similar to previous phase) or with a monoclinic unit cell (with the *b* axis as the unique axis, β about 60°). This LC phase may be smectic G (tilted phase with a pseudohexagonal unit cell) or smectic H (tilted phase with a monoclinic unit cell).[21,22] The phase at room temperature is a crystalline phase.

Polymerization Behavior of the Monomers. We have found the 8-8DABP monomer is very reactive to photonic radiation. As irradiated by UV (λ = 254 nm), it immediately underwent polymerization and the color changed from white to vivid blue. Its polymerization can also be initiated by other kinds of radiation including ^{60}Co γ-rays, an electron beam, X-rays, or even a red laser beam (discussed later). The color change is due to the conjugated PDA backbone. Irradiation for longer times caused the color to change from blue to deep purple, brown, and finally reddish gold, with a metallic luster in reflectance. The UV–visible spectra (not shown here) showed that the initial blue phase has an absorption maxima about 620 nm. At longer polymerization times, the absorption maxima gradually blue-shifted to a new maxima at about 555 nm. This phenomenon is normally observed in diacetylenes with the aliphatic side groups, for example, in our synthesized aliphatic diacetylenic acids (*m*-*n*DA acids), the dialkyldiacetylenes,[23] the α,ω-alkyldiyne dimers,[24] or monolayers of amphiphilic diacetylenic acids.[25] The blue shift has been associated with the imposed strain occurring during the polymerization process.[26] The strain forced the polymer chains to adapt different packing, thus altering the electronic structure and causing the blue shift.[26]

8-8DABP showed chromic transitions. Its color changes upon being subjected to applied heat or stress. The polymer film in the blue phase (at a low polymer conversion) continually changed its color to purple, orange, and yellowish gold as the temperature is increased to 35, 50–55, and 110–120 °C, respectively. The thermochromic behavior was found to be reversible and quickly occurred upon temperature change between room temperature and about 125 °C. The reversibility was found to be permanent over many cycles of heating and cooling (at least up to 100 times). This polymerized film can be utilized as a temperature indicator. A reversible chromic change was also observed when stress was applied to the blue polymer film, the color changed from blue to reddish purple and returned to blue when the stress was released.

3-8DABP was similar to 8-8DABP. The initial polymerized material was pink in color. Upon polymerization its color gradually changes from light beige to pink to red. Like 8-8DABP, its polymers also showed reversible thermochromic transitions, the color changed from pink to red and finally orange upon increasing the temperature. However, 3-8DABP is less reactive than 8-8DABP.

Raman Spectroscopy of *m*-*n*DABP. Transforming monomer to polymer changes the chemical environment of the carbons on the diacetylene backbone (see Figure 1). This process should show two features in the Raman spectra, one is the presence of the $\nu(\mathrm{C{=}C})$ str mode and another is the shift of the $\nu(\mathrm{C{\equiv}C})$ to a lower wave number because the resonance effect in the PDA backbone weakens the triple-bond strength.[27]

A Raman spectrum of 8-8DABP polymer powder is shown in Figure 3B. Several strong peaks are observed due to the resonance Raman effect resulting from the absorption of a red laser beam (λ = 750.7 nm) by the blue-colored polymer sample. The presence of the C=C bond stretching at 1457 cm^{-1} and the polymer C≡C bond stretching at 2078 cm^{-1} indicates the acetylenic type, $(=\mathrm{C(R)C{\equiv}CC(R)}=)_n$, of PDA backbone.[27]

The striking peaks at 699, 1198, and 1236 cm^{-1} are expected to be the Raman-active (A_g) modes of the in-plane stretching vibrations of the PDA backbone. In accordance with the simple force field models calculated by Bloor et al.,[28] these vibrations should be the symmetric (A_g) mode 2, mode 3, and mode 4, respectively.

Because the pure monomer spectrum can not be obtained from the monomer powder due to its polymerization by the red laser beam used (to be discussed later), the solution spectrum of 8-8DABP monomer (7 wt %) in chloroform, shown in Figure 3A, was used. The monomer $\nu(\mathrm{C{\equiv}C})$ stretching peak appeared at 2261 cm^{-1}. Comparing the $\nu(\mathrm{C{\equiv}C})$ stretching of the monomer and its polymer, the shift from 2261 cm^{-1} for the monomer to 2078 cm^{-1} for the polymer is due to electron delocalization in long-chain conjugated systems, which causes the bond strength to be weaker.[29]

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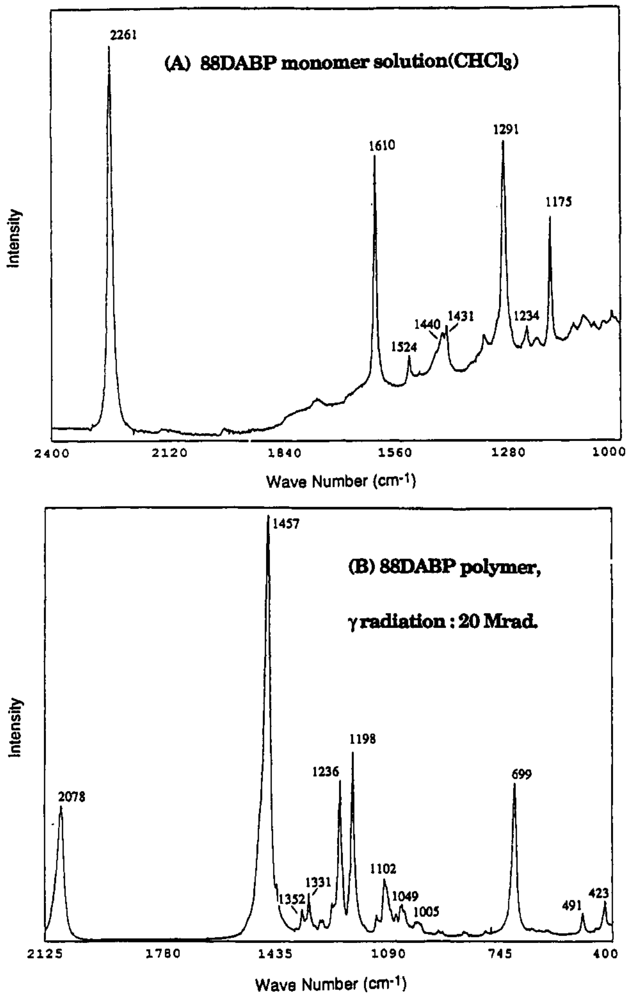

Figure 3. Raman spectra of 8-8DABP (A) monomer solution (7% in $CHCl_3$) and (B) polymer powder.

Polymerization of 8-8DABP monomer by a red laser light was concluded after several attempts to obtain the monomer spectrum from the powder sample failed, resulting in the same spectrum as obtained from the polymer sample. Also a blue color was observed on the sample exposed to the laser beam. The effect of laser power on the polymerization of the monomer at the same integration time (5 s) is shown in Figure 5. With the low power of 300 mW, the presence of polymer can be seen from the ν(C=C) peak at 1475 cm^{-1} and the ν(C≡C) peak at ≈2080 cm^{-1}, but the monomer color was unchanged. When the higher power of 600 mW was used, the intensity of both peaks was greatly increased, especially at ν(C=C) peak, and the ν(C≡C) peak also shifted to a lower wave number. It was found that increasing the exposure (integration) time at the same low power gave the same effect as increasing the power. We also checked the possibility of a thermally-induced polymerization which may occur during the laser irradiation. 8-8DABP monomer was subjected to several heating scans from a room temperature to 125 °C (above its melting point) in the DSC instrument and it was found that all of the endothermic and exothermic peaks of the monomer in the DSC thermograms remained unchanged. Thus, a thermally induced polymerization does not occur. These facts indicate that 8-8DABP monomer is polymerized by the laser beam. However, a clear explanation and the mechanism of this laser polymerization are not known at this time.

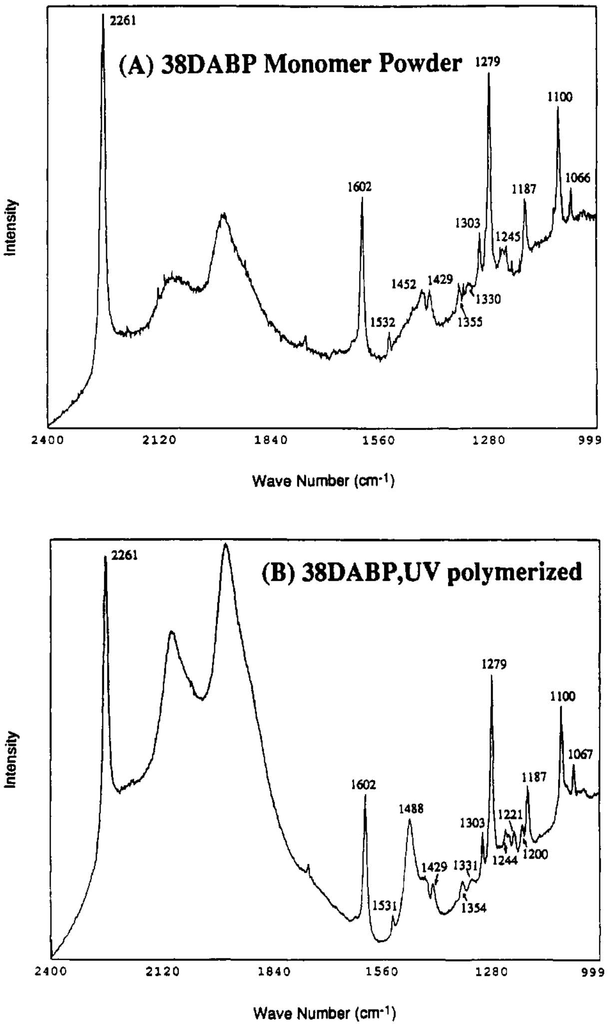

Figure 4. Raman spectra of 3-8DABP (A) monomer powder and (B) monomer with UV polymerized for 2.5 h.

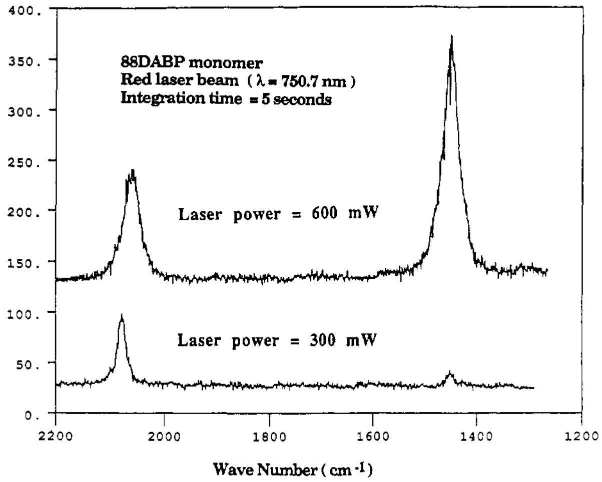

Figure 5. Raman spectra showing the effect of different laser power (λ = 750.7 nm) at the same integration time (5 s) on the polymerization of 8-8DABP monomer.

The polymerization behavior of 8-8DABP monomer is unusual. Most diacetylenes can be polymerized photonically by the higher-frequency radiation (UV, X-ray, electrons or γ-ray). Laser-induced polymerization was also

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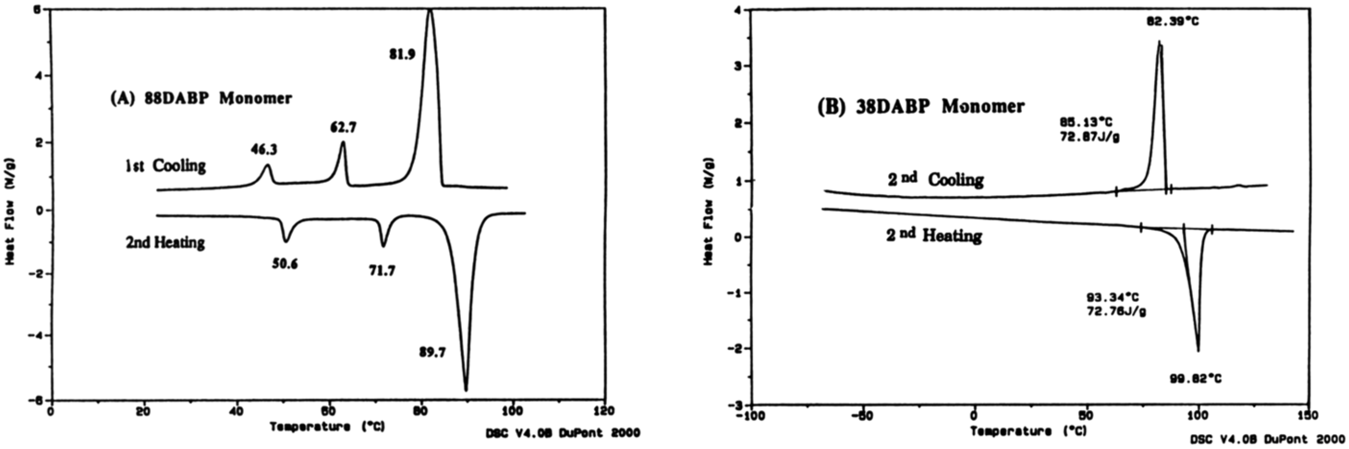

Figure 6. DSC thermograms of (A) 8-8DABP and (B) 3-8DABP monomers. The scanning rates were 15 °C/min for 8-8DABP and 10 °C/min for 3-8DABP.

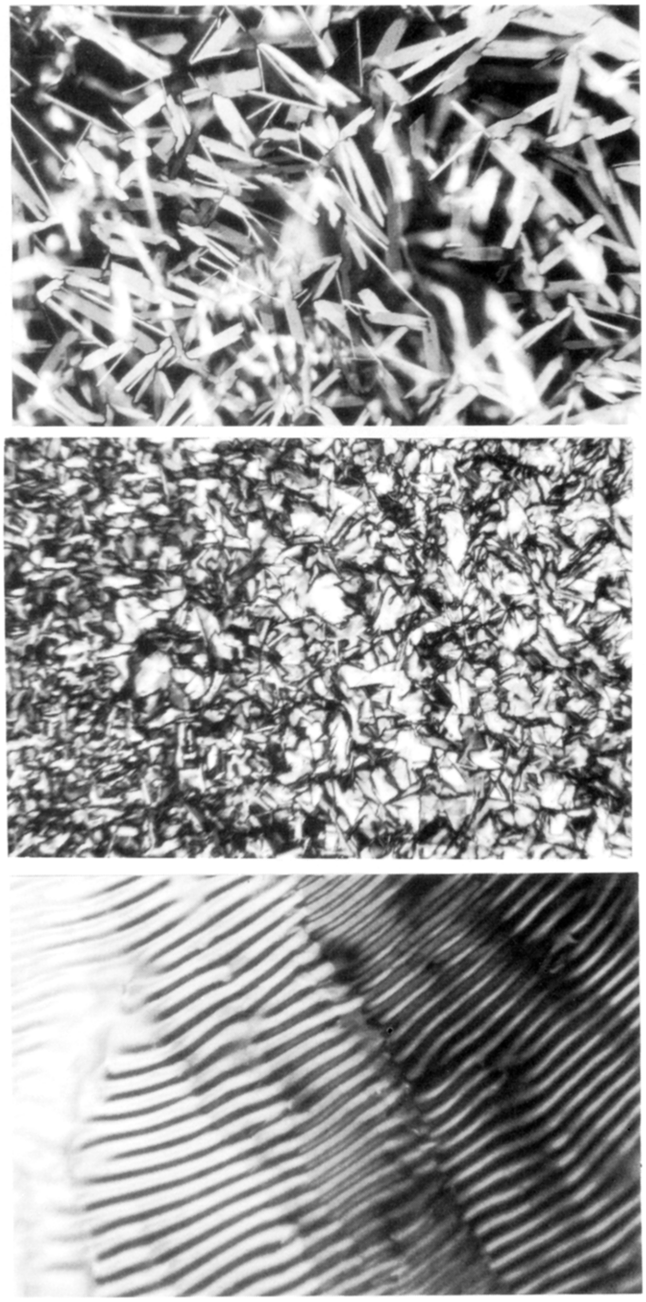

Figure 7. Optical micrographs of (A, top) 8-8DABP monomer at 82 °C (100×), (B, middle) 8-8DABP monomer at 55 °C (75×), and (C, bottom) 3-8DABP monomer at 80 °C (75×).

found in some highly reactive diacetylenes,[27] but it was not of interest because its occurrence was found to be a thermal effect induced by the laser beam. In our case, the ability of diacetylenes to undergo polymerization initiated by the visible (red) laser light without the aid of a doping photosensitizer is interesting and could be very useful. This ability should allow a more convenient and controllable polymerization method for this diacetylene, as compared to the limited penetration of UV light and the restricted accessibility of a γ-ray source.

Raman spectra of the 3-8DABP monomer powder and the partially polymerized sample (UV 2.5 hr, pink in color) are shown in Figure 4. Unlike in 8-8DABP, the laser beam did not polymerize the sample and a strong resonance effect was not observed in 3-8DABP, resulting in the low-intensity peaks with a large beam background around 1800–2200 cm^{-1}. The 3-8DABP monomer spectrum showed a strong ν(C≡C) peak at 2261 cm^{-1}. Although the partially polymerized sample still contained a large portion of monomer as seen from the remaining large peak at 2261 cm^{-1}, the polymerization can be followed by the ν(C═C) peak of the PDA backbone at 1488 cm^{-1}. The polymer ν(C≡C) peak (at about 2100 cm^{-1}) was not observed since it was buried in the background.

WAXD of 8-8DABP Polymer. Figure 9 shows a WAXD pattern of 8-8DABP polymer at room temperature. The similarity between this pattern and its monomer pattern in crystalline state (Figure 8A) further confirms a topochemical mechanism. Only a small lattice displacement occurs during the polymerization so that the unit cell and the symmetry of the newly created polymer are very similar to those of its monomer. The d_{001} of the polymer pattern, about 4.9 Å, corresponds to the repeat along the chain axis.[30]

Polymerization in the Liquid-Crystalline States. During X-ray scanning we found that 8-8DABP monomer was polymerized by the X-ray beam (as visualized from the color change from white to dark blue) at 55 °C. This demonstrates that the monomer can be polymerized in the LC phase (S_G or S_H). This was confirmed when we

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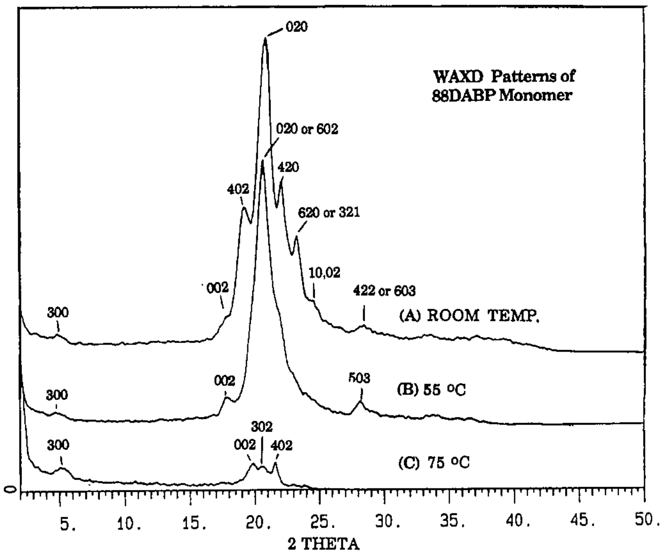

Figure 8. Powder WAXD patterns of the 8-8DABP monomer at (A) room temperature (ca. 20 °C), (B) 55 °C, and (C) 75 °C.

found its color quickly changed from colorless to purple and then deep red (maroon) upon UV irradiation of a monomer film at about 55 °C. The polymerized film showed a purple color at room temperature and a reversible thermochromic behavior (color changes between purple ↔ deep red ↔ orange), similar to that found in the films polymerized at room temperature. The polymerizability in the LC state suggested that the incorporated mesogenic group and the alkyl spacers can maintain a sufficient packing order of the diacetylene molecules to allow the diacetylene groups to undergo polymerization. The fact that the packing order within the smectic layers of smectic liquid crystals is normally observed in WAXD patterns, as strong and sharp peak(s), at d spacings of 4–5 Å ($2\theta \approx$ 18–20)[22b] and the known packing distance of many reactive diacetylenes is also around 4.5–5.0 Å,[31] it should not be so surprising that a liquid-crystalline diacetylene monomer can be polymerized in the high-ordered smectic state.

Conclusions

The synthesized m-nDABP monomers ($n = 8$ and $m =$ 3 and 8) showed liquid-crystalline state(s) at elevated temperatures and were polymerizable by radiation. The chemical structure of the side group (i.e., the outer spacer length, m) had an influence on the polymerizability of the monomers. The longer and even spacer length ($m = 8$) provides a higher reactivity than that of the shorter and odd spacer length ($m = 3$).

8-8DABP has an unusual property. It can be polymerized by a red laser beam ($\lambda = 750.7$ nm). This should allow a practical and controllable method of polymerizing this kind of diacetylene. 8-8DABP can also undergo polymerization in the liquid crystalline phase (S_G or S_H).

The above suggested that m-nDABP monomer, i.e., 8-8DABP, can have all the properties needed for producing a molecular composite system. The resulting (polymerized) product should behave like a molecular composite, the polydiacetylene chains providing the rigid molecular "fibers" while the mesogenic groups and the alkyl spacers provide the flexibility and impact resistance. Thus this polymer could be utilized as an engineering material with a unique mix of mechanical properties.

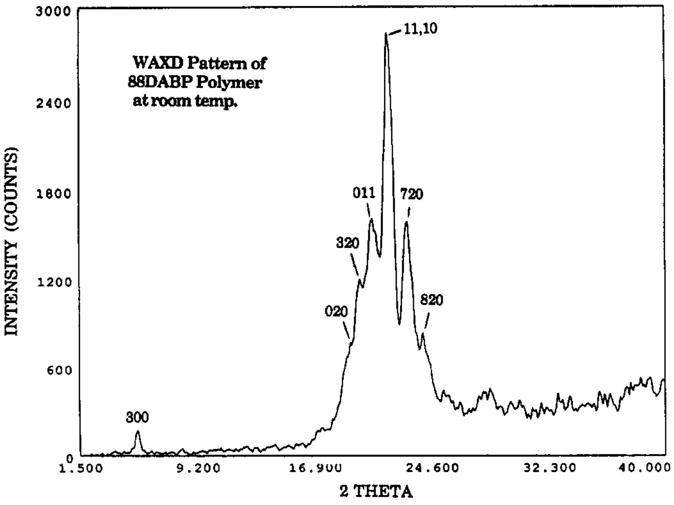

Figure 9. Powder WAXD pattern of the polymerized 8-8DABP at room temperature.

The observed reversible thermochromic and mechanochromic transitions in 8-8DABP polymer also suggest other possible applications of this material as thermal and nanostress sensors.

Since it has been known that the alkyl-functionalized diacetylene monomers do not polymerize in an isotropic state and are soluble in many common solvents,[32] this will facilitate the processing of MCs, since the monomers can be processed from solution or the melt. Various forms and shapes can be preformed in either an isotropic or a liquid-crystalline state before the in situ polymerization in the crystalline or liquid-crystalline state.

Further studies of the polymerization behavior of the monomers (polymerization in different ordered states and polymerization by a visible laser light) and the chromic transitions of their polymers are underway. Studies of the physical and mechanical properties of these polymers as a function of spacer length and mesogen type are planned.

Acknowledgment. We gratefully acknowledge Prof. Stephen Cheng from the University of Akron for providing the WAXD spectrometer equipped with temperature controller and Prof. Hatsuo Ishida from Case Western Reserve University for providing the Raman spectrometer for this study. This research was supported by the Center for Molecular and Microstructure of Composites (CMMC), a National Science Foundation State/industry/university Cooperative Research Center. Special thanks are also given to the Thai government for financial support of S.A. under a DPST scholarship.

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