Macromolecules

Volume 28, Number 4 February 13, 1995

Synthesis and Characterization of New Mesogenic Diacetylene Monomers and Their Polymers

Paula T. Hammond and Michael F. Rubner*

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received July 7, 1994; Revised Manuscript Received September 23, 1994®

ABSTRACT: Three functionalized semirigid aromatic thermotropic diacetylene liquid crystals were prepared: an aromatic diacid containing tetramethylene spacers on either side of the diacetylene group (5,7DODBA) and aromatic diols with four and nine methylene spacers (5,7DHDP and 10,12DHDP). This paper addresses the design and synthesis of the monomers, their liquid crystalline behavior, and the reactivity of their diacetylene groups. 5,7DODBA and 5,7DHDP each exhibited smectic phases. For the 5,7DODBA diacid, in particular, hydrogen bonding is thought to play a significant role in the mesogenic behavior and the high stability of the mesophase. The mesogenic nature of 10,12DHDP was inconclusive, though a liquid crystalline phase may exist within a narrow temperature range. Each of the monomers was photoreactive, producing deeply colored, conjugated poly(diacetylene) chains via topochemical polymerization upon exposure to UV or electron beam irradiation. The degree of reactivity in the solid state was much greater for the 10,12DHDP monomer than for the 5,7 monomers due to the added flexibility of the longer methylene spacer. On the other hand, thermally induced liquid-state polymerization appeared to be much faster in 5,7-DHDP and 5,7-DODBA, due perhaps to the more rigid nature of these molecules in the melt. Polymers obtained from the liquid crystalline monomers are poly(diacetylenes) with functionalized mesogenic side chains. The partially polymerized diacetylene of 10,12DHDP monomer exhibited clear mesogenic melt behavior based on thermal analysis, optical microscopy, and wide-angle X-ray diffraction.

Introduction

Diacetylene liquid crystals make up an exciting and relatively new class of optical materials well suited to molecular design. Conjugated poly(diacetylene) chains are the products of the solid-state, topochemical reaction of a diacetylene-containing compound or diacetylene groups incorporated into the repeat unit of a linear polymer.[1] The creation of liquid crystalline diacetylene monomers and macromonomers has just begun in the last decade,[2-9] with particular emphasis on optimization of the nonlinear optical properties of the conjugated poly(diacetylene) chains formed upon polymerization. The potential to control the orientation of diacetylene monomers in the liquid crystalline state and induce topochemical diacetylene polymerization in the ordered phase could present a means of producing highly oriented poly(diacetylene) materials with anisotropic linear and nonlinear optical properties. In addition, there are several as yet unexplored aspects of the chromic nature of mesogenic poly(diacetylene) chains which may lead to important applications such as temperature sensors or temperature-controlled optical filters. It is well known that poly(diacetylene) chains often undergo dramatic color changes in response to changes in temperature[10,11] and mechanical stress;[12] these chromic effects are usually associated with conformational changes of the polymer side chains.[13]

The schematic in Figure 1 presents the topochemical polymerization of a semirigid mesogenic diacetylene monomer. When the liquid crystalline diacetylene polymerizes, a poly(diacetylene) with mesogenic side chains is created. It is reasonable to believe that the conformation of the poly(diacetylene) backbone and its side chains must be greatly affected by the mesogenic transitions of the polymer or the host monomeric matrix in which the polymer resides. These conformational changes can in turn trigger chromic changes. For these reasons, the multiphasic behavior of liquid crystals provides an ideal host environment for the expression of conformationally induced thermochromic behavior at precise temperature ranges determined by liquid crystalline transitions.

® Abstract published in *Advance ACS Abstracts,* November 15, 1994.

0024-9297/95/2228-0795$09.00/0

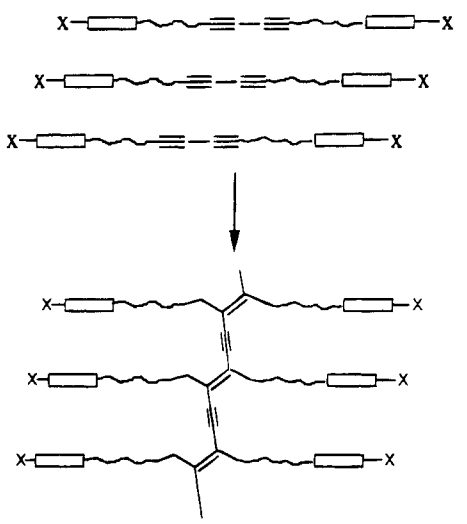

Figure 1. Schematic illustrating design and polymerization of diacetylene-containing functionalized monomers. Rectangle indicates rigid portion of molecule, squiggled line indicates flexible spacer, and X indicates functional group.

In this series of investigations, we attempt for the first time to control the chromic behavior of poly(diacetylene) chains using these concepts of molecular and supermolecular design. Continued development of these poly(diacetylene) systems should lead to the more complete exploitation of chromic behavior in poly(diacetylenes) for device applications. The results from the studies described here also contribute to the general field of knowledge on liquid crystal diacetylenes.

In this paper, the design and syntheses of diol and dicarboxylic acid functionalized mesogens are described. These functionalities allow the exploration of hydrogen-bonded liquid crystalline diacetylenes and open the opportunity for further functionalization of the monomers or their poly(diacetylenes). For example, a diacid-functionalized poly(diacetylene) might be cross-linked using diamines or diols, or a diol-terminated diacetylene could be used as a monomer for a polycondensation. In fact, a second paper addresses the properties of liquid crystalline polyester–diacetylenes formed from the polycondensation of the diacetylene monomers with aromatic comonomers.[14] Finally, the thermochromic behavior of the monomer and polyester systems will be discussed in a third paper.[15]

Experimental Section

Synthetic Methods. The basic synthetic routes of the diacetylene diacid and diol compounds are shown in Figure 2. The detailed synthetic procedures and analyses are described below. Each of the monomers was characterized using Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance spectroscopy (^{1}H NMR). Elemental analyses on new compounds were performed by Schwarzkopf analytical laboratories. Melting points and thermal behavior of the three aromatic diacetylene monomer products are discussed in detail in the Results and Discussion.

5,7-Dodecadiyne-1,12-diol. This compound was prepared using the method of Hay.[16] Tetramethyleneethylenediamine (2.4 mL, 0.015 mol) and CuCl (2.0 g, 0.02 mol) were dissolved in 100 mL of methanol. The solution was stirred as oxygen was bubbled into the container. 5-Hexyn-1-ol (20 g, 0.2 mol) was added dropwise to the solution over a period of 30 min, and the solution was allowed to stir at room temperature overnight. It was then acidified with 5 N HCl to a pH of 1, diluted with a small amount of water, and extracted with diethyl ether repeatedly. The resulting organic phase was dried over $MgSO_4$, filtered, concentrated, and vacuum dried to yield a white crystalline solid. The diol was recrystallized 1–2 times in diethyl ether at 0 °C. Melting point: 49–50 °C. Yields ranged from 75 to 90%.

1,12-Dibromo-5,7-dodecadiyne. Phosphorus tribromide (2.05 mL, 0.0216 mol) was added dropwise under nitrogen to a stirred slurry of 5,7-dodecadiyne-1,12-diol (3.5 g, 0.0180 mol) in 80 mL of benzene. An ice water bath was used to maintain the temperature at 0 °C; the reaction mixture was allowed to warm to room temperature during the course of the reaction. The mixture was allowed to stir for 3 days to obtain optimal yield. The reaction solution was extracted using water and diethyl ether. After drying the organic phase over $MgSO_4$ and concentrating the liquid with a rotary evaporator to obtain a clear yellow oil, the oil was redissolved in benzene, passed through a silica gel plug, and reconcentrated. The resulting pale amber oil was then dried under high vacuum overnight to remove residual solvent. Yield: 3.9 g, 67%.

4,4′-(5,7-Dodecadiyn-1,12-diyldioxy)dibenzoic Acid (5,7-DODBA). The 5,7DODBA diacetylene diacid was synthesized by directly reacting the potassium salt of *p*-hydroxybenzoic acid with 1,12-dibromo-5,7-dodecadiyne. The dibromodiacetylene (4.0 g, 0.0125 mol) was dissolved in 80 mL of dimethylformamide in a round bottom flask fitted with a water-cooled condenser. An aqueous solution of hydroxybenzoic acid (3.09 g, 0.02750 mol; 10% molar excess) and potassium hydroxide (3.09 g, 0.0550 mol) was prepared using 40 mL of water to maintain a DMF:H_2O ratio of 2:1. The potassium salt was added dropwise to the DMF reaction solution. The solution was heated to a light reflux for 8 h and then allowed to stir overnight at room temperature. The water/DMF solvent was concentrated, and the resulting white paste was dissolved in water and acidified using concentrated HCl. The precipitated product was purified by recrystallization in chloroform. Yield was approximately 50%. Purity of the 5,7DODBA is estimated to be 91–93%, based on elemental analysis, which indicated the presence of bromine. The bromine is thought to come from approximately 3% residual potassium bromide salt; the remainder of the impurity is thought to be monosubstituted byproduct. ^{1}H NMR (THF-*d*) and FTIR verified the structure of the diacid. The presence of impurities is anticipated to have lowered the melting point of the 5,7DODBA monomer; however, it is believed that the overall thermodynamic behavior and diacetylene reactivity of 5,7DODBA were not greatly affected by its level of purity. Thermal and optical observations were quite similar from batch to batch, including a small batch of diacid obtained from an alternate synthetic route involving the saponification of the diacetylene benzoate diester. FTIR (cm^{-1}): 2949.53 (m), 2600 (w), 2700 (w), 1682.14 (s), 1606.91 (s), 1514 (m), 1429, 1254, 1167, 1104.39 (w), 850, 770.

1,12-Bis(4-hydroxyphenoxy)-5,7-dodecadiyne (5,7DHDP). Seventy-five milliliters of dry, deaerated 95% ethanol (with 5% methanol, i.e., denatured alcohol) was added to a round bottom flask under nitrogen. A catalytic amount of sodium hydrosulfite (0.05 g) and 10 times molar excess of hydroquinone (10.3125 g, 0.094 mol) were added and dissolved. 1,12-Dibromo-5,7-dodecadiyne (3.0 g, 0.0094 mol) was added, and the solution was heated to reflux. A solution of potassium hydroxide (1.578 g, 0.028 mol) in 20 mL of dry, deaerated 95% ethanol was then added dropwise. The resulting cloudy solution was refluxed for 4 h and allowed to stir at room temperature overnight. The reaction solution was then acidified with 33% sulfuric acid solution to a pH of 1.0. The resulting slurry was reheated to reflux temperature, and the reaction solution was hot filtered and rinsed many times with hot 95% ethanol. The filtrate was concentrated to a thick white paste, which was washed with warm water and then recrystallized in 95% ethanol. Estimated purity is approximately 98% from NMR and elemental analysis. Yield was 30%. FTIR: 3345 (br), 2952 (m), 1600 (w), 1514 (s), 1239 (s), 1103 (m), 1057 (m), 955 (m), 824 (m).

10,12-Docosadiyne-1,22-diol. 10-Undecyn-1-ol (15 g, 0.089 mol) was coupled to produce a diol using the same Hay oxidative coupling procedure as that described for 5,7-dodecadiyne-1,12-diol. A white crystalline powder is formed which

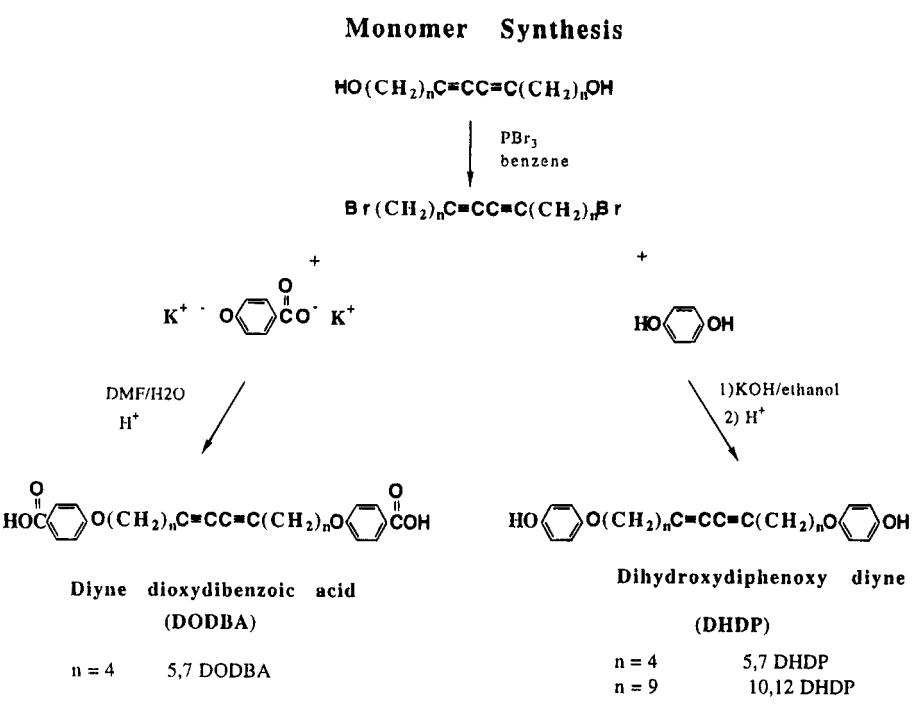

Figure 2. Synthetic routes of diacetylene-containing functionalized monomers.

turns light blue under UV irradiation. Yield was 87%. The melting point was 80–82 °C.

1,22-Dibromo-10,12-docosadiyne. 10,12-Docosadiyne-1,-22-diol (6 g, 0.018 mol) was brominated using phosphorus tribromide in the same procedure as that described for 1,12-dibromo-5,7-dodecadiyne. The product was a waxy solid/viscous liquid at or near its melting point at room temperature. The yield was 97%.

1,22-Bis(4-hydroxyphenoxy)-10,12-docosadiyne (10,-12DHDP). The 1,22-dihydroxy-10,12-docosadiyne was synthesized from 1,22-dibromo-10,12-docosadiyne (5 g) and excess hydroquinone using the same procedure described for the 5,-7DHDP. A very light reflux was used due to the high diacetylene reactivity of the starting material and the product. The reflux was continued overnight (12 h), and the reaction was allowed to stir at room temperature for another 24 h. A white powder was produced after recrystallization in 95% ethanol. Estimated purity is approximately 98% as calculated from NMR and elemental analysis. The yield was 63%. FTIR (cm^{-1}): 3400 (br), 2932 (s), 2851 (s), 1513 (s), 1233 (m, br), 826 (m), 768 (m).

Thermal Analysis Techniques. Differential scanning calorimetry experiments were conducted using a Perkin-Elmer DSC 7 thermal analyzer calibrated with an indium standard. A 20 °C/min heating rate was used, and a nitrogen purge was maintained over the samples at all times. Transition temperatures were taken from the maximum points on the endotherms. Enthalpies were measured using DSC 7 software to measure areas under the endotherms, and transition entropies were determined by dividing the enthalpy by the transition temperature. Thermogravimetric analysis was performed using a Seiko TG/DTA to obtain weight loss as a function of temperature for degradation and stability studies at a heating rate of 20 °C/min under a dry nitrogen purge.

Optical Microscopy. Optical microscopy studies were performed on a Zeiss optical microscope equipped with crossed polarizers and a Mettler FP-80 hot stage. Samples were prepared by placing thin films or solid powder samples onto a glass slide and adding a coverslip or a second glass slide.

X-ray Diffraction Measurements. Wide-angle X-ray diffractograms were obtained with a Rigaku 300 X-ray generator with a rotating anode, adjustable pole figure goniometer, and diffractometer. The generator was operated at 50 V and 60 or 200 mA unless otherwise specified. Ni-filtered Cu Kα radiation (1.54 Å) was used. The typical sampling interval was 0.05°, and the scan rates varied from 2 to 5°/min. Powder samples were prepared with a small quantity of powder sample and a nondiffractive binder solution on glass slides; these samples were examined in X-ray reflection mode. Most of the diacetylene-containing monomers exhibited slight color changes when exposed to X-rays; however, the solubility of materials exposed to X-rays for these time periods did not change significantly, indicating only low extents of polymerization.

Irradiation Methods. The as-synthesized powders of the monomers were irradiated with an electron beam from a Van de Graff accelerator operated at 2.6 MeV. The accelerator is located at the M.I.T. High Voltage Research Laboratory. Dosages of up to 100 Mrad were administered in intervals of 10–20 Mrad to prevent overheating of the samples. The materials were contained in polyethylene vials during irradiation. Ultraviolet irradiation was carried out by placing thin films of monomer under an ultraviolet lamp for varying amounts of time.

Results and Discussion

Monomer Design and Synthesis. The compounds synthesized in this study include 4,4′-(5,7-dodecadiynediyl-1,12-dioxy)dibenzoic acid (5,7DODBA), 1,12-bis(4-hydroxyphenoxy)-5,7-dodecadiyne (5,7DHDP), and 1,22-bis(4-hydroxyphenoxy)-10,12-docosadiyne (10,12DHDP). The chemical structures of these monomers are shown as structures I, II, and III, respectively.

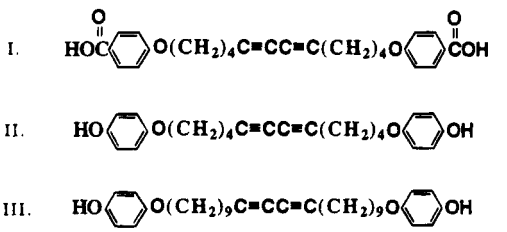

Figure 1 illustrates the general design of these diacetylene monomers, as well as the resulting conjugated poly(diacetylene) chain with mesogenic side chains that is expected upon polymerization of the diacetylene group. Each molecule contains a reactive diacetylene group at its center, which can undergo solid (i.e., condensed) state polymerization to a form a poly-

Table 1. Phase Transitions for Diacetylene Monomers from First Heating[a]

monomer	transitions
5,7DODBA	K (113 °C) LC (196 °C) I
5,7DHDP	K (138 °C) LC (153 °C) I
10,12DHDP	K1 (75 °C) K2 or LC (96 °C) I

[a] K = crystal, LC = liquid crystal, I = isotropic.

Table 2. Diacetylene Monomer Heats of Transition from DSC

monomer	T(K–LC) (°C)	enthalpy (kJ mol^{-1})	entropy (kJ mol^{-1} K^{-1})
5,7DODBA	113	7	0.018
5,7DHDP	138	29	0.065
10,12DHDP	75	8	0.022
monomer	T(LC–I) (°C)	enthalpy (kJ mol^{-1})	entropy (kJ mol^{-1} K^{-1})
5,7DODBA	196	11	0.024
5,7DHDP	153	27	0.059
10,12DHDP	96	36	0.098

(diacetylene) chain. To obtain mesogenic melt behavior, aromatic phenoxy groups were added to either end, introducing a semirigid nature to the monomers. The aliphatic spacer groups surrounding the diacetylene group in these centrosymmetric molecules serve two functions. The flexibility of the spacer allows the mobility necessary for the diacetylene groups to order into a lattice which is conducive with solid-state topochemical polymerization. This added mobility also lowers the transition temperatures, allowing the exhibition of liquid crystalline characteristics at temperatures below that of thermal degradation. Finally, the aromatic rings are functionalized with hydroxy or carboxylic acid groups so that they can be polymerized with difunctional aromatic comonomers to obtain mesogenic diacetylene-containing polyesters.[14]

Characterization of Monomers. Table 1 contains the transition temperatures of the three diacetylenic monomers examined in this study as obtained from the first heating. The transition enthalpies and entropies of each of these monomers are found in Table 2. As indicated, each of the monomers exhibits some form of mesogenic behavior, although liquid crystalline phases are more evident for 5,7DODBA and 5,7DHDP than for 10,12DHDP, as will be discussed shortly. Characterization of the monomers involved thermal analysis, optical microscopy, and X-ray diffraction; in cases in which the liquid crystalline phases are not easily identifiable, only general statements are made concerning the nature of the mesophase.

5,7DODBA. 5,7DODBA, an aromatic diacid with four methylene spacers surrounding the diacetylene group, exhibits an enantiotropic liquid crystalline phase over a wide temperature range from 113 to 200 °C. The first and second heating and cooling DSC thermograms of this material are shown in Figure 3. The first broad endotherm at 113 °C marks a transition from the crystalline to liquid crystalline state. When the as-prepared 5,7DODBA monomer powder is placed between a glass slide and a coverslip and heated, the powder melts to form a translucent, shearable, and highly viscous film between the glass substrates, and a complex, fine texture is observed. Upon heating beyond the small 130 °C endotherm, which appears to be the result of melting of a second crystalline form, the optical field brightens as more of this fine texture is seen. The melt has a sticky, gel-like consistency and can be

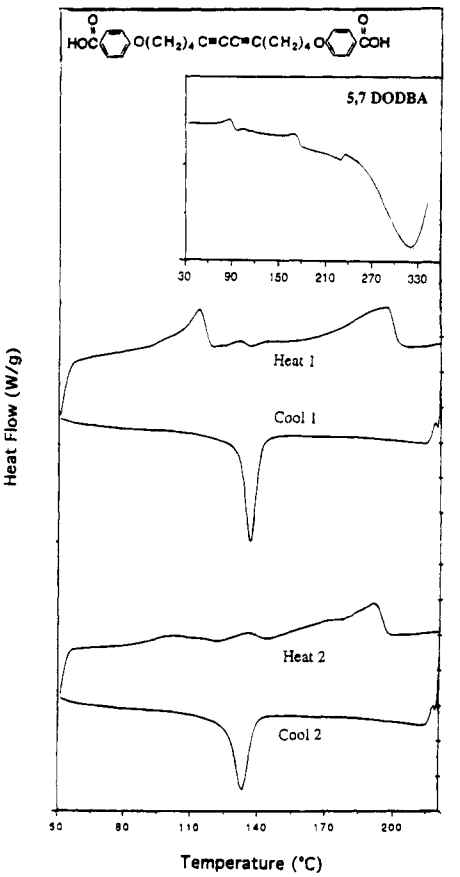

Figure 3. DSC thermal cycles of 5,7DODBA (endotherm peaks up); inset shows high-temperature DSC thermogram.

sheared in the liquid crystalline state to produce aligned birefringent regions. A large and broad endotherm corresponding to the clearing transition is observed at 196 °C. The isotropization enthalpy of 5,7DODBA (see Table 2) falls close to the range of clearing enthalpies for dimerized *p-n*-alkoxybenzoic acids, which vary from 8 to 12 kJ/mol.[17] The broad shape of the transition endotherms of the monomers discussed in this paper is thought to be due to the presence of a range of hydrogen-bonding strengths between the functional groups. A DSC thermogram of 5,7DODBA taken to 350 °C is shown in the inset in Figure 3. The small endotherm at 250 °C is believed to be due to an endothermic degradation process. The large exotherm at 326 °C is associated with large-scale thermally induced polymerization of the diacetylene groups, coupled with degradation of the monomer. Similar exotherms were observed for each of the monomers and will be discussed further in a following section on diacetylene monomer polymerization.

The first cooling curve indicates an exothermic transition from the isotropic to the liquid crystalline state at 135 °C. This transition is highly supercooled, suggesting a high-viscosity melt. When cooled from 200 °C, batonnets begin to form at approximately 140–135 °C (see Figure 4a); this temperature coincides with the exotherm in the cooling curve of 5,7-DODBA. The batonnets begin to coalesce into larger domains with plate and fanlike focal conic regions as shown in Figure 4b. The batonnets and focal conic fans are characteristic of a smectic A phase, which is often observed in dimerized carboxylic acid liquid crystals. Upon further cooling, no recrystallization endotherm is produced, and optical microscopy indicates the presence of the liquid crystalline texture near room temperature. Apparently,

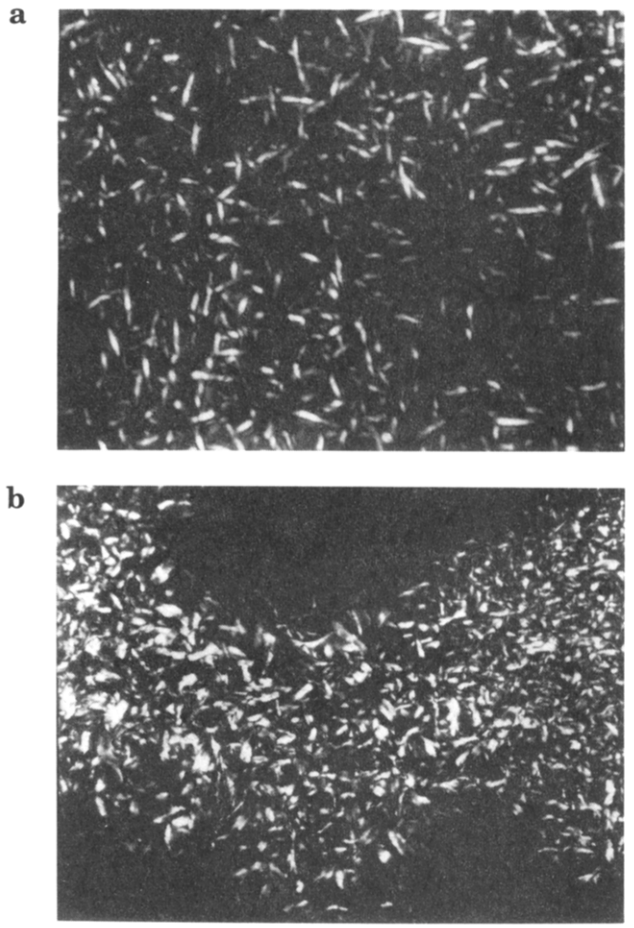

Figure 4. (a) Batonnets formed on cooling from isotropic phase (200 °C) of 5,7DODBA to 120 °C (1600 magnification, crossed polarizers). (b) Coalescence of batonnets of 5,7DODBA cooled to 67 °C (800 magnification).

the liquid crystalline ordering becomes substantially quenched in at lower temperatures, probably due to the kinetic effects of recrystallization from the viscous smectic mesophase. An example of similar kinetic effects was found in a study by Schen, who reported a cyanobiphenyl-substituted diacetylene which would not recrystallize unless reheated from room temperature, at which point recrystallization occurred at 39 °C.[18]

The second heating of 5,7DODBA indicated a large decrease in the area of the original melting endotherm, due in part to the incomplete recrystallization of the monomer. However, it is notable that the small endotherm at 130 °C has increased in size from about 1.2 to 2.6 kJ/mol and that a shoulder from 145 to 180 °C has appeared along the side of the clearing endotherm. The 5,7DODBA monomer is polymorphic, and some of the recrystallization that does occur during the cooling process or during the second heating cycle apparently results in more stable solid-state forms that melt at higher temperatures. The conclusions drawn from DSC results are confirmed by microscopic observations. A second heating does not produce a truly shearable melt until 165 °C, and a third heating results in even higher observed melting temperatures. Another potential cause of the decreased melt enthalpy and higher melt temperatures observed in subsequent heat cycles could be thermally induced polymerization of the diacetylene groups in the liquid crystalline state during each thermal cycle. Slight color changes in the samples after heating indicate that a small degree of polymerization may have taken place during the experiment.

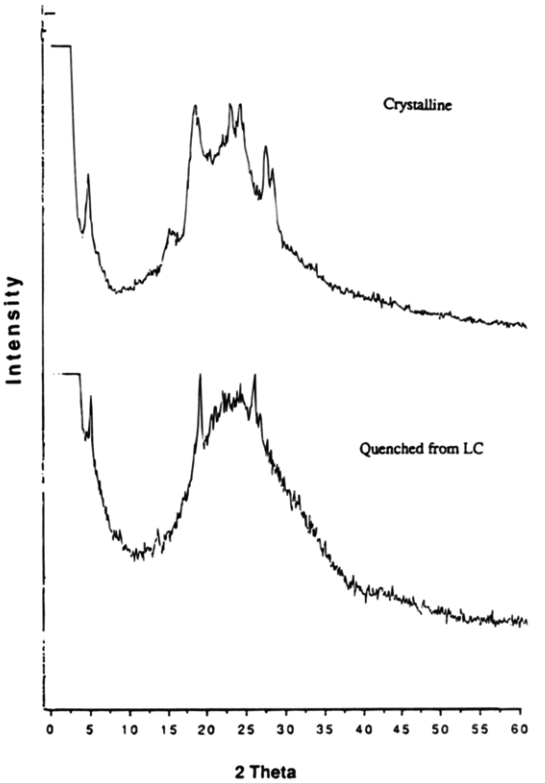

Figure 5. Wide-angle X-ray diffraction pattern of 5,7DODBA: (top) crystalline; (bottom) quenched state.

As mentioned earlier, the liquid crystallinity of 5,7DODBA is believed to be facilitated by hydrogen bonding of the carboxylic acid groups. In fact, it is well known that the liquid crystallinity of the fairly simple *p-n*-alkoxybenzoic acids is due to the dimerization of the carboxylic acid groups to form a rigid mesogenic core. When the alkyl groups of these acids contain six or more methylene groups, a smectic phase is exhibited at melt temperature ranging from 85 to 102 °C.[17] The smectic phase of 5,7DODBA is especially stable, probably due to its ability to dimerize on both ends of the molecule. A material that more closely resembles 5,7DODBA is an aromatic diacid with simply 12 methylene spacers in place of the tetramethylene/diacetylene/tetramethylene spacer. This compound is reported to melt at approximately 250 °C, and there is no mention of a liquid crystalline phase.[19] It should be noted here that the melting point of the 5,7DODBA monomer is expected to have been slightly lowered by the presence of impurities that were difficult to remove; however, impurity does not account for the over 130 °C difference in melting point between these two compounds. The presence of the diacetylene group in the center of the DODBA molecule seems to have a strong influence on the melt behavior and mesogenic nature of the diacid.

Wide-angle X-ray diffraction was used to verify the existence of a liquid crystalline phase as well as to further understand the ordering of the 5,7DODBA crystalline form. The diffractogram of 5,7DODBA in the solid state, shown at the top of Figure 5, contains several strong peaks situated atop a broad halo. The breadth of the peaks is large, indicating that the size of the crystals is quite small. Although the diacid is crystalline, there is a large amount of disordered material present in the monomer, judging from the diffuse halo at the base of the peaks. The peak at low angle corresponds to a *d*-spacing of approximately 16 Å and is most probably a second-order reflection. The esti-

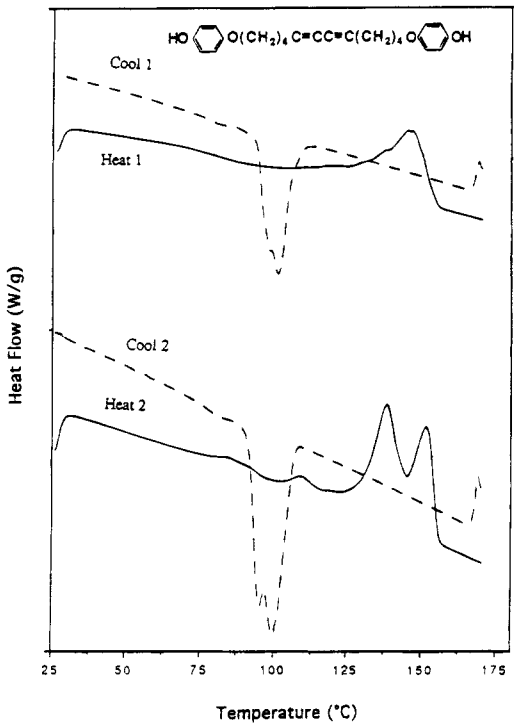

Figure 6. DSC thermal cycles of 5,7DHDP monomer.

mated fully extended length of a single DODBA molecule is 29 Å based on a computer model (Molecular Simulations Quanta Program); therefore it appears that in its predominant crystalline state, the diacid molecule is in its fully extended form. Although this cannot be confirmed without small-angle X-ray analysis, it seems a likely possibility, since the diacid can dimerize on both ends of the molecule. IR studies of the liquid crystalline melt of 5,7DODBA, which will be addressed in a subsequent paper,[15] indicate that hydrogen bonding is actually maintained in the smectic phase. Indeed, this phenomenon has been observed for the *n*-alkoxybenzoic acids; their liquid crystalline phases consist of dimerized acid molecules.

The liquid crystalline pattern of 5,7DODBA, shown in the bottom half of Figure 5, was obtained by heating a sample to 145 °C and quenching it in a dry ice/2-propanol bath. The resulting broad wide-angle halo and the sharp peak at smaller angle are typical of patterns seen for two-dimensional smectic phases such as smectic A or C. The spacing of the layers in the mesophase also correspond well to the extended length of the 5,7DODBA molecule, indicative of a smectic A phase with the molecular axis perpendicular to the smectic layers. The two peaks atop the amorphous halo suggest that some very regular interplanar or intermolecular spacing remains.

5,7DHDP. Figure 6 contains the heat/cool thermal cycles for the 5,7DHDP monomer, which has diol functional groups in place of the carboxylic acid groups of 5,7DODBA. In the first heating, 5,7DHDP monomer exhibits only one broad endotherm at 145 °C with a slight shoulder at 130 °C. However, the second heating of 5,7DHDP in a heat/cool cycle reveals that it does, indeed, exhibit two large endotherms: a crystal to liquid crystal transition at 138 °C and an isotropic clearing point at 153 °C. There are also small endotherms at 85 and 110 °C corresponding to solid-state transitions of the monomer.

Cooling 5,7DHDP from the isotropic melt brings about the growth of a highly birefringent phase from 134 to

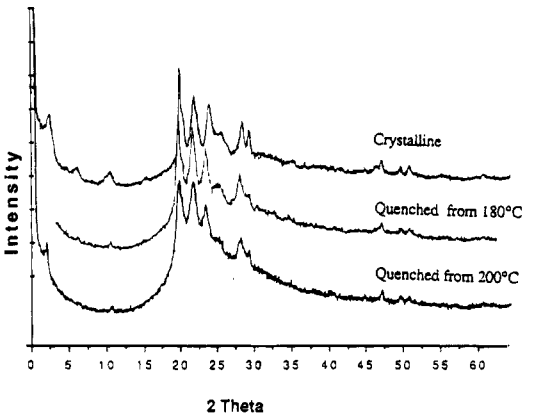

Figure 7. Wide-angle X-ray diffraction patterns of 5,7DHDP quenched in a dry ice/2-propanol bath from various temperatures.

129 °C. For reasons not fully understood at this time, there was no exotherm corresponding to the transition at 130 °C observed in the optical microscope. The DSC cooling curve has an exotherm at 100 °C, believed to be due to the transition to a second, metastable liquid crystalline phase. At this temperature, a platelike texture much like the threaded nematic mosaic textures found in some three-dimensional smectic phases such as F or I is found in regions of the monomer film. The first cooling peak is shouldered with a second peak at 95 °C, corresponding to recrystallization, as determined by optical microscopy. From these observations, it appears that the monomer exhibits a smectic phase from 138 to 153 °C upon heating; cooling from the isotropic melt results in the development of the original smectic at 130 °C, plus the appearance of a second monotropic smectic phase with a mosaic texture at 100 °C. The polymerization/degradation exotherm of 5,7DHDP occurs at 288 °C and has an enthalpy of 305 kJ/mol (not shown).

It is interesting to note here that 5,7DHDP, an aromatic diol with four methylene spacers on either side of the diacetylene group, has a melting point which is only slightly lower than a similar diphenoxy dihydroxy compound containing aliphatic spacers in place of the diacetylene group;[19] the latter compound was not reported to exhibit any liquid crystalline behavior. The similar melting points of the diol with and without the diacetylene is in contrast to the aromatic dicarboxylic acid, 5,7DODBA, for which the presence of the diacetylene moiety results in significantly lower melt temperatures and multiple melt behavior. This suggests that quite a different type of solid-state crystalline packing should be expected in 5,7DHDP versus 5,7DODBA. However, in both the cases of the diol and the diacid, the presence of the diacetylene group has facilitated the observation of liquid crystalline phases.

Although 5,7DHDP has a more thermally stable crystalline structure, its liquid crystalline phase is less stable, with only a 15–20 °C range of mesogenic behavior exhibited; this probably has to do with differences in the type of molecular packing and hydrogen bonding present in each of the two mesophases. Room temperature WAXD results of 5,7DHDP are shown in Figure 7. The diffraction peaks of 5,7DHDP are much sharper and narrower than those of 5,7DODBA, a sign that the 5,7DHDP sample contains larger crystallites, with more perfect crystalline ordering. The lower angle peaks of 5,7DHDP between 2 and 10° 2θ indicate spacings of 20.3, 11.9, and 7.8 Å. It is clear that by

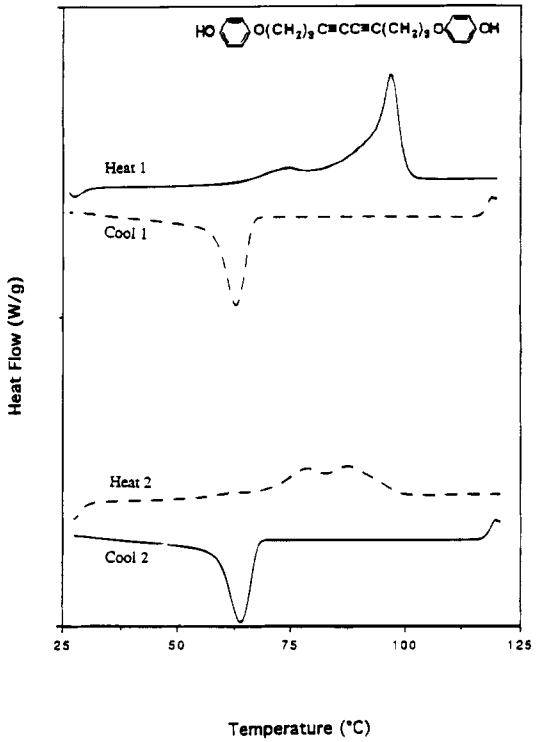

Figure 8. DSC thermal cycles of 10,12DHDP monomer.

comparison the lattice parameters of these two monomers are also quite different.

Quenching of the mesophase of 5,7DHDP proved quite difficult, and even when cooled from temperatures well above the clearing point by quenching in liquid nitrogen, the same crystalline pattern was often obtained, or only partial quenching was achieved, as shown in Figure 7. The relative sizes and the positions of the peaks between 15 and 25° 2θ change slightly upon quenching, indicating possible changes in the ordering of the monomer lattice. Given the optical microscopy and DSC results described above, there is evidence that 5,7DHDP exhibits one or more three-dimensional smectic phases.

10,12DHDP. As shown in Figure 8, two endotherms were found for the first heating of 10,12DHDP, the aromatic diol analog with nine flexible spacer units, at 75 and 96 °C. The second heating resulted in peaks at 80 and 90 °C. These peaks are listed in Table 1 as possible melting and isotropic clearing endotherms, although there is not enough evidence at this time to assert that this compound exhibits a true mesogenic phase. Like 5,7DHDP, when the monomer is melted in a capillary tube, it melts to form an opaque liquid at 75–80 °C and then clears to become an isotropic liquid at 90–96 °C. The enthalpy of the first endotherm is relatively small for a crystal to isotropic liquid transition but does fit into the high range of crystal to smectic phase transition enthalpies. Heat/cool DSC thermal cycles show that the compound exhibits two clearly defined transitions on heating and one visible transition exotherm at 65 °C on cooling. There is a third, smaller transition at 60 °C in the heating curves, which is probably a solid–solid transition. Optical microscopy indicates a complex, ill-defined birefringence between the two primary endotherms, which exists for a brief 10 deg range. Batonnets are seen at temperatures close to the clearing point. The temperature range in which the birefringent phase is present is small, and it is difficult to discern whether a shearable liquid crystalline phase or a recrystallization process is observed under the microscope. In any case, if a liquid crystalline phase does exist for 10,12DHDP, it is a relatively unstable one with a narrow temperature range. The polymerization/degradation exotherm of this compound appears at 337 °C.

Table 3. Relative Diacetylene Monomer Reactivities[a]

	thermal			UV	e-beam
monomer	LC state	isotropic liquid	solid state	solid state	solid state % (color) conv
5,7DODBA	moderate	high	low	low	low 25% (red)
5,7DHDP	moderate	high	low	low	moderate 40% (yellow)
10,12DHDP	low	low	moderate	very high	high 80% (purple)

[a] Based on observations of color change and thermal analysis.

Like 5,7DHDP, it was also difficult to quench the 10,12DHDP monomer at a temperature between its two endotherms. By heating to higher temperatures and quenching, a diffractogram which was thought to reflect the structure at midtransition was obtained (not shown). The original small-angle peak and its reflections at low angle (corresponding to d-spacings of 32.1, 16.7, 11.2, and 8.6 Å) nearly disappear. Peaks at high angles that were small and weak in the original monomer lattice appear to sharpen and increase slightly in intensity, and one or two new peaks appear as well (corresponding to d-spacings 1.0 and 1.6 Å). Like 5,7DHDP, this monomer may exhibit a three-dimensional smectic phase. A second possibility is the presence of a crystal–crystal phase transition.

Of the three monomers synthesized for this study, the diacid monomer, 5,7DODBA, exhibited a stable liquid crystalline phase over a wide temperature range, which existed at temperatures as high as 200 °C. The high degree of mesophase stability is thought to be due to the dimerization of hydrogen-bonded diacid molecules in the liquid crystalline phase. The two aromatic diol monomers exhibited very similar thermal behavior; in fact, the DSC thermograms for the two monomers differ primarily in the temperature range of the thermal transitions. For both cases, the liquid crystalline region was relatively small, and the clearing points were lower than in the diacid. Also, the mesophases of the diols appeared to be complex three-dimensional smectic phases rather than the simpler smectic A phase observed in 5,7DODBA.

Polymerization of Diacetylene Monomers. Relative Diacetylene Monomer Reactivities. Liquid crystalline diacetylenes may potentially undergo polymerization in one of at least three phases: the solid state, the liquid crystalline phase(s), and the isotropic liquid. Each mode of diacetylene polymerization is of interest. Solid-state polymerization frequently results in a poly(diacetylene) in the original or a slightly modified version of the monomer crystalline lattice. Polymerization in the mesogenic phase could allow the orientation of mesogens prior to polymerization, to produce highly aligned poly(diacetylenes) samples with anisotropic linear and nonlinear properties. Both liquid crystalline state and isotropic liquid state polymerizations often result in a noncrystalline poly(diacetylene). These methods are of interest for the formation of amorphous, optically clear poly(diacetylene) materials. Several researchers have reported the liquid and liquid crystalline state polymerization of diacetylenes to produce colored polymers, including Garito,[5] Schen,[8] and Tsibouklis et al.[9a] Table 3 gives a qualitative sense of

the relative reactivities observed for each of the aromatic diacetylene monomers. As with many diacetylene compounds, the DODBA and DHDP monomers were reactive in the liquid state as well as the solid state. During the thermal analysis and optical microscopy of these materials, observations were made of the relative reactivities of the monomers in both the liquid crystalline and isotropic liquid phases. Extensive kinetic studies have not yet been carried out on the monomers; however, preliminary observations do suggest some trends. One of the most obvious differences is the difference in liquid-state reactivities between the 5,7 monomers and 10,12DHDP.

When held in the liquid crystalline state for a few hours, 5,7DODBA gradually converts to a reddish orange poly(diacetylene) which is only partially soluble in acetone (a good solvent for the monomer). Infrared spectroscopy and thermogravimetry indicate that no significant chemical degradation occurs during polymerization in the mesophase; however, when heated in the isotropic liquid state above 200 °C, 5,7DODBA undergoes a fairly rapid polymerization to form viscous brown low conjugation length poly(diacetylene). It is possible that some portion of the isotropic state polymerization product is the result of 1,2 rather than 1,3 diacetylene polymerization or other cross-linking reactions. Like 5,7DODBA, the 5,7DHDP monomer is quite thermally reactive. In the liquid crystalline state, the monomer forms a gold-brown, nonbirefringent polymer after holding at 150 °C for 30 min to an hour. Polymerization takes place within 5–10 min in the isotropic liquid state.

On the other hand, the 10,12DHDP monomer is quite thermally stable above its melting point, and heated samples maintain the white color of the original monomer or turn a very faint, pale blue color after several hours at 80–100 °C. In short, the rate of polymerization of 10,12DHDP in the liquid state is apparently much slower than that of 5,7DHDP or 5,7DODBA. The only differences between the two DHDP monomers is the length of the aliphatic spacer. It thus appears that for the series of diacetylenes examined in this study, the shorter, less flexible molecules are much more thermally reactive. In studies of the *n*OBOA series of poly(diacetylenes), Schen et al.[8,18] conclude that monomers with a more rigid-rod character tend to maintain intermolecular correlations in the liquid state which facilitate polymerization of neighboring diacetylene groups. The large differences in liquid-state polymerization of the 5,7 monomers, which have four methylene spacer groups, versus 10,12DHDP with nine spacer groups confirm this observation.

Examination of Table 3 reveals that the comparative reactivities of the monomers are virtually reversed in the solid state; 10,12DHDP is far more reactive than 5,7DHDP and 5,7DODBA. It is noted here that conversion is best estimated using the monomer extraction method; however, the small sample sizes available precluded use of this method for the 5,7 monomers. It was found that for 10,12DHDP, the degree of conversion estimated from DSC measurements of the melt endotherm was quite close to that found from monomer extraction. The conversions listed in Table 3 were therefore calculated using DSC data. The longer length of 10,12DHDP apparently provided the flexibility needed to rearrange and thereby accommodate the formation of poly(diacetylene) chains. On the other hand, many diacetylenes exist in the literature that have just one, two, or four methylene spacers and are quite reactive.

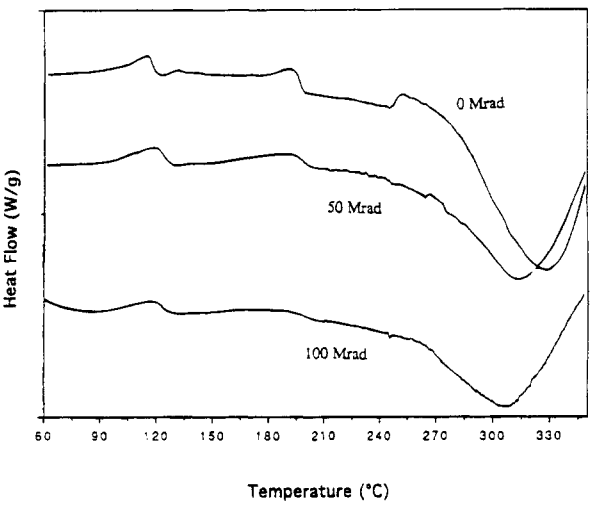

Figure 9. DSC of 5,7DODBA at increasing electron beam irradiation levels.

The increased spacer length therefore has some influence on the reactivity in these systems, but other factors must also be accounted for. For example, the distances between diacetylene groups and the angles of the monomer lattice have been found to be important parameters in diacetylene solid-state reactivity.[20] Finally, degree of conversion is undoubtedly affected by the perfection of the crystalline structure, which provides the alignment of diacetylene groups needed for solid-state reactivity. 5,7DODBA appears to have the smallest number of well-ordered crystalline regions, and it also displays the lowest conversion levels following electron beam irradiation. More detailed observations from solid-state polymerization will be discussed in the next section. Results from the preliminary characterizations of the resulting poly(diacetylenes) are also discussed below.

Poly(diacetylenes) from Solid-State Polymerization. Polymerization of 5,7DODBA. Thin solvent-cast samples of 5,7DODBA are transformed from white to deep pink upon exposure to ultraviolet irradiation for 6–8 h. The monomer turns a dark burgundy red color when electron beam irradiated at a dosage of 50–100 Mrads. The resulting partially polymerized solid is only partly soluble in tetrahydrofuran and acetone, solvents which easily dissolve the monomer. The effects of conversion due to electron beam initiated polymerization of 5,7DODBA can be observed from the DSC thermograms shown in Figure 9. The thermal characteristics of 5,7DODBA remained relatively unchanged at low electron beam dosages (<5 Mrad), and significant differences were only detected at very high levels of irradiation. The monomer exposed to 50 Mrad of irradiation shows an increase in the melting point of the monomer from 113 to 120 °C and from 120 to 122 °C in the 100 Mrad sample. This increase is due to the introduction of rigid conjugated polymer chains into the monomer crystal lattice.[21] The enthalpy of the melting endotherm has decreased relative to that of the fresh monomer; the decrease in enthalpy is due to a 20–25% degree of conversion of the monomer at 100 Mrad. These relatively low levels of conversion at very high radiation dosages indicate that the crystalline structure and/or order of 5,7DODBA is not completely conducive to solid-state polymerization.

The liquid crystalline to isotropic liquid transition is much more greatly affected by diacetylene polymerization. The clearing point broadens considerably, and it

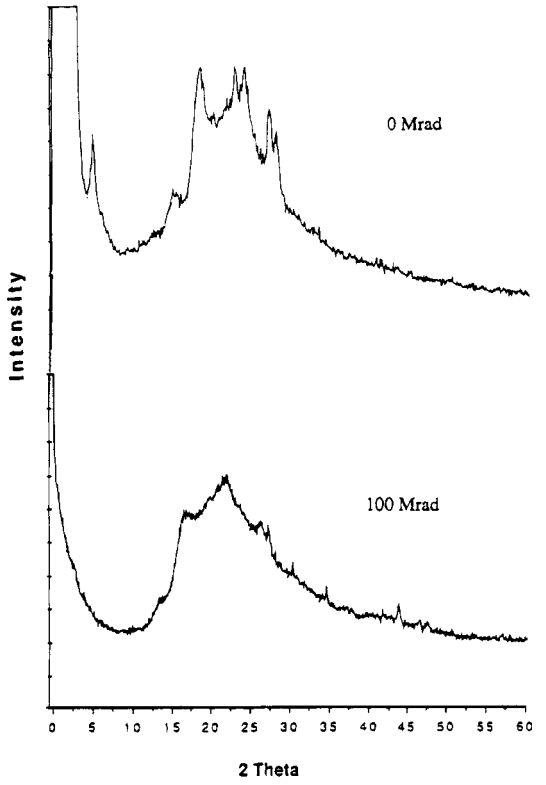

Figure 10. Wide-angle X-ray diffraction patterns of 5,7DODBA before (top) and after (bottom) 100 Mrad dosage irradiation.

appears from optical microscopy results that the partially polymerized monomer maintains liquid crystallinity up to temperatures 10 or 20 deg higher. This suggests an increase in the stability of the liquid crystalline phase. Polymer formation can stabilize the liquid crystalline phase in two possible ways: (1) the increased viscosity due to the presence of polymer chains can decrease the ease with which the residual monomer can achieve isotropic ordering and (2) the monomer converts to liquid crystalline oligomer or high polymer which reach isotropization at higher temperatures than the original monomer.

The large exotherm observed for the nonirradiated monomer at 326 °C is due to a combination of thermally induced polymerization of the diacetylene groups and an exothermic thermal degradation of the monomer, as noted earlier (see also inset, Figure 3). Thermogravimetric analysis indicates that a large weight loss of greater than 50% is associated with this exotherm. The enthalpy of the high-temperature exotherm decreases with irradiation, an indication that some portion of the exotherm is truly attributable to the polymerization of diacetylene units. Similar decreases in the size of the polymerization/degradation exotherm were observed for 5,7DHDP and 10,12DHDP as well. Thermograms for partially polymerized 5,7DODBA show no transitions characteristic of the poly-DODBA, and wide-angle X-ray diffraction data provide evidence that glassy amorphous poly(diacetylene) is formed when 5,7DODBA is polymerized, as shown in Figure 10. It is apparent that solid-state polymerization of 5,7DODBA yields a poly(diacetylene)/monomer mixture with very low levels of crystallinity. Assuming that the poly(diacetylene) is amorphous by nature, it is possible that the amorphous polymer transition may be hidden among the melting or clearing transitions of the residual monomer.

Although 5,7DODBA becomes disordered during the radiation process, the monomer produces a deeply colored red poly(diacetylene) of moderate conjugation length. Apparently, poly(diacetylene) chains are formed in localized ordered domains within the original monomer matrix. The visible absorption spectrum of lightly polymerized 5,7DODBA indicates a well-developed excitonic transition, which is characteristic of ordered poly(diacetylene) regions. A red amorphous poly(diacetylene) also has been produced by Schen via thermal polymerization of a monomer in the isotropic phase.[18]

Polymerization of 5,7DHDP. The 5,7DHDP monomer turns pale yellow when exposed to ultraviolet irradiation for several hours and yields a deep yellow-gold color when electron beam irradiated to 100 Mrad. Thermal analyses of 5,7DHDP at various levels of electron beam irradiation indicate a decrease in the transition enthalpies with increased irradiation, as was the case for 5,7DODBA. There is also a shift to lower monomer melt temperatures; this could be due to presence of poly(diacetylene) as an impurity in isolated monomer-rich domains. The conversion of the monomer, as estimated from the decrease of the melt enthalpy, is approximately 50%. There is no indication of the development of new polymeric peaks in the irradiated version of 5,7DHDP; wide-angle X-ray data suggest that 5,7DHDP also forms an amorphous polymer.

Thus from thermal analysis and diffraction studies, it is clear that both the 5,7DODBA and 5,7DHDP monomers produce amorphous poly(diacetylenes). The polymers formed from 5,7DODBA and DHDP have mesogenic side groups attached to the backbone by tetramethylene spacers and could potentially exhibit a liquid crystalline phase above the glass transition point. However, the presence of large amounts of monomer in each of these partially polymerized diacetylenes makes identification of the polymer transitions, if present, difficult.

Polymerization of 10,12DHDP. The most reactive monomer of the series is 10,12DHDP, which has nine flexible spacer units between the aromatic rings and the diacetylene groups. A thin cast film of the material will turn a deep purple-blue color following 5 min of UV light exposure, and the electron beam irradiated powder turns a dark reddish purple color at 50 Mrad dosages. This powder is not soluble in common organic solvents, and the monomer may be extracted out with denatured alcohol to obtain a burgundy colored poly(diacetylene). The estimated conversion derived from this extraction experiment is 80%.

Figure 11 contains the DSC thermograms of 10,12DHDP before and after irradiation. At 50 Mrad, the partially polymerized poly(diacetylene) clearly exhibits two transitions separate from the original monomer melting endotherm: a broad peak at 120 °C and a smaller, even broader transition centered at 180 °C. It is clear that some monomer is still present; the conversion estimated from the change in the melt endotherm enthalpy is 75% at 50 Mrad, which is consistent with the 80% estimate from extraction experiments. It appears that the 10,12 monomer will react readily to achieve appreciable yields of conjugated poly(diacetylene), and the purple-red color of the resulting polymer suggests a long effective conjugation length. Because the monomeric transitions appear at much lower temperatures, it is easy to observe the optical texture of poly-10,12DHDP. At room temperature, the powder

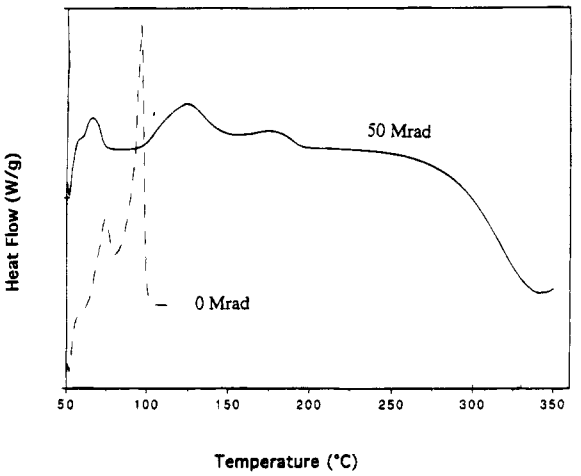

Figure 11. DSC of 10,12DHDP at 0 and 50 Mrad electron beam irradiation levels.

appears as dark purple-red particles; however, upon heating to 50–60 °C, a spherulitic crystalline structure becomes more evident as the residual monomer melts out. A gradual melting process from 100 to 130 °C produces a birefringent melt in which spherulitic forms coexist with a broken focal conic fan texture. Shearing the melt causes coalescence and alignment of liquid crystalline regions. The birefringence begins to dim at 180 °C, but some birefringence remains up to 215 °C. WAXD results indicate that a smectic C phase is probably formed by the 10,12DHDP poly(diacetylene)/monomer mixture. DSC results of the extracted poly(diacetylene) show higher transition temperatures at 160 and 193 °C, with a broad melt endotherm that is shouldered into the clearing transition. Optical observations indicate much smaller amounts of birefringent texture in the extracted polymer than in the 50 Mrad unextracted sample. It appears that in the partially polymerized (80% converted) diacetylene, the molten monomer acts as a diluent for the poly(diacetylene), effectively lowering the transition temperatures and enabling the exhibition of a liquid crystalline phase.

Heat/cool DSC experiments of the nonextracted 10,12DHDP poly(diacetylene) indicated that its transitions are not reversible when heated to 200 °C; no transition endo- or exotherms are visible at all after the first heating. The reasons for this irreversibility are unknown at this time. However, these observations are similar to those found for the thermally polymerized hexoxybenzoate poly(diacetylenes) investigated by Belina et al.[22] In the case of 10,12DHDP, the unreacted monomer may polymerize upon heating in the DSC, resulting in loss of the molten monomer diluent needed to facilitate exhibition of a liquid crystalline phase, or effectively increasing the transition temperatures by increasing the molecular weight of the sample.

The 10,12DHDP monomer has a relatively simple diffraction pattern compared to the other two monomers. As shown at the top of Figure 12, strong peaks at 4.4 and 3.8 Å are the major features of the pattern. The crystalline peaks are somewhat broad, but well-defined, suggesting a well-organized crystalline structure. There are may peaks visible at lower angles, including reflections corresponding to spacings of 32.1, 16.7, and 11.2 Å; these indicate crystalline long spacings of 33 Å. The presence of higher order peaks for the small- and wide-angle reflections in the diffractogram illustrates the excellent ordering of the crystalline phase.

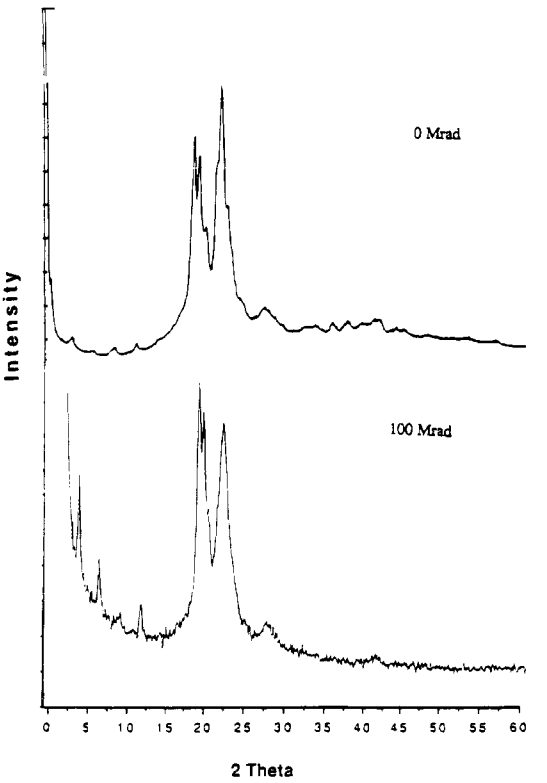

Figure 12. Wide-angle X-ray diffraction patterns of 10,12DHDP before (top) and after (bottom) 100 Mrad dosage irradiation.

The high level of reactivity of 10,12DHDP is probably due in part to its high degree of ordering, as well as the added flexibility of the long methylene sequences surrounding the diacetylene molecule. The irradiation of 10,12DHDP yields a crystalline poly(diacetylene) at high conversions (estimated at 80%), as seen by the diffractogram of the polymerized sample in the lower half of Figure 12. The topochemical polymerization takes place without altering the basic crystalline structure. Most noticeable is the increased relative intensity of the small-angle peaks by two- or threefold. Improved long-range ordering implies that the creation of the poly(diacetylene) backbone has enhanced the layer spacing of the monomer, which now exists as a mesogenic side chain connected to the poly(diacetylene) backbone. The *d*-spacing of the lowest order visible peak has shifted from 16.7 to 18.8 Å, and the 11.2 Å peak has shifted to 12.3 Å. These shifts indicate a change in lamellar spacing from approximately 33 to 38 Å, which is a sizable increase in lattice parameters. This information sheds light on the cross-polymerization process in the 10,12DHDP monomer. As the monomer converts to polymer, the mismatch in lattice spacings between monomer and polymer causes an adjustment in the arrangement of the side chains to allow expansion of the poly(diacetylene) chain. Changes in the intermolecular spacing included in this rearrangement are a shift from 3.8 to 3.9 Å and the disappearance of the weak peak at 8.6 Å. This shift is probably facilitated by the rotation of methylene groups in the DHDP side chain, and the end result is a realignment of the side chains at an angle closer to the normal of the lamellar layers. The change in angle is seen as an increase in *d*-spacing, and the degree of tilt in the side chains is decreased from that in the original monomer lattice. As discussed earlier, the resulting poly(diacetylene) is a

side chain liquid crystalline polymer that melts from 100 to 120 °C and clears above 180 °C.

Conclusions

Three new mesogenic, semirigid aromatic monomers were synthesized: 4,4'-(5,7-dodecadiynediyl-1,12-dioxy)-dibenzoic acid (5,7DODBA) 1,12-bis(4-hydroxyphenoxy)-5,7-dodecadiyne (5,7DHDP), and 1,22-bis(4-hydroxyphenoxy)-10,12-docosadiyne (10,12DHDP). Thermal analysis, optical microscopy, and wide-angle X-ray diffraction were used to characterize the crystalline and liquid crystalline properties of these materials.

5,7DODBA exhibited a highly stable mesophase from 113 to 200 °C. The stability of the mesophase was attributed to dimerization of the diacid groups to form a hydrogen-bonded smectic phase. The 5,7DHDP monomer appeared to exhibit at least one smectic phase of three-dimensional order, and optical microscopy and thermal analysis suggest that a second, metastable smectic phase exists as well. Conclusions could not be made about the mesogenic nature of 10,12DHDP, although it does exhibit what appears to be a liquid crystalline phase over a very narrow temperature range.

The 5,7DODBA and 5,7DHDP monomers were thermally reactive in the liquid crystalline and isotropic phase but were only moderately reactive when annealed in the solid state. The opposite was true of the 10,-12DHDP monomer, which was polymerized to high conversions using electron beam irradiation but was relatively stable to heat in the liquid crystalline and isotropic states. The high liquid-state reactivities of the 5,7 monomers could be attributable to higher levels of ordering in the isotropic and mesogenic states due to their more rodlike nature. Differences in solid-state reactivity varied as a factor of the degree of ordering in the crystalline state of the monomer and the length of the flexible spacer. It was found from wide-angle diffraction studies that the 10,12DHDP monomer was able to better accommodate the growing poly(diacetylene) chain during the solid-state polymerization reaction, thus allowing the production of a highly conjugated, well-ordered poly(diacetylene) chain.

The 10,12DHDP monomer was irradiated to form a crystalline polymer that melted at temperatures above that of the original monomer to form a liquid crystalline melt. The new melting and clearing endotherms of the 10,12DHDP poly(diacetylene) were visible in DSC thermograms, and WAXD indicated the crystalline nature of the product. Above the melting point of the 10,-12DHDP poly(diacetylene), a smectic phase is observed using optical microscopy and WAXD, which resembles a smectic C mesophase.

These polymerized materials are unique examples of functionalized poly(diacetylenes) with liquid crystalline side chains. Highly oriented, anisotropic optical materials might be made by processing these materials in the mesophase. Finally, the mesogenic transitions that the diacetylenes and poly(diacetylenes) in this study undergo provide the framework for thermochromism studies at the phase transitions of these materials. Separate papers will discuss polyesters made from these monomers and the thermochromic properties of both the monomers and the polyesters.

References and Notes

(1) (a) Wegner, G. *Z. Naturforsch.* **1969**, *246*, 824. (b) Wegner, G. *Makromol. Chem.* **1970**, *134*, 219.
(2) (a) Ozcayir, Y.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1986**, *135*, 237. (b) Ozcayir, Y.; Asrar, J.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 263.
(3) (a) Ozcayir, Y.; Asrar, J.; Clough, S. B.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1986**, *138*, 167. (b) Ozcayir, Y.; Blumstein, A. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 1217.
(4) (a) Grant, B.; Clecak, N. J.; Cox, R. J. *Mol. Cryst. Liq. Cryst.* **1979**, *51*, 209. (b) Grant, B. *Mol. Cryst. Liq. Cryst.* **1978**, *48*, 175.
(5) Garito, A. F.; Teng, C. C.; Wong, K. Y.; Zammani'Khamiri, O. *Mol. Cryst. Liq. Cryst.*, **1984**, *106*, 219.
(6) Plachetta, C.; Rau, N. O.; Schulz, R. C. *Mol. Cryst. Liq. Cryst.* **1983**, *96*, 141.
(7) Schen, M. A. *Nonlinear Opt. Prop. Org. Mater.* **1988**, *971*, 178.
(8) (a) Schen, M. A.; Briber, R.; Cline, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (2), 151. (b) Schen, M. A.; Kotowski, K.; Cline, J. *Polymer* **1991**, *32*, 1843.
(9) (a) Tsibouklis, J.; Werninck, A. R.; Shand, A. J.; Milburn, G. H. W. *Liq. Cryst.* **1988**, *3*, 1393. (b) Hardy, G.; Milburn, G. H. W.; Nyitrai, K.; Horvath, J.; Balazs, G.; Varga, J.; Shand, A. J. *New Polym. Mater.* **1989**, *1* (3), 209.
(10) Exarhos, G. J.; Risen, W. K. M.; Baughman, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 481.
(11) (a) Rubner, M. F. *Macromolecules* **1986**, *19*, 2114. (b) Rubner, M. F. *Macromolecules* **1986**, *19*, 2129.
(12) (a) Nallicheri, R. N.; Rubner, M. F. *Macromolecules* **1991**, *24*, 517. (b) Hammond, P. T.; Nallicheri, R. N.; Rubner, M. F. *Mater. Sci. Eng.* **1990**, *A126*, 281.
(13) Beckham, H. W.; Rubner, M. F. *Macromolecules* **1993**, *26*, 5198.
(14) Hammond, P. T.; Rubner, M. F. *Macromolecules*, to be submitted (Part 2).
(15) Hammond, P. T.; Rubner, M. F. *Macromolecules*, to be submitted (Part 4).
(16) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320.
(17) (a) Barrall, E. M., II; Johnson, J. F. *Liquid Crystals and Plastic Crystals*; Gray, G. W., Winsor, P. A., Eds.; John Wiley & Sons: New York, 1974; Vol. 2, Chapter 10, p 263. (b) Gray, G. W.; Jones, B. J. *J. Chem. Soc.* **1953**, 4179. (c) Maier, W. M.; Englert, G. *Z. Phys. Chem.* **1959**, *19*, 168.
(18) Schen, M. A. *Adv. Nonlinear Polym. Inorg. Cryst., Liq. Cryst., Laser Media* **1987**, *824*, 93.
(19) Havens, S. J. Polymeric Liquid Crystals Structurally Related to 4-Alkoxyphenyl 4'-Alkoxy Benzoates. Doctoral Dissertation, University of Southern Mississippi, August 1979.
(20) Bloor, D. *Crystallographically Ordered Polymers*; Sandman, D. J., Ed.; ACS Symposium Series 337; American Chemical Society: Washington, DC, 1987; Chapter 10.
(21) Patel, G. N. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1591.
(22) Belina, K.; Balazs, G.; Varga, J.; Hardy, G. Y.; Horvath, J.; Nyitrai, K.; Werninck, A. R.; Shand, A. J.; Milburn, G. H. W. *Liq. Cryst.* **1990**, *7*, 399.

MA940978E