Synthesis and Characterization of Branched Liquid-Crystalline Polyethers Containing Cyclotetraveratrylene-Based Disklike Mesogens

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ABSTRACT: The synthesis and characterization of branched liquid-crystalline polyethers containing disklike mesogens are described. The particular disklike molecules employed for these experiments are octaalkyloxy-substituted cyclotetraveratrylene derivatives (CTTV-*n*). The model compounds of the monomeric structural units (i.e., asymmetrically disubstituted [CTTV-*n*[*m*(*x*/*y*)]]) were synthesized by the electrophilic cocyclotetramerization of 3,4-bis(*n*-alkyloxy)benzyl alcohols [1(*n*)], while the branched polymers were synthesized by the cocyclotetramerization of various ratios of a mixture containing 3,4-(di-*n*-alkyloxy)benzyl alcohol and α,ω-bis[[2-(*n*-alkyloxy)-5-(hydroxymethyl)phenyl]oxy]alkane [2(*n,m*)]. CF₃COOH was used as the cyclotetramerization catalyst. This novel polymerization reaction constructs the disklike CTTV-*n* molecules during the polymerization process. In a columnar mesophase the backbone of a main-chain liquid-crystalline polymer containing disklike mesogens can either connect mesogens from adjacent columns (intercolumnar bridging) or link two mesogens within the same column (intracolumnar backfolding). Therefore, since such a polymer resembles a rigid networklike structure, we believe that the branched structure described in this publication represents a rational architecture for polymers containing disklike mesogens. Preliminary data on the characterization of the mesomorphic behavior of model compounds of the monomeric structural units, of a twin discotic dimer, and of the branched oligomers, obtained by a combination of differential scanning calorimetry and thermal polarized optical microscopy, have shown that all exhibit discotic mesophases.

Introduction

Thermotropic discotic liquid crystals exhibiting columnar mesophases have received considerable interest since their discovery in 1977.[1,2] Several reviews have been written.[3–5] Discotic liquid-crystalline compounds, such as hexasubstituted triphenylenes,[4] are typically composed of flat rigid polyaromatic cores symmetrically substituted with three, four, six, or eight long alkyl side chains. Molecules with flexible cores which can adopt a quasi-flat conformation, such as octasubstituted cyclotetraveratrylene (CTTV-*n*),[6] tetra- and hexasubstituted cyclic polyamines,[7] and hexasubstituted *scyllo*-inositol,[8] also form columnar mesophases. However, even hexasubstituted cyclotriveratrylene (CTV-*n*) derivatives, which have a conelike shape,[9] and phasmidic derivatives[10] form columnar mesophases.

In addition to the lenticular nematic phase (N_D), disklike molecules form hexagonal (D_h), rectangular (D_r), and oblique (D_ob) columnar discotic mesophases which are further distinguished by the order (e.g., D_ho) or disorder (e.g., D_hd) of the mesogens within the column.[11] Several of these discotic mesophases can be identified by their characteristic optical textures.[11]

Polymers containing both phasmidic[12] and disklike mesogens[13–15] in three different architectures have been synthesized. These include polymers containing the disklike mesogen either as side groups[13] or in the main chain[14] and spinal columnar liquid-crystalline polymers in which the polymer backbone links the centers of each disklike unit.[15] Several twin dimers of liquid-crystalline disklike molecules have also been reported.[16] Investigations of both the structure[17] and the dynamics[18] of polymers containing disklike mesogens have demonstrated that they can be macroscopically oriented either by magnetic fields[18a] or by mechanical forces.[17a,18c] This orientation is frozen within the system at temperatures below the polymer glass transition temperature, resulting in highly ordered anisotropic glasses.

Chart I
Discotic Ordered Hexagonal (D_ho) Arrangement of a Main-Chain Liquid-Crystalline Polymer Containing Disklike Units: (a) Viewed from the Side of the Columns; (b) Viewed from the Top of the Columns; (c) Top Disk Layer of the Columns; (d) Top Two Disk Layers of the Columns
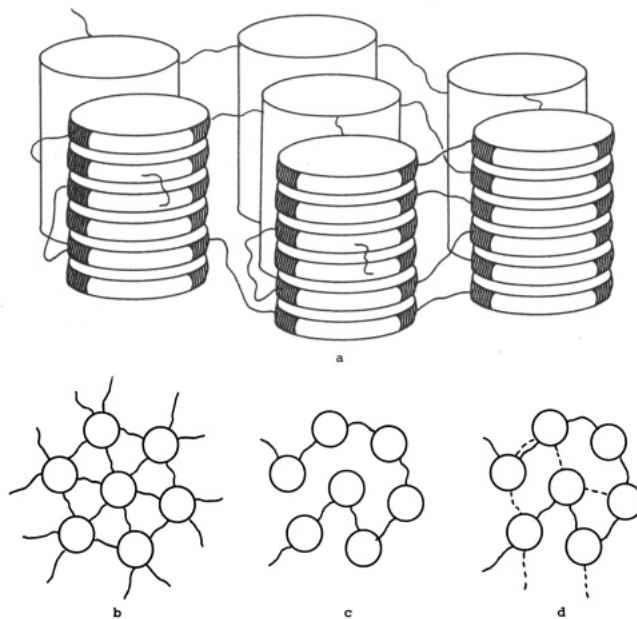
This paper describes the synthesis of the first series of branched polymers containing the disklike mesogens at the branch points. In this case, polymers based on *n*-octaalkyloxy-substituted cyclotetraveratrylene (CTTV-*n*) groups are used as an example of branched polymers containing disklike units which are formed during the polymerization process. That is, the CTTV-*n* moiety is constructed as part of the polymer structure through an electrophilic cyclopolymerization reaction. We and others[14b,17a] believe that a networklike structure results

Scheme I
Formation of Six Possible CTTV-Based Isomers by Cocyclotetramerization of Two Different 3,4-Bis(n-alkyloxy)-benzyl Alcohols
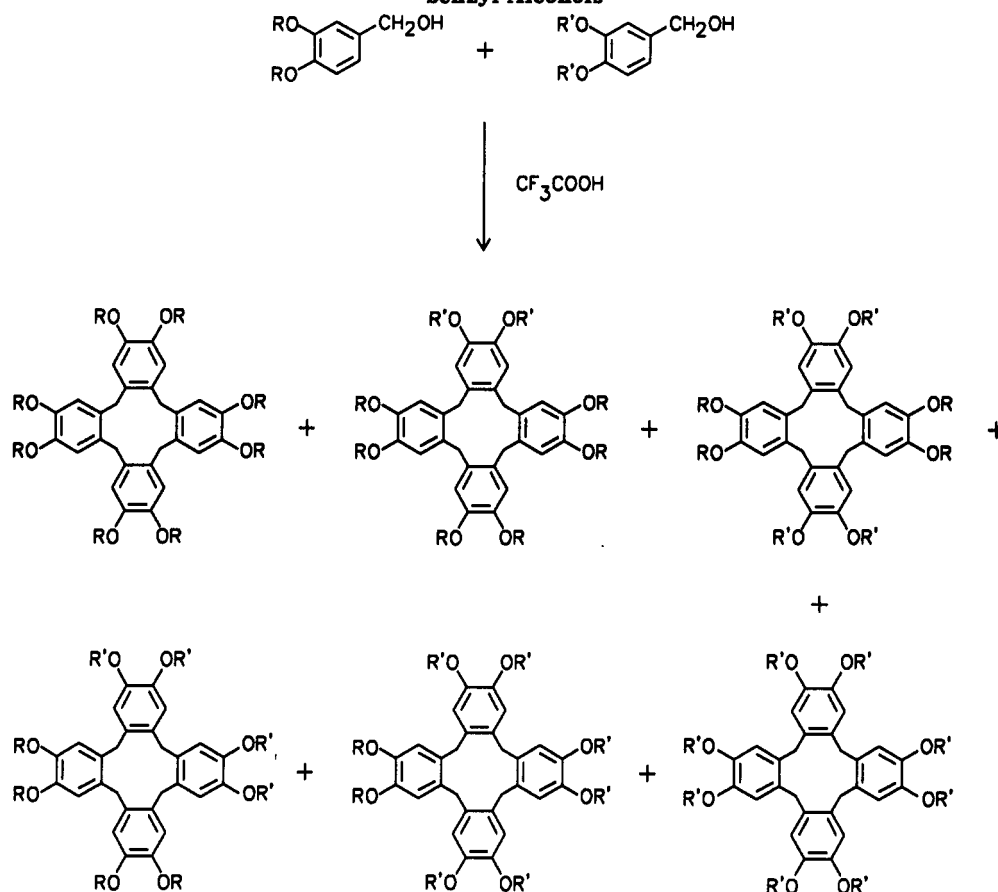
Results and Discussion

Chart I illustrates the discotic ordered hexagonal (D_{ho}) phase of a main-chain liquid-crystalline polymer which contains disklike mesogenic groups. Chart Ia displays the columns composed of disklike molecules in a hexagonal arrangement. The main chain of the polymer can either connect adjacent columns (intercolumnar bridging) or link two mesogens within the same column (intracolumnar backfolding).[14b,17a] In the hexagonal packing, the distance between each column and its nearest neighbor at either of the six corners of the hexagon is equal to the distance between the same columns and the column at the center of the hexagon. Therefore, the polymer backbone can statistically interconnect the disk-shaped molecules in any of these seven columns, resulting in a rigid networklike structure. In addition, two columns can be interconnected through the polymer backbone by bridging two disks located either within the same plane or in different planes. Chart Ib views this hexagonal arrangement from the top and demonstrates that the seven columns appear to form a rigid network. Alternatively, if only the upper level of the disk molecules is viewed from the top as in Chart Ic, a linear arrangement of the polymer main chain might be observed. However, this view is oversimplified since it illustrates interconnection by the polymer backbone of disks located only within the same plane. If we instead consider the first two planes, the arrangement of columns as viewed from the top already resembles a network (Chart Id).

Liquid-crystalline polymers containing the disklike mesogens as side groups should also display such a network structure. Therefore, there is little difference between the architecture of main-chain and side-chain polymers containing disklike mesogens. Since a highly branched structure is intermediate between a network and a linear polymer structure, we believe that the branched structure represents a rational architecture for polymers containing disklike mesogens in general.

In order to demonstrate this idea, we have prepared branched polymers based on CTTV-n mesogens. CTTV-n mesogens were selected partially because the CTTV disk is very flexible. The dynamics of mesophase formation are therefore very fast compared to that of rigid disklike molecules. In addition, we have developed a method which selectively forms CTTV-n units by the CF_3COOH-catalyzed electrophilic cyclotetramerization of 3,4-bis(n-alkyloxy)benzyl alcohols.[6b,19] The phase behavior of octa-n-alkyloxy (n = 4–15) derivatives of CTTV prepared by both alkylation of octahydroxytetrabenzocyclododecatetraenes (CTTV-OH) and by cyclotetramerization of the corresponding 3,4-bis(n-alkyloxy)benzyl alcohols was presented and compared in a previous publication.[6b]

In order to form branched polymers containing octa-substituted CTTV derivatives, various ratios of a 3,4-bis-(n-alkyloxy)benzyl alcohol were cocyclotetramerized with an α,ω-bis[[2-(n-alkyloxy)-5-(hydroxymethyl)phenyl]oxy]-alkane. Since the resulting CTTV-n unit will be asymmetric, we must first determine whether asymmetrically substituted disklike molecules can form columnar mesophases and, if so, whether the various asymmetrically

Table I
Synthesis of CTTV-6/12(x/y), Poly(CTTV)-6/6,12(x/y), Poly(CTTV)-7/7,12(x/y), and Poly(CTTV)-7/7,16(x/y) by Electrophilic
Cocyclotetramerization Reactions (Reaction Solvent, CH_2Cl_2 (9.6 mL); Temperature = 20 °C; Reaction Time = 4.5 h; Catalyst,
CF_3COOH (0.5 mL))

monomer [mmol]	CF_3COOH/CH_2OH, mol/mol	product	convn, %	GPC	
				$M_n \times 10^{-3}$	M_w/M_n
1(6) [0.114] 1(12) [0.350]	14.0	CTTV-6/12(1/3)	65.8		
1(6) [0.256] 1(12) [0.254]	13.0	CTTV-6/12(2/2)	64.9		
1(6) [0.428] 1(12) [0.143]	11.0	CTTV-6/12(3/1)	54.3		
1(6) [0.486] 2(6,12) [0.081]	10.0	poly(CTTV)-6/6,12(6/1)	50.5	2.8	1.6
1(6) [0.431] 2(6,12)] [0.109]	10.0	poly(CTTV)-6/6,12(4/1)	58.5	2.8	1.7
1(6) [0.389] 2(6,12) [0.130]	10.0	poly(CTTV)-6/6,12(3/1)	55.5	2.6	1.7
1(6) [0.324] 2(6,12) [0.163]	10.0	poly(CTTV)-6/6,12(2/1)	59.0	3.0	1.7
1(7) [0.451] 2(7,12) [0.075]	10.8	poly(CTTV)-7/7,12(6/1)	68.0	1.8	1.5
1(7) [0.401] 2(7,12) [0.101]	10.8	poly(CTTV)-7/7,12(4/1)	61.5	2.1	1.6
1(7) [0.362] 2(7,12) [0.121]	10.8	poly(CTTV)-7/7,12(3/1)	66.5	2.2	1.6
1(7) [0.303] 2(7,12) [0.152]	10.8	poly(CTTV)-7/7,12(2/1)	57.5	2.7	1.7
1(7) [0.443] 2(7,16) [0.073]	11.0	poly(CTTV)-7/7,16(6/1)	67.0	3.7	1.6
1(7) [0.443] 2(7,16) [0.073]	11.0	di(CTTV)-7/7,16(6/1) dimer[a]		1.4	1.0
1(7) [0.392] 2(7,16) [0.097]	11.0	poly(CTTV)-7/7,16(4/1)	73.0	4.3	1.5
1(7) [0.351] 2(7,16) [0.17]	11.1	poly(CTTV)-7/7,16(3/1)	73.0	4.8	1.7
1(7) [0.291] 2(7,16) [0.146]	11.1	poly(CTTV)-7/7,16(2/1)	70.0	5.8	1.9
1(7) [0.250] 2(7,16) [0.166]	11.1	poly(CTTV)-7/7,16(3/2)	85.0	3.4	1.9
1(7) [0.291] 2(7,16) [0.146]	11.1	poly(CTTV)-7/7,16(2/1)[b]		7.3	1.5
1(7) [0.250] 2(7,16) [0.166]	11.1	poly(CTTV)-7/7,16(3/2)[b]		7.8	1.5

[a] Pure dimer separated by chromatography. [b] Polymer free of oligomers separated by two precipitations in acetone.

substituted disklike isomers within a certain column are isomorphic within a certain mesophase. We expect the answers to both questions to be affirmative. For example, it has already been demonstrated that two asymmetric hexasubstituted isomers of triphenylene exhibit columnar mesophases.[19] These isomers exhibit lower transition temperatures than either of the corresponding symmetrically hexasubstituted triphenylenes. In addition, both the symmetric and the asymmetric substituted triphenylenes are isomorphic within their columnar mesophase.[19]

Cocyclotetramerization of 3,4-Bis(*n*-hexyloxy)benzyl Alcohol [1(6)] and 3,4-Bis(*n*-dodecyloxy)benzyl Alcohol [1(12)]. In order to determine whether asymmetric octasubstituted CTTV can be tolerated within a columnar mesophase, 3,4-bis(*n*-hexyloxy)benzyl alcohol [1(6)] was cocyclotetramerized with 3,4-bis(*n*-dodecyloxy)benzyl alcohol [1(12)] in three different ratios. The phase behavior of the resulting CTTV mixtures was characterized by differential scanning calorimetry and polarized optical microscopy and compared to that of the analogous symmetrically octasubstituted CTTV-6 and CTTV-12.

Since the reactivities of 1(6) and 1(12) are equal, cocylotetramerization should result in a statistical distribution of the two substituents. Six CTTV molecules are possible (Scheme I). The distribution of these six CTTV isomers is influenced by the ratio of 1(6) and 1(12) in the initial reaction mixture. Figure 1 presents the heating and cooling DSC traces of CTTV-6 and CTTV-12 prepared by alkylation of CTTV-OH.[6b] Figure 1 also presents the DSC traces of the CTTV-6/12(1/3), CTTV-6/12(1/1), and CTTV-6/12(3/1) mixtures obtained by cocyclotetramerization of 1:3, 1:1, and 3:1 molar ratios of 1(6) and 1(12), respectively. The results of these cyclotetramerization experiments are summarized in Table I.

CTTV-*n* with various alkyloxy groups was previously considered to exhibit only a single columnar mesophase and multiple crystalline phases.[6] However, we have recently discovered that some of the crystalline phases are in fact discotic mesophases. Although definitive assignment of all the mesophases requires support by X-ray diffraction experiments, the mesophases of CTTV-6, CTTV-7, and CTTV-12 can tentatively be assigned based on a combination of polarized optical microscopy and differential scanning calorimetry (DSC).

CTTV-6 exhibits a very fluid mesophase when heated above 161.6 °C. This mesophase undergoes isotropization at 172.4 °C (Figure 1 and Table II). An polarized optical microscopic texture with digitated contours which merge into mosaic domains is obtained by slowly cooling from the isotropic melt. This texture is characteristic of a D_h mesophase.[3c,11a,b] The large change in enthalpy of isotropization (4.7 kcal/mol) is also indicative of a D_h mesophase. Further cooling causes the D_h domains to break at 153 °C, forming banded domains which are also characteristic of a D_x (unassigned) phase.[11b] The mesophase formed at 153 °C is monotropic and crystallizes upon further cooling. The textures exhibited by CTTV-6 are similar to those exhibited by CTTV-7, which will be presented subsequently.

The DSC traces of CTTV-12 are also presented in Figure 1. On the basis of both polarized optical microscopy and DSC experiments, this compound exhibits two enantiotropic discotic (D_h and unassigned D_x) phases, an inverse monotropic columnar mesophase, which was not assigned, and a crystalline phase. The D_h phase exhibits a fanlike texture which nucleates from singular points,[11a,b] as is seen in Figure 2A. Very large fans grow if the isotropic melt is held for a long period of time at the temperature where an anisotropic point is first observed (Figure 2B). Further cooling results in faster growth of small domains (Figure 2B,C). However, thin anisotropic strips are also seen growing in the homeotropic domains of Figure 2C due to the transition from D_h to the unassigned D_x phase. Once the transition is complete, as in Figure 2D, all of the homeotropic regions and much of the fan domains have become striped (Figure 2D).[11c] The formation of both textures occurs at higher temperatures on the optical microscope since the rate of cooling is lower than on the DSC. In addition, nucleation of the highest temperature columnar mesophase occurs at a much higher temperature than that at which the major growth occurs.

The DSC traces obtained on heating and cooling CTTV-7 are presented in Figure 3. Its thermal behavior is summarized in Table II. CTTV-7 exhibits enantiotropic D_h and unassigned D_x phases with textures almost identical to the D_h and unassigned D_x textures of CTTV-6. Representative polarized optical micrographs of this phase obtained with different cooling rates are presented in
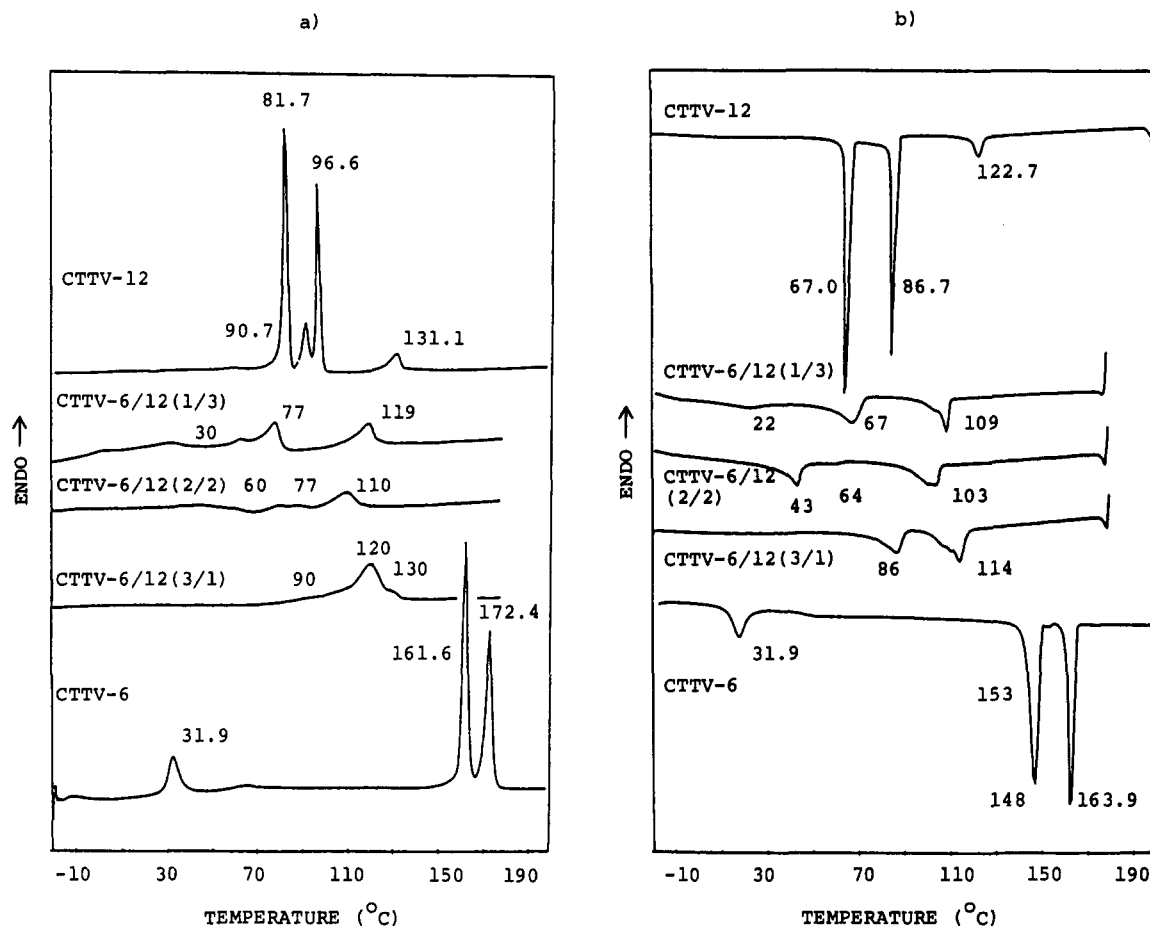
Figure 1. DSC (a) heating and (b) cooling scans (20 °C/min) of CTTV-6/12(x/y) cocyclotetramers prepared by cocyclotetramerization of x mol of 3,4-bis(n-hexyloxy)benzyl alcohol and y mol of 3,4-bis(n-dodecyloxy)benzyl alcohol, and of pure CTTV-6 and CTTV-12 prepared by alkylation of CTTV-OH.

Table II
Characterization of CTTV-6, CTTV-7, CTTV-12, CTTV-6/12(x/y), Poly(CTTV)-6/6,12(x/y), Poly(CTTV)-7/7,12(x/y), and Poly(CTTV)-7/7,16(x/y)

| | thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses | |
sample	heating	cooling
CTTV-6	k 31.9 (1.9) k 161.6 (6.5) D_h 172.4 (4.7) i	i 163.9 (5.4) D_h 153 (−) D_x 148 (7.1) k 18.0 (2.1) k
CTTV-7	k 90.1 (11.2) k 123.8 (2.3) D_x 139.1 (3.6) D_h 161.6 (4.6) i	i 154.3 (4.8) D_h 131.5 (4.1) D_x 119.7 (2.4) k 82.0 (11.6) k
CTTV-12	k 81.7 (20.4) D_{x1} 90.7 (4.9) D_{x2} 96.6 (11.9) D_h 131.2 (3.1) i	i 122.7 (2.3) D_h 86.7 (13.7) D_{x1} + D_{x2} 67.0 (19.6) k
CTTV-6/12(1/3)	k 30 (1.2) D_{x1} 70 D_{x2} 77 (4.4) D_h 119 (3.3) i	i 109 (3.1) D_h 67 (4.5) D_{x1} + D_{x2} 22.0 (0.9) k
CTTV-6/12(2/2)	k 40 (1.2) D_{x1} && (−) D_h 110 (2.1[a]) i	i 103 (2.5) D_h 64 (−[a]) D_{x1} 43 (2.1) k
CTTV-6/12(3/1)	k 90 (−[a]) D_{x1} 120 (7.1[a]) D_h 130 (−[a]) i	i 114 (3.4) D_h 86 (2.6) D_{x1}
poly(CTTV)-6/6,12(6/1)	g 15 D_{x1} 102 D_{x2} 120 D_h 145 i	i 114 D_h 91 D_{x2} 80 D_{x1}
poly(CTTV)-6/6,12(4/1)	g 18 D_{x1} 99 D_{x2} 120 D_h 139 i	i 107 D_h 100 D_{x2} 86 D_{x1}
poly(CTTV)-6/6,12(3/1)	g 20 D_{x1} 98 D_{x2} 120 D_h 136 i	i 102 D_h 83 D_{x2} + D_{x1}
poly(CTTV)-6/6,12(2/1)	g 20 D_{x1} 95 D_h 118 i	i D_h 92 78 D_{x1}
poly(CTTV)-7/7,12(6/1)	D_{x1} 90 D_{x2} 103 D_{x3} 116 D_h 141 i	i 122 D_h 112 D_{x3} 98 D_{x2} D_{x1}
poly(CTTV)-7/7,12(4/1)	D_{x1} 103D_{x2} 103 D_{x3} 114 D_h 139 i	i 118 D_h 97 D_{x3} 76 D_{x2}
poly(CTTV)-7/7,12(3/1)	D_{x1} 64 D_{x2} 92 D_h 110 i	i 101 D_h 90 D_{x2} 71 D_{x1}
poly(CTTV)-7/7,12(2/1)	D_{x1} 89 D_h 103 i	i 97 D_h 87 D_{x2} 65 D_{x1}
poly(CTTV)-7/7,16(6/1)	g 14 D_{x1} 90 D_{x2} 105 D_{x3} 120 D_h 127 D_h 142 i	i 124 D_h 117 D_{x3} 102 D_{x2} 80 D_{x1}
di(CTTV)-7/7,16(6/1)[a] dimer	D_{x1} 81 D_{x2} 122 D_h 136 i	i 124 D_h 117 D_{x2} 71 D_{x1}
poly(CTTV)-7/7,16(4/1)	g 18 D_{x1} 87 D_{x2} 103 D_{x3} 117 D_h 134 i	i 109 D_h 98 D_{x3} 76 D_{x2}
poly(CTTV)-7/7,16(3/1)	g 18 D_{x1} 86 D_{x2} 102 D_{x3} 112 D_h 129 i	i 106 D_h 96 D_{x2} 72 D_{x1}
poly(CTTV)-7/7,16(2/1) poly(CTTV)-7/7,16(3/2)	g 19 D_{x1} 83 D_{x2} 99 D_{x3} 107 D_h 120 i	i 100 D_h 91 D_{x2} 64 D_{x1}
poly(CTTV)-7/7,16(2/1)[b]	g 20 D_{x1} 83 D_{x2} 109 D_h 122 i	i 102 D_h 95 D_{x2} 64 D_{x1}
poly(CTTV)-7/7,16(3/2)[b]	g 20 D_h 102 i	i 99 D_h 91 D_{x2} 64 D_{x1}

[a] Overlapped transition peaks; the enthalpy change refers to both peaks; when enthalpy changes are not reported, all peaks are overlapped.

Figure 4. The D_h phase grows dendritically from the isotropic melt as fingerlike contours (Figure 4A; −10 °C/min), which merge into mosaic domains (Figure 4B). On further cooling, the mosaic structures breaks (Figure 4C) at the D_h–D_x transition. Figure 4A can be compared with parts D–F of Figure 4, which were obtained by very slow cooling from the isotropic melt. In this case, very large fingerlike structures were obtained by cooling at −3 °C
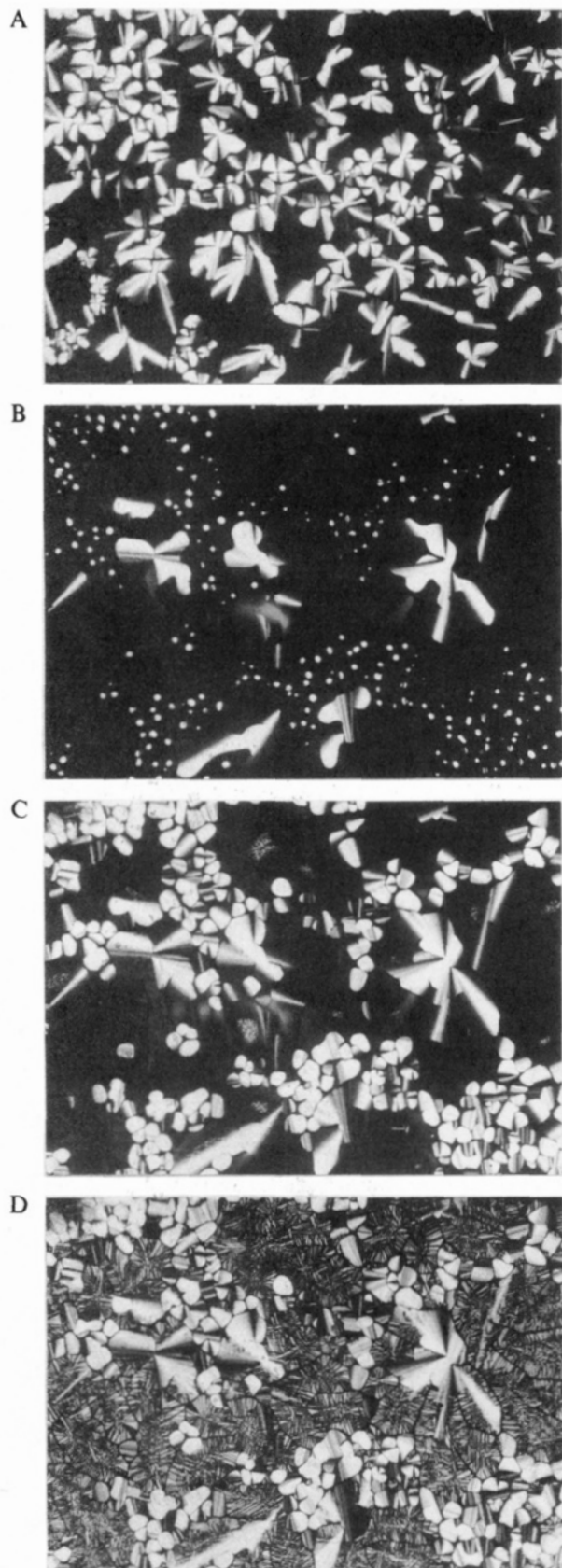
A

B

C

D

Figure 2. Polarized optical micrographs obtained by cooling CTTV-12 from the isotropic melt: (A) 122.4 °C, smaller fan domains typical of a D_h mesophase formed by cooling the isotropic melt at −3 °C/min; (B) 128.9 °C, large fan domains typical of a D_h mesophase formed isothermally at 129.2 °C for 7 h; (C) 117.1 °C, initial growth of anisotropic stripes typical of a transition to the D_x mesophase in the homeotropic domains; (D) 107.6 °C, banded paramorphotic fan texture typical of the D_x mesophase formed from a D_h mesophase.
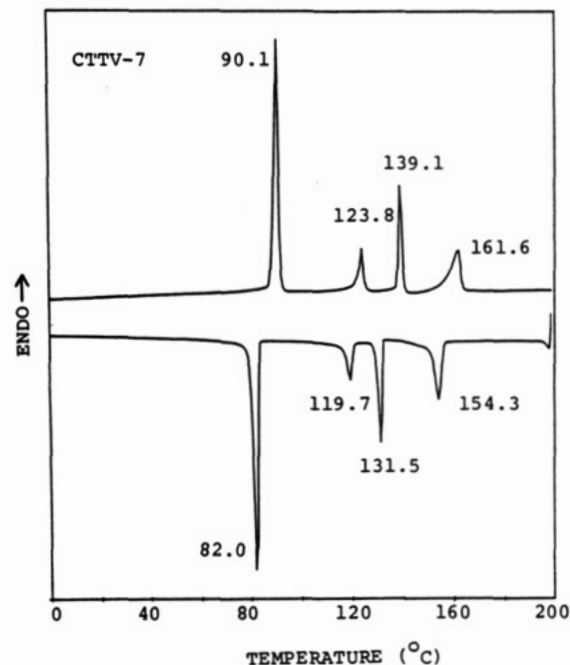
Figure 3. DSC heating and cooling scans (20 °C/min) of CTTV-7 prepared by alkylation of CTTV-OH.

until an anisotropic point was observed at 158.1 °C. The sample was held at this temperature for approximately 10 min until the fingerlike branches covered the entire field of view. However, smaller branches in which the dendritic growth is still obvious are also found in the thinner regions of the sample (Figure 4E). As shown in Figure 4G, the large domains of the Figure 4D, F, E sequence break into smaller regions at the D_h–D_x transition.

The DSC traces of the CTTv-6/12 cocyclotetramers presented in Figure 1 are interpretable based on the phase behavior of CTTV-6 and CTTV-12. Incorporating two dissimilar alkyloxy groups within the CTTV structure results in a decrease in both the liquid-crystalline and the crystalline phase transitions. Although the CTTV-6/12 cocyclotetramers are composed of up to six isomers, all exhibit two columnar mesophases. The isomers are therefore isomorphic within their columnar mesophases. The texture of the high-temperature mesophase of CTTV-6/12(3/1) shown in Figure 5A resembles the D_h phase of CTTV-12. As shown in Figure 5B, the fan-shaped texture breaks into a texture characteristic of a D_x phase on further cooling. The mesophases exhibited by CTTV cocyclotetramers containing alkyloxy groups of dissimilar length are therefore determined by the longest of the two alkyloxy substituents. This is reasonable assuming the longest alkyloxy substituent determines the overall diameter of the column, which in turn determines the overall packing in the hexagonal phase. Table II summarizes the phase transitions of the CTTV-6/12 cocyclotetramers.

CTTV-Based Oligomers Obtained by Cocyclopolymerization of 1(n) and 2(n,m). The synthesis of poly-(CTTV)-*n*/*n*,*m*(*x*/*y*) by an electrophilic cocyclotetramerization of 1(*n*) with 2(*n*,*m*) is outlined in Scheme II. As shown in this scheme, the electrophilic cocyclotetramerization reactions of 2(*n*,*m*) can provide both interdisk and intradisk links. Also, the resulting branched polymers are composed of an even greater number of discotic isomers than the asymmetrically substituted CTTV-*n*/*m* cocyclotetramers. If the difunctional 2(*n*,*m*) monomer is represented by an asymmetric 3,4-bis(alkyloxy)benzyl alcohol as shown in Scheme III, then cocyclotetramerization with the corresponding symmetrically substituted
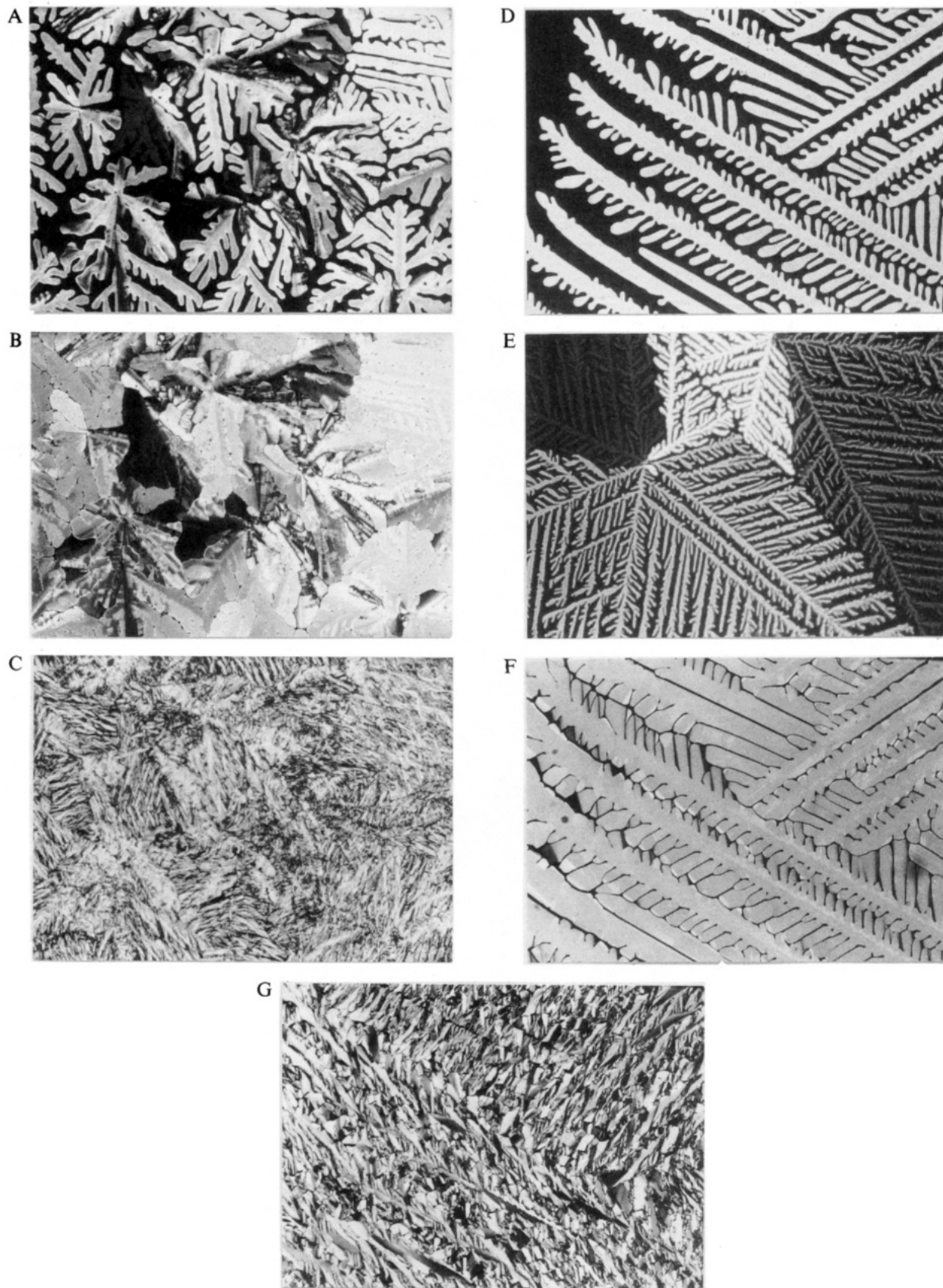
Figure 4. Polarized optical micrographs obtained by cooling CTTV-7 from the isotropic melt: (A) 158.6 °C, dendritic growth of fingerlike contours typical of a D_{ho} mesophase formed by cooling at −10 °C/min; (B) 141.6 °C, final D_h mosaic texture formed at −10 °C/min from Figure 4A; (C) 126.5 °C, broken paramorphotic mosaic texture typical of a D_x mesophase formed by cooling the Figure 4A,B textures at −10 °C/min; (D) 158.1 °C, dendritic growth of fingerlike contours typical of a D_h mesophase formed isothermally over 10 min (corresponds to Figure 4A); (E) 158.1 °C, dendritic growth of fingerlike contours typical of a D_h mesophase formed isothermally over 10 min (another section; corresponds to Figures 4A,D); (F) 140.0 °C, final D_h mosaic texture corresponding to Figure 4C formed by cooling Figure 4D at −3 °C/min; (G) 132.9 °C, broken paramorphotic mosaic texture corresponding to Figure 4C formed by cooling Figure 4F at −3 °C/min.

Scheme II
Synthesis of a Twin Discotic Dimer and Branched Oligomers Based on CTTV-7 Mesogens Interconnected through a Hexadecane Spacer
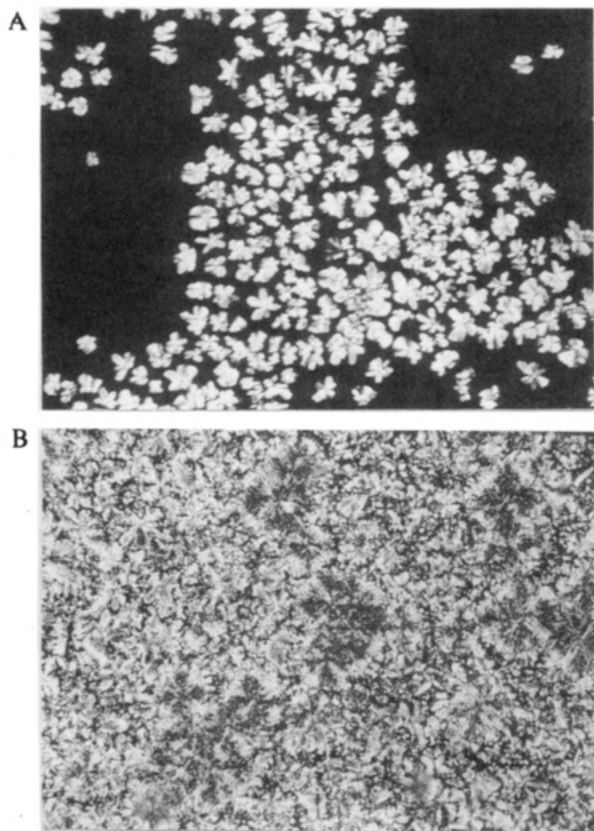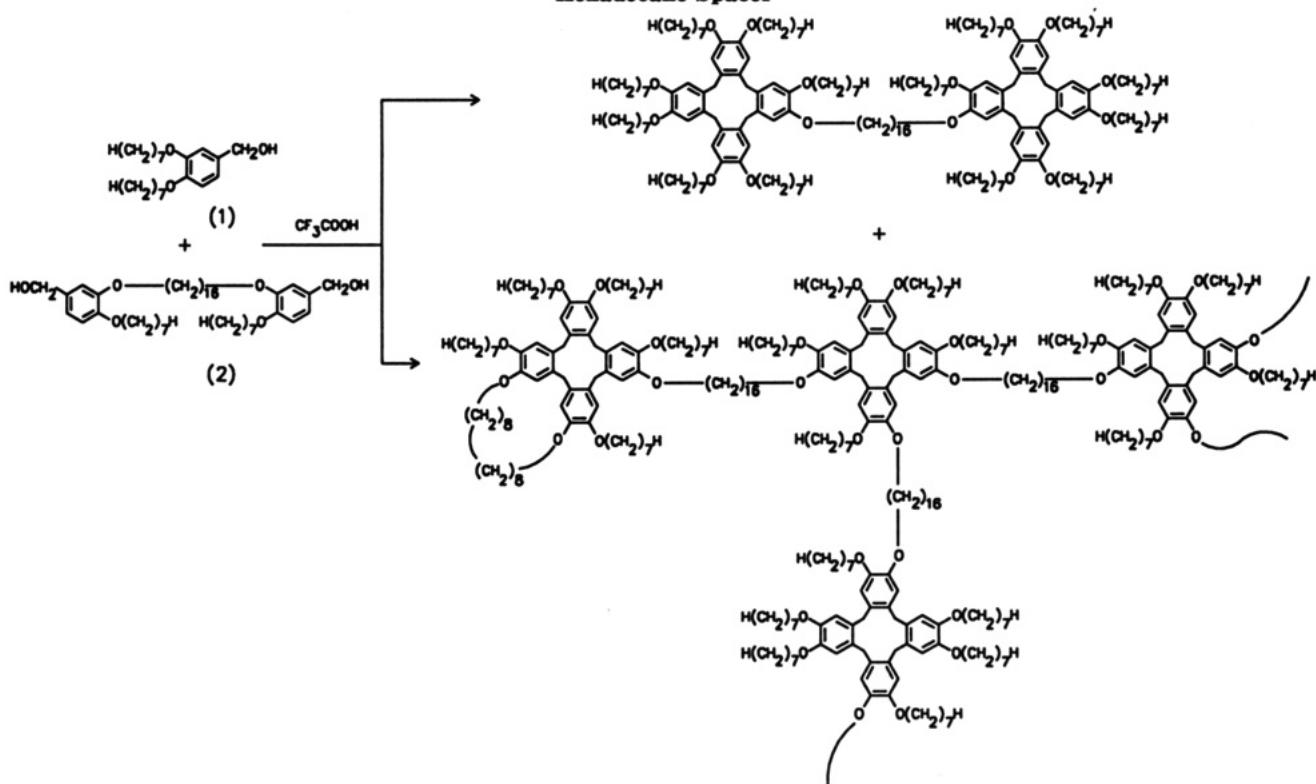

Figure 5. Polarized optical micrographs obtained by cooling CTTV-6/12(3/1) from the isotropic melt: (A) 124.9 °C, growth of fan domains typical of a D_h mesophase; (B) 100.0 °C, sanded fan texture.

Figure 6. GPC chromatograms of the poly(CTTV)-6/6,12(*x*,*y*) oligomers presented in Table I prepared by cocyclotetramerization of *x* moles of CTTV-6 and *y* moles of 1,12-bis[[2-(*n*-hexyloxy)-5-(hydroxymethyl)phenyl]oxy]dodecane.

3,4-bis(*n*-alkyloxy)benzyl alcohol will result in up to 14 CTTV isomers. However, the symmetric monomeric CTTV-*n* will not be present in the branched polymer since
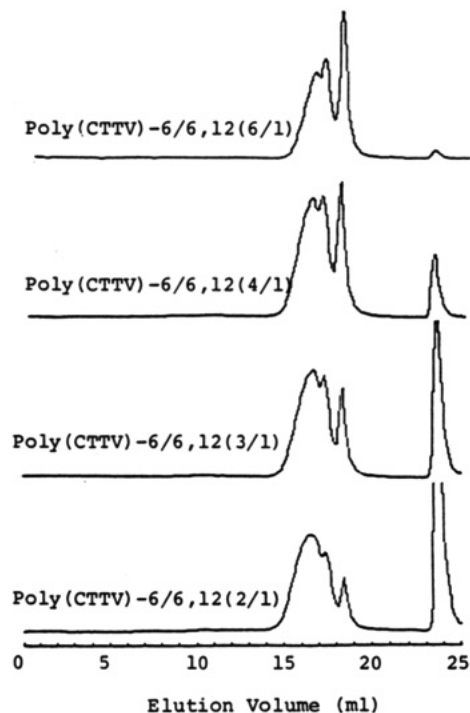
it is removed by reprecipitation. In addition, the high molar ratio of 1(*n*) to 2(*n*,*m*) used in the polymerization experiments makes it unlikely that the branched polymer will contain any of the CTTV mesogens connected through spacers to four other disks. This is confirmed by the fact that the branched polymers are completely soluble. There is, however, a high probability that the polymers will
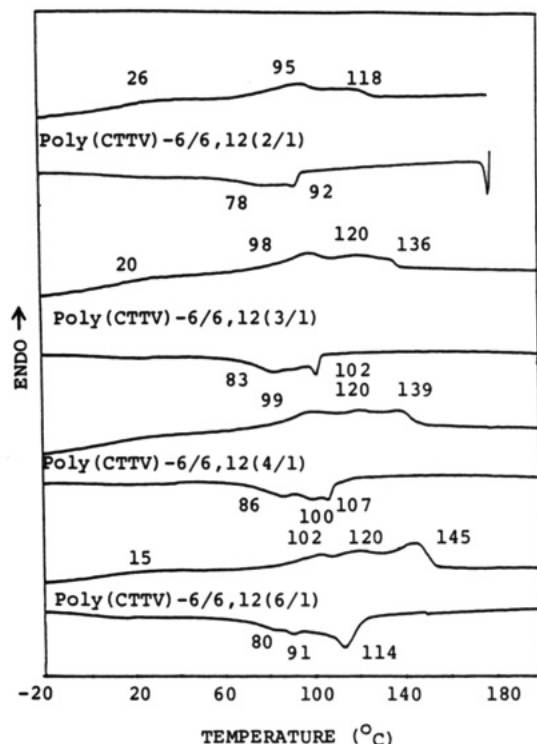
Figure 7. DSC heating and cooling scans (20 °C/min) of the poly(CTTV)-6/6,12(x,y) presented in Tables I and II prepared by cocyclotetramerization of x moles of 3,4-bis(n-hexyloxy)benzyl alcohol and y moles of 1,12-bis[[2-(n-hexyloxy)-5-(hydroxymethyl)phenyl]oxy]dodecane.
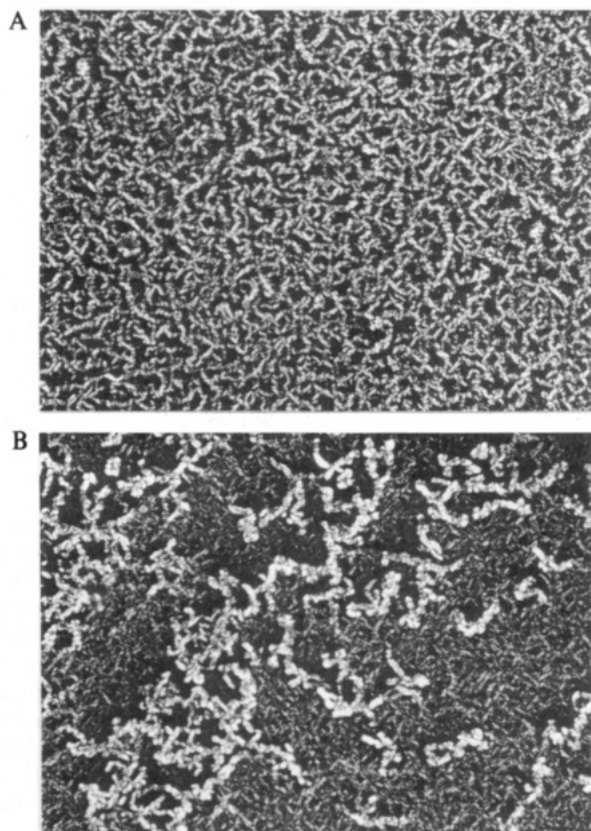

Figure 8. Polarized optical micrographs of the columnar mesophase obtained on cooling the isotropic melt of (A) poly(CTTV)-6/6,12(6/1), 85.6 °C, and (B) poly(CTTV)-7/7,12(6/1), 111.5 °C.

contain some CTTV units linked to three other disklike mesogens.

The results of the cocyclotetramerization experiments using various ratios of 1(6) and 2(6,12) are summarized in
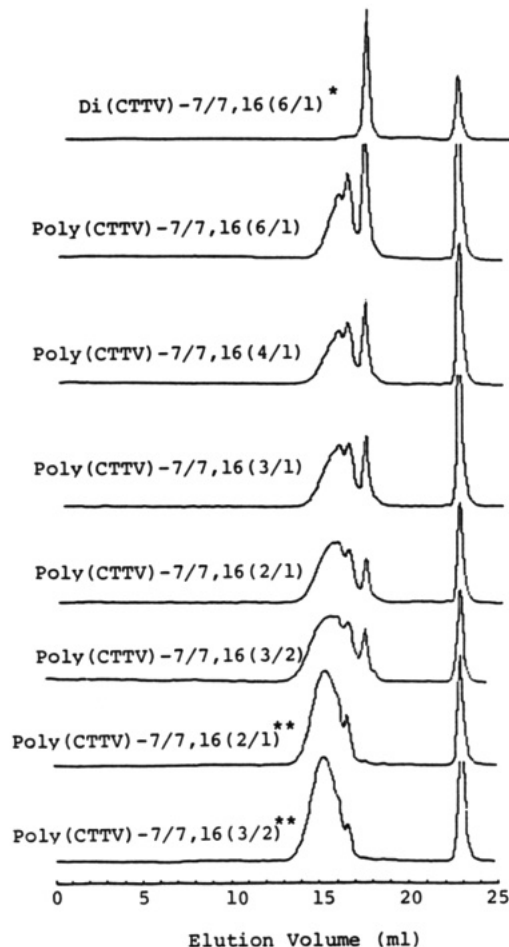

Figure 9. GPC chromatograms of the poly(CTTV)-7/7,16(x,y) dimer and oligomers prepared by cocyclotetramerization of x moles of 3,4-bis(n-heptyloxy)benzyl alcohol and y molecules of 1,16-bis[[2-(n-heptyloxy)-5-(hydroxymethyl)phenyl]oxy]hexadecane.

Table I. Since the molecular weight of these polymers is controlled by varying the molar ratio of 1(6) to 2(6,12), the composition of the polymers will also be different. The molecular weights reported in Table I were obtained by gel permeation chromatography calibrated with polystyrene standards and will therefore be correct only on a relative basis. The GPC traces of the poly(CTTV)-6/6,-12(x,y) oligomers presented in Figure 6 demonstrate that the concentration of the lowest molecular weight oligomer decreases by decreasing the feed ratio of 1(6) to 2(6,-12). The lowest molecular weight oligomer from the poly(CTTV)-7/7,16(x/y) experiments was separated and found to be a dimer. Its molecular weight determined by GPC is approximately half of its real value. Therefore, all real molecular weights are higher than the experimental values. If the real molecular weights of these oligomers are approximately twice those reported in Table I, the average degree of polymerization of the highest molecular weight polymer is 6. However, the experimental molecular weights are biased by the presence of a substantial amount of dimer.

The DSC scans obtained on heating and cooling the poly(CTTV)-6/6,12(x,y) samples are shown in Figure 7. Since the oligomers have different molecular weights, different compositions, and different amounts of dimer present, their thermal behavior can not be quantitatively compared. Nevertheless, some general trends are observed. All of the oligomers exhibit two columnar mesophases. As the concentration of dodecyl spacers increases,

Scheme III
Fourteen Isomers Which Can Form by Cocyclotetramerization of an Asymmetrically Substituted 3,4-Bis(alkyloxy)-benzyl Alcohol and a 3,4-Bis(n-alkyloxy)benzyl Alcohol
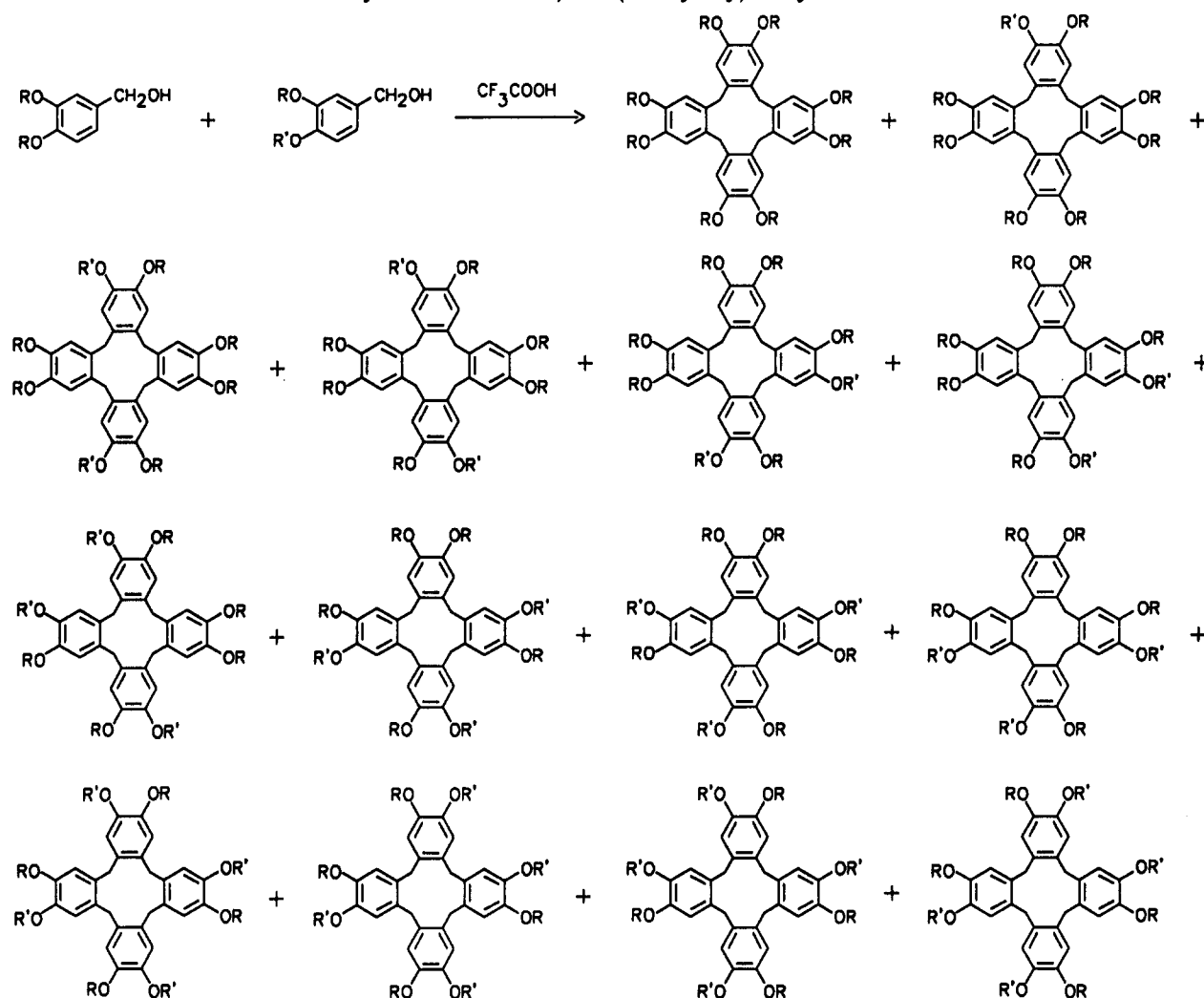
the temperature of isotropization decreases. This is consistent with the lower isotropization temperature of CTTV-12 compared to CTTV-6 (Table II). The synthesis and characterization of poly(CTTV)-7/7,12(x/y) is also summarized in Tables I and II, respectively. The behavior of these oligomers resembles that of poly(CTTV)-6/6,-12(x/y).

Representative textures exhibited by poly(CTTV)-6/6,12(6/1) and poly(CTTV)-7/7,12(6/1) are presented in parts A and B of Figure 8, respectively. Although only very fine textures with some fanlike characteristics are observed in all of the oligomers even after extensive annealing, the textures do change as a function of copolymer composition. As the concentration of the dodecyl spacer, and therefore the concentration of branched CTTV units, increases the textures become finer and no longer resemble those exhibited by either the monomers or dimers. Nevertheless, a tentative assignment of the phase transition temperatures is presented in Table II.

The results of the 1(7) and 2(7/7,16) copolymerizations are summarized in Table I. The GPC traces of poly-(CTTV)-7/7,16(x/y) with various compositions are shown in Figure 9, along with that of a separated dimer and those of some polymers purified of the dimer by fractional precipitation. The dimer was separated from poly(CTTV)-7/7,16(6/1) in 92% purity. Although the calculated molecular weight of the dimer is 2574, the GPC determined molecular weight is 1370 ($M_w/M_n = 1.02$).

As shown in Figure 9, the concentration of the dimer present in the polymer samples decreases by decreasing the content of monomer 1(7) in the initial reaction mixture. The relative amount of polymer formed and its molecular weight therefore increase. The dimer was completely removed from two polymer samples [poly(CTTV)-7/7,-16(2/1) and poly(CTTV)-7/7,16(3/2)] by two reprecipitations in acetone.

The DSC traces obtained on heating and cooling the poly(CTTV)-7,7/16(x,y) samples are presented in Figure 10. The pure di(CTTV)-7/7,16(6/1) dimer, which represents a discotic twin, shows three enantiotropic phase transitions. Polarized optical microscopy demonstrates that all three phases are fluid columnar mesophases. This dimer therefore does not crystallize either on heating or on cooling at 20 °C/min. The first mesophase formed from the isotropic melt nucleates and grows with a fingerlike structure (Figure 11A,B). Therefore, the highest temperature mesophase exhibited by the CTTV-7/7,16 dimer is also a D_h phase (Table II). Figure 11C shows the texture of the next mesophase formed on cooling.

The isotropization temperature of the twin dimer is lower than that of the corresponding CTTV-7 monomer. This may be because the length of the hexadecane spacer interconnecting the two CTTV-7 disks does not correspond to the distance between the columns formed by hexagonal packing of CTTV-7. This spacer length therefore depresses both the order in the CTTV-7 mesophase and the
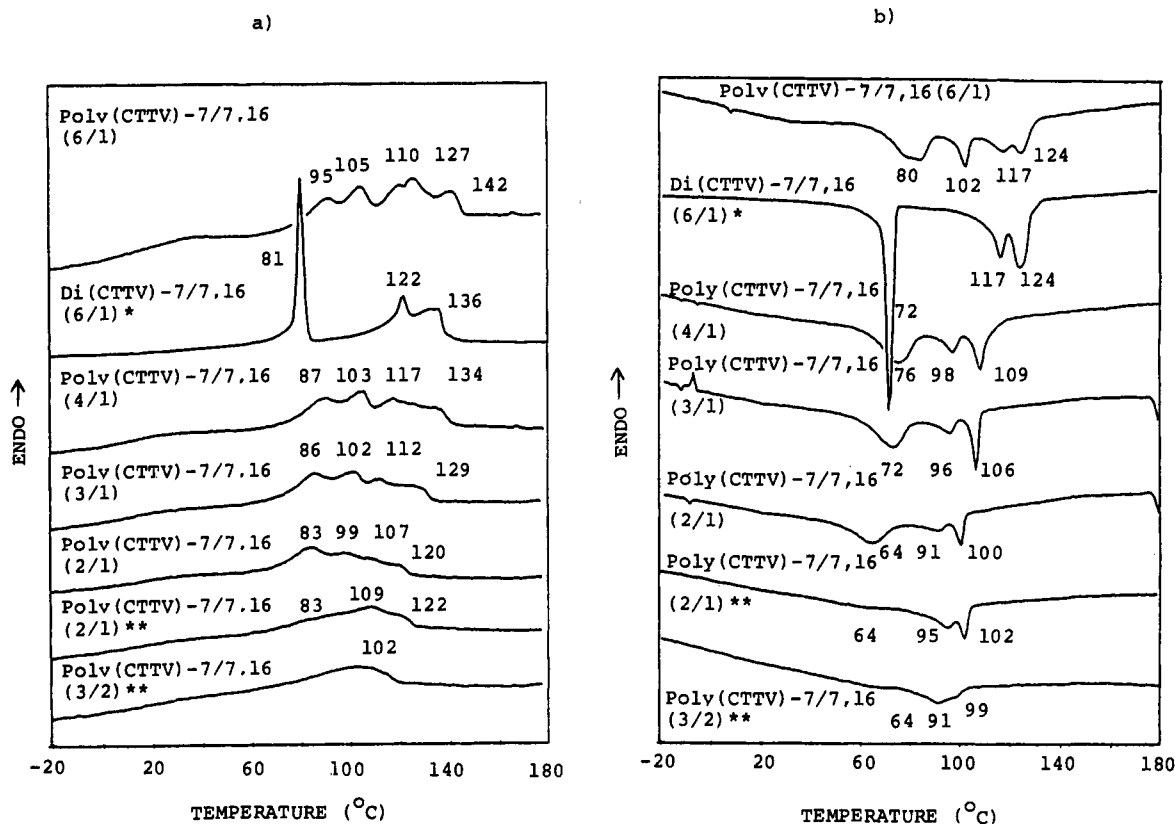
Figure 10. DSC heating and cooling scans (20 °C/min) of the poly(CTTV)-7/7,16(*x,y*) dimer and oligomers prepared by cocyclotetramerization of *x* moles of 3,4-bis(*n*-heptyloxy)benzyl alcohol and *y* moles of 1,16-bis[[2-(*n*-heptyloxy)-5-(hydroxymethyl)phenyl]oxy]hexadecane.

ability of the twin dimer to crystallize. Although subtle, the small mosaic texture of the D_h mesophase changes upon cooling to a broken fanlike texture (Figure 11D,E) which is maintained and remains fluid up to room temperature (Figure 11F).

As shown in Figure 10, the higher molecular weight samples also undergo three transitions on cooling. However, all transitions decrease in temperature as the molecular weight increases. Although the phase behavior of CTTV-16 has not been reported, it is known that the isotropization temperatures of CTTV-*n* derivatives decrease with increasing *n*-alkyloxy chain length.[6b] Therefore, the decrease in the isotropization temperatures of the higher molecular weight poly(CTTV)-7/7,16(*x,y*)s is evidently due to the increasing content of the hexadecane spacers.

Most of the polymer samples whose DSC traces are shown in Figure 10 contain the twin dimer as an impurity. However, the overall shape of the DSC traces is maintained in the poly(CTTV)-7/7/16(*x/y*) samples with *x/y* = 2/1 and 3/2 after the dimer has been removed. Therefore, with the exception of poly(CTTV)-7/7,16(6/1), the mesophases exhibited by the twin dimer are isomorphic with those of the poly(CTTV)-7/7,16(*x,y*). Poly(CTTV)-7,7/16 exhibits four peaks on cooling. The peak at 102 °C is evidently due to the higher molecular weight poly(CTTV)-7/7,16(6/1) fraction, while those at 117 and 124 °C are due to the twin dimer. The peak at 80 °C is due to peaks of both the dimer and polymer that overlap in temperature. In this case, the phase transition temperatures of the lowest molecular weight polymer and the twin dimer are too different for the isomorphic phases to mix, and they therefore exhibit four peaks.

More phase transition temperatures are observed in the DSC heating scans than in the cooling scans. This is probably because the mesophases of the twin dimer do

not always overlap the mesophases of the oligomers. An exception is provided by the purified samples of poly-(CTTV)-7/7,16(2/1) and poly(CTTV)-7/7,16(3/2). That is, while the first poly(CTTV)-7/7,16(2/1) shows three peaks on both heating and cooling, the purified poly-(CTTV)-7/7,16(3/2) shows a broad peak on heating corresponding to the three mesophase peaks.

Although there are many synthetic and characterization aspects of this research which are requiring further experiments, we believe that the results reported in this paper have demonstrated both a new preparative and a new architecture of interest for the field of liquid-crystalline polymers containing disklike mesogens.

Experimental Section

Materials. 1-Bromoheptane (Fluka; 99%), 3,4-dihydroxybenzaldehyde (Lancaster Synthesis; 97%), trifluoroacetic acid (Fisher Scientific; 99.7%), and all other reagents were used as received. 1,12-Dibromododecane (Aldrich; technical, mp 38–41 °C) and 1,16-dibromohexadecane (Pfaltz & Bauer; mp 56–57 °C) were recrystallized from methanol. CH_2Cl_2 used as cyclotetramerization solvent was distilled from CaH_2.

Techniques. ¹H NMR (200 MHz) spectra (δ, ppm) were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as the internal standard. All spectra of CTTV oligomers were recorded at 55 °C; the other spectra were recorded at room temperature.

Purity was determined by high-pressure liquid chromatography/gel permeation chromatography with a Perkin-Elmer Series 10 LC instrument equipped with an LC-100 column oven (40 °C), an LC-600 autosampler, and a Nelson Analytical 900 Series data station. Measurements were made using a UV detector with $CHCl_3$ as solvent (0.9–1.0 mL/min) and a 100-Å PL gel column or a set of 500- and 10⁴-Å PL gel columns. Molecular weights were determined using the same instrument, the set of 500- and 10⁴-Å PL gel columns, and a calibration plot constructed with polystyrene standards (Supelco).
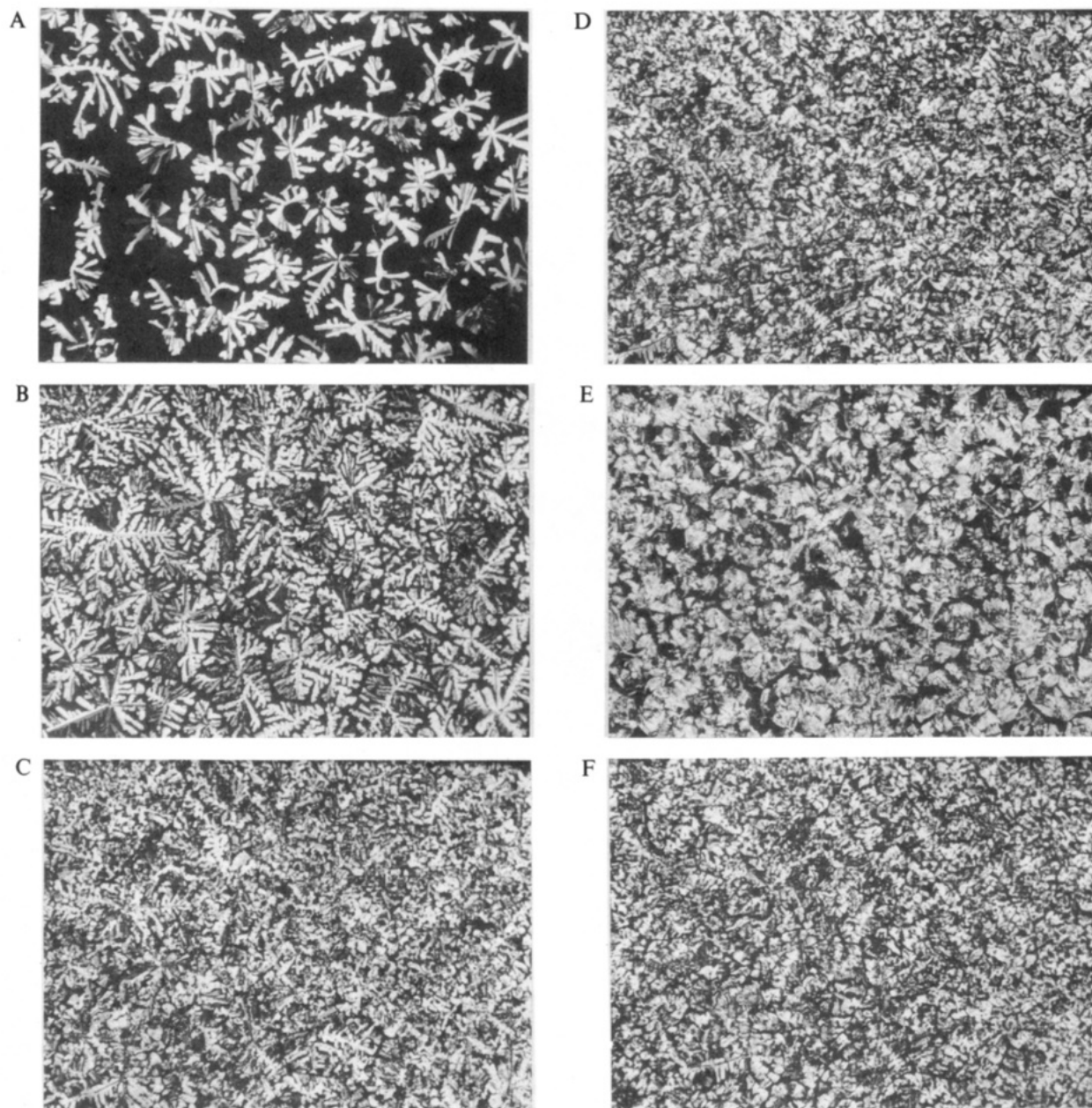
Figure 11. Polarized optical micrographs obtained on cooling (−10 °C/min) di(CTTV)-7/7,16(6/1) from the isotropic melt: (A) 141.2 °C, dendritic growth of fingerlike contours; (B) 137.2 °C, final mosaic texture typical of the D_h mesophase; (C) 127.3 °C, columnar mesophase obtained on cooling Figure 11B; (D) 72.1 °C, columnar mesophase obtained on cooling Figure 11C; (E) 72.6 °C, third columnar mesophase (another section); (F) 31.7 °C, same fluid anisotropic texture as Figure 11D.

A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions which were read as the maximum or minimum of the endothermic or exothermic peaks. All heating and cooling rates were 20 °C/min. Tabulated thermal transitions were read from reproducible second or later heating scans and first or later cooling scans. Both enthalpy changes and transition temperatures were determined using indium as a calibration standard.

A Carl Zeiss polarized optical microscope (magnification 100×) equipped with a Mettler FP-82 hot stage and a Mettler FP-800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[11,21,22]

Synthesis of CTTV-6, CTTV-7, and CTTV-12. CTTV-6, CTTV-7, and CTTV-12 were synthesized as described previously;[6b] purity ≥ 99.9%.

Synthesis of 3,4-Bis(n-hexyloxy)benzyl Alcohol [1(6)] and 3,4-Bis(n-heptyloxy)benzyl Alcohol [1(7)]. 3,4-Bis(n-hexyloxy)benzyl alcohol [97.8%, mp 31.9 °C (DSC, 20 °C/min)] and 3,4-bis(n-heptyloxy)benzyl alcohol (98.7%, mp 39–41 °C) were prepared by etherification of 3,4-dihydroxybenzaldehyde with

1-bromohexane or 1-bromoheptane, followed by reduction of the aldehyde group with $NaBH_4$ as described in detail in a previous publication.[6b] Both compounds have identical ^1H NMR chemical shifts: 0.95 (t, CH_3, 6 H), 1.34 (m, $[CH_2]_{n-3}$, 4[n − 3] H), 1.84 (m, OCH_2CH_2, 4 H), 4.02 (t, OCH_2, 4 H), 4.64 (s, OH), 6.89 (s, 2 aromatic H ortho to OR), 6.95 (s, 1 aromatic H meta to OR).

Synthesis of 3-Hydroxy-4-(n-hexyloxy)benzaldehyde and 3-Hydroxy-4-(n-heptyloxy)benzaldehyde. 3-Hydroxy-4-(n-hexyloxy)benzaldehyde [99.6%, mp 47.4 °C (DSC, 20 °C/min)] and 3-hydroxy-4-(n-heptyloxy)benzaldehyde were prepared as in the following synthesis of 3-hydroxy-4-(n-heptyloxy)benzaldehyde. A solution of 3,4-dihydroxybenzaldehyde (6.0 g, 43 mmol), 1-bromo-n-heptane (7.7 g, 43 mmol), K_2CO_3 (3.0 g, 22 mmol), and KI (0.10 g, 0.60 mmol) in ethanol (50 mL) was stirred at reflux for 8 h under nitrogen. The reaction mixture was then filtered to remove KBr, and the KBr was washed several times with ethanol. The filtrate was condensed by rotary evaporation, and Et_2O and 5% NaOH were added to the residue until two clear layers formed. Following extraction of the aqueous phase with Et_2O and extraction of the Et_2O extracts with H_2O, the solvent was removed from the ether extracts to yield 2.0 g (14%)

of 3,4-bis(*n*-heptyloxy)benzaldehyde. The combined aqueous layer was then acidified (pH = 2) with HCl and extracted with Et₂O. These ether extracts were washed with H₂O, and the solvent was removed by rotary evaporation. The resulting dark brown residue was purified by column chromatography on silica gel using acetone–hexanes (2:1) as eluant to yield 5.5 g (53%) 3-hydroxy-4-(*n*-heptyloxy)benzaldeyde, mp 61–63 °C, purity 98.9%. 3-Hydroxy-4-(*n*-hexyloxy)benzaldehyde and 3-hydroxy-4-(*n*-heptyloxy)benzaldehyde have identical ¹H NMR chemical shifts: 0.95 (t, *CH₃*), 1.35 (m, [*CH₂*]ₙ₋₃), 1.91 (m, CH₂*CH₂*), 4.18 (t, O*CH₂*), 5.81 (s, O*H*), 6.98 (d, 1 aromatic H meta to CHO), 7.20 (d, 2 aromatic H ortho to CHO), 9.87 (d, C*HO*).

Synthesis of 1,12-Bis[[2-(*n*-hexyloxy)-5-formylphenyl]oxy]dodecane, 1,12-Bis[[2-(*n*-heptyloxy)-5-formylphenyl]oxy]dodecane, and 1,16-Bis[[2-(*n*-heptyloxy)-5-formylphenyl]oxy]hexadecane. The 1,12-bis[[2-(*n*-alkyloxy)-5-formylphenyl]oxy]dodecanes and 1,16-bis[[2-(*n*-heptyloxy)-5-formylphenyl]oxy]hexadecane were prepared as in the following example. A solution of 3-hydroxy-4-(*n*-heptyloxy)benzaldehyde (0.71 g, 3.0 mmol), 1,16-dibromohexadecane (0.50 g, 1.3 mmol), K₂CO₃ (0.43 g, 3.1 mmol), and KI (30 mg, 0.18 mmol) in ethanol (30 mL) was stirred at reflux for 2 days. The contents of the flask solidified upon cooling. Methanol (75 mL) and water (75 mL) were added, and the precipitate was collected in a fritted glass funnel, washed several times with water and with methanol, and dried in vacuo to yield 0.90 g (86%) of 1,16-bis[[2-(*n*-heptyloxy)-4-formylphenyl]oxy]hexadecane, mp 80–81 °C, purity >99.9%. ¹H NMR: 0.90 (t, *CH₃*, 6 H), 1.30 (m, [*CH₂*]₄ and [*CH₂*]₁₂, 40 H), 1.86 (m, OCH₂*CH₂*, 8 H), 4.08 (2 overlapping t, O*CH₂*, 8 H), 6.96 (d, 2 aromatic H meta to CHO), 7.43 (d, 4 aromatic H ortho to CHO), 9.88 (s, C*HO*, 2 H).

1,12-Bis[[2-(*n*-hexyloxy)-5-formylphenyl]oxy]dodecane [88.5%, mp 34–37 °C (DSC, 20 °C/min)] and 1,12-bis[[2-(*n*-heptyloxy)-5-formylphenyl]oxy]dodecane have identical ¹H NMR chemical shifts: 0.91 (t, *CH₃*, 6 H), 1.28 (m, [*CH₂*]₃ and [*CH₂*]₈, 28 H), 1.84 (m, OCH₂*CH₂*, 8 H), 4.08 (2 overlapping t, O*CH₂*, 8 H), 6.97 (d, 2 aromatic H meta to CHO), 7.39 (d, 4 aromatic H ortho to CHO), 9.82 (s, C*HO*, 2 H).

Synthesis of 1,12-Bis[[2-(*n*-hexyloxy)-5-(hydroxymethyl)phenyl]oxy]dodecane [2(6,12)], 1,12-Bis[[2-(*n*-heptyloxy)-5-(hydroxymethyl)phenyl]oxy]dodecane [2(7,12)], and 1,16-Bis[[2-(*n*-heptyloxy)-5-(hydroxymethyl)phenyl]oxy]hexadecane [2(7,16)]. The 1,12-bis[[2-(*n*-alkyloxy)-5-(hydroxymethyl)phenyl]oxy]dodecanes and 1,16-bis[[2-(*n*-heptyloxy)-5-(hydroxymethyl)phenyl]oxy]hexadecane were prepared as in the following example. A solution of NaBH₄ (70 mg, 1.9 mmol) and NaOH (50 mg, 1,2 mmol) in a mixture of ethanol (20 mL) and H₂O (3 mL) was added dropwise to a mixture of 1,-16-bis[[2-(*n*-heptyloxy)-5-formylphenyl]oxy]hexadecane (0.79 g, 1.1 mmol) in THF (20 mL). The reaction mixture was stirred at reflux for 10 h. The solvent was removed on a rotary evaporator, and the residue was washed several times with water and recrystallized from ethanol to yield 0.77 g (97%) of 1,16-bis[[2-(*n*-heptyloxy)-5-(hydroxymethyl)phenyl]oxy]hexadecane, mp 74–75 °C, purity 97.7%. ¹H NMR: 0.88 (t, *CH₃*, 6 H), 1.27 (m, [*CH₂*]₄ and [*CH₂*]₁₂, 40 H), 1.83 (m, OCH₂*CH₂*, 8 H), 3.98 (t, O*CH₂*, 8 H), 4.62 (s, *CH₂*OH, 4 H), 6.88 (s, 4 aromatic H ortho to OR), 6.94 (s, 2 aromatic H meta to OR).

1,12-Bis[[2-(*n*-hexyloxy)-5-(hydroxymethyl)phenyl]oxy]dodecane [94.5% mp 71.3 °C (DSC, 20 °C/min)] and 1,12-bis[[2-(*n*-heptyloxy)-5-(hydroxymethyl)phenyl]oxy]dodecane have identical ¹H NMR chemical shifts: 0.90 (t, *CH₃*, 6 H), 1.30 (m, [*CH₂*]₄ and [*CH₂*]₈, 32 H), 1.81 (m, OCH₂*CH₂*, 8 H), 3.99 (t, O*CH₂*, 8 H), 4.59 (s, *CH₂*OH, 4 H), 6.85 (s, 4 aromatic ortho to OR), 6.92 (s, 2 aromatic H meta to OR).

Cocyclotetramerizations of 3,4-Bis(*n*-hexyloxy)benzyl Alcohol [1(6)] and 3,4-Bis(*n*-dodecyloxy)benzyl Alcohol [1(12)]. Mixtures of up to six CTTV isomers containing hexyloxy and dodecyloxy substituents (CTTV-6/12) were prepared by cocyclotetramerization of varying ratios of *x* moles of 3,4-bis(*n*-hexyloxy)benzyl alcohol with *y* moles of 3,4-bis(*n*-dodecyloxy)benzyl alcohol [CTTV-6/12(*x/y*)] as in the following example describing the synthesis of CTTV-6/12(1/3). Trifluoroacetic acid (0.50 mL, 6.5 mmol) was added to a solution of 3,4-bis(*n*-hexyloxy)benzyl alcohol (0.035 g, 0.11 mmol) and 3,4-bis(*n*-dodecyloxy)benzyl alcohol (0.16 g, 0.35 mmol) in CH₂Cl₂

(9.5 mL). After stirring at room temperature for 4.5 h, the purple reaction mixture was quenched with triethylamine (0.5 ml), and the resulting yellow organic layer was washed three times with water and precipitated in methanol (100 mL). The precipitate was filtered, washed twice with acetone, and dried in vacuo to yield 0.13 g (66%) of CTTV-6/12(1/3). The results of the synthesis of CTTV-6/12 are summarized in Table I.

Cocyclotetramerizations of 3,4-Bis(*n*-alkyloxy)benzyl Alcohols [1(*n*)] and α,ω-Bis[[2-(*n*-alkyloxy)-5-(hydroxymethyl)phenyl]oxy]alkanes [2(*n,m*)]. CTTV-*n/n,m*(*x,y*) oligomers were prepared by cocyclotetramerization of varying ratios of a 3,4-bis(*n*-alkyloxy)benzyl alcohol with an α,ω-bis[[2-(*n*-alkyloxy)-5-(hydroxymethyl)phenyl]oxy]alkane as in the following dimer preparation. Trifluoroacetic acid (0.50 mL, 6.5 mmol) was added to a solution of 3,4-bis(*n*-heptyloxy)benzyl alcohol (0.15 g, 44 mmol) and 1,16-bis[[2-(*n*-heptyloxy)-5-(hydroxymethyl)phenyl]oxy]hexadecane (51 mg, 0.073 mmol) in CH₂Cl₂ (9.5 mL). After stirring at room temperature for 4 h, the purple reaction mixture was quenched with triethylamine (0.5 mL), and the resulting yellow organic layer was washed three times with water. The CH₂Cl₂ oligomer solution was then precipitated in methanol, and the precipitate was washed with acetone and with methanol and dried in vacuo: yield 0.13 g; M_n = 3700, M_w/M_n = 1.57. The pure CTTV-7/7,16(6/1) dimer (92%) was obtained by precipitating a CHCl₃ solution of the above mixture with acetone, filtering off the precipitated higher oligomers, and purifying the acetone-soluble portion by column chromatography on silica gel using CHCl₃–hexanes (1:1) as eluant. ¹H NMR: 0.89 (t, *CH₃*, 36 H), 1.30 (m, [*CH₂*]₄ and [*CH₂*]₁₂, 136 H), 1.76 (m, OCH₂*CH₂*, 32 H), 3.51 (b s, Ar*CH₂*Ar, 16 H), 3.89 (t, OH*H₂*, 32 H), 6.60 (s, 16 aromatic H).

The results of the cocyclotetramerization reactions are presented in Table II. Poly(CTTV)-7/7,16(2/1) and poly(CTTV)7/7,16(3/2) free of CTTV-7/7,16(6/1) dimer were obtained by two precipitations from CHCl₃ with acetone. The ¹H NMR spectra of all oligomers were free of the resonances at 6.84 (s, aromatic protons), 4.78 (d, Hₐₓ), and 3.56 (d, Hₑ𝓆) due to CTTV-based mesogens.

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