Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Phase Transfer Pd(0) Catalyzed Polymerization Reactions. 2. Thermal Characterization of Liquid Crystalline 1,2-(4,4′-Dialkoxyaryl)acetylene Derivatives

C. Pugh [a] & V. Percec [a]

[a] Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio, 44106, USA

Version of record first published: 04 Oct 2006.

To cite this article: C. Pugh & V. Percec (1990): Phase Transfer Pd(0) Catalyzed Polymerization Reactions. 2. Thermal Characterization of Liquid Crystalline 1,2-(4,4′-Dialkoxyaryl)acetylene Derivatives, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 178:1, 193-217

To link to this article: http://dx.doi.org/10.1080/00268949008042719

Mol. Cryst. Liq. Cryst., 1990, Vol. 178, pp. 193–217
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Phase Transfer Pd(O) Catalyzed Polymerization Reactions. 2. Thermal Characterization of Liquid Crystalline 1,2-(4,4′-Dialkoxyaryl)acetylene Derivatives†

C. PUGH and V. PERCEC‡

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106 USA

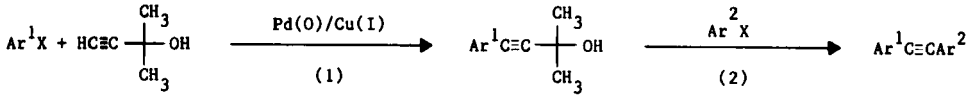
(*Received July 18, 1989*)

A homologous series of 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes with n = 1,3–12 was prepared by a one pot phase transfer Pd(O)/Cu(I) catalyzed three step coupling of an aryl halide with 2-methyl-3-butyn-2-ol, followed by deprotection of the carbinol group and finally a second coupling with either the same or another aryl halide. The lower members of this series with n = 1–3 are crystalline. In addition to a nematic phase, the compounds with from four to eight methylenic units in the alkoxy substituents present crystalline polymorphism due to the proximity of the crystallization temperatures and the low rates of crystallization. Therefore, under the nonequilibrium conditions at which the compounds were analyzed, these immiscible crystalline phases coexist. The higher homologs of n = 10–12 display an unusual enantiotropic smectic C phase directly below a nematic phase. These compounds also exhibit an additional monotropic smectic phase, possibly smectic B, below the smectic C phase. Methyl branches were introduced into either the aromatic ring(s) of the mesogen or the alkoxy substituent of several 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes. This acts to depress liquid crystallinity more than crystallinity. However, the assymetrically substituted branched derivatives display a nematic phase in addition to the crystalline phase(s).

INTRODUCTION

The first paper[1] in this series described the synthesis of several 1,2-(4,4′-dialkoxyaryl)acetylenes and 1,4-*bis*[2-(4′,4″-dialkoxyphenyl)ethynyl]benzene derivatives containing similar or dissimilar substituents by four variations of a one pot phase transfer Pd(O)/Cu(I) catalyzed coupling of aryl halides with a protected acetylene. This synthetic procedure was originally developed by Carpita et al.[2] for the synthesis of 1,2-(diheteroaryl)acetylenes. Three steps are performed in the same flask with isolation and purification of only the final 1,2-diarylacetylene product. In the first

†Part 1 in this series: C. Pugh and V. Percec, J. Polym. Sci., Polym. Chem. Ed., in press.
‡To whom correspondence should be sent.



Method A - liquid-liquid PTC
(1) - 16-50 hrs @ room temperature
(2) - 40-50 hrs @ 70-80°C

Method B (1) - concentrated aq. K_2CO_3 phase
- PTC
- reflux
(2) - solid NaOH, reflux

Method C (1) = (2) - 2 eq. ArX + 1 eq. HC≡C-
- solid-liquid PTC:solid KOH
- reflux

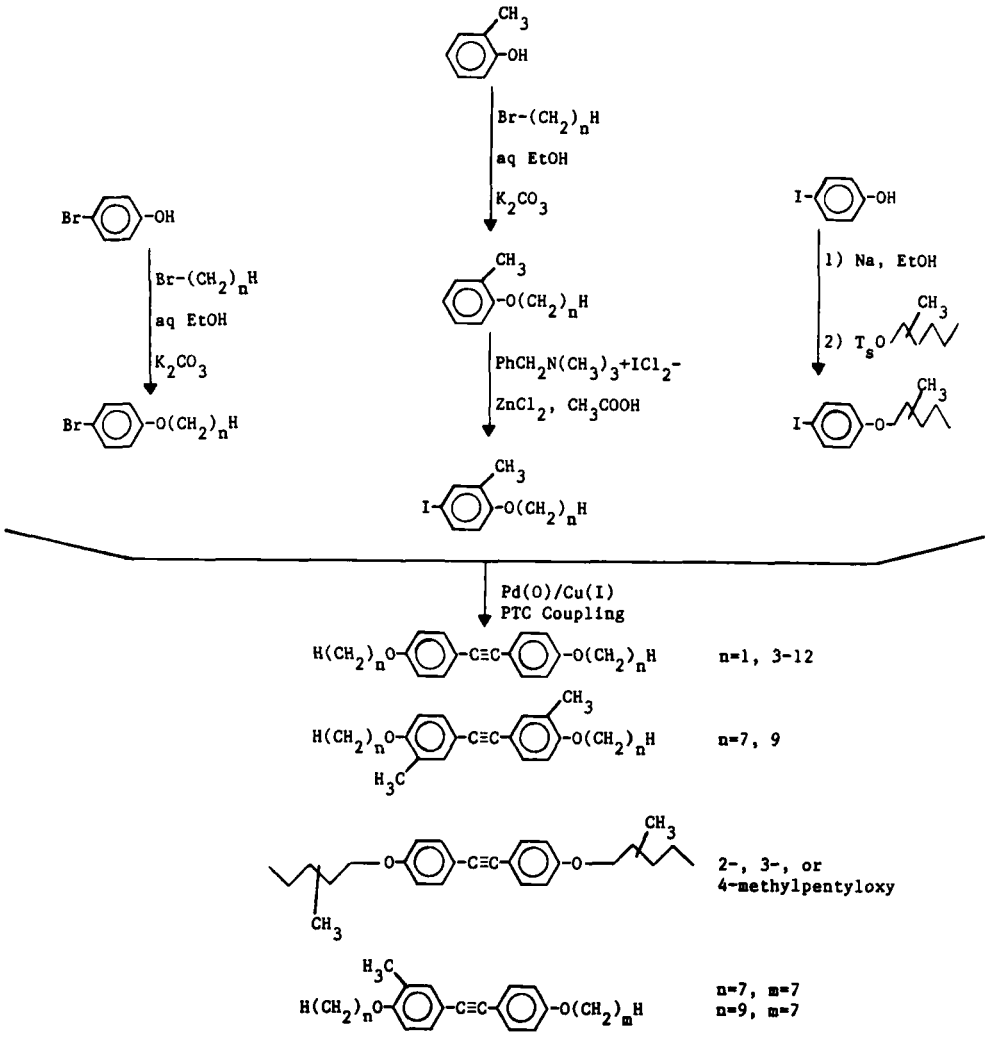
Method D (1) - non-PTC:2 eq. NEt_3 in benzene
- reflux
(2) - solid-liquid PTC:solid KOH
- reflux

SCHEME 1 The four variants of the one pot phase transfer Pd(O)/Cu(I) catalyzed synthesis of 1,2-(diaryl)acetylenes. PTC = phase transfer catalyzed.

step, an aromatic halide is coupled with 2-methyl-3-butyn-2-ol as the monoprotected acetylene. In the second step, the resulting compound is deprotected with formation of an aryl acetylene. The final step involves the coupling of this aryl acetylene with a second aryl halide. Deprotection of the 1-aryl-2-(isopropanol)acetylene is the rate determining step.[1]

Carpita et al.'s original procedure (Scheme 1, Method A) performs the first coupling step in benzene at room temperature using 5.5 *N* NaOH as the aqueous phase. The catalytic system included a phase transfer catalyst, tetrakis(triphenylphosphine) palladium and cuprous iodide. The second coupling step and deprotection were performed simultaneously after addition of the second aryl halide by increasing the temperature to 70–80°C.

The 1,2-(4,4′-dialkoxyaryl)acetylenes found in Scheme 2 were most successfully prepared from the corresponding aryl halides by variations of Method A. Symmetrically substituted 1,2-diarylacetylenes were most conveniently synthesized by performing all three steps simultaneously in a solid-liquid phase transfer catalyzed system (Scheme 1, Method C). On the other hand, assymmetrically substituted 1,2-diarylacetylenes were prepared by Method D (Scheme 1) involving non phase transfer catalyzed coupling in the first step. Scheme 2 outlines the general synthetic



SCHEME 2 1,2-(4,4′-Dialkoxyaryl)acetylene derivatives synthesized by phase transfer Pd(O)/Cu(I) catalyzed coupling of acetylenes with the 1-halo-4-alkoxybenzene derivatives shown.

route used to prepare the 1,2-(4,4′-dialkoxyphenyl)acetylenes described in this paper and their precursors.

The symmetrical 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes shown in Scheme 2 where $n = 1-8,10$ have been prepared previously by the alkaline rearrangement and elimination of 1,1-disubstituted-2,2′-diarylethylenes.[3,4] With the exception of 1,2-(4,4′-didecyloxyphenyl)acetylene,[5a,b] their complete thermal behaviour was not reported. However, all compounds were reported to display nematic mesophases and multiple crystalline transitions. The thermal transitions of 1,2-(4,4′-didecyloxyphenyl)acetylene were reported as: *k* 86.5 s_C 89 s_A 95.5 *n* 101.[4]

This paper will report the complete thermal behavior of the symmetrically substituted 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes with one and from three to twelve

methylenic units in the *n*-alkoxy substituents. To our knowledge, the 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes with $n = 9,11,12$ have not been reported previously. In addition, we are also interested in understanding how a methyl branch affects the liquid crystalline behavior of 1,2-diarylacetylenes and their derivatives. Therefore, several 1,2-(4,4′-dialkoxyaryl)acetylenes were prepared with a methyl branch in either the aromatic ring(s) of the mesogen or the alkoxy side chains.

At this time, we are primarily interested in the synthesis of low molar mass and oligomeric liquid crystals based on 1,2-(4,4′-dialkoxyaryl)acetylene units. These monomers can undergo either linear polymerization leading to polyacetylenes, or cyclotrimerization leading to hexa(alkoxyaryl)benzene derivatives. The hexasubstituted benzene derivatives may be low molar mass disc-like liquid crystals. In addition, several potentially interesting classes of oligomers and polymers containing 1,2-diarylacetylene units will be investigated. In our opinion, these can be most conveniently synthesized by coupling reactions of aryl halides with aryl acetylides, especially by the one pot sequential coupling of two aryl halides with a protected acetylene as reported previously.[1,2]

RESULTS AND DISCUSSION

In addition to symmetrically substituted 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes,[3,4] assymetrically substituted 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes,[3] symmetric and assymmetric 1,2-(4,4′-dialkylphenyl)acetylenes[5a,b] and 1-(4-alkoxyphenyl)-2-(4′-alkylphenyl)acetylenes[3,6] have been reported. All of these compounds display nematic mesophases. The dialkyl-[5b], and as will be demonstrated subsequently, the dialkoxy-derivatives also display smectic mesophase(s). The temperature of isotropization decreases in the order 1,2-(4,4′-dialkoxyphenyl)acetylene > 1-(4-alkoxyphenyl)-2-(4′-alkylphenyl)acetylene > 1,2-(4,4′-dialkylphenyl)acetylene, and wider nematic temperature windows are observed when the two alkyl or alkoxy substituents are of different lengths. Chiral 1-(4-*n*-alkoxyphenyl)-2-{4-[S-(+)-2-methylbutyl]phenyl}-acetylenes[7] have also been synthesized, and display cholesteric mesophases.

Several additional classes of diarylacetylenes have been previously reported, including 1-(4-alkoxyphenyl)-2-(4′-alkanoyloxyphenyl)acetylenes,[8] 1-(4-alkoxyphenyl)-2-(4′-alkoxycarbonyloxyphenyl)acetylenes,[8] 1-(4-alkylphenyl)-2-(4′-cyanophenyl)acetylenes[9–12] and 1-(4-alkoxyphenyl)-2-(4′-cyanophenyl)acetylenes,[10–13] 1-(4-alkylphenyl)-2-(4′-[ω-cyanoalkoxy]phenyl)acetylenes[12] and 1,2-(4,4′-acyloyloxyphenyl)acetylene.[14] These compounds display monotropic or enantiotropic nematic mesophases. 1,2-(4,4′-Dialkanoyloxyphenyl)acetylenes, which are crystalline, have also been synthesized.[8]

Symmetrically substituted 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes

The DSC traces observed on heating and cooling the symmetrically substituted 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes with $n = 1,3–12$ methylenic units are presented in Figures 1 and 2 respectively. Their complete thermal transitions are summarized

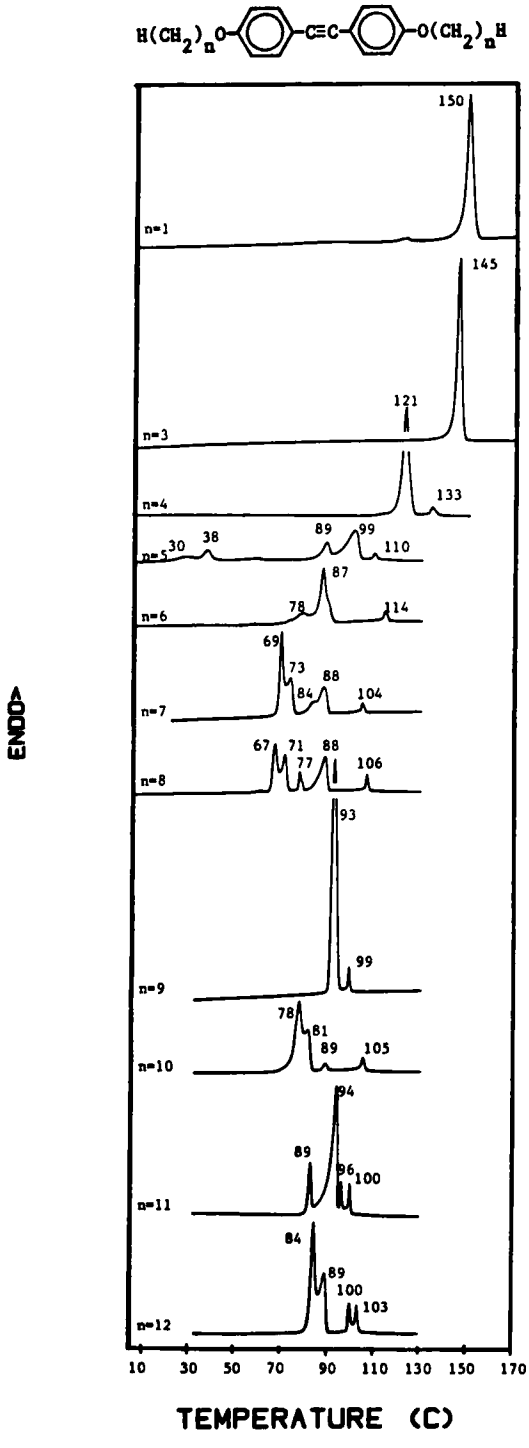


FIGURE 1 DSC heating scans of symmetrically substituted 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes.

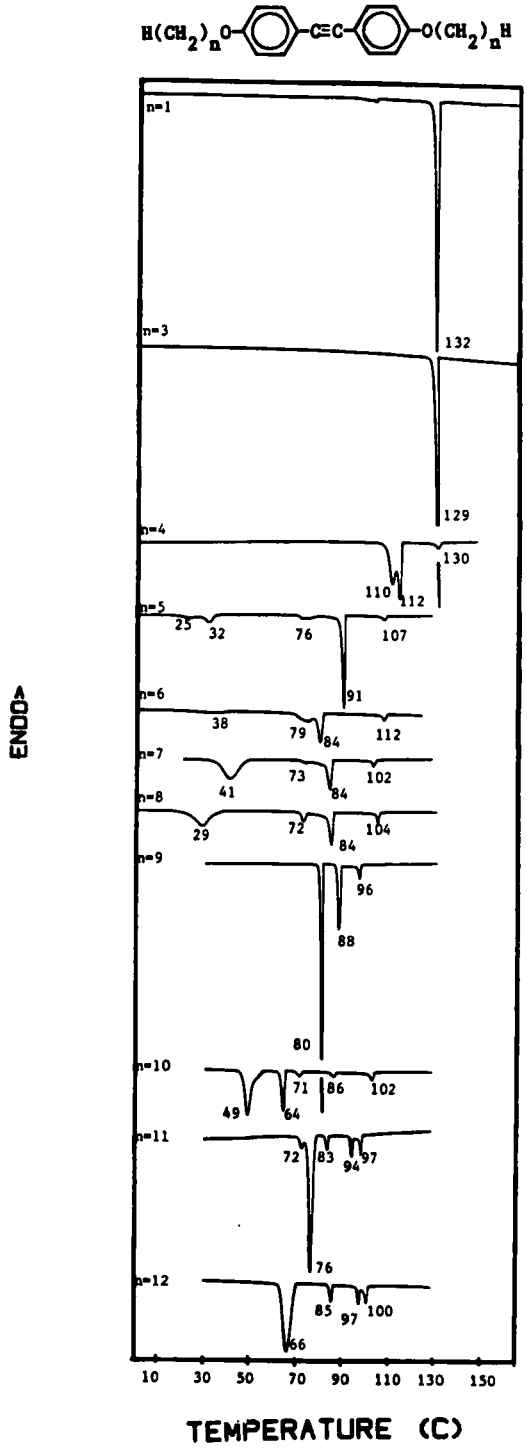
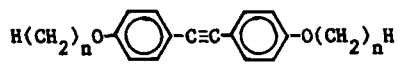


FIGURE 2 DSC cooling scans of symmetrically substituted 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes.

TABLE I

Thermal transitions and thermodynamic parameters of symmetrically substituted 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes.†



n	Phase Transitions (°C) and the Corresponding Enthalpy Changes (in parentheses, kcal/mol)
1	k 150.2 (7.03) i i 131.9 (6.71) k
3	k 144.9 (8.23) i i 129.3 (7.77) k
4	k 121.4 (6.77) n 133.2 (0.42) i i 130.4 (0.52) n 112.2 k 109.8 (6.69)* k
5	k 30.2 k 38.0 (1.52)* k 88.7 k 99.4 (5.05)* n 109.8 (0.32) i i 107.1 (0.37) n 91.1 k 75.6 (5.02)* k 31.8 k 24.8 (1.64)* k
6	k 78.2 k 86.9 (6.12)* n 113.8 (0.51) i i 111.5 (0.59) n 84.0 k 78.6 (4.36)* k 38.3 (0.87) k
7	k 69.4 k 73.4 (6.21)* k 83.7 k 87.6 (3.17)* n 104.4 (0.42) i i 102.4 (0.56) n 83.8 k 73.4 (3.26)* k 40.9 (5.53) k
8	k 66.5 k 70.8 (5.00)* k 77.3 (0.65) k 88.3 (3.10) n 106.4 (0.71) i i 104.2 (0.78) n 84.3 k 72.1 (3.99)* k 28.8 (5.07) k
9	k 92.7 (14.8) n 98.8 (0.53) i i 96.2 (0.63) n 87.5 (3.44) s 80.3 (8.95) k
10	k 77.5 k 81.4 (10.3) s_C 88.8 (0.45) n 105.0 (0.95) i i 101.9 (0.87) n 85.6 (0.38) s_C 70.7 (0.53) s 63.9 (2.65) k 48.7 (6.90) k
11	k 88.8 (1.68) k 93.8 (14.2) s_C 96.1 (0.61) n 99.7 (0.66) i i 97.4 (1.05) n 93.7 (1.09) s_C 83.2 (0.81) s 76.3 k 72.3 (13.3)* k
12	k 84.4 k 89.2 (13.8)* s_C 100.0 n 103.2 (2.61)* i i 100.4 n 97.2 (2.57)* s_C 85.4 (1.00) s 66.4 (13.3) k

†k = crystalline, s = smectic, n = nematic, i = isotropic melt; first line of data obtained on heating, second line on cooling

*overlapping with the previous transition(s)

in Table I. 1,2-(4,4′-Dimethyloxyphenyl)acetylene, 1,2-(4,4′-diethyloxyphenyl)-acetylene[6] and 1,2-(4,4′-dipropyloxyphenyl)acetylene are only crystalline and therefore melt into an isotropic state. However, once the alkoxy substituent is composed of at least four methylenic units, crystallization is sufficiently suppressed that a nematic mesophase is also realized. As shown in Figure 3, melting and crystallization continue to drop until the alkoxy substituents contain approximately six methylenic units. When the alkoxy substituent reaches nine methylenic units, melting increases in temperature and crystallization drops relative to the shorter homologs; both alternate thereafter in an odd-even manner. It is interesting to note that in these

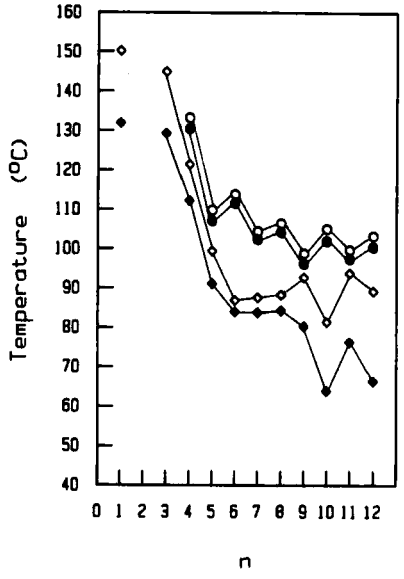


FIGURE 3 Melting (◇), crystallization (◆), isotropization (○) and isotropic→nematic (●) transition temperatures of symmetrically substituted 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes as a function of *n*.

compounds, isotropization and crystallization/melting display opposite odd-even alternation. Such a trend is also observed in the homologous 1-(4-alkylphenyl)-2-(4′-cyanophenyl)acetylenes,[9–12] although the authors did not note it as unusual. The effect is so great in the cyanophenylacetylenes that they alternate in displaying monotropic (even *n*) and enantiotropic (odd *n*) nematic mesophases. We have no explanation for this phenomena at this time.

With the exception of 1,2-(4,4′-dinonyloxyphenyl)acetylenes, further examination of Figures 1 and 2 demonstrate that the homologous series of compounds displaying nematic mesophases can be grouped into two categories. 1,2-(4,4′-Dibutyloxyphenyl)acetylene through 1,2-(4,4′-dioctyloxyphenyl)acetylene behave similarly, while 1,2-(4,4′-didecyloxyphenyl)acetylene through 1,2-(4,4′-didodecyloxyphenyl)acetylene can be grouped into a second category which displays similar transitions.

Figure 4 shows a series of optical micrographs obtained by cooling 1,2-(4,4′-dioctyloxyphenyl)acetylene from the nematic mesophase. These micrographs are representative of the first category involving the shorter homologs. Upon solidification from the nematic state, two immiscible phases are formed by those compounds with from four to eight methylenic units in the alkoxy chains. Although there is some resolution of the first phase formed from the nematic state of 1,2-(4,4′-dibutyloxyphenyl)acetylene, the second immiscible phase forms almost simultaneously due to the proximity in transition temperatures. In this first set of compounds, one first observes the appearance of two phases of approximately equally small domain size (Figure 4A). These two immiscible phases then grow somewhat and separate further (Figure 4B). Immiscibility persists throughout the additional phase transitions observed on cooling (Figures 4C–E).

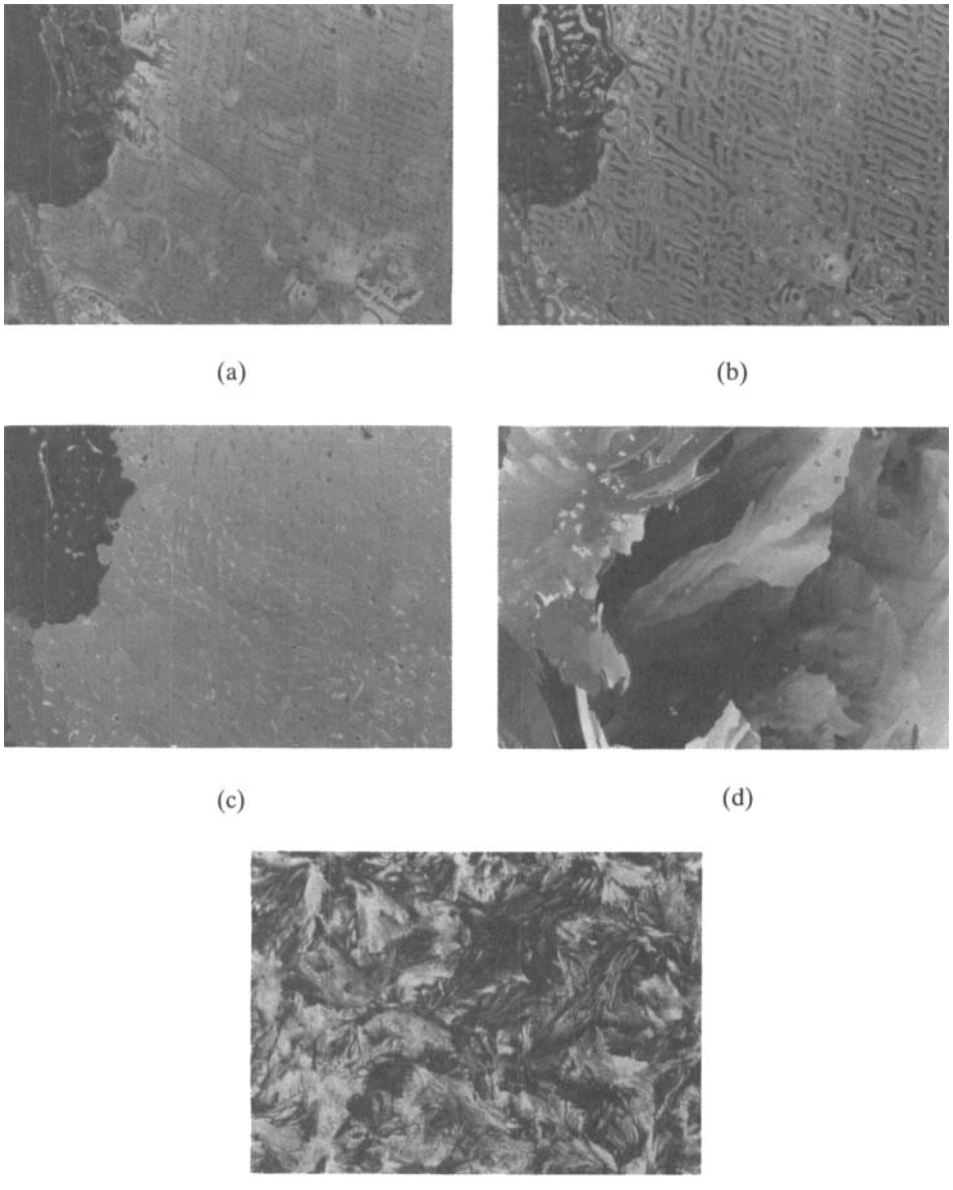


FIGURE 4 Microscopic textures (100×) observed on cooling 1,2-(4,4′-dioctyloxyphenyl)acetylene from the nematic mesophase; thin sample. (A) 85.6°C, $n \rightarrow k_3$; same section as (B)–(D) (B) 85.6°C, $n \rightarrow k_3$ a few seconds later (C) 80.8°C, k_3 (D) 72.9°C, $k_3 \rightarrow k_2$ (E) room temperature k_1; annealed 3.5 days at room temperature.

The question is, whether these immiscible phases involve only crystalline phases, or perhaps both crystalline phase(s) and smectic phase(s). Both phases become more distinct with more developed growth patterns, and the phase transitions become more obvious, upon going from shorter to longer alkoxy chain length. Although the amount of supercooling at these transitions is often quite small and therefore indicative of transitions to a liquid crystalline state, the total change in enthalpy upon cooling from the nematic state to 0°C adds up to only 6.69 to 9.06 kcal/mol. This enthalpy is comparable to that of the melting/crystallization of 1,2-(4,4′-dimethyloxyphenyl)acetylene, 1,2-(4,4′-dipropyloxyphenyl)acetylene and 1,2-(4,4′-dinonyloxyphenyl)acetylene, and is much lower than that of the higher homologs. We therefore tend to believe that both immiscible phases are crystalline, and that only crystalline polymorphism occurs in addition to the nematic mesophase.

The crystallization of these compounds is evidently difficult and leads to the coexistence of polymorphic crystalline phases under nonequilibrium conditions. In addition, the rate of crystallization is apparently slow, and the crystallization of consecutive polymorphic phases therefore overlap. Nevertheless, a single phase should form under equilibrium conditions after sufficient annealing at the appropriate temperature. The optical micrographs observed after several days at room temperature show the coexistence of two, more developed, crystalline phases. Because both phases are frozen at this temperature, it is necessary to anneal the sample at a temperature slightly above the lowest temperature crystalline–crystalline transition in order to form a single phase of the more thermodynamically stable crystal. Gray and Mosley[10] have also observed the coexistence of two crystalline phases (needles and platelets) in 1-(4-decylphenyl)-2-(4′-cyanophenyl)acetylene. It must be emphasized at this point that these compounds displaying the simultaneous occurrence of immiscible phases are greater than 99.6% pure.

1,2-(4,4′-Dinonyloxyphenyl)acetylene displays only one crystalline phase and a nematic mesophase on heating. On cooling, crystallization is somewhat depressed relative to the previous homologs, and a monotropic smectic mesophase is observed in addition to the crystalline and nematic phases. As shown in Figure 5, this unidentified smectic mesophase displays a mosaic texture, as is typical of smectic B, F, G and H mesophases.

1,2-(4,4′-Di-*n*-alkoxyphenyl)acetylenes with ten to twelve methylenic units in the alkoxy substituents display a nematic mesophase and two smectic mesophases. In addition, 1,2-(4,4′-didecyloxyphenyl)acetylene undergoes two crystallization transitions. As stated in the introduction, the phases exhibited by 1,2-(4,4′-didecyloxyphenyl)acetylene have been previously assigned to: *k* 86.5 s_C 89 s_A 95.5 *n* 101.[4] However, we have identified the enantiotropic smectic phase observed below the nematic state of this series of compounds as a smectic C (s_C) phase. This can be seen most clearly from microscope slides prepared by the method of Neubert and De Vries,[15] which results in thicker samples.

The smectic C phase was identified in thick microscope samples by the existence of an intermediate texture which occurs at the nematic-smectic C transition.[16] This intermediate texture was mentioned in the book on textures by Demus and Rich-

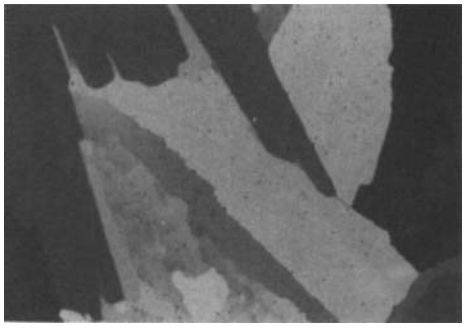


FIGURE 5 Microscopic smectic texture (100×) observed on cooling 1,2-(4,4′-dinonyloxyphenyl)acetylene from the nematic mesophase; 88.5°C, thin sample.

ter,[17] and in reports of chlorophenyldiamines[18] and 4-*n*-alkoxybenzoic acids.[19] It was then discussed in detail using primarily 4-*n*-alkoxybenzoic acids as examples by Neubert and De Vries.[15] As shown in Figure 6 for a thick sample of 1,2-(4,4′-didecyloxyphenyl)acetylene, when this transition is reached, the nematic threads (Figure 6A) appear to multiply and fill the field of vision (Figure 6B), causing increasing graininess of the texture on cooling. These lines then retract (Figure 6C), and the intermediate texture is replaced by a nematic-like smectic C phase (Figure 6D). Nearly identical textures are displayed by both the thin and thick microscope sample preparations of 1,2-(4,4′-didecyloxyphenyl)acetylene, 1,2-(4,4′-diundecyloxyphenyl)acetylene and 1,2-(4,4′-didodecyloxyphenyl)acetylene, and arguments concerning any of these three compounds can therefore be used interchangeably.

Fan type regions are also often observed in thick samples displaying s_C textures below a nematic mesophase.[16] However, the fan type s_C textures are observed much more easily in thin samples. In contrast, it is more difficult to detect the nematic to s_C intermediate texture in thin samples. A fan type s_C texture is presented by the optical micrograph of 1,2-(4,4′-didodecyloxyphenyl)acetylene in Figure 7A. Upon further cooling within the smectic C phase, we have noticed little additional color changes which would occur as a result of changes in the tilt angle.[20] However, De Vries concluded from X-ray studies that the tilt angle of s_C phases which occur below nematic mesophases have no temperature dependence.[21] ESR studies suggest that the intermediate $n \rightarrow s_C$ state has smectic A-like character,[22] which may account for the fan type textures observed in these s_C phases. The existence of a s_C phase below a nematic phase has been observed in only a few compounds, which were recently tabulated.[15]

Further cooling of, for example, 1,2-(4,4′-didodecyloxyphenyl)acetylene from the smectic C phase causes transition bars to appear across the fan regions (Figure 7B, D & E) before a mosaic texture develops (Figure 7C & F). However, this mosaic texture includes fan type regions that are less distinct than in the s_C texture, resulting in a paramorphotic fan/mosaic texture. It is quite probable that the monotropic smectic phases exhibited by these compounds is the same monotropic smec-

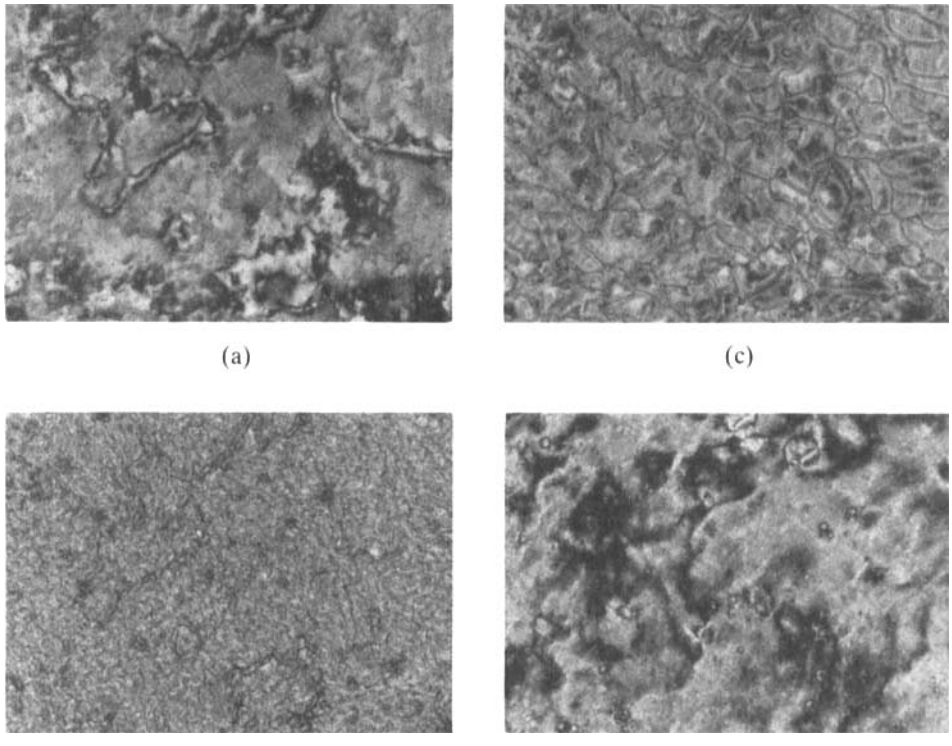


FIGURE 6 Microscopic textures (100×) observed on cooling 1,2-(4,4′-didecyloxyphenyl)acetylene from the isotropic state; thick sample preparation. (A) 99.8°C, *n* (B) 88.8°C, initial stages of $n \rightarrow s_C$ (C) 88.0°C, continued $n \rightarrow S_C$ (D) 83.6°C, s_C.

tic phases exhibited by 1,2-(4,4′-dinonyloxyphenyl)acetylene. If this is the case, the natural texture of these paramorphotic fan/mosaic textures would be the mosaic texture formed by cooling 1,2-(4,4′-dinonyloxyphenyl)acetylene from the nematic mesophase. As stated previously, such a mosaic texture may be exhibited by smectic B, F, G and H mesophases. However, the paramorphotic fan/mosaic textures observed here do not resemble the paramorphotic patchwork mosaic and broken fan textures typical of smectic F, G and H mesophases. In addition, the transition bars are neither L-shaped (s_F) nor dark patches (s_G and s_H).[20] Therefore, the monotropic smectic mesophases observed in 1,2-(4,4′-dinonyloxyphenyl)acetylene through 1,2-(4,4′-didodecyloxyphenyl)acetylene are more typical of s_B mesophases than s_F, s_G and s_H phases.

De Vries has found that the nematic phases which occur directly above s_C phases are different from other nematic phases in that they have smectic C-like order. He labelled them "skewed cybotactic nematic" phases.[23,24] This smectic-like order is necessary for a nematic phase to be considered skewed, since there must be some reference within the molecular arrangement for the molecular axes to be tilted in

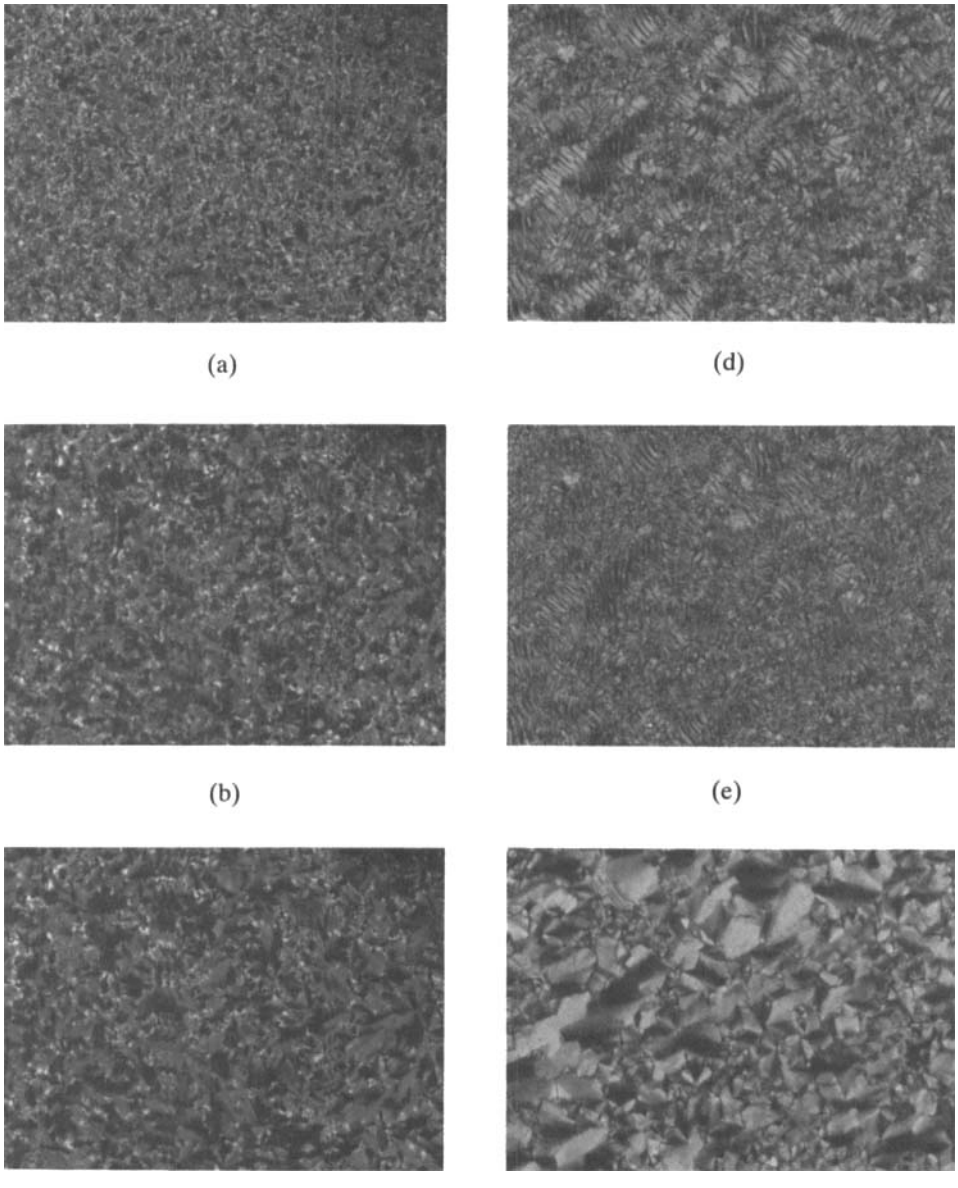


FIGURE 7 Microscopic textures (100×) observed on cooling 1,2-(4,4′-didodecyloxyphenyl)acetylene from the nematic mesophase; (A)–(C) thin samples; (D)–(F) thick samples. (A) 94.8°C, s_C (B) 86.8°C, $s_C \rightarrow s$ (C) 83.3°C, s (D) 86.9°C, $s_C \rightarrow s$ (E) 86.9°C, $s_C \rightarrow s$ a few seconds later (F) 82.8°C, s.

relation to. In addition, since it is necessary for the molecular axes within a nematic phase to undergo both layering and skewing in order to transform into a smectic C phase, it is reasonable that part of this transformation would begin in the nematic state with decreasing temperature. Indeed, color and textural changes have been observed with temperature variations in nematic phases near a nematic/s_C transition.[15] It is therefore interesting to note the changes in the nematic textures observed in this homologous series of 1,2-(4,4′-*n*-alkoxyphenyl)acetylenes. As shown in Figure 8, while the compounds which exhibit crystalline polymorphism develop threaded marbled nematic textures (Figure 8, A–F), those with longer *n*-alkoxy substituents of from nine to twelve methylenic units develop schlieren nematic textures (Figure 8, G–J).

The nematic texture of 1,2-(4,4′-dibutyloxyphenyl)acetylene is also interesting. In addition to regions of the simple threaded marbled nematic texture (Figure 8A), there are regions with an extremely high number of inversion lines (Figure 8B) as is usually obtained in an electric field.[25]

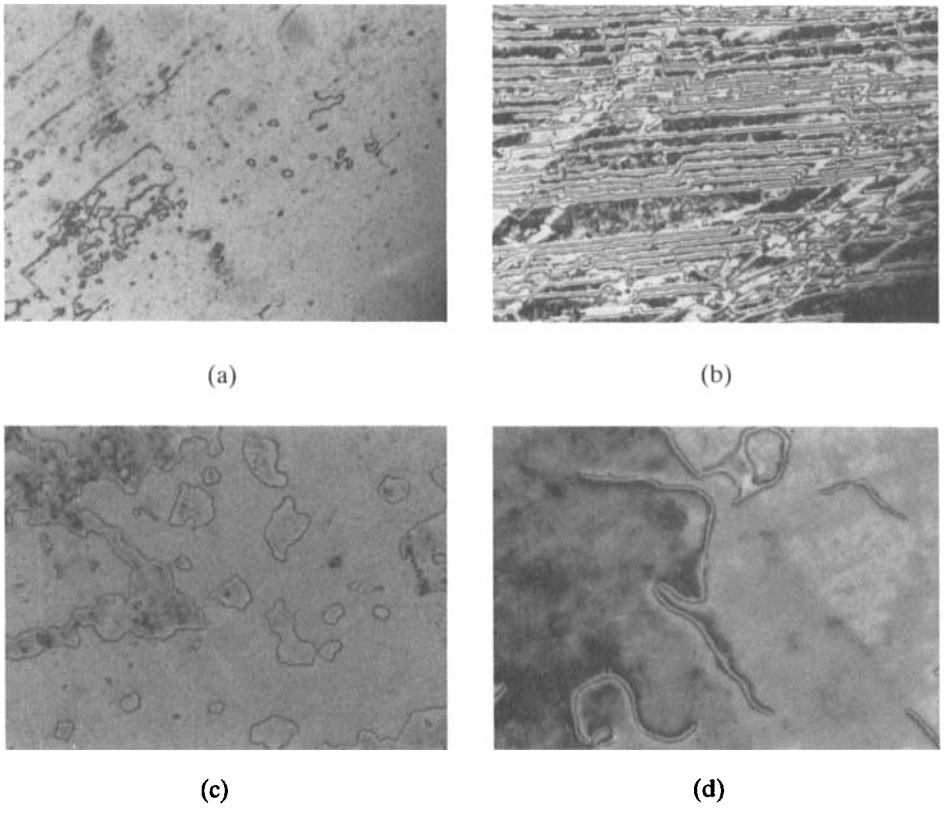


FIGURE 8 Microscopic nematic textures (100×) observed on cooling 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes from the isotropic state; thin sample preparation. (A) $n=4$, 127.7°C (B) $n=4$, 127.7°C (C) $n=5$, 105.5°C (D) $n=6$, 110.0°C (E) $n=7$, 99.5°C (F) $n=8$, 103.6°C (G) $n=9$, 95.7°C (H) $n=10$, 103.4°C (I) $n=11$, 97.0°C (J) $n=12$, 99.3°C.

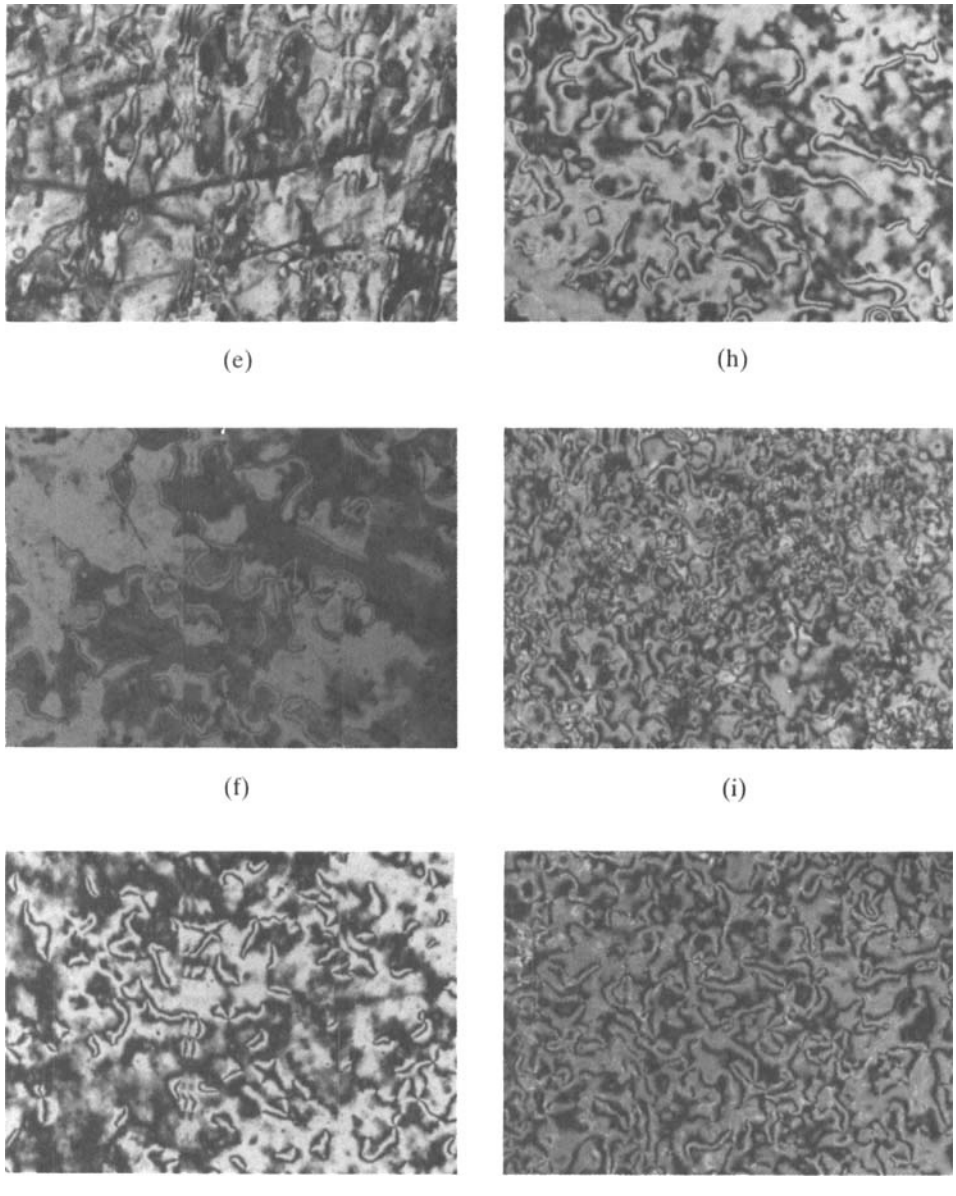


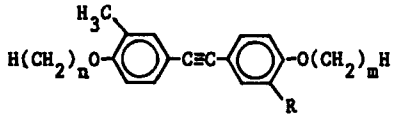
FIGURE 8 (continued)

1,2-(4,4′-Dialkoxyphenyl)acetylenes with a methyl branch in the mesogen

Both symmetrically and assymmetrically substituted 1,2-(4,4′-dialkoxyphenyl)acetylenes were prepared with a methyl branch in one or both of the aromatic rings of the mesogen. Table II summarizes the thermal transitions and

TABLE II

Thermal transitions and thermodynamic parameters of symmetrically and asymmetrically substituted 1,2-(4,4′-dialkoxyphenyl)acetylenes with a methyl branch in the mesogen.†



n	m	R	Phase Transitions (°C) and the Corresponding Enthalpy Changes (in parentheses, kcal/mol)
7	7	CH_3	k 74.8 (8.45) i i 54.6 (8.07) k
9	9	CH_3	k 63.3 (8.37) i i 48.6 (8.01) k
7	7	H	k 65.6 n 69.6 (7.82)* i i 66.9 (0.36) n 52.1 (6.70) i
9	7	H	k 60.3 (7.26) n 66.4 (0.29) i i 64.3 (0.38) n 43.2 (3.26) k 31.5 (1.34) k 20.0 (1.06) k

†k = crystalline, s = smectic, n = nematic, i = isotropic melt; first line of data obtained on heating, second line on cooling

*overlapping with the previous transition

enthalpy changes exhibited by these four compounds. Their heating and cooling DSC traces, as well as those of their corresponding unbranched analogues, are plotted in Figures 9 and 10. Both Figures 9 and 10 demonstrate that the introduction of a methyl branch in both aromatic rings of the mesogen strongly depresses both crystallinity and liquid crystallinity. However, the lack of either a nematic or a smectic phase demonstrates that the liquid crystalline phases are more strongly depressed than crystalline phases. That is, both 1,2-[4,4′-diheptyloxy(3,3′-dimethyl)phenyl]acetylene and 1,2-[4,4′-dinonyloxy(3,3′-dimethyl)phenyl]acetylene are only crystalline and melt into an isotropic state.

A thorough review of the literature, or at least those compounds tabulated in Reference 5a, demonstrate that the introduction of a methyl branch in an aromatic ring of the mesogen almost always depresses liquid crystallinity more than crystallinity. Three such homologous examples are listed in Table III. In many cases, melting actually increases while isotropization is depressed.

Although the symmetric compounds do not exhibit a liquid crystalline phase, when the methyl branch is introduced in only one of the aromatic rings of the mesogen, a nematic phase is also exhibited. This is apparently because crystallization is further depressed below the virtual liquid crystalline transition of the symmetrically branched compounds.

The nematic temperature window is quite small in 1,2-[3-methyl(4,4′-dihepty-

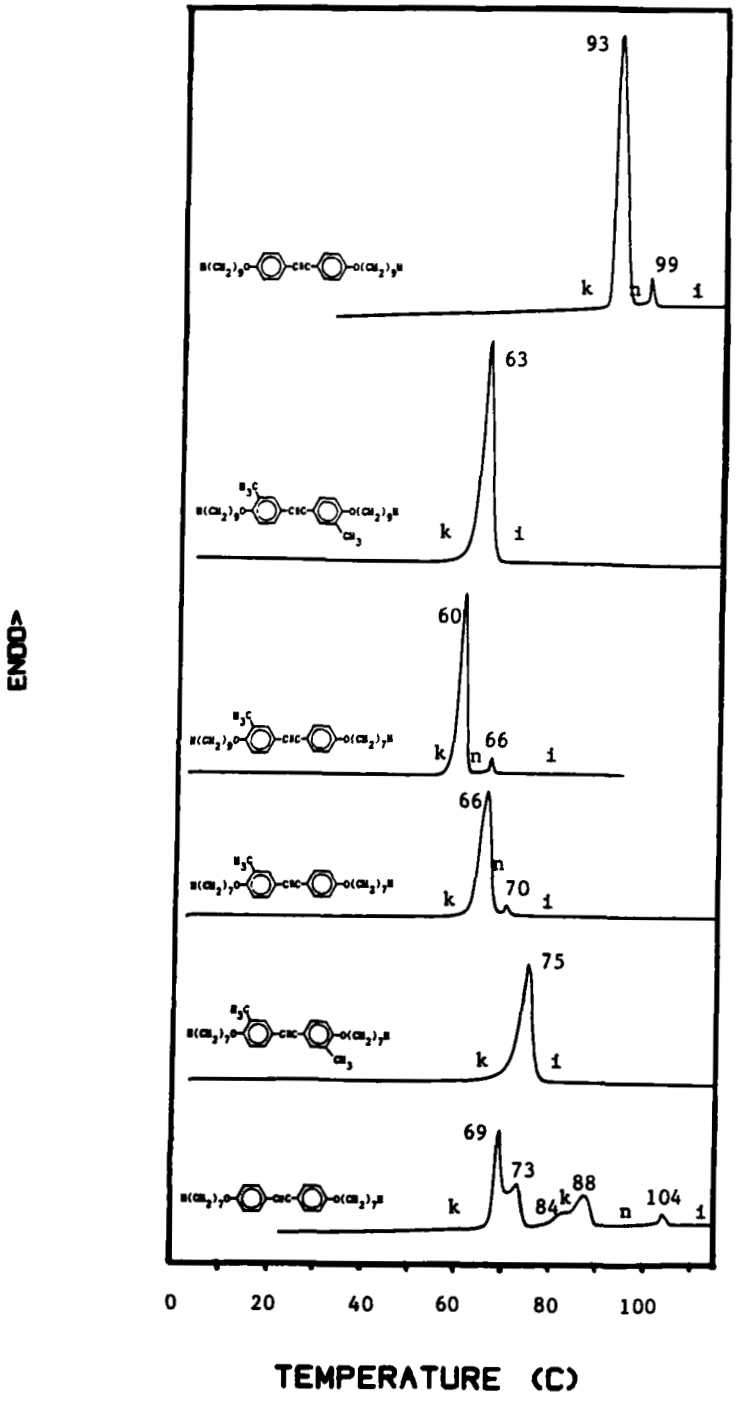


FIGURE 9 DSC heating scans of 1,2-(4,4′-dialkoxyphenyl)acetylenes with a methyl branch in the mesogen and their unbranched analogues.

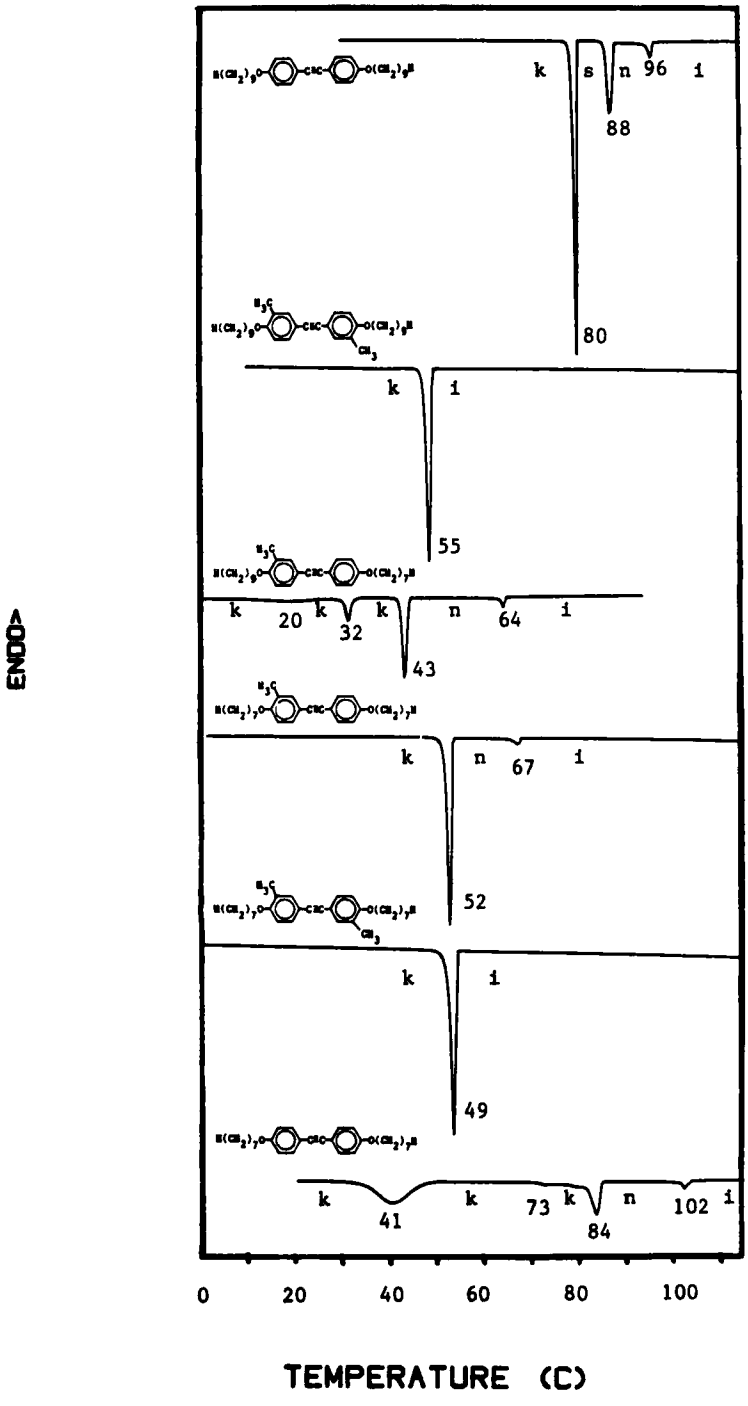
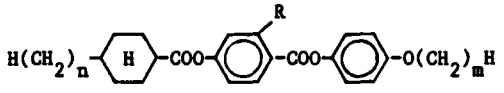


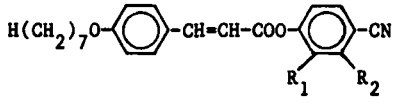
FIGURE 10 DSC cooling scans of 1,2-(4,4′-dialkoxyphenyl)acetylenes with a methyl branch in the mesogen and their unbranched analogues.

TABLE III

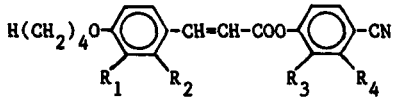
Thermal transitions (°C) of representative liquid crystals with a methyl branch in the mesogen and their unbranched analogues.†



n	m	R=CH_3	ref.	R=H	ref.
2	4	k 82 n 151 i	26,27	k 70.5 n 206 i	26,27
2	7	k 64 n 127 i	26,27	k 63 n 184 i	26,29
3	4	k 69 n 169 i	26-28	k 75 n 222 i	26,29
3	7	k 65 n 145 i	26,28	k 75 (s_A 70) n 203 i	26,29
4	4	k 70 n 162 i	27	k 75 s_A 88 n 218 i	26,29,30
4	7	k 67 n 142 i	26,27	k 67 s_A 126 n 196 i	26,29
5	4	k 67 n 165 i	27	k 85 (s_B 70) s_A 124 n 216 i	26,29
5	7	k 66 n 145 i	27	k 66 s_B 88 s_A 150 n 202 i	26,29
6	4	k 72 n 157 i	27	k 61 s_B 98 s_A 136 n 207.5 i	26,27
6	7	k 60 n 136 i	26,27	k 57 s_B 95 s_A 168 n 194 i	26,29



R_1	R_2		ref.	R_1=R_2=H	ref.
CH_3	H	k 88.3 (n 81.0) i	31	k 72.4 n 128.9 i	30-33
H	CH_3	k 79.8 (n 60.0) i	31		



R_1	R_2	R_3	R_4		Ref.	R_1=R_2=R_3=R_4=H	ref.
CH_3	H	H	H	k 101 (n 72.4) i	32	k 91.5 n 144.5 i	31,32
H	CH_3	H	H	k 97.5 (n 93.0) i	32		
H	H	CH_3	H	k 100.8 (n 92.6) i	32		
H	H	H	CH_3	k 88.5 (n 61.2) i	32		

†k = crystalline, s = smectic, n = nematic, i = isotropic melt

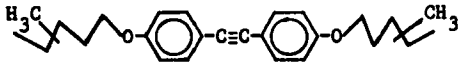
loxyphenyl)acetylene (4°C on heating and 14.8°C on cooling). However, when further assymmetry is introduced by using two different lengths of the alkoxy substituents, the nematic temperature window is stabilized. For example, 1-[(3-methyl)-4-nonyloxyphenyl]-2-(4′-heptyloxyphenyl)acetylene exhibits nematic windows of 6.1°C and 21.1°C on heating and cooling, respectively. In addition, this compound undergoes multiple crystalline-crystalline transitions in a stepwise crystallization process. This is further evidence that the multiple transitions in the lower homologues of the unbranched 1,2-(4,4′-dialkoxyphenyl)acetylenes are crystalline–crystalline transitions.

1,2-(4,4′-Dialkoxyphenyl)acetylenes with a methyl branch in the alkoxy substituents

The thermal transitions and the corresponding enthalpy changes of the symmetrically substituted 1,2-(4,4′-dipentyloxyphenyl)acetylenes with a methyl branch in either the 2-, 3- or 4-position of the pentyloxy substituent are listed in Table IV. Their DSC traces on heating and cooling are plotted in Figure 11 and 12, respectively. As with the 1,2-(4,4′-dialkoxyphenyl)acetylenes with a methyl branch in the mesogen, isotropization is depressed more than melting. In fact, melting is actually higher in the 4-methylpentyloxy derivative relative to 1,2-(4,4′-dipentyloxyphenyl)acetylene. Again, a review of Reference 5a demonstrates that the isotropization temperature is always depressed upon going from unbranched alkyl chains to methyl-branched chains. Melting may be depressed, stay about the same, or

TABLE IV

Thermal transitions and thermodynamic parameters of symmetrically branched 1,2-(4,4′-dipentyloxyphenyl)acetylene.†



Position of $-CH_3$ branch	Phase Transitions (°C) and the Corresponding Enthalpy Changes (in parentheses, kcal/mol)
2	k 36.4 (0.49)†† k 51.5 (5.7) i i 11.5 (3.74) k
3	k 71.1 k 80.1 (5.42)* i i 69.2 k 60.5 (5.18)* k
4	k 127.9 (6.75) i i 118.8 (6.52) k

†k = crystalline, s = smectic, n = nematic, i = isotropic melt; first line of data obtained on heating, second line on cooling

††endotherm

*overlapping with previous transition

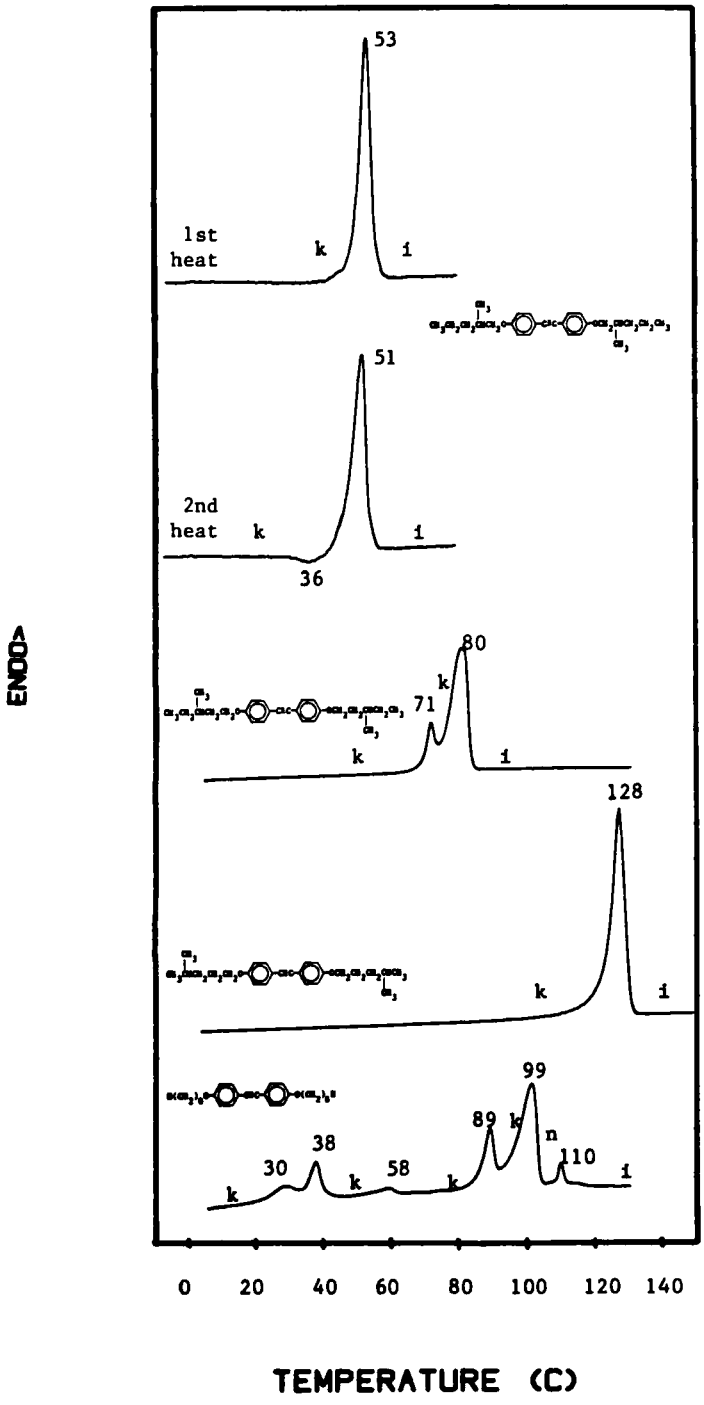


FIGURE 11 DSC heating scans of branched 1,2-(4,4′-dipentyloxyphenyl)acetylene with a methyl branch in both alkoxy chains at the 2-, 3- or 4-positions.

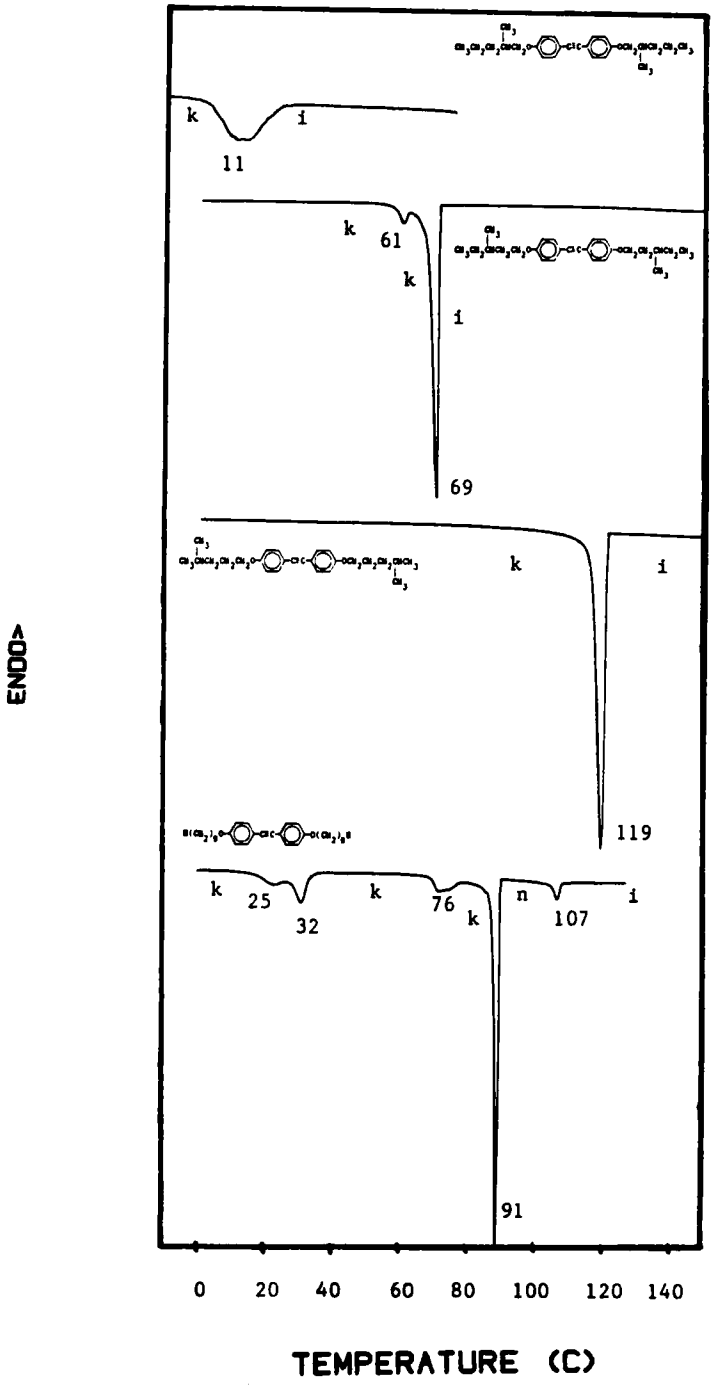


FIGURE 12 DSC cooling scans of branched 1,2-(4,4′-dipentyloxyphenyl)acetylene with a methyl branch in both alkoxy chains at the 2-, 3- or 4-positions.

increase in temperature. Melting point elevation is usually observed in those compounds with the methyl branch at the end of the chain, as is the case here. Stated another way, Figures 11 and 12 demonstrate that melting and crystallization increase in temperature upon going from methyl branching close to the mesogen, to methyl branching in the middle of the chain, to methyl branching at the end of the chain. Crystallization of the 2-methylpentyloxy derivative is not completed during the cooling scan, and therefore is completed in the next heating scan before melting takes place. The 3-methylpentyloxy derivative exhibits two melting/crystalline transitions.

Figures 11 and 12 demonstrate that none of these symmetrically substituted diphenylacetylene derivatives exhibit liquid crystallinity. In analogy to the 1,2-(4,4′-dialkoxyphenyl)acetylenes with a methyl branch in the mesogen and those compounds listed in Reference 5a, we expect that compounds with only one methyl-branched alkoxy chain will show at least a nematic phase.

As stated in the introduction, we are interested in the trimers of 1,2-(4,4′-dialkoxyphenyl)acetylenes as possible low molar mass disc-like liquid crystals. In a recent publication, methyl branches were introduced into the side chains of hexakis(octanoyloxy)benzene.[34] In the disc-like compounds, a methyl branch in the middle of the chain widened the temperature range over which the columnar mesophase was stable by depressing melting. It will therefore be interesting to see if the methyl branching in the pentyloxy chain has the opposite effect on the phase transitions of hexakis(4-pentyloxyphenyl)benzene versus 1,2-(4,4′-dipentyloxyphenyl)acetylene. That is, will methyl-branching in the pentyloxy chain stabilize the mesophase of hexakis(4-pentyloxyphenyl)benzene rather than destabilize the mesophase as in 1,2-(4,4′-dipentyloxyphenyl)acetylene?

EXPERIMENTAL

Materials

The synthesis of the 1,2-(4,4′-dialkoxyaryl)acetylene derivatives and their 1-halo-4-alkoxybenzene precursors were reported in the previous paper[1] in this series and is outlined in Scheme 2. With the exception of 1,2-(4,4′-dinonyloxyphenyl)acetylene (98.8% pure) and 1-(4-heptyloxyphenyl)-2-[4′-nonyloxy(3′-methyl)phenyl]acetylene (98.1% pure), the purity of all compounds reported here is greater than 99.6%.

Techniques

Purity was determined by high pressure liquid chromatography (HPLC) with a Perkin-Elmer Series 10 LC instrument equipped with an LC-100 column oven (40 or 50°C), an L-600 autosampler, and a Sigma 15 data station. Measurements were made using a UV detector after ^{1}H-NMR demonstrated that non-UV-absorbing impurities were absent, with THF or $CHCl_3$ as solvent, either a single 100 Å PL gel column (1.5 ml/min) or a set of PL gel columns of 10^2, 5×10^2, 10^3 and 10^4 Å (1.0 ml/min).

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 of the endothermic or exothermic peaks. All heating and cooling rates were 10°C/min. Tabulated thermal transitions were read from reproducible second or later heating scans, and reproducible first or later cooling scans. Both enthalpy changes and transition temperatures were determined using indium as a calibration standard.

A Carl-Zeiss optical polarized 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.[17,20] Thin samples were prepared by melting a minimum amount of sample on a clean glass slide, covering this with a cover slip, and rubbing the coverslip with a spatula. Thick samples were prepared as reported by Neubert and De Vries.[15] That is, a great amount of sample was placed on a freshly cleaned (acetone) glass slide and covered with a freshly cleaned (acetone) cover slip. This was then placed on the hot stage a few degrees below the clearing temperature and heated at 3°C/min to the isotropic liquid. All further examinations of both preparations were carried out at cooling and heating rates of 3°C/min.

Acknowledgements

Financial support from the U.S. Army Research Office is gratefully acknowledged. Helpful discussions with Dr. M. Neubert of the Liquid Crystal Institute, Kent State University, Kent, Ohio are also acknowledged.

References

1. C. Pugh and V. Percec, *J. Polym. Sci.*, Polym. Chem. Ed., in press.
2. A. Carpita, A. Lessi and R. Rossi, *Synthesis*, 571 (1984).
3. J. Malthete, M. Leclercq, M. Dvolaitzky, J. Gabard, J. Billard, V. Pontikis and J. Jacques, *Mol. Cryst. Liq. Cryst.*, **23**, 233 (1973).
4. L. Liebert, W. B. Daniel, J. Billard and J. Malthete, *Compt. Rend. Acad. Sci., Ser. C*, **285**, 451 (1977).
5. a) D. Demus and H. Zaschke, "Flussige Kristalle in Tabellen II," VEB Deutscher Verlag fur Grundstoffindustrie, Liepzig, 1984; b) page 104 in Reference 5a.
6. J. Malthete, J. Canceill, J. Gabard and J. Jacques, *Tetrahedron*, **37**, 2815 (1981).
7. R. Benotas and P. Adamenas, in "Advances in Liquid Crystal Research and Application," R. Bata ed., Vol. II, Pergamon Press, Oxford, 1980, p. 1019.
8. J. C. Dubois, A. Zann and A. Coutlet, *Mol. Cryst. Liq. Cryst.*, **27**, 187 (1974).
9. R. J. Cox and N. J. Clecak, *Mol. Cryst. Liq. Cryst.*, **37**, 241 (1976).
10. G. W. Gray and A. Mosley, *Mol. Cryst. Liq. Cryst.*, **37**, 213 (1976).
11. F. J. Cox and R. C. Gaskill, J. F. Johnson and N. J. Clecak, *Thermochim. Acta*, **18**, 37 (1977).
12. P. Adomenas, V. Butkus, J. Daugvila, J. Dienyte and D. Girdziunaite, in "Advances in Liquid Crystalline Research and Applications," L. Bata Ed., Vol. II, Pergamon Press, Oxford, 1980, p. 1029.
13. B. Grant, N. J. Clecak and R. J. Cox, *Mol. Cryst. Liq. Cryst.*, **51**, 209 (1979).
14. L. Strzelecki and L. Liebert, *Bull. Soc. Chim. France*, 605 (1973).
15. M. E. Neubert and A. De Vries, *Mol. Cryst. Liq. Cryst.*, **145**, 1 (1987).
16. This was confirmed by personal communication with and observation by M. E. Neubert of the Liquid Crystal Institute of Kent State University, Kent, Ohio.
17. D. Demus and L. Richter, "Textures of Liquid Crystals," Verlag Chemie, Weinheim, 1978.
18. S. L. Arora, J. L. Fergason and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **10**, 243 (1970).

19. T. S. Scheffer, H. Grueler and G. Meier, *Solid State Comm.*, **11**, 253 (1972).
20. G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals. Textures and Structures," Leonard Hill, Glasgow, 1984.
21. A. De Vries, *J. Phys.* (*Paris*), **36**, C1-1 (1975).
22. G. R. Luckhurst, M. Ptak and A. Sanson, *J. Chem. Soc.*, Faraday Trans. II, 1752 (1973).
23. A. De Vries, *Mol. Cryst. Liq. Cryst.*, **10**, 31 (1970).
24. A. De Vries, *Mol. Cryst. Liq. Cryst.*, **10**, 219 (1970).
25. Reference 5a, p. 115.
26. H.-J. Deutscher, C. Seidel, M. Koerber and H. Schubert, *J. Prakt. Chem.*, **321**, 47 (1979); Reference 159a in Reference 5a.
27. C. Seidel, Dissertation, Halle 1978; Reference 525a in Reference 5a.
28. H.-J. Deutscher, Dissertation B, Halle 1980; Reference 165a in Reference 5a.
29. H.-J. Deutscher, H. Schubert, C. Seidel, D. Demus and H. Kresse, DE-OS 2 752 975; Reference 159 in Reference 5a.
30. H.-J. Deutscher, C. Zoemisch and H. Altmann, *Z. Chem.*, **19**, 454 (1979); Reference 161 in Reference 5a.
31. A. I. Pavluchenko, N. I. Smirnova, E. I. Kovshev and V. V. Titov, *Zh. Org. Khim.*, **12**, 1511 (1976); Reference 461 in Reference 5a.
32. V. A. Grozkile and P. Adomenas, *Opt. Spektrosk.*, **44**, 1028 (1978); Reference 296 in Reference 5a.
33. V. V. Titov, E. I. Kovshev and A. I. Pavluchenko, *J. Phys.* (*Paris*), *Coll. C 1*, **36**, C 1-387 (1975); Reference 586 in Reference 5a.
34. D. M. Collard and C. P. Lillya, *J. Am. Chem. Soc.*, **111**, 1829 (1989).