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Phase transfer Pd(0) catalyzed polymerization reactions

4. Thermal characterization of 1,4-bis[2-(4′,4″-dialkoxyaryl)ethynyl]benzene derivatives and their electron-donor-acceptor complexes with p-chloranil*

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SUMMARY

1,4-Bis[2-(4',4"-diheptyloxyphenyl)ethynyl]benzene and 1,4-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]-benzene were synthesized by a one pot phase transfer Pd(0)/Cu(I) catalyzed three step coupling of 1,4-diiodobenzene with 2-methyl-3-butyn-2-ol and the appropriate aryl halide. Both compounds display mesomorphic behavior similar to that of the analogous 1,2-(4,4'-dialkoxyaryl)acetylenes, except that the temperature window of each phase is stabilized, such that an enantiotropic mesophase is even observed in the derivative containing a methyl branch in the mesogen. Both compounds form mesomorphic EDA complexes with p-chloranil as electron acceptor, and display a depression of the nematic-isotropic transition temperature.

INTRODUCTION

The first paper (1) in this series described the synthesis of both symmetrically and assymmetrically substituted 1,2-(4,4'-dialkoxyphenyl)acetylene monomers and 1,4-bis[2-(4',4"-dialkoxyphenyl)ethynyl]benzene derivatives by a one pot phase transfer Pd(0)/Cu(I) catalyzed coupling of aryl halides with a monoprotected acetylene. While the second paper (2) in this series described the liquid crystalline behavior of the 1,2-(4,4'-dialkoxyphenyl)acetylene monomers, this paper will describe the liquid crystalline behavior of the 1,4-bis[2-(4',4"-dialkoxyphenyl)ethynyl]benzene derivatives in which the mesogenic unit has been extended by one phenylethynyl unit. Because of this extended conjugation, we have also investigated their ability to form electron-donor-acceptor (EDA) complexes with an electron acceptor, and the resulting thermal behavior.

EXPERIMENTAL

Materials

The synthesis of 1,4-bis[2-(4',4"-diheptyloxyphenyl)-ethynyl]benzene and 1,4-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]benzene was described in detail previously (1). p-Chloranil (m.p. 290°C) used as electron acceptor was recrystallized from 1:1 (v/v) toluene / diethyl ether to obtain yellow platelets. Yellow EDA complexes were

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prepared by separate dissolution of the electron donor and p-chloranil in chloroform, mixing, and slow evaporation at room temperature. They were then dried in vacuo overnight.

Techniques

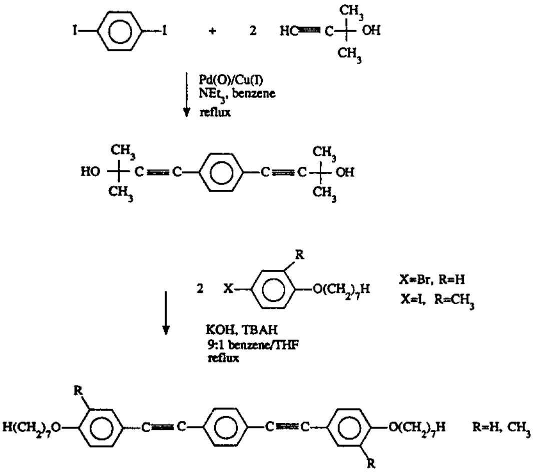
A Perkin Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine thermal transitions (10^oC/min). Unless noted otherwise, the first and second heating scans were identical. Indium was used as the calibration standard.

A Carl-Zeiss optical polarized microscope 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 (3,4).

RESULTS AND DISCUSSION

1,4-Bis[2-(4,4'-diheptyloxyphenyl)ethynyl]benzene Derivatives

The synthesis of 1,4-bis[2-(4',4"-diheptyloxyphenyl)-ethynyl]benzene and 1,4-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]benzene is outlined in Scheme 1. The three step synthesis was performed in the same flask, with isolation and purification of only the final product. In the first step, 1,4-diiodobenzene was coupled with 2-methyl-3-butyn-2-ol by a traditional non-phase-transfer-catalyzed Pd(0)/Cu(I) coupling procedure using two equivalents of triethylamine as base. In refluxing benzene, this coupling step is complete within two hours. The resulting dicarbinol was then deprotected and coupled with either 1-bromo-4-heptyloxybenzene or 1-iodo-3-methyl-4-heptyloxybenzene in a



Scheme 1. One pot phase transfer Pd(0)/Cu(I) catalyzed synthesis of 1,4-bis[2-(4',4"-diheptyloxyphenyl)ethynyl]-benzene and 1,4-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]benzene.

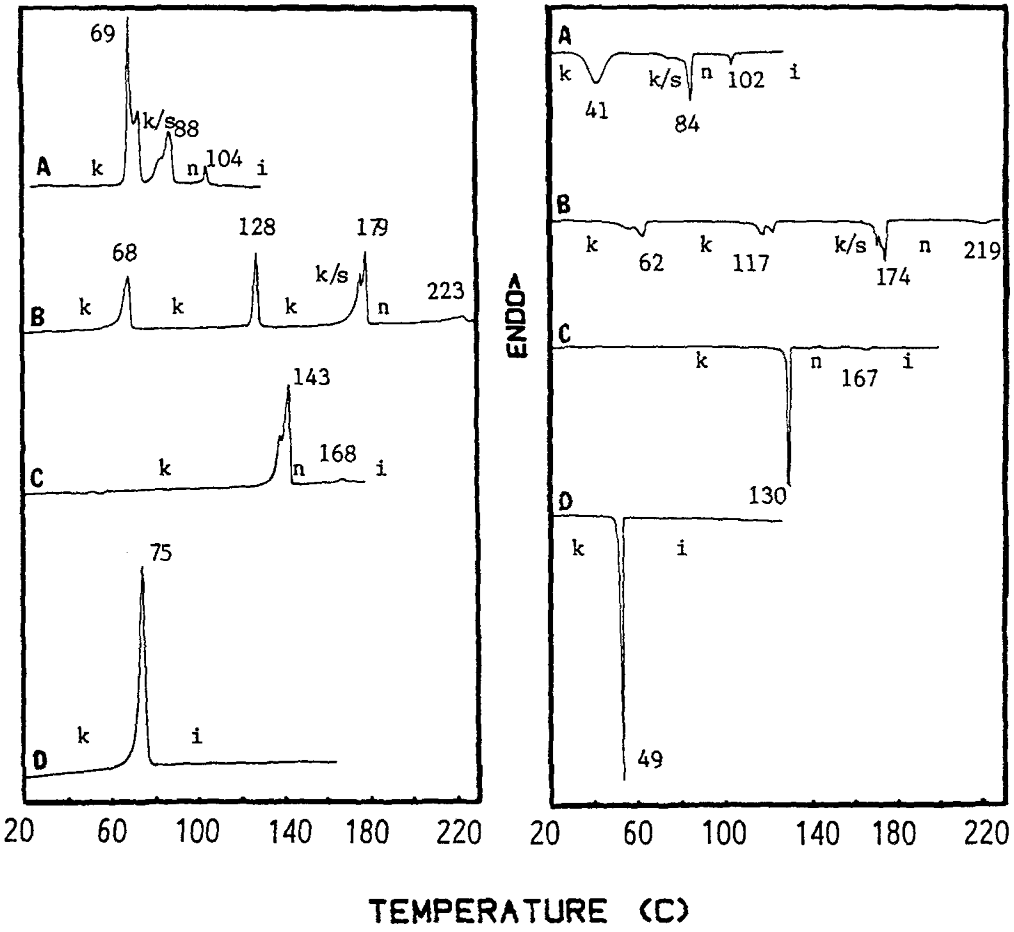
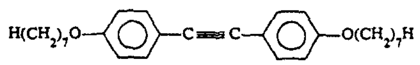


Figure 1. DSC heating and cooling scans of 1,2-(4,4'-diheptyloxyaryl)acetylene and 1,4-bis[2-(4',4"-diheptyloxyaryl)ethynyl]benzene derivatives.

A)



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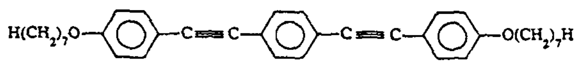

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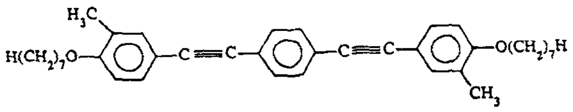

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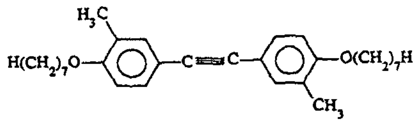
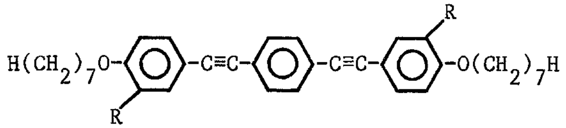


Table 1. Thermal transitions and thermodynamic parameters of 1,4-bis[2-(4',4"-diheptyloxyphenyl)ethynyl]benzene derivatives.+



R	Phase Transitions (°C) and the Corresponding Enthalpy Changes (in parentheses, kcal/mol)
H	k 68.1 (3.41) k 127.7 (2.62) k 176.8 k/s 178.8 (4.66)* n 223.1 (0.56) i i 218.5 (0.61) n 173.5* s/k 170.0 (4.91)* k 121.6 k 117.0 (2.62)* k 61.8 k 55.4 (3.40)*
CH_3	k 139.5 k 142.9 (6.80)* n 167.7 (0.33) i i 167.0 (0.34) n 130.3 (6.49) k

+k=crystalline, s=smectic, n=nematic, i=isotropic melt; first line of data obtained from second and later heating scans, second line from cooling scans.

*overlapping with previous transition

solid-liquid phase transfer catalyzed system. That is, solid KOH and tetrabutylammonium hydrogen sulfate (TBAH) as phase transfer catalyst were added to the Pd(0)/Cu(I) system with the second aryl halide addition. The Pd(0)/Cu(I) catalyst system included $PdCl_2(PPh_3)_2$ (1.2-4.3 mol% relative to -I), cuprous iodide and triphenylphosphine ($CuI:Pd:PPh_3$ = 3.8-3.9 : 1 : 4.9-5.7 molar ratio).

The thermal transitions of 1,4-bis[2-(4',4"-diheptyloxyphenyl)ethynylbenzene and 1,4-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]benzene are summarized in Table 1. Their DSC traces observed on heating and cooling are plotted in Figure 1, along with those of the analogous 1,2-(4,4'-diheptyloxyphenyl)acetylene derivatives (2). As with the 1,2-(4,4'-dialkoxyphenyl)acetylenes (2), the symmetrical introduction of a methyl branch into the aromatic rings of 1,4-bis[2-(4',4"-diheptyloxyphenyl)ethynyl]benzene strongly depresses both melting and isotropization, with melting being affected the most. The methyl branches also decrease the tendency towards multi-step melting and crystallization.

Figure 1 demonstrates that increasing the length of the 1,2-diarylacetylene mesogen by one phenylethynyl unit both increases the temperature of melting and isotropization, and increases the resolution of all phase transitions. Increasing the length of the mesogen also stabilizes the liquid crystalline mesophases. This is demonstrated by the fact that symmetrical methyl branching in the mesogen of 1,2-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]benzene does not eliminate the nematic mesophase. That is, while 1,2-(3,3'-dimethyl-4,4'-dihepthyloxyphenyl)acetylene is only crystalline and melts into the isotropic state, 1,4-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]benzene displays an enantiotropic nematic mesophase.

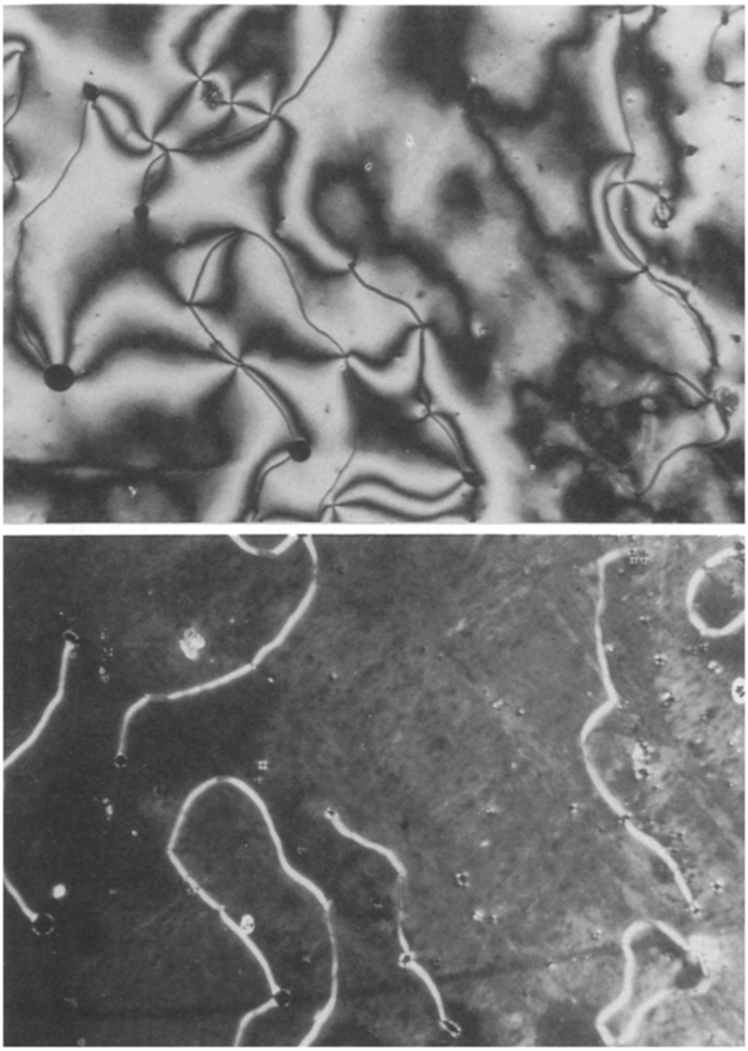
As discussed in a previous paper in this series (2), the 1,2-(4,4'-di-**n**-alkoxyphenyl)acetylenes with from four to eight methylenic units in the **n**-alkoxy substituents solidify from the nematic state into two immiscible phases. The presence of immiscilbe polymorphs is retained in even the lowest temperature crystalline phase(s). This is due to the close proximity of the crystalline temperatures and the low rates of crystallization, as observed under nonequilibrium conditions. It is questionable however, as to whether the immiscible phases involve only crystalline phases, or both crystalline and smectic phase(s). While the degree of supercooling of the transition directly below the nematic mesophase is small enough to indicate that a nematic/smectic transition occurs, the total enthalpy change upon cooling from the nematic state to 0°C is indicative of crystalline transitions (2). In addition, only subtle optical changes occur upon further cooling through the crystalline/crystalline transitions. We concluded that all the immiscible phases were probably crystalline, with only crystalline polymorphism occurring in addition to the nematic mesophases in the series 1,2-(4,4'-dibutyloxyphenyl)acetylene through 1,2-(4,4'-dioctyloxyphenyl)acetylene (2).

1,4-Bis[2-(4',4"-diheptyloxyphenyl)ethynyl]benzene displays the same trend in phase transitions as 1,2-(4,4'-diheptyloxyphenyl)acetylene, except that the transition temperatures are further separated. For example, the nematic mesophase is observed over 44°C upon cooling 1,4-bis[2-(4',4"-diheptyloxyphenyl)ethynyl]benzene, and only 18°C upon cooling 1,2-(4,4'-diheptyloxyphenyl)acetylene. As shown in Figure 2, substantial color changes are observed by polarized optical microscopy upon cooling the nematic mesophase of 1,4-bis[2-(4',4"-diheptyloxyphenyl)ethynyl]benzene. In addition to the texture darkening with decreasing temperature as a result of the sample becoming more homeotropic, some of the inversion lines become very bright. Such color changes within the nematic mesophase are not unusual in a temperature range this large (5).

Upon further cooling, a transition of only 5°C supercooling occurs. The initial platelets observed form reversibly with the nematic mesophase and are therefore indicative of a liquid crystalline mesophase. However, the texture rapidly becomes biphasic as is also observed in 1,2-(4,4'-diheptyloxyphenyl)acetylene. We therefore believe that a smectic mesophase overlaps the transition from the nematic to the crystalline phase of 1,4-bis[2-(4',4"-diheptyoxyphenyl)ethynyl]benzene, and possibly 1,2-(4,4'-di-**n**-heptyloxyphenyl)acetylene. The additional phase transitions are polymorphic crystalline transitions. Except for the second melting transition which occurs at 127°C on the first heating scan, all transitions are identical in temperature from one heating or cooling scan to the next.

EDA Complexes

Because both the conjugation and electron donor character of 1,4-bis[2-(4',4"-dialkoxyphenyl)ethynyl]benzene derivatives have been extended by one phenylethynyl unit relative to the 1,2-(4,4'-dialkoxyphenyl)acetylenes, we have investigated the effect of adding an electron acceptor on their phase behavior. The thermal transitions of the EDA complexes of 1,4-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]benzene and 1,4-bis[2-(4',4"-diheptyloxyphenyl)ethynyl]benzene with p-chloranil are summarized in Table 2. Only the first heating scans are reported because 1,4-bis[2-(4',4"-



A) 205.8°C

B) 180.5°C

Figure 2. Microscopic textures (100x) observed on cooling the nematic mesophase of 1,4-bis[2-(4',4"-diheptyloxyphenyl)-ethynyl]benzene.

Table 2. Thermal transitions of the EDA complexes of p-chloranil and 1,4-bis[2-(4',4"-diheptyloxy)ethynyl]benzene derivatives[+]

R[++]	% p-chloranil mol	% p-chloranil wt	Phase Transitions (°C)
H	0	0	k 67.5 k 131.1 k/s 176.4 n 222.3 i
	30	17	k 73.1 k 132.3 k/s 169.8 n 189.1 i
	34	20	k 73.2 k 132.8 k/s 170.3 n 190.0 i
	54	36	k 68.0 k 127.3 k/s 169.9 n 188.0 i
	74	44	k 72.2 k 131.6 k/s 168.6 n 186.7 i
CH_3	0	0	k 139.5 k 143.1 n 169.6 i
	37	21	k 139.3 n 146.7-156.4* i
	52	33	k 139.4 n 142.2-157.6** i

[+] k=crystalline, s=smectic, n=nematic; data obtained from first heating scan

[*] observed only by microscopy, second heating scan, 3°C/min

[**] observed by microscopy, second heating scan, 3°C/min

[++] See Scheme 1 for R

diheptyloxyphenyl)ethynyl]benzene and/or p-chloranil rapidly sublime from the DSC sample pan at elevated temperatures. The two highest temperature endotherms sit on top of a broader endotherm which is evidently decomplexation. There is therefore an enthalpy loss observed in all further cooling and heating scans, and isotropization is subsequently that of the pure donor as observed by optical microscopy. In contrast, the complexes of 1,4-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]benzene show reversible phase behavior since the isotropization temperature is much lower in temperature than the decomplexation endotherm. However, if these complexes are also heated to 240°C, a decomplexation endotherm is observed at 226°C, and one or both components of the complex sublime from the sample pan. Decomplexation endotherms have also been observed by DSC in polymeric EDA complexes (6).

Addition of p-chloranil to form EDA complexes has little effect on the crystalline transition temperatures. However, isotropization and the suspected smectic-nematic transition temperatures are depressed. This behavior is typical of that occurring upon addition of normal non-mesogenic solutes to a mesogenic solvent, but is in contrast to the increase in the nematic-isotropic transition temperature and the decrease in crystalline transition temperatures observed when the solvent and solute can form donor-acceptor interactions (7). In addition, nematic (8), smectic (8) and discotic (9) mesophases have been induced in mixtures of potentially mesogenic donors and acceptors, and smectic mesophases have been induced in mixtures of nematic donors and acceptors (10). It is well known that EDA interactions induce increased order and even miscibility in polymer blends (6,11). No new liquid crystalline phases were induced in the mixtures of p-chloranil and the 1,4-bis[2-(4',4"-diheptyloxyphenyl)ethynyl]benzene derivatives. Although both the depression of isotropization and the lack of induced additional mesophases indicate that donor-acceptor interactions are absent, EDA complexes are evidently formed since a decomplexation endotherm is observed, and since the mixtures display a single phase both in the anisotropic and isotropic phases as observed by optical microscopy. That is, there is no uncomplexed p-chloranil detected at temperatures above isotropization. This previously unobserved behavior results from p-chloranil not being potentially mesogenic. Therefore, although it interacts with these liquid crystalline electron donors, its size and shape are so different from those of the 1,4-bis[2-(4',4"-dialkxoyphenyl)ethynyl]benzene derivatives that complexation destabilizes the order of the liquid crystalline phases. However, similar electron acceptors have proved to be pro-discogens (9).

The other effect of p-chloranil is that the rate of isotropization decreases. Isotropization is so broad in the mixtures involving 1,4-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]benzene that it is not observed by DSC, although it can be followed by optical microscopy. As with uncomplexed 1,4-bis[2-(3',3"-dimethyl-4',4"-diheptyloxyphenyl)ethynyl]benzene, the nematic mesophase of the complexes display a threaded nematic texture.

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