Reactivity of mesogenic diacetylenes coupled with phase transitions between crystal and liquid crystal phases

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Among mesogenic diacetylenes, *N*-[4-(5-hydroxypenta-1,3-diynyl)benzylidene]-4-alkoxyaniline (DA-C*n*), in which *n* is the number of carbon atoms in the alkoxy group, DA-C8 has been found to have four phases divided by three endothermic transition temperatures. The four phases have been assigned to crystal phase I (T < 96 °C), crystal phase II ($T_{CI–CII}$ = 96 °C), crystal phase G ($T_{CII–CG}$ = 115 °C) and nematic phase ($T_{CG–N}$ = 123 °C), based on DCS measurements and observation under a microscope. The crystal structure of DA-C8 in phase I has been determined. Crystal data are triclinic, space group $P\bar{1}$, a = 14.580(3), b = 17.451(4), c = 10.219(3) Å, α = 93.40(2), β = 103.83(2), γ = 116.85(3)° and Z = 4. Four molecules in a unit cell are hydrogen-bonded to each other at the hydroxymethyl groups and/or the imino-nitrogens of the benzylideneaniline moieties to form a checker-like structure. The phase transitions have been monitored by X-ray powder diffraction measurements. The checker-like structure in crystal I is transformed to a layered structure in crystal phase II and in crystal phase G. The structural transformation may be coupled with a change in the hydrogen-bonding scheme. Whereas crystal phase I is inactive towards the solid state polymerization, crystal phase II polymerizes with a long induction time of 50 h at 110 °C. However, the induction time of the polymerization is shortened greatly in crystal phase G, and the polymerization in the nematic phase proceeds smoothly with almost no induction time. The results are interpreted in terms of the relative orientation of diacetylene molecules in each phase.

Introduction

Solid state reactions have been a recent topic of interest in materials science.[1] They provide new possibilities for obtaining a desired product in a highly regio- and/or stereo-selective manner. Since the chemical reactivity in the solid state depends heavily on the relative orientation of reactant molecules, it is of particular interest to investigate the solid state reactivity of a certain molecule which undergoes successive phase transitions and to examine the relative reactivities in each phase, by focusing on the mutual orientations of reaction sites of neighboring reactant molecules.

Solid state polymerization of diacetylenes, in particular, is worthwhile investigating in detail, because of the potential interest concerning opto-electrical properties of the obtained polydiacetylenes. In the case of the solid state polymerization of diacetylenes *via* a 1,4-addition mechanism,[2] the reaction proceeds only when the relative orientation of monomers satisfies Baughmann's criterion:[3] the stacking interval (d) is to be in the range of 4.2–5.7 Å, and the inclination angle (θ) between the molecular axis and the stack direction is in the range of 40–60° (Fig. 1). Under such circumstances, the distance between reaction sites of diacetylenyl groups of neighboring molecules is substantially shorter than 4.0 Å.

For obtaining diacetylene derivatives with an enhanced third order non-optical property,[4] it is desirable to prepare unsymmetrical diacetylenes substituted with phenyl groups attached directly to the diacetylenic moiety: in such a case, optical properties are supposed to be modulated by substituents on the phenyl groups. The unsymmetrical polydiacetylenes are also potentially useful for obtaining high spin polymers.[5] Although many solid state reactive diacetylenes have been developed so far, most of them are symmetrically substituted ones.[6] Reactive unsymmetrical diphenyldiacetylene derivatives, in particular, have been scarcely developed, except for diacetylene derivatives with a *p*-trifluoromethylphenyl group at one end.[7]

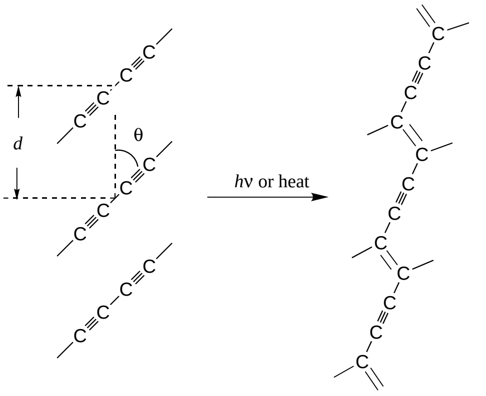

Fig. 1 Schematic drawing of formation of polydiacetylenes through 1,4-addition of diacetylenes

We have examined here the reactivity of unsymmetrically substituted phenyldiacetylene derivatives in various molecular alignments realized by the structural phase transitions,[8] including liquid crystal phases.[9] Some of the diacetylenes, *e.g.* bis(2-phenyldivinyl)diacetylene, are found to have liquid crystal phases and the obtained diacetylenes also exhibit mesogenic properties.[10] Even if a crystal of a diacetylene derivative is inactive towards polymerization, it may become reactive as the morphology of crystals changes. For this purpose, we prepared

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mesogenic diacetylenes, in which the diacetylene moiety is substituted with a hydroxymethyl group at one end, and a benzylideneaniline carrying an alkoxy group at the other, as a mesogenic core.

The crystal of *N*-[4-(5-hydroxypenta-1,3-diynyl)benzylidene]-4-methoxyaniline (**DA-C1**), in which a methoxy group is introduced at the *para*-position of the anilino group, turns out to satisfy Baughmann's criterion. In an asymmetric unit, two independent diacetylene molecules are doubly hydrogen-bonded side-by-side between the hydroxymethyl and the imino groups (*vide infra*). They stack along the *c*-axis at an interval of 4.80 Å, and the molecular axis is inclined to the *c*-axis at 54°. The distance between the potentially reactive carbons of two adjacent molecules is 3.96 Å within the stack [*cf.* Fig. 7(*b*)]. In fact, the crystal of **DA-C1** is found to afford polydiacetylene as a result of heating or UV irradiation.[11]

Although **DA-C1** undergoes a phase transition from the crystal phase to the nematic one, the temperature of the phase transition is as high as 148 °C. The diacetylene **DA-C1**, therefore, starts to polymerize before being transformed to the nematic phase. In order to lower the phase transition temperature of the nematic phase, we have prepared **DA-C*n*** (***n*** = 2–8) in which the alkoxy group is varied from ethoxy to octyloxy. The transition temperature of the nematic phase ($T_{\mathrm{CG–N}}$) becomes lower when the chain-length of the alkoxy group increases. Among the diacetylene derivatives explored, the transition temperature of **DA-C8**, with an octyloxy group, is the lowest. Accordingly, **DA-C8** was chosen as a target molecule for examining the correlation between the reactivity of polymerization and the relative orientation of diacetylenes in the molecular assembly. **DA-C8** has four phases divided by three endothermic transition temperatures, and the reactivity of each phase turns out to be different. While phase I is inactive, phases II and III exhibit polymerization reactivity after an induction time, and the polymerization proceeds smoothly in phase IV. These reactivities are discussed based on its crystal and liquid crystal structures. A part of the unique kinetic behavior of **DA-C8** in the nematic phase has been reported separately.[12]

Experimental

General

X-Ray powder diffraction patterns were measured on a RIGAKU D-9C diffractometer with graphite monochromatic Cu-Kα radiation (λ = 1.540 56 Å) using an electric oven. UV–VIS and IR spectra were recorded on a SHIMADZU 3100PC and a Perkin-Elmer 1640 spectrometer, respectively. ^{1}H and ^{13}C NMR spectra were measured on a JEOL GSH-270 spectrometer. High resolution solid state ^{13}C NMR (CP/MAS) measurement was carried out on a JEOL GSH-270 spectrometer at 67.8 MHz with a repetition time of 10 s and a contact time of 10 ms. Gel Permeation Chromatography (Japan Analytical Industry Co., Ltd. Model LC-908) equipped with JAIGEL 1H-2H was used for purification of **DA-C8**. EPS spectra were recorded on a JEOL JES-RE2X spectrometer equipped with a temperature controller of Scientific Instrument 3700.

Differential scanning calorimetry (DSC) measurement

DSC measurement was performed on a SHIMADZU DSC-50 calorimeter. A sample (*ca.* 2.0 mg) was sealed in an aluminium cell under N_2 atmosphere and heated. Heating or cooling rates were 2.5 °C min^{-1}. Usually transformation temperatures of liquid crystalline phases are determined based on a thermogram obtained from a cooling-and-heating cycle starting from an isotropic phase. In the case of mesogenic diacetylenes **DA-C*n***, including **DA-C8**, however, the phase transition temperatures were determined during the initial heating process, because the compound **DA-C*n*** starts to polymerize in the nematic phase, even in a rapid scan rate.

Table 1 Crystal data, data collection and refinement details of phase I

Crystal data	
$C_{26}H_{29}NO_2$	$D_x = 1.35$ Mg m^{-3}
$M_r = 387.5$	$D_m = 1.33$ Mg m^{-3}
Triclinic	flotation in CCl_4–benzene
$P\bar{1}$	Mo-Kα radiation
$a = 14.580(3)$ Å	$\lambda = 0.710\ 73$ Å
$b = 17.451(4)$ Å	Cell parameters from 25 reflections
$c = 10.219(3)$ Å	$\theta = 10.0–12.5°$
$\alpha = 93.40(2)°$	$\mu = 0.07$ mm^{-1}
$\beta = 103.83(2)°$	$T = 293$ K
$\gamma = 116.85(3)°$	Plate
$V = 2210.0(9)$ Å^3	Yellow
$Z = 4$	0.6 × 0.3 × 0.1 mm
Data collection	
Rigaku AFC-5 diffractometer	$\theta_{\max} = 27.5°$
ω scan: 2–20°, ω–2θ scan: 20–27.5°	$h = -19 \to 19$
Absorption correction: none	$k = -23 \to 23$
10 915 measured reflections	$l = 0 \to 13$
10 245 unique reflections	3 standard reflections monitored every 200 reflections intensity variation <±2%
4220 observed reflections [$I > 3\sigma(F)$]	
$R_{\mathrm{int}} = 0.039$	
Refinement	
Refinement on F	$(\Delta/\sigma)_{\max} = 0.12$
Final $R = 0.098$	$\Delta\rho_{\max} = 0.23$ Å^{-3}
$wR = 0.092$	$\Delta\rho_{\min} = -0.30$ Å^{-3}
$w = 1/[\sigma(F)^2 + 0.0005\lvert F\rvert^2]$	
$S = 1.94$	
4220 reflections	
524 parameters	
H-atom positions: calculated	
H-atom parameters: not refined	

X-Ray crystal structure determination and refinement

Crystals of **DA-C8** were obtained by slow evaporation from an ethanol solution. Crystal data and details of data collection and refinement conditions are given in Table 1. The structure was solved by direct methods using SHELX 86[13] and refined by a block-diagonal least squares method using UNICS III.[14] Atomic scattering factors were obtained from ref. 15.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/123.

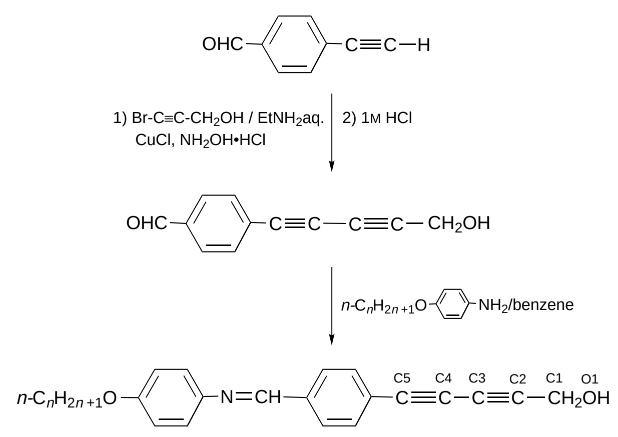
Polymerization

Polymerization of diacetylene **DA-C8** was carried out in an electric oven. Accuracy of the temperature of the samples is ±2 °C. A sample (50 mg) was sealed in a Pyrex tube with an exchange gas of Argon (*ca.* 5 mmHg). The decay of the monomer was monitored by intensities of the $C{\equiv}C$ stretching mode at 2250 cm^{-1}.

Materials

Preparative routes of the mesogenic diacetylenes **DA-C1–C8** are shown in Scheme 1. Condensation of *p*-ethynylbenzaldehyde[16] with 3-bromopropargyl alcohol was performed in aqueous ethylamine in the presence of cuprous chloride.[17] After hydrolysis with aq. HCl, the diacetylene derivative was condensed with the corresponding alkoxyaniline.

***p*-Octyloxyacetoanilide.** A solution of 10.0 g (66 mmol) of *p*-hydroxyacetanilide, 26 g (130 mmol) of octyl bromide and 50 g (360 mmol) of K_2CO_3 in 300 ml of cyclohexanone was refluxed for 1 day. After solvent was removed under reduced pressure, the residue was extracted by diethyl ether. The organic layer was washed with water, dried over $MgSO_4$ and concentrated by



DA–C*n* (*n* =1–8)

Scheme 1 Preparation of diacetylene derivatives **DA-C1–C8**

rotary evaporation. The crude product was recrystallized from hexane to give 12.0 g (69%) of a white powder of *p*-octyloxyacetanilide. δ_H(270 MHz; $CDCl_3$) 0.9 (3H, t, $-CH_3$), 1.4 [10H, m, $-(CH_2)_5-CH_3$], 1.80 (2H, m, $-CH_2-CH_2O-$), 2.05 (3H, s, $CO-CH_3$), 3.9 (2H, t, $-OCH_2-$), 6.80 (2H, d, *m*-ArH), 7.35 (2H, d, *o*-ArH).

***p*-Octyloxyaniline.** To a suspension of 1.3 g (5 mmol) of acetanilide derivative in 40 ml of 6 M HCl was added 2 ml of benzene and the mixture was refluxed for 1 day under N_2 atmosphere. After removal of benzene on a rotary evaporator, the solution was poured into aq. NaOH and extracted by diethyl ether. The organic layer was washed with water and dried over $MgSO_4$, and was concentrated under reduced pressure to give 0.90 g (60%) of *p*-octyloxyaniline. δ_H(270 MHz; $CDCl_3$) 0.9 (3H, t, $-CH_3$), 1.4 [10H, m, $-(CH_2)_5-CH_3$], 1.80 (2H, m, $-CH_2-CH_2O-$), 3.2 (s, 2H, $-NH_2$), 3.85 (2H, t, $-OCH_2-$), 6.55 (2H, d, *m*-ArH), 6.70 (2H, d, *o*-ArH).

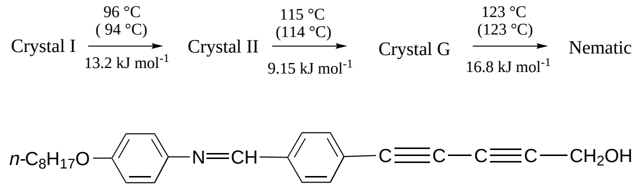
4-(5-Hydroxypenta-1,3-diynyl)benzaldehyde. 4-(5-Hydroxypenta-1,3-diynyl)benzaldehyde was prepared according to refs. 10 and 17.

***N*-[4-(5-Hydroxypenta-1,3-diynyl)benzylidene]-4-octyloxyaniline DA-C8.** A solution of 1.0 g (5.4 mmol) of 4-(5-hydroxypenta-1,3-diynyl)benzaldehyde and 1.5 g (6.8 mmol) of *p*-octyloxyaniline in benzene (100 ml) was refluxed in the presence of molecular sieves (4 Å, 1/16) for 12 hours under N_2 atmosphere. After filtration, the solvent was removed under a reduced pressure. The residue was purified by gel permeation chromatography (GPC) and recrystallized from ethanol to give 1.90 g (95%) of yellow powder of **DA-C8**: mp 122–123 °C; δ_H(270 MHz; $CDCl_3$) 0.90 (3H, t, $-CH_3$), 1.35 [10H, m, $-(CH_2)_5-$ CH_3], 1.80 (2H, m, $-CH_2-CH_2O-$), 3.95 (2H, t, $-OCH_2-CH_2$), 4.40 (2H, d, $-CH_2OH$), 6.75 (2H, d, 3-ArH), 7.22 (2H, d, 2-ArH), 7.55 (2H, d, 3-ArHCN–), 7.82 (2H, d, 2-ArHCN–), 8.45 (1H, s, –N=CH–); δ_C(67.5 MHz; $CDCl_3$) 14.0 ($-CH_3$), 22.8, 26.2, 29.43, 29.46, 29.54, 32.0 [$-(CH_2)_6-$], 51.7 ($-CH_2OH$), 68.5 ($-CH_2OAr$), 69.8 ($-CCCH_2OH$), 75.1 (ArC*C*–), 78.1 (–*C*CH$_2$OH), 82.2 (Ar*C*C–), 115.1 (C3,5), 122.5 (C2,6), 123.7 (C4, Bn), 128.5 (C3,5, Bn), 133.1 (C2,6, Bn), 137.5 (C1, Bn), 144.2 (C1), 156.6 (N=CH), 159.2 (C4) (Calc. for $C_{26}H_{29}NO_2$: C, 80.58; H, 7.54; N, 3.61. Found: C, 80.30; H, 7.60; N, 3.71%).

Results

Observation of phases transition of DA-C8 by means of DSC measurements

Thermal analysis of the phase transitions of **DA-C8** was performed by DSC measurements (Scheme 2). The thermogram of DSC of **DA-C8** is shown in Fig. 2. In the heating process, **DA-C8** exhibited three endothermic peaks at 96, 115 and 123 °C with endothermicities of 13.2, 9.15 and 16.8 kJ mol^{-1}, respectively. Four phases, identified by the presence of three peaks, were assigned to be crystal phase I, crystal phase II, crystal phase G and nematic phase, respectively, based on observations under a microscope, X-ray diffraction and IR spectroscopy (*vide infra*). The results suggest that these transitions are coupled with the change in the hydrogen-bonding scheme.



DA–C8

Scheme 2 Transition temperature and thermodynamic change for the phase transition of **DA-C8**

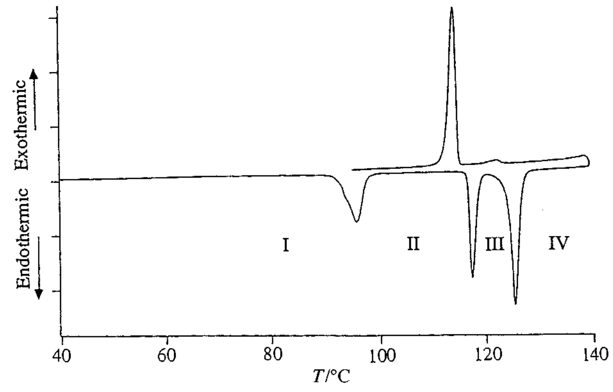


Fig. 2 DSC thermograms of the mesogenic diacetylene **DA-C8**

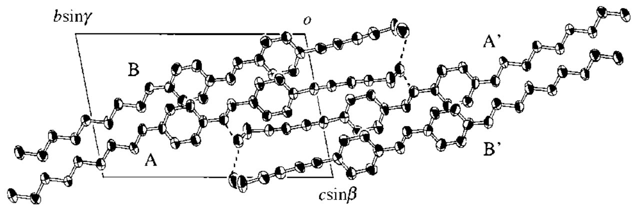


Fig. 3 Crystal structure of phase I viewed along the *a*-axis

Crystal structure of DA-C8 of phase I

The crystal structure of the diacetylene monomer, **DA-C8**, of phase I (Fig. 3) was determined by X-ray crystallographic analysis. There are two symmetrically independent molecules, A and B, in an asymmetric unit. Conformations of the two monomers are similar. Since the conformation of the octyloxy group is all antiperiplanar, the length of the long axis of the monomer extends about 28 Å. Bond-alternation between the triple and the single bonds is observed in the diacetylene moiety. The averaged bond distances of the triple and single bonds are 1.18 and 1.37 Å, respectively. The OH bond of the hydroxymethyl group is twisted about 90° from the plane of the phenyl ring attached to the diacetylene moiety. The dihedral angles between the two phenyl rings are 11 and 4°, and the C=N bond lengths are 1.28 and 1.26 Å for monomers A and B, respectively. The conformation of the benzylideneaniline moiety is *anti*. The geometrical features of the benzylideneaniline moiety in this work are in good agreement with those of known benzylideneaniline derivatives.[18]

Two pairs of monomers related by an inversion symmetry at (0, 0, $\frac{1}{2}$) are denoted by A–A′ and B–B′. The octyloxy chains of A and B are located side-by-side, and the oxygen atom of the hydroxymethyl group of B is hydrogen-bonded to that of A with the OH···O distance of 2.73 Å. The hydroxymethyl

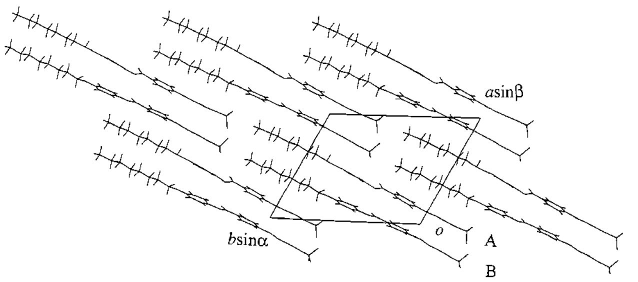


Fig. 4 Crystal structure of diacetylene phase I viewed along the *c*-axis

group of A is, in turn, hydrogen-bonded to the imino-nitrogen of the monomer A′ to form an antiparallel pair, A–A′, the OH · · · N distance being 2.85 Å (or *vice versa*, starting from B′). Accordingly four monomers, A, A′, B and B′, constitute a tetrameric hydrogen-bonded cluster. It is to be noticed that the imino-nitrogen of B or B′ is free from hydrogen bonds. The monomers A and B′ are nearly in the plane parallel to $\bar{4}\,2\,0$, and in another parallel plane are located the monomers A′ and B. A quasi-double sheet structure is, thus, formed with the interplanar distance of 3.5 Å. The antiparallel pairs of the diacetylenyl moieties of B–A–A′–B′–B are stacked along the *c*-axis. Although the intermolecular distances of the active sites of diacetylenyl groups are in a range of 3.8–4.8 Å within the stack, the relative orientation does not satisfy the condition for 1,4-addition.

The crystal structure viewed along the *c*-axis is shown in Fig. 4. The dimeric stackings of diacetylenyl groups of A and B are sandwiched by stackings of alkyl groups to form a checker-like image. Since van der Waals' radii of the diacetylenyl and the benzylideneaniline parts are a little smaller than those of the octyloxy part, this checker-like arrangement is considered to be preferred by the crystal packing compared with the layered structure. Thus a relative orientation for the 1,4-addition is not satisfied along the *a*- or *b*-axes either, in spite of the relatively short distance of the A–B dimer.

Phase transitions of DA-C8 monitored by X-ray powder diffractometry, IR spectroscopy and microscopic observation

The powder X-ray diffraction (XRD) patterns of **DA-C8** in each phase are shown in Fig. 5. In phase I [Fig. 5(*a*)], three intense peaks are observed at $2\theta = 19.5^\circ$ ($d = 4.55$ Å), $2\theta = 24.3^\circ$ ($d = 3.67$ Å) and $2\theta = 25.2^\circ$ ($d = 3.53$ Å) which are assigned to $\bar{2}\,0\,2$, $2\,\bar{2}\,2$, $\bar{4}\,2\,0$, respectively. The interplanar distance of $\bar{4}\,2\,0$ approximately corresponds to the double-sheet distance of monomer A and B. Phase II is assigned to the crystal phase as well, although the crystal structure of phase II has not been determined [Fig. 5(*b*)]. Three strong diffraction peaks are observed at $2\theta = 19.7$, 22.5 and 23.1° ($d = 4.49$, 3.95 and 3.84 Å). Note that a new peak appears at the lower angle region of $2\theta = 4.26^\circ$ ($d = 20.72$ Å). In phase III, most of the diffraction peaks in the lower range disappeared, except for a sharp peak at $2\theta = 3.96^\circ$ ($d = 22.3$ Å) [Fig. 5(*c*)], although diffraction peaks in the range $15 < 2\theta/^\circ < 25$ are still observed. All of the diffraction peaks disappeared, when the sample was heated to the nematic phase at temperatures higher than 123 °C.

The change was also monitored by microscopic observation. Neither fluidity nor texture was observed in phases I, II and III. Taking the results of X-ray powder diffraction patterns into account, phase III can be assigned to crystal phase G according to Gray's classification.[19] The long axis of the component molecule is inclined within the layer and the order in the local environment of molecules is almost as high as that in the crystal phase. In contrast, the sample became fluid and showed a Shlieren texture under a microscope through a polarimeter in phase IV. When an external electric field was applied, the sample showed dynamic scattering mode with a threshold value of 2500 V cm^{-1}.[12] Phase IV was, therefore, assigned to the nematic phase.

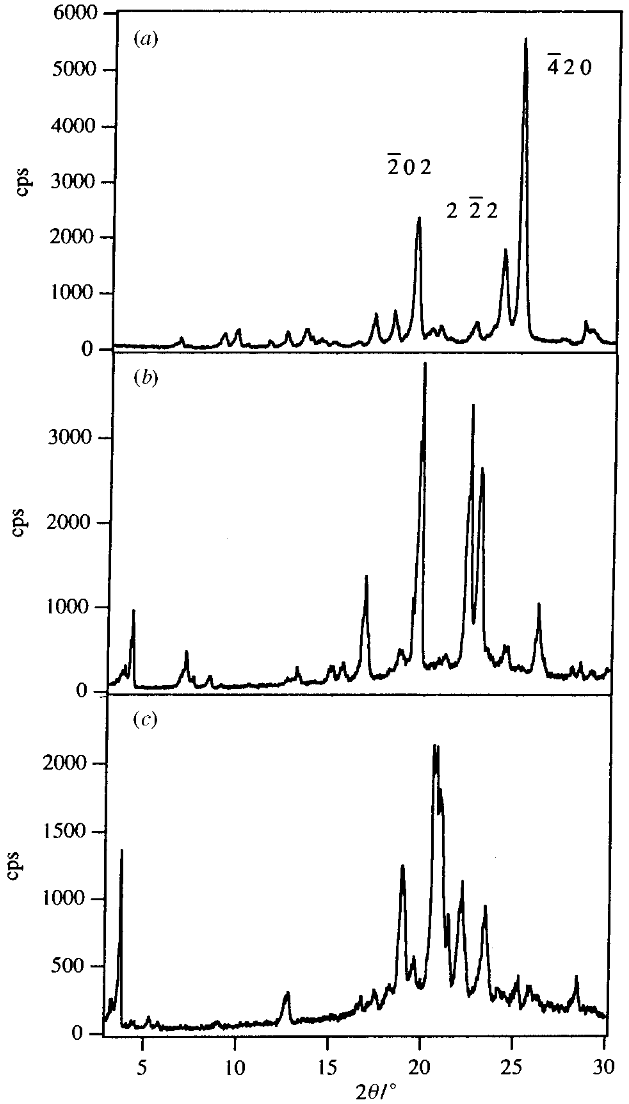


Fig. 5 Powder X-ray diffraction patterns of **DA-C8**: (*a*) crystal phase I at 25 °C; (*b*) crystal phase II at 102 °C; (*c*) crystal G phase at 115 °C

The IR spectrum of **DA-C8** in each phase was recorded to obtain information on the difference in the hydrogen-bonding scheme. The IR bands of the OH stretching band (ν_{OH}) of phase I were detected at 3336 and 3160 cm^{-1} at 25 °C. In phase II, only one hydrogen-bonded ν_{OH} band was observed at 3305 cm^{-1}. The ν_{OH} band in phase III (117 °C) was detected at 3310 cm^{-1}, and it was shifted to 3307 cm^{-1} in the nematic phase (130 °C).

Reactivity of DA-C8 in various phases

The reactivity of polymerization of **DA-C8** was examined by thermal annealing under an Ar atmosphere in the four phases. The decay curves of the monomer, which were traced by the decrease in intensities of the $\nu_{C\equiv C}$ stretching mode at 2250 cm^{-1}, are shown in Fig. 6. Thermal reactivity could not be observed in crystal I, as predicted from the crystal structure, even though the sample was annealed for 100 h at 90 °C. However, the polymerization in crystal phase II at 110 °C proceeded after an induction period of *ca.* 50 h, and it was completed after 150 h to afford insoluble polymers. In the crystal phase G at 118 °C, the polymerization proceeded after several hours of an induction period as in the case of crystal phase II. Thus the local environment of the monomer in crystal phase G should be similar to that of crystal phase II, although the monomers are slightly distorted in a two-dimensional lattice. The nematic phase polymerization at 130 °C, however, proceeded smoothly

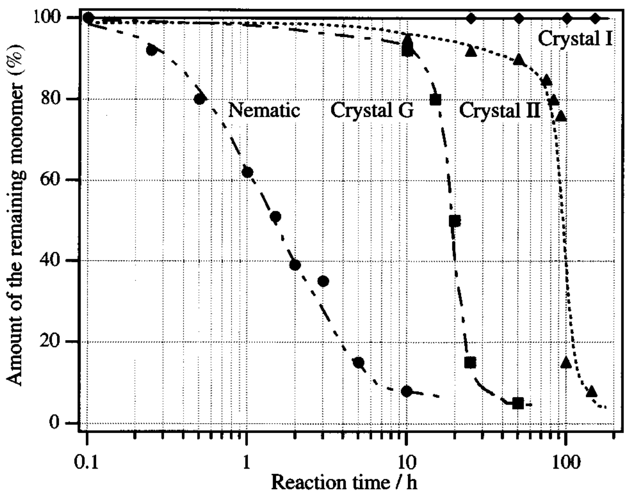


Fig. 6 Decay curves of monomer **DA-C8** in each phase

with almost no induction period, and the reaction was almost completed within 10 h.

The high resolution solid state ^{13}C NMR (CP/MAS) spectra were recorded on the diacetylene monomer **DA-C8**, and on the polymer obtained by its thermal annealing. Regardless of whether the reaction phases are crystal II, crystal G or nematic phase, the spectra of the polymers are practically the same. The spectrum of the monomer shows the signals of four acetylenic carbons at 71, 76, 79 and 86 ppm. However, the spectrum of the polymer shows novel signals at 117, 130 ppm at the expense of signals of the acetylenic carbons of the monomer. Since these signals can be assigned to those of the ene–yne type backbone carbons of polydiacetylenes,[20] it is strongly suggested that the polymer is formed through 1,4-addition of the monomers as shown in Fig. 1.

UV–VIS spectra of the polymer dispersed into KBr disks indicate that the edge of the absorption extends to 600 nm, but that no excitonic transitions characteristic to the polydiacetylene are observed. This is presumably because the high structural regularity of the growing polymers cannot be maintained during the thermal polymerization.

Discussion

Intermolecular interactions of **DA-C*n*** in the crystals are classified into the following three types: intermolecular hydrogen-bonds between hydroxymethyl groups, dipolar interactions between imino groups of benzylideneaniline moieties and van der Waals' interactions of a dispersion-type between alkyl groups substituted at the *para*-position of the anilino groups. In the case of **DA-C1**, whose alkoxy chain is the shortest among **DA-C*n***, two **DA-C1** molecules form an antiparallel dimer through the intermolecular hydrogen bonds between hydroxymethyl groups and the imino nitrogens [Fig. 7(*a*)].[11] The dimers stack along the *c*-axis inclined at about 50°, keeping the appropriate orientation for 1,4-addition [Fig. 7(*b*)]. In the case of **DA-C8**, the hydrogen-bond scheme is more complicated compared with that of **DA-C1**. The antiparallel dimer of A and A′ is formed as in the case of **DA-C1** through the hydrogen bonds between the hydroxy group and the imino one. In addition, molecule B is hydrogen-bonded to the hydroxymethyl group of monomer A. The octyloxy chains of A and B are arranged side-by-side, presumably due to the enhanced dispersion force compared with that of the methoxy group in **DA-C1**. Therefore the **DA-C8** molecules, A, B, A′ and B′, form a tetrameric hydrogen-bonded cluster (Fig. 3). The relative orientation of diacetylenyl groups in the checker-like structure is not appropriate for 1,4-addition in all directions, although the distances between the active sites of diacetylenyl groups are reasonably short within the dimer. As a result, the crystal phase I of diacetylene derivative **DA-C8** is inactive.

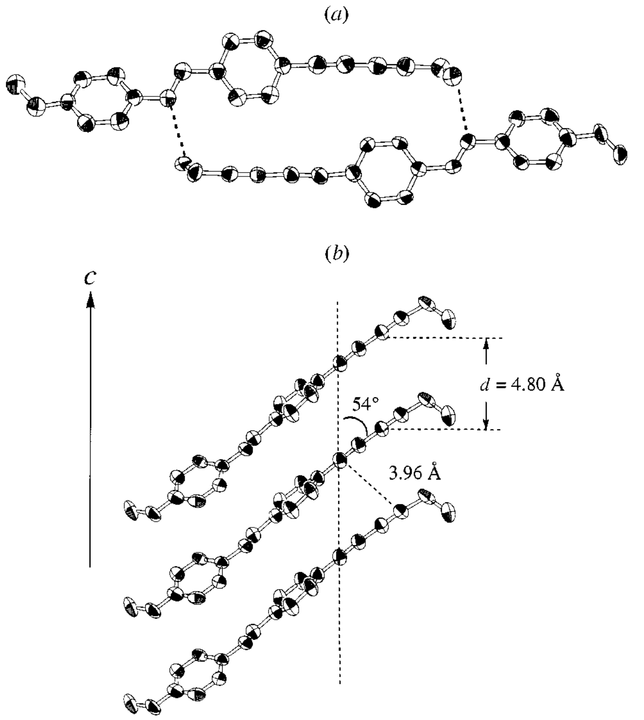


Fig. 7 Crystal structure of **DA-C1**: (*a*) hydrogen-bonded dimer of **DA-C1**; (*b*) stacking of **DA-C1** along the *c*-axis

Since **DA-C8** has the multi-centers for the intermolecular interaction as mentioned above, these interactions should cause multi-local minima for the stable arrangements of monomers in the molecular assembly. This may be the reason why **DA-C8** undergoes a sequential phase transitions. The endothermicities related to the phase transitions between crystals I, II, and G are evaluated to be 13.2 and 9.15 kJ mol^{-1}, respectively. Since the third transition is from the crystal phase G to the nematic phase, the endothermicity of 16.8 kJ mol^{-1} is larger than the former two.

The transformation of the crystal structure from crystal phase I to phases II and III might be directed toward the formation of the layered structure from the checker-like structure, because of the appearance of the peak at $2\theta = 4.26°$ (phase II) and 3.96° (phase III) in the X-ray powder diffraction patterns. The relative orientation of **DA-C8** may become appropriate for polymerization through the 1,4-addition mechanism upon transformation from phase I to phase II. In phase III (crystal phase G), the lowest diffraction peak shifts to the lower angle side, and the relative intensity of the peak is strengthened compared with that of phase II. Since the long axis of **DA-C8** molecule is estimated to be about 28 Å, the molecule is supposed to be inclined by 36° in the layer in phase III. The value corresponds to the inclination angle of 54° in **DA-C1** for 1,4-addition. The structural transformation from crystals I, II to crystal III is schematically depicted in Fig. 8.

The changes in the OH stretching in IR spectra of **DA-C8**, coupled with the phase transitions, reflect the change in the hydrogen-bonding scheme in each phase. The assignment of ν_{OH} to 3160 and 3336 cm^{-1} in phase I is performed by virtue of IR spectra and crystal structures of both **DA-C1** and **DA-C5**.[21] In the crystal of **DA-C1**, ν_{OH} is observed at 3146 cm^{-1}. Since the distance between the oxygen atom of the hydroxymethyl group and the imino-nitrogen of the adjacent molecule is 2.84 Å in the crystal of **DA-C1** [Fig. 7(*a*)], the hydroxy group of **DA-C1** is considered to be hydrogen-bonded to the imino-nitrogen. Consequently, ν_{OH} at 3160 cm^{-1} for **DA-C8** is to be assigned to the hydrogen-bonded hydroxy group of the OH · · · N type ($d = 2.83$ Å). Whereas ν_{OH} at 3336 cm^{-1} for **DA-C8** may be assigned to the

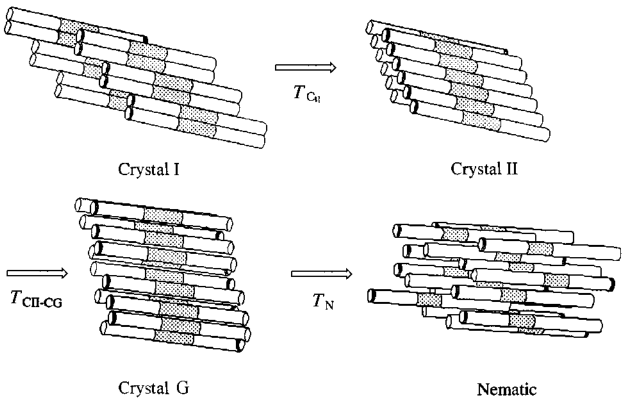


Fig. 8 Schematic drawing of the phase transition of **DA-C8**. A shaded zone at the edge of a rod-like molecule represents a hydroxymethyl group and a dotted zone for a benzylideneaniline group

hydrogen-bonded hydroxy group of the OH···O ($d = 2.71$ Å) type, because ν_{OH} frequency of **DA-C5** is observed at 3315 cm^{-1}, under the distance of OH···O of 2.73 Å. Since phase II is active in the solid state polymerization, the relative orientation of **DA-C8** should be changed significantly. Only one ν_{OH} peak is observed at 3305 cm^{-1} in phase II at 102 °C. Taking the change in the IR absorption of ν_{OH} into account, the hydrogen bond between OH and the imino nitrogen is considered to be cleaved in phase II. Whereas the OH···O type hydrogen bond between the hydroxy groups remains. In phase III, ν_{OH} is observed at 3310 cm^{-1} at 117 °C. The peak may also be assigned to the OH···O type hydrogen bond. This interpretation of the IR data is consistent with the result of the X-ray powder diffraction patterns, suggesting layered structures for both phase II and phase III.

The difference in the induction time of polymerization (Fig. 6) is explained as follows: since the molecular motion in phase II is restricted by the crystal lattice, the reaction during the induction time is very slow. After the local concentration of polymer increases to a certain extent, a sort of the structural transition occurs and the mother lattice is replaced by the daughter lattice. The reaction, thereafter, proceeds smoothly. Since no excitonic transition was observed in the absorption spectrum of the obtained polydiacetylene, the order of the reaction environment may decrease as the reaction proceeds, leading to the loss in the structural regularity of the polydiacetylene.[22] The polymerization of **DA-C8** in phase III also proceeds after an induction period. This is presumably because the local environment in the crystal phase G is similar to that of the crystal II. The shortening of the induction period, however, may reflect the local flexibility in the crystal phase G. The reaction in the nematic phase proceeded with little induction period, which clearly shows that the diacetylene molecules **DA-C8** in the nematic phase are free from the restriction of the crystal lattice. The diacetylene molecules react immediately when they are aligned in a suitable orientation for 1,4-addition in the fluid environment. The chance for the monomers to encounter such a relative orientation may be related to the local order in the nematic phase. The importance of the relative orientation of the nematic phase polymerization is supported by the enhanced reactivity of polymerization in a thin film sample and the effect of applying an external electric field upon the rate of polymerization.[12]

Conclusions

We have prepared the mesogenic diacetylene, **DA-C8**, which has four phases, including three crystal phases and a nematic phase. The correlation between the reactivity and the relative orientation of the monomers was studied based on the diffraction data. Although crystal phase I of **DA-C8** is inactive towards polymerization, **DA-C8** will polymerize in other phases. This behavior may be generalized as follows. When diacetylene monomers are inactive towards polymerization in crystals as grown, they become active as a result of structural transformations. This method may be applied to diacetylenes with a variety of substituents to obtain polydiacetylenes.

Note that the obtained polydiacetylenes are substituted by aromatic rings. It is rather rare for diacetylene derivatives substituted directly with an aromatic ring to polymerize.[23] Unsymmetrically aryl-substituted polydiacetylenes, in particular, have drawn much attention for their optical non-linearity, photo-conductivity or magnetism. In particular, non-linear optical susceptibility should be enhanced by introducing an aryl group attached directly to the acetylenic moiety.[4] The unsymmetrical (head-to-tail) substitution pattern in polydiacetylenes is also crucial in realizing a high spin ground state based on the topochemical requirement of the spin correlation in conjugated π-systems.[24] If a mesogenic group of polydiacetylenes can be removed after polymerization, and be switched with other functional groups, this synthetic method is extremely useful for constructing functional diacetylenes.

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