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Online publication date: 06 August 2010

To cite this Article Sekine, Chizu , Iwakura, Kazunori , Minai, Masayoshi and Fujisawa, Koichi(2001) 'High birefringence photopolymerizable phenylacetylene liquid crystals', Liquid Crystals, 28: 10, 1505 — 1512
To link to this Article: DOI: 10.1080/02678290110068947
URL: http://dx.doi.org/10.1080/02678290110068947

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LIQUID CRYSTALS, 2001, VOL. 28, NO. 10, 1505–1512

High birefringence photopolymerizable phenylacetylene liquid crystals

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(*Received 20 November 2000; in final form 20 February 2001; accepted 7 May 2001*)

Photopolymerizable three-ring phenylacetylene (3PA) liquid crystalline compounds were synthesized and the physical properties of the monomers and polymers were characterized in the expectation of obtaining high birefringence polymers. 3PA monomers containing acrylate substituents exhibited enantiotropic nematic phases and high Δn values of around 0.35. Homogeneous alignment was retained after polymerization and high values of Δn ($\sim$0.34) for the polymers were obtained. The orientation of the monomers at the photopolymerization temperature was almost fixed, such that Δn and the order parameter of the polymers varied with the polymerization temperature.

1. Introduction

Polymerizable liquid crystals are useful for many applications in electronic devices. Many types of liquid crystal monomers, oligomers and polymers have been investigated for use as LCD components [1–3]. Liquid crystal monomers, which have one polymerizable group, have been and continue to be extensively studied because pendant-type polymers have application potential in switching devices and as optical freestanding films. Cyanobiphenyl-containing materials, which are representative nematic compounds, were investigated and the physical properties of the monomers and polymers compared [4]. The birefringence was reduced by polymerization because the orientational order decreased. Recently liquid crystal monomers containing two polymerizable groups have been investigated. This type of polymer, for which nematic orientations were frozen by photopolymerization, were called *in situ* photopolymerized polymers [5–9]. These materials are better suited for static applications, such as optical films. Three-ring phenylbenzoate monomers with either one or two polymerizable groups and their polymers were systematically studied. This revealed that the relationships between the optical properties of the monomers and polymers are complex.

High birefringence (Δn) liquid crystals are useful materials for application in reflective-type LCDs, spatial light modulators, compensation films, reflectors and polarizers [10–12]. The fabrication of such optical components, requires high Δn polymerizable liquid crystal monomers. We have studied three-ring phenylacetylene (PA) compounds as high Δn liquid crystals having improved liquid crystal temperature ranges, solubility and photostability [13–15]. On the basis of these results, we have incorporated the core structures of these series into photopolymerizable liquid crystal monomers. In this paper, we report the physical properties of new photopolymerizable three-ring phenylacetylene (3PA) diacrylate monomers and of their polymeric networks.

2. Experimental

We synthesized the three-ring phenylacetylene derivatives **1** and **2** as shown in scheme 1 and the derivatives **3** and **4** as shown in scheme 2. All the compounds were synthesized by the coupling of an acrylic chloride with hydroxyl derivatives. The main synthetic procedures are described in § 5. The structures of the final compounds and various synthetic intermediates were characterized by ^{1}H NMR spectroscopy. All spectra were recorded in $CDCl_3$ with TMS as internal standard. The ^{1}H NMR spectra (Unity 300, Varian 300 MHz) are in accord with the proposed structures. Mass spectra (SX102, Jeol) were also measured and revealed the expected molecular weights. All the compounds of this series were greater than 99% pure according to HPLC (ODS A-212 column, Sumika Chemical Analysis Service).

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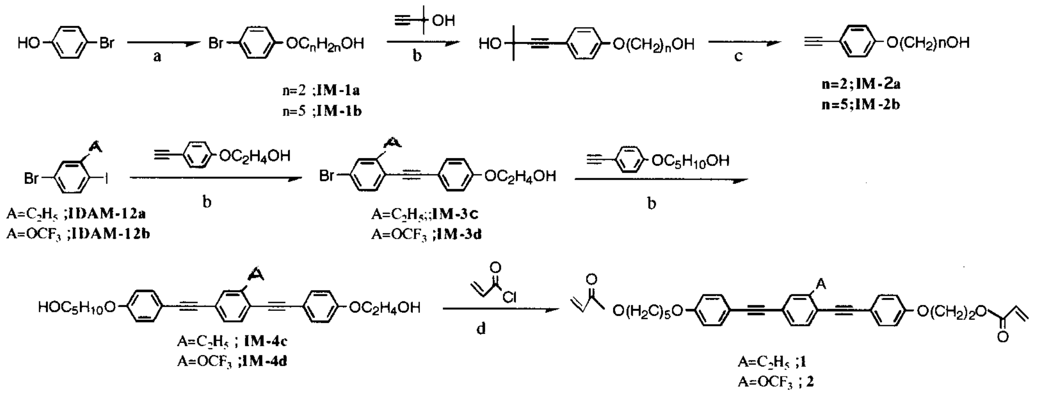
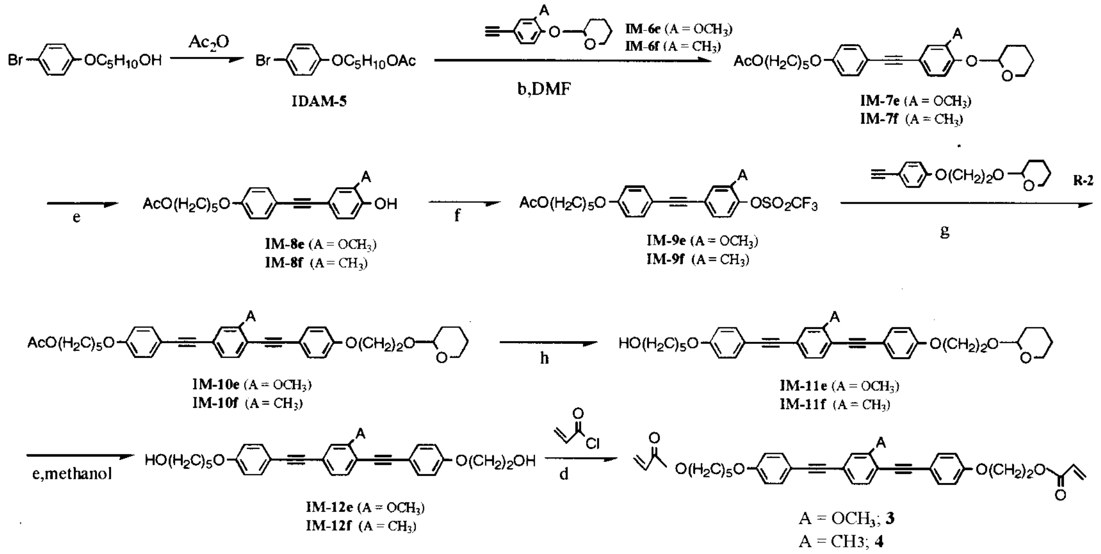
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110068947



Scheme 1. a $Br(CH_2)_5OH/K_2CO_3$; b $PdCl_2(PPh_3)_2/PPh_3$/Triethylamine/CuI; c NaOH/Toluene; d THF.



Scheme 2. e p-Toluenesulfonic acid/methanol; f $(CF_3SO_2)_2O$/pyridine/4-pyrrolidin-1-yl pyridine; g $PdCl_2(PPh_3)_2$/triethylamine/DMF; h $LiAlH_4$/THF.

Transition temperatures and phase sequences were measured using a Mettler FP82 hot stage and control unit in conjunction with an optical microscope (Optiphot2-Pol, Nikon) and were confirmed using differential scanning calorimetry (DSC-200, Seiko Instruments Inc.).

Refractive indices were evaluated as extrapolated values from mixtures containing 10 wt % of each test compound in MJ931381 (Merck, Japan). An Abbe refractometer (2T, Atago) was used to measure the refractive indices of the mixtures at 20°C, a sodium lamp providing the light source at 589 nm. The birefringence of single monomers and polymers was measured also by the hollow prism method [16]; the experimental set-up for the measurement is shown in figure 1. A temperature controlled parallel aligned wedge cell mounted on a rotating stage equipped with a stepping motor (D80, Suruga Seiki) and encoder system (resolution; 1 arcsec, K1 and Cr-16, Canon) was used for these measurements. Each reflection angle of the incident He-Ne laser ($\lambda = 633$ nm) light polarized parallel and perpendicular to the rubbing direction was measured for the calculation of n_o and n_e.

Order parameters were estimated by measuring polarized IR absorption spectra (FTIR, Magna860, Nicolet); 15–20 µm thick homogeneously aligned cells were prepared for this measurement. The substrates were CaF_2 crystal plates coated with polyimide (LX-1800, Hitachi Chemicals), and rubbed in one direction. Order parameters were calculated from the dicroic ratio [17] of the acetylene, C≡C, stretching absorption bonds (centred around 2220 cm^{-1}) of the compounds, according to the equation

$$S = (D + 1)/(D - 2)$$

where D is the dicroic ratio, and S the order parameter.

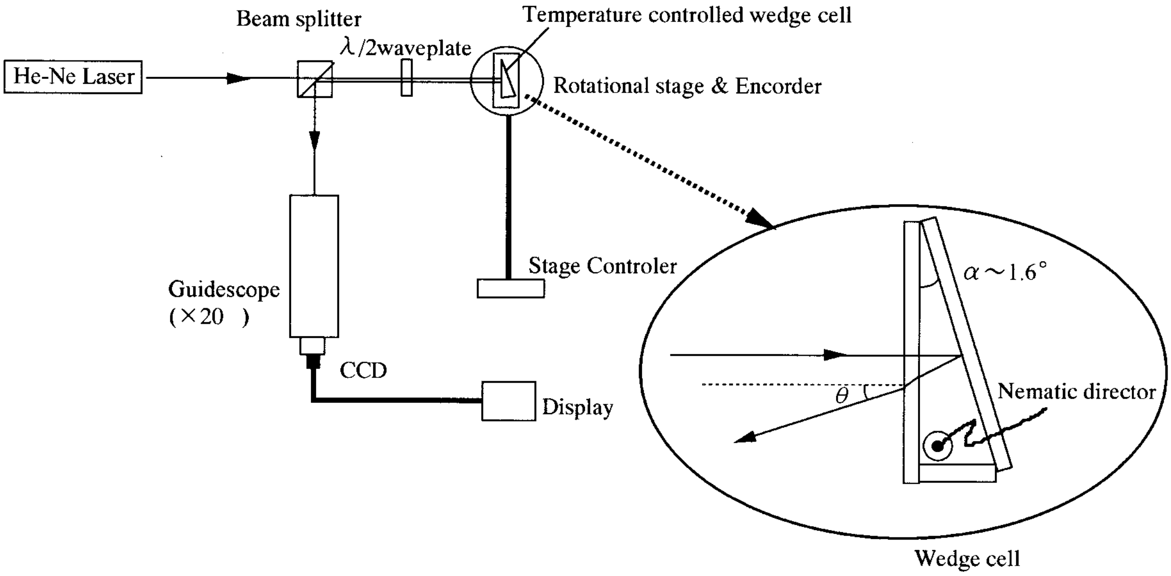


Figure 1. Optical set-up for refractive index measurement.

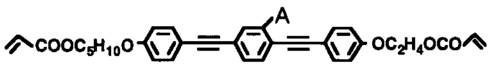
3. Results and discussion

The phase transition temperatures of the acrylic phenylacetylene monomers are listed in the table; they all exhibited a nematic phase. Compounds **1** ($A = C_2H_5$) and **4** ($A = CH_3$) exhibited enantiotropical nematic phases. The presence of an acrylic terminal group narrowed the nematic range compared with the non-acrylic homologues [18]. As shown in figure 2, the effects of the substituent group (A) on the transition temperatures of the liquid crystal phases were similar to those observed for compounds with alkyl terminal chains [18].

The Δn values of these monomers were high at around 0.35; acrylic groups tended to lower Δn as estimated from the mixtures with the host nematic. A comparison of Δn, measured for single compounds, for the acrylic and non-acrylic compounds is shown in figure 3. There were no differences between these compounds, and so the lower Δn values estimated from the mixtures (see figure 2) were a result not of the difference in polarizability but of the decrease in T_{NI} of the mixtures with the host nematic at 20°C.

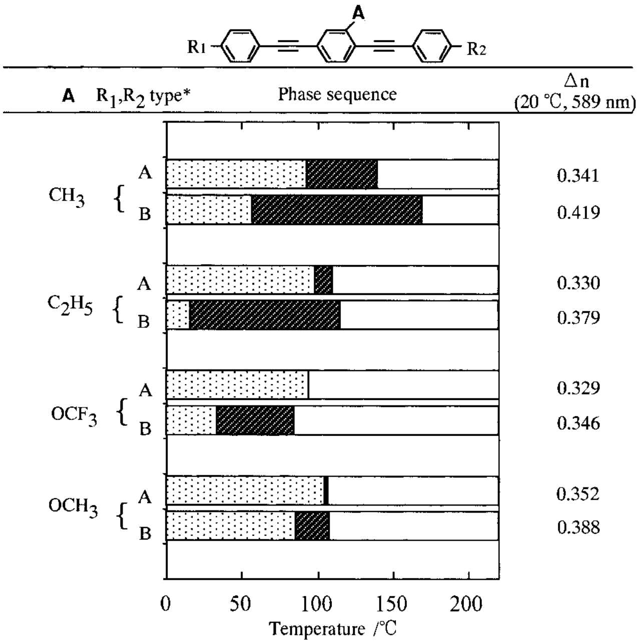
Compounds **1** and **4**, which exhibited an enantiotropic nematic phase, were polymerized in order to evaluate the physical properties of the corresponding polymers. Figure 4 shows the refractive indices (at 633 nm) before and after the polymerization of **1**. Compound **1** with 1 wt% Irgacure 651 as photoinitiator was irradiated with a high pressure mercury lamp (1.4 J cm^{-2}) in a cell with rubbed polyimide as the alignment layer at 105°C in the nematic phase. Polymerization was confirmed by the IR spectrum, and specifically the band associated with the acrylate C=C double bonds disappeared. The optical texture after polymerization was homogeneous and almost the same as that of the monomer. Defects were not generated by polymerization and no haze was observed. Therefore, the arrangements of the cores was thought to be retained and significant shrinkage was not observed. The temperature dependences of n_e and Δn

Table. Phase sequences, refractive indices and Δn of the phenylacetylene monomers.



Compound	A	Transition temperatures/°C	n_o[a]	n_e[a]	Δn[a]
1	C_2H_5	Cr • 98 • N • 110 • I	1.523	1.854	0.330
2	OCF_3	Cr • 94 • (N • 91) I	1.504	1.833	0.329
3	OCH_3	Cr • 105 • N • 107 • I	1.525	1.877	0.352
4	CH_3	Cr • 93 • N • 140 • I	1.516	1.857	0.341

[a] Extrapolated values (20°C, 589 nm) of the mixture: monomer 10 wt % in MJ931381.



* Type A; $R_1 = OC_5H_{10}OCOCHCH_2$, $R_2 = OC_2H_4OCOCHCH_2$
Type B; $R_1 = C_6H_{13}$, $R_2 = C_3H_7$

▨ Crystal phase, ■ Nematic phase, ☐ Isotropic phase

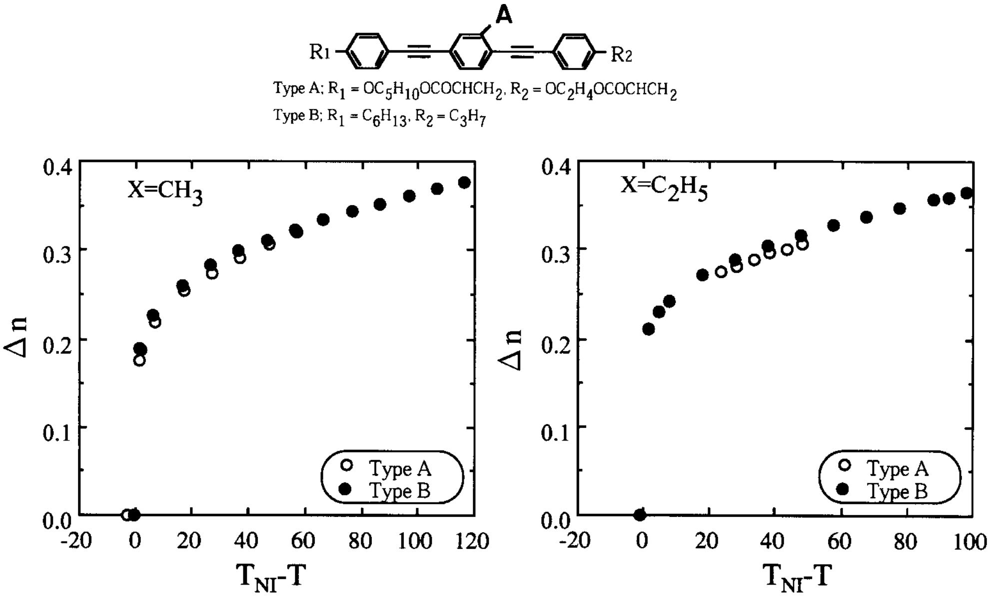
Figure 2. Effect of acrylic groups on transition temperatures and birefringence.

were smaller than those of the monomer. The values of Δn, n_o and n_e of the monomer were almost captured by polymerization, which is consistent with the observation that no textural changes occur after polymerization.

The order parameter of compound **1** is shown in figure 5. The temperature dependence of the order parameter also decreased after polymerization. The order parameter at the polymerization temperature was captured in the polymer and it showed similar behaviour after polymerization as the refractive indices.

Compound **4** had a wider nematic range than **1** and thus was polymerized at two different temperatures, 105 and 140°C. The polymerization conditions were the same as that used to polymerize **1**. As shown in figure 6, Δn of polymer **1** (irradiated at 105°C) was essentially the same as the value of the monomer at the polymerization temperature, but n_o decreased and n_e also became slightly smaller on polymerization. The order parameter of polymer **1** was almost the same as that of the monomer at 105°C (see figure 7). It was considered that the orientational order in the nematic phase was essentially captured after polymerization with regard to monomer **4**, as for **1**. The dichroic ratio of the C=C double bond of monomer **4** in the IR spectrum was negative so that the contribution of the bond to n_o as clearly decreased by polymerization. A decrease in n_e was also apparent for the same reason.

Δn, n_e and the order parameter of polymer **2** (irradiated at 140°C) were smaller than those of polymer **1**, but they increased compared with the monomer values. Monomer **4** began its transition from nematic to isotropic phase at 140°C, but exhibited a narrow transition range. Thus the orientation was increased by polymerization in the co-existence of nematic and isotropic phases.



(*a*) (*b*)

Figure 3. Effect of acrylic groups on birefringence (*a*) A = CH_3, (*b*) A = C_2H_5.

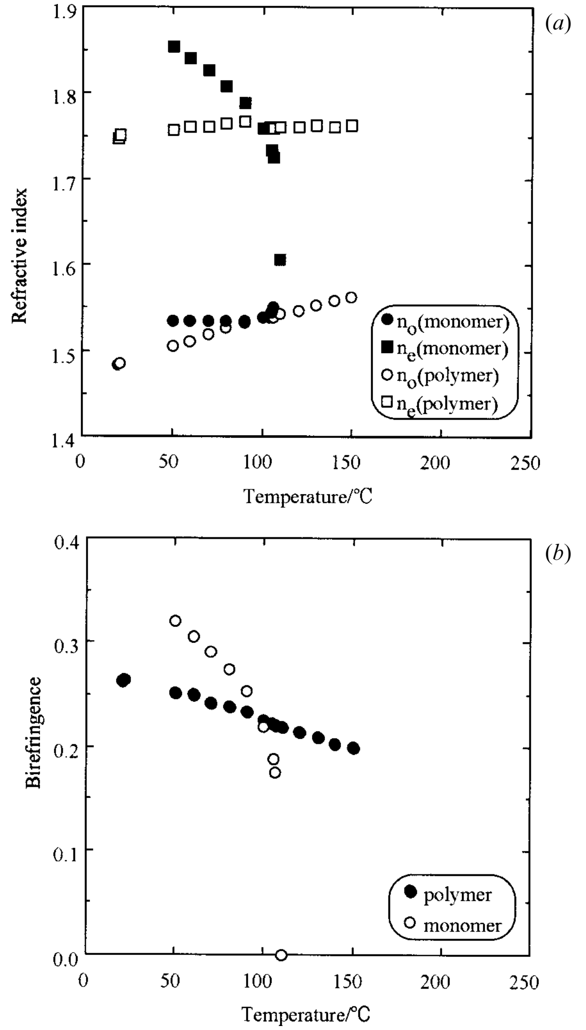


Figure 4. Refractive index (*a*) and birefringence (*b*) of diacrylate monomer **1** and its crosslinked polymer.

Δn and the order parameter of the polymer varied with polymerization temperature; the lower temperature gave the higher Δn and order parameter. The orientation at photopolymerization was almost fixed such that Δn and order parameter varied with polymerization temperature.

4. Conclusions

We synthesized and characterized photopolymerizable phenylacetylene liquid crystals. The compounds evaluated here exhibit a nematic phase and high birefringence as expected from the corresponding alkyl containing homologues. The homogeneous alignment of the monomers was retained after polymerization such that the birefringence and the order parameters were almost fixed at the values of the monomers. Therefore, Δn and S varied with polymerization temperature and hence, the higher Δn value was obtained by polymerization at lower temperature.

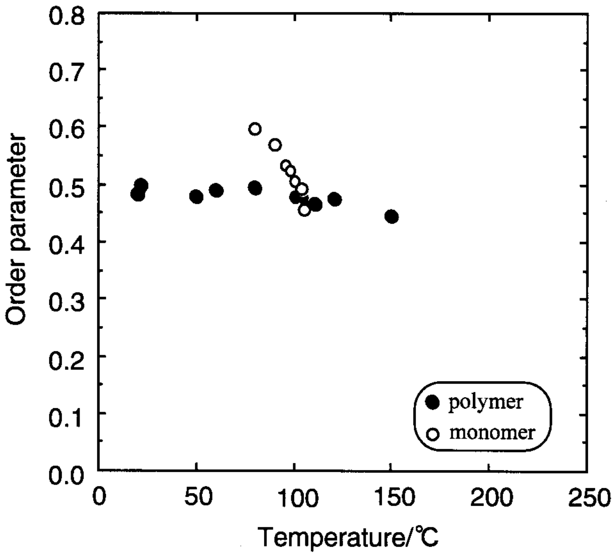


Figure 5. Order parameter of diacrylate monomer **1** and its crosslinked polymer.

5. Synthesis

5.1. *1-{[4-(2-Acryloyloxyethoxy)phenyl]ethynyl}-2-ethyl-4-{[4-[5-acryloyloxypentoxy)phenyl]-ethynyl}benzene (1)*

A solution of 4-bromophenol (4.29 g) in dried DMF (40 ml) was degassed with nitrogen. 2-Bromoethanol (5.0 g) and potassium carbonate (4.14 g) were added at room temperature and the mixture was stirred for 5 h at 50–55°C. Water and ethyl acetate were added and the product was extracted into the organic solvent. The organic solution was washed with saturated brine and dried with anhydrous sodium sulphate. The extract was filtered, concentrated and purified by column chromatography (silica gel, *n*-hexane/ethyl acetate) to give **IM-1a**; yield 7.8 g (75%).

A solution of **IM-1a** (7.8 g) in triethylamine (62 ml) was degassed with nitrogen; 3-methyl-1-butyn-3-ol (2.72 g), copper(I) iodide (48.7 mg), triphenylphosphine (0.6 g) and dichlorobis(triphenylphosphine)palladium (48.7 mg) were added at room temperature and the mixture was stirred under reflux for 5 h. The mixture was filtered and the solvent removed under vacuum. The product was extracted using ethyl acetate acidified with 1N hydrochloric acid. The extract was washed with saturated brine, dried with anhydrous sodium sulfate, filtered and the solvent removed. Sodium hydroxide (0.73 g) and toluene (30 ml) were added to the extract and stirred for 4 h. The product was extracted using ethylacetate acidified by IN hydrochloric acid. The organic solution was washed with saturated brine, dried with anhydrous sodium sulfate, filtered and the solvent removed to give **1M-2a**; yield 1.48 g (100%).

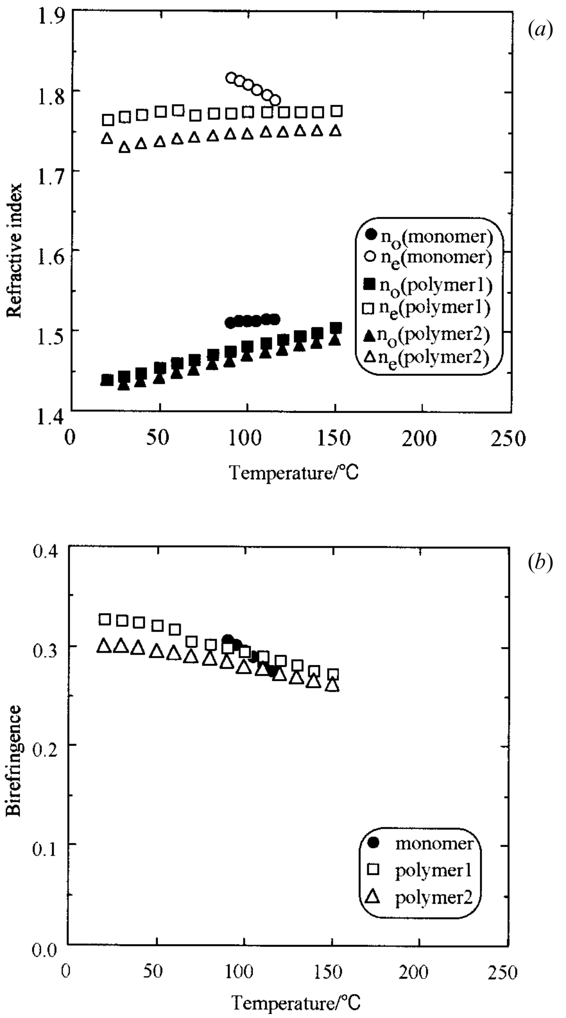


Figure 6. Refractive index (*a*) and birefringence (*b*) of diacrylate monomer **4** and its crosslinked polymers.

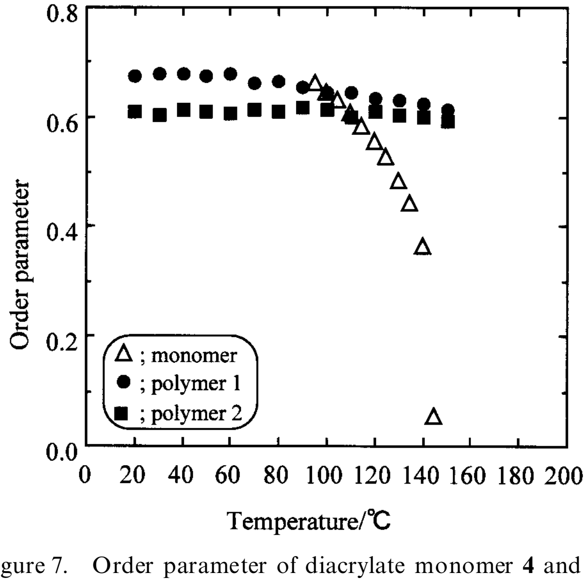


Figure 7. Order parameter of diacrylate monomer **4** and its crosslinked polymers.

A mixture of **IM-1b** (synthesized using the same route as for **IM-1a**, but using 1-bromopentanol instead of 2-bromoethanol), toluene (70 ml) and sodium hydroxide (1.65 g) was degassed with nitrogen and stirred while heating at reflux for 4 h. The product was extracted with ethyl acetate acidified by 1N hydrochloric acid. The organic solution was washed with saturated brine, dried with anhydrous sodium sulfate, filtered and the solvent removed to give **IM-2b**; yield 4.13 g (99%).

4-Bromo-2-ethyl-1-iodobenzene (3.83 g) plus triethylamine (19 ml) was degassed with nitrogen. **IM-2a** (1.48 g), copper(I) iodide (13.7 g), triphenylphosphine (0.632 g) and dichlorobis(triphenylphosphine)palladium (13.7 g) were added at room temperature and the mixture stirred while heating at reflux for 6 h. The solvent was evaporated after filtration, and the product extracted with ethyl acetate acidified with 1N hydrochloric acid. The extract was washed with saturated brine, dried over anhydrous sodium sulfate, filtered, concentrated and purified by column chromatography (silica gel, *n*-hexane/ethylacetate) to give **IM-3c**; yield 3.1 g (82%).

IM-3c (3.1 g) with triethylamine (16 ml) was degassed with nitrogen. **IM-2b** (1.52 g), copper(I) iodide (11.2 mg), triphenylphosphine (51.5 mg) and dichlorobis(triphenylphosphine)palladium (11.2 mg) were added at room temperature and the mixture was stirred while heating at reflux for 6.5 h. The solvent was removed after filtration, and the product extracted with ethyl acetate acidified with 1N hydrochloric acid. The extract was washed with saturated brine, dried with anydrous sodium sulfate, filtered, concentrated and purified by column chromatography (silica gel, *n*-hexane/ethylacetate) to give **IM-4c**; yield 3.22 g (82%).

A solution of **IM-4c** (2.7 g) and triethylamine (16 ml) in THF (50 ml) was degassed with nitrogen and cooled in ice. Acryloyl chloride (1.03 g) was added and the mixture stirred for 0.5 h at 0°C and then for 2 h at room temperature. A 5% aqueous solution of sodium carbonate was added after cooling, and the product was extracted with ethyl acetate. The extract was washed with water and saturated brine, dried over anhydrous sodium sulfate and filtered. The solvent was removed and the product purified by recrystallization from *n*-hexane/chloroform (5/1 and 1/1) to give compound **1**; yield 1.86 g (33%). ^{1}H NMR (CDCl$_3$, δ): 1.31 (t, 3H, $J = 7.8$ Hz), 1.52–1.63 (m, 2H), 1.71–1.89 (m, 4H), 2.87 (q, 2H, $J = 7.8$ Hz), 3.99 (t, 2H, $J = 6.3$ Hz), 4.17–4.26 (m, 4H), 4.51–4.55 (m, 2H), 5.80–5.89 (m, 2H), 6.07–6.22 (m, 2H), 6.37–6.49 (m, 2H), 6.84–6.92 (m, 4H), 7.28–7.49 (m, 7H). IR (CaF$_2$ cell) ν_{max}: 3040, 2940, 2872, 2525, 2205, 1890, 1726, 1731, 1636, 1603, 1568, 1512, 1457, 1408, 1294, 1270 cm^{-1}. MS m/z 576, 577 (M$^+$).

5.2. *1-{[4-(2-Acryloyloxyethoxy)phenyl]ethynyl}-2-trifluoromethoxy-4-{[4-[5-acryloyloxypentoxy)-phenyl]ethynyl}benzene (**2**)*

Compound **2** was synthesized using the same route as for compound **1** but using 2-trifluoromethoxy-4-bromo-1-iodobenzene in place of 2-ethyl-4-bromo-1-iodobenzene ^{1}H NMR ($CDCl_3$, δ): 1.52–1.63 (m, 2H), 1.71–1.90 (m, 4H), 4.00 (t, 2H, $J = 6.5$ Hz), 4.17–4.26 (m, 4H), 4.51–4.55 (m, 2H), 5.80–5.89 (m, 2H), 6.07–6.22 (m, 2H), 6.37–6.49 (m, 2H), 6.81–6.93 (m, 4H), 7.37–7.52 (m, 7H). IR (CaF_2 cell) ν_{max}: 2947, 2216, 1728, 1603, 1518, 1408, 1248, 1220 cm^{-1}. MS *m*/*z* 632 (M^+).

5.3. *1-{[4-(2-Acryloyloxyethoxy)phenyl]ethynyl}-2-methoxy-4-{[4-[5-acryloyloxypentoxy)phenyl]-ethynyl}benzene (**3**)*

A solution of **IM-2b** (80 g) in acetic anhydride (36.4 g) was degassed with nitrogen gas. Acetic anhydride (320 g) was added and stirred for 5 h at 55°C. The organic solution was concentrated and purified by column chromatography (silica gel, ethylacetate/*n*-hexane = 1/10) to give **IDAM-5**; yield 93 g (100%).

IDAM-5 (26 g) was degassed. Dichlorobis(triphenylphosphine)palladium (0.182 g), copper(I) iodide (0.15 g), triphenylphosphine (0.68 g) and triethylamine (182 ml) were added at 65°C. A solution of **IM-6e** (28.0 g) in triethylamine (30 ml) was added and the mixture stirred for 5 h at 89°C. The product was filtered and washed with ethyl acetate. The filtrate was concentrated and purified by column chromatography (silica gel, *n*-hexane/ethylacetate with 0.1% triethylamine) to give **IM-7e**; yield 39.1 g (74.4%).

IM-7e (28.1 g), methanol (413.1 ml) and *p*-toluenesulphonic acid (0.83 g) were degassed with nitrogen and stirred at 3–6°C. Triethylamine (10 ml) was added; the mixture was concentrated and purified by column chromatography (silica gel, *n*-hexane/ethylacetate = 3/1) to give **IM-8e**; yield 22.91 g (85.2%).

IM-8e (19.5 g), 4-pyrrolidin-1-yl pyridine (2.3 g), pyridine (82 ml) and dichloromethane were degassed with nitrogen and the mixture was stirred at 0°C. A solution of trifluoromethanesulphonic anhydride (15.4 ml) in dichloromethane (20 ml) was added and the resulting mixture stirred for 1 h at 0°C. Water and dichloromethane were added and the product was extracted into the organic solvent. The organic layer was washed with water, concentrated and purified by column chromatography (silica gel, *n*-hexane/ethylacetate = 4/1 with 0.1% triethylamine) to give **IM-9e**; yield 25.6 g (99.9%).

A solution of **IM-9e** (23.5 g), dichlorobis(triphenylphosphine)palladium (0.6 g), copper(I) iodide (0.15 g) and triethylamine (20.4 ml) in dried DMF (243 ml) was degassed with nitrogen and heated at 65°C. A solution of **R-2** (12.0 g) in DMF (12 ml) was added and the mixture stirred for 5.5 h. Ethyl acetate, *n*-hexane and water were added and the product was extracted into the organic solvent. The extract was washed with water, dried and concentrated. The crude product was purified by column chromatography (silica gel, *n*-hexane/ethylacetate = 3/1 with 0.1% triethylamine) to give **IM-10e**; yield 2.9 g (80.4%).

IM-10e (23.31 g), THF (195 ml) and lithium aluminium hydride (1.8 g) were degassed with nitrogen and stirred for 1 h at 0°C. A 10% aqueous solution of sodium hydroxide (21.69 g) was added and the product extracted with ethyl acetate. The combined organic extract was washed with water and concentrated to give **IM-11e**; yield 22.28 g (80.4%).

IM-11e (22.28 g), chloroform (10 ml), methanol (100 ml) and *p*-toluenesulphonic acid (0.6 g) were degassed with nitrogen and stirred for 12 h at room temperature. Triethylamine (63 ml) was added and the mixture concentrated. The crude product was purified by column chromatography (silica gel, *n*-hexane/ethylacetate = 3/1 with 0.1% triethylamine) to give **IM-12e**; yield 18.4 g (81.0%).

IM-12e (5.4 g), dried triethylamine (4 ml) and dried THF (117 ml) were degassed with nitrogen. Acryloyl acidic chloride (2.3 ml) was added at 0°C and the mixture stirred for 0.5 h. A 5% aqueous solution of sodium carbonate (50 ml) was added at room temperature. The product was extracted with ethyl acetate and washed with water and saturated brine. The organic solution was dried, the mixture concentrated and purified by column chromatography (silica gel, chloroform/*n*-hexane = 5/1 with 0.1% triethylamine) to give compound **3**; yield 6.4 g (43.8%). ^{1}H NMR ($CDCl_3$, δ): 1.52–1.61 (m, 2H), 1.71–1.87 (m, 4H), 3.93 (s, 3H), 3.99 (t, 2H, $J = 6.3$ Hz), 4.19–4.25 (m, 4H), 4.53 (t, 2H, $J = 4.8$ Hz), 5.84–5.90 (m, 2H), 6.08–6.22 (m, 2H), 6.38–6.50 (m, 2H), 6.85–6.91 (m, 4H), 7.02–7.16 (m, 2H), 7.41–7.52 (m, 5H). IR (CaF_2 cell) ν_{max}: 2946, 2870, 2209, 1726, 1635, 1603, 1566, 1544, 1515, 1495, 1458, 1407, 1275, 1246 cm^{-1}. MS *m*/*z* 578 (M^+).

5.4. *1-{[4-(2-Acryloyloxyethoxy)phenyl]ethynyl}-2-methyl-4-{[4-(5-acryloyloxypentoxy)-phenyl]ethynyl}benzene (**4**)*

Compound **4** was synthesized using the same synthetic route as for compound **3** but using **IM-5f**–**IM-11f** in place of **IM-5e**–**IM-11e**. ^{1}H NMR ($CDCl_3$, δ): 1.52–1.61 (m, 2H), 1.71–1.87 (m, 4H), 2.49 (s, 3H), 3.98 (t, 2H, $J = 6.3$ Hz), 4.19–4.25 (m, 4H), 4.53 (t, 2H, $J = 4.8$ Hz), 5.84–5.90 (m, 2H), 6.08–6.22 (m, 2H), 6.38–6.50 (m, 2H), 6.84–6.98 (m, 4H), 7.29–7.52 (m, 7H). IR (CaF_2 cell) ν_{max}: 3040, 2948, 2871, 2529, 2208, 1891, 1732, 1721, 1635, 1603, 1567, 1512, 1471, 1456, 1408, 1294, 1270, 1246 cm^{-1}. MS *m*/*z* 562 (M^+).

This work was performed under the management of ASET and in the MITI Program of Super-Advanced Electronic Technologies supported by NEDO.

References

[1] Broer, D. J., van Harren, J. A. M. M., Mol, G. N., and Leenhouts, F., 1995, *SID'95*, Asia Display, 735.

[2] Stohr, A., and Strohriegl, P., 1997, *Mol. Cryst. liq. Cryst.*, **299,** 211.

[3] Hikmet, R. A. M., and Kemperman, H., 1999, *Liq. Cryst.*, **26,** 1645.

[4] Plte, N. A., Talroze, R. V., and Shibaev, V. P., 1987, *Makromol. Chem., macromol. Symp.*, **12,** 203.

[5] Broer, D. J., Finkelmann, H., and Kondo, K., 1988, *Makromol. Chem.*, **189,** 185.

[6] Broer, D. J., Mol. G. N., and Challa, G., 1989, *Makromol. Chem.*, **190,** 19.

[7] Broer, D. J., Boven, J., Mol, G. N., and Challa, G., 1989, *Makromol. Chem.*, **190,** 2255.

[8] Broer, D. J., Hikmet, R. A. M., and Challa, G., 1989, *Makromol. Chem.*, **190,** 3201.

[9] Broer, D. J., Mol, G. N., and Challa, G., 1990, *Makromol. Chem.*, **192,** 59.

[10] Wu, S. T., 1995, *Mol. Cryst. liq. Cryst.*, **261,** 79.

[11] Takatsu, H., Takeuchi, K., Tanaka, Y., and Sasaki, M., 1986, *Mol. Cryst. liq. Cryst.*, **141,** 279.

[12] Wu, S. T., Finkenzeller, U., and Reiffenrath, V., 1989, *J. appl. Phys.*, **65,** 4372.

[13] JP98-43 289, 1998, Sumitomo Chemical Co., Ltd.

[14] Sekine, C., Fujisawa, K., Konya, N., and Minai, M., 1998, in Proceedings of Liquid Crystal Conference of Japan, 2B11.

[15] Sekine, C., Fujisawa, K., Konya, N., and Minai, M., 1998, *Proc. IDW99*, 411.

[16] Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., and Vill, V. (editors), 1998, *Handbook of Liquid Crystals*, Vol. 2A (Wiley-VCH).

[17] Fontana, M. P., Rosi, B., Korov, N., and Dozov, I., 1986, *Phys. Rev. A*, **33,** 4132.

[18] Sekine, C., Iwakura, K., Minai, M., and Fujisawa, K., *Mol. Cryst. liq. Cryst.* (in the press).