New side chain liquid crystalline polymers: synthesis and thermal properties of side chain polyacrylates having segmented spacers

Eiichi Akiyama; Yu Nagase; Naoyuki Koide; Kazuo Araki

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New side chain liquid crystalline polymers: synthesis and thermal properties of side chain polyacrylates having segmented spacers

EIICHI AKIYAMA*, YU NAGASE

Sagami Chemical Research Center, 4-4-1 Nishi-ohnuma, Sagamihara,
Kanagawa 229-0012, Japan

NAOYUKI KOIDE

Department of Chemistry, Faculty of Science, Science University of Tokyo,
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-0825, Japan

and KAZUO ARAKI

Department of Materials Science and Engineering,
Faculty of Science and Engineering, Science University of Tokyo in Yamaguchi,
1-1-1 Daigaku-dori, Onoda, Yamaguchi 756-0884, Japan

In order to acquire high mobility of a mesogenic group, we propose a new type of side chain liquid crystal polymer having segmented spacers, consisting of binary moieties of an oligo-(ethylene oxide) segment and an alkylene segment. Six kinds of polyacrylates having segmented spacers consisting of different lengths of an oligo(ethylene oxide) and an alkylene, and having 4′-cyanobiphenyl as a mesogenic group have been synthesized, and their thermal properties investigated. Some of these polyacrylates exhibit a mesophase and show an extremely low glass transition temperature compared with LC polyacrylates having ordinary alkylene spacers.

1. Introduction

Side chain liquid crystalline polymers (SCLCPs) which offer possibilities for various applications have attracted the attention of numerous scientific researchers and engineers [1]. In general, SCLCPs can be classified into mainly two categories, the first in which SCLCP is a static anisotropic dielectric and the second where the anisotropy is controlled by an external field. We have been interested in the latter. That is, a basic object of our study is to obtain an SCLCP having both the fast response of low molar mass liquid crystals (LMMLCs) and good polymer processing properties. Our approach has been to modify the chemical structure of the spacer part in order to decouple the motions of the polymer backbone and mesogenic groups. Since Finkelmann *et al.* developed SCLCPs in 1978 [2], alkylene chains as flexible spacers have been mainly used [3]. As a flexible spacer chain alternative to alkylene chains, the introduction of a siloxane linkage into an alkylene chain, or an oligo(ethylene oxide) spacer into the chain was proposed by M. Engel *et al.* [4].

Recently we also reported the mesomorphic properties of polyacrylates having the so-called 'siloxane spacer' [5]. It was seen that the introduction of a siloxane linkage into a spacer decreased the glass transition temperature (T_g) of a polymer compared with the case of an ordinary alkylene spacer, while a relatively large mesogenic group such as the three phenylene ring of 4′-cyanobiphenylyl benzoate was necessary to obtain a mesophase, because the bulk of the dimethylsiloxane unit prevented the mesogenic side chain from aniso-tropically ordering. Furthermore, we adopted the oligo-(ethylene oxide) chain as a very flexible and non-bulky spacer chain [6]. From our result and that reported by M. Engel *et al.* [4], it was found that the polyacrylate having a very flexible and non-bulky spacer chain did not yet exhibit a mesophase in the case of a small mesogenic group (such as the two phenylene rings of 4-cyanophenyl benzoate). It was concluded that a spacer chain worked not only to decouple the motion of a polymer backbone and a mesogenic group, but also to control part of the interaction between mesogenic groups.

In previous papers, we reported the influence of the spacer chemical structure on the mobilities of poly-mer backbone and mesogenic groups using dielectric

*Author for correspondence; e-mail: eiichi@pluto.dti.ne.jp

relaxation spectroscopy (DRS) [6, 7]. For an SCLCP whose optical anisotropic director is switchable by electric field, its switching properties are affected not only by the amplitude of the anisotropic dipole moment, but also by the rotational viscosity in the macro and/or micro scale. However, the relaxation time (τ_R) of a δ-relaxation process, in relation to the motion of a mesogenic side chain evaluated from DRS, should reflect the characteristics of an optical switching property. Therefore, we reported that the size of a mesogenic core mainly affects τ_R. That is, as small a mesogenic group as possible should be introduced to get fast response. Hence, in this paper we wish to describe a concept to guide the synthesis of SCLCPs, designed for fast electro-optic response.

Our concept of the synthesis is illustrated in figure 1. That is, a high response SCLCP should consist of the following four parts, A to D, and address the issues indicated.

(A) Polymer backbone: control of T_g of a polymer and the fluidity (or macroscopic viscosity).
(B) Oligo(ethylene oxide) chain: decoupling of the motions of the polymer backbone and mesogenic group.
(C) Alkylene chain: control of the interaction between mesogenic groups.
(D) Mesogenic group: introduce as small a mesogenic core as possible for the purpose of obtaining fast response to external stimulus.
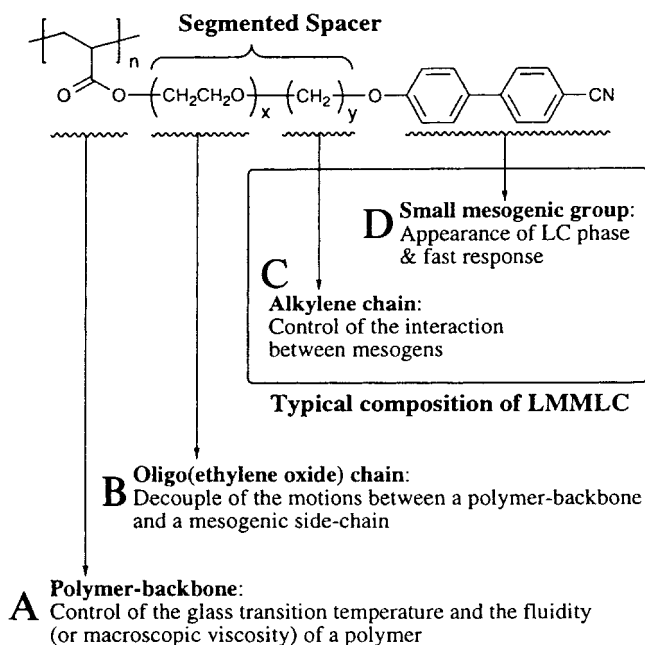
We use the term 'segmented spacer' to distinguish such a spacer group (i.e. the binary chain composed of parts B and C) from the ordinary spacer chain of one composition, such as an alkylene chain. The side chain moiety composed of parts C and D is a typical composition of a LMMLC, such as 5OCB (4-cyano-4′-pentyloxybiphenyl).

In order to verify our concept six kinds of polymers were synthesized, having the following components: A polyacrylate; B tri- or tetra-(ethylene oxide); C an alkylene chain with number of carbons $y = 4$, 6 or 11; and D 4′-cyanobiphenyl moiety as a typical small mesogenic group. Their thermal properties were then investigated using differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). In addition, the thermal properties of two kinds of the corresponding tri- and tetra-(ethylene oxide) spacer type polyacrylates were investigated for comparison with those of the segmented spacer type polyacrylates.

2. Experimental
2.1. *Materials*

4-Hydroxy-4′-cyanobiphenyl (Tokyo Kasei Industries), 1,4-dibromobutane (Tokyo Kasei Industries), 1,6-dibromo-hexane (Tokyo Kasei Industries), potassium carbonate (Kanto Chemical Co.), potassium iodide (Kanto Chemical Co.), sodium hydride (60% in oil, Kishida Chemical Co., Ltd.), diethyl azodicarboxylate (DEAD, 40% in toluene, Nacalai Tesque, Inc.), pyridine (Wako Pure Chemical Industries, Ltd.) and 2,2′-azobis(isobutyronitrile) (AIBN, Wako Pure Chemical Industries, Ltd) were commercially available and used as received. Tri(ethylene glycol) (Kanto Chemical Co.) and tetra(ethylene glycol) (Kanto Chemical Co.) were dried *in vacuo* at 100°C overnight before use. Triphenylphosphine (TPP, Kanto Chemical Co.) and 4-toluenesulphonyl chloride (Tokyo Kasei Industries) were recrystallized from ethanol and *n*-hexane, respectively. Acryloyl chloride (Tokyo Kasei Industries) was distilled under argon before use. Tetrahydrofuran (THF) and triethylamine (TEA) were distilled over sodium and calcium hydride, respectively.

2.2. *Characterization*

^{1}H NMR was conducted with Hitachi R-90H FT NMR (90 MHz) and Bruker AM-400 FT NMR (400 MHz) spectrometers using CDCl$_3$ as the solvent, Infrared (IR) spectra were recorded on a Jasco FTIR-5300 spectrometer. Mass spectrometry used a Hitachi Mass Spectrometer M80B with the electron ionization method (EI). Gel-permeation chromatography (GPC) was carried out with a Tosoh HLC-802A instrument using THF as an eluent. It was equipped with four columns of TSK gels: G5000H$_6$, G4000H$_6$, G3000H$_6$

Figure 1. Illustration of the new type of SCLCP having a segmented spacer.

and G2000H$_6$; standard polystyrenes were used for calibration.

Differential scanning calorimetry (DSC) was performed with a Seiko Electronic DSC-20 with SSC-580 thermal controller. DSC measurements of the polymers were carried out at a scanning rate of $\pm 5°C \, min^{-1}$. A Nikon Microphot-UFX polarizing optical microscope equipped with a Mettler FP-82 hot stage and an FP-80 central processor was used to observe thermal transitions and analyse anisotropic textures under a flow of cool nitrogen. XRD patterns were recorded on a MAC Science MXP^3 X-ray diffractometer at room temperature (25°C).

2.3. *Synthesis of compounds 1 and 2*

In this and the following sections, compound numbers refer to the structures defined in schemes 1 and 2. 4-Hydroxy-4′-cyanobiphenyl (2.00 g, 10.2 mmol) and 1,4-dibromobutane (20.0 g, 92.6 mmol) were dissolved in acetone (10 ml). After adding potassium carbonate (1.50 g, 10.9 mmol) and potassium iodide (0.2 g) as catalyst, the mixture was stirred at reflux for 15 h. *n*-Hexane
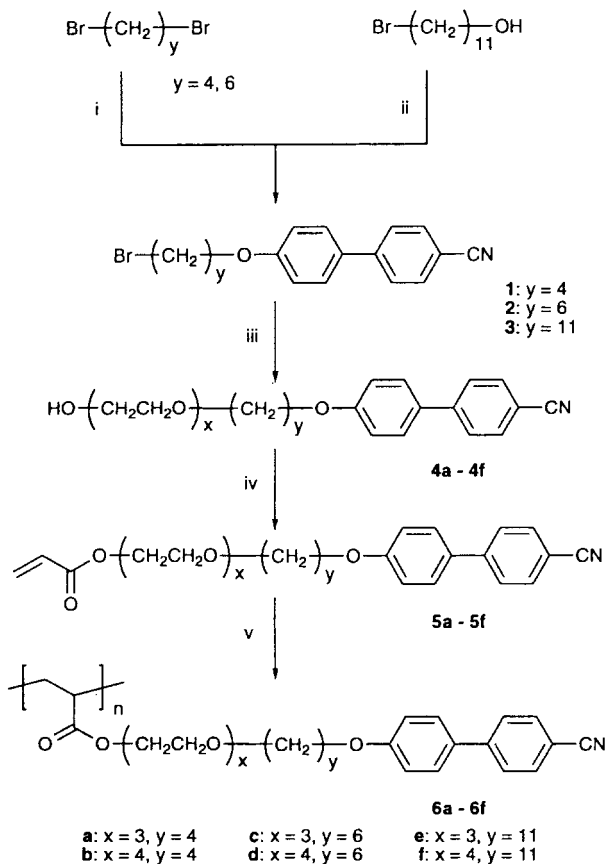

Scheme 1. Reagents and conditions: i, K$_2$CO$_3$, acetone, 4-cyano-4′-hydroxybiphenyl; ii, 4-cyano-4′-hydroxybiphenyl, DEAD, PPh$_3$, CHCl$_3$, 0°C, 1 h; iii, tri- or tetra-(ethylene glycol), NaH, THF, 0°C reflux; iv, acryloyl chloride, TEA, THF; v, AIBN, THF, 60°C, 18 h.

Scheme 2. Reagents and conditions: i, *p*-toluenesulfonyl chloride, pyridine, ether; ii, 4-cyano-4′-hydroxybiphenyl, K$_2$CO$_3$, acetone, reflux; iii, acryloyl chloride, TEA, THF; iv, AIBN, THF, 60°C, 18 h.

(200 ml) was added and insoluble salts filtered off. The filtrate was then concentrated, and the residue purified by recrystallization from *n*-hexane to afford 1 (2.26 g, 66.8% yield) as colourless, needle-like crystals. ^{1}H NMR, δ (ppm, CDCl$_3$, 90 MHz): 1.9–2.1 (m, 4H), 3.50 (t, 2H), 4.05 (t, 2H), 6.98 (d, $J = 8.8$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 7.65 (s, 4H).

Compound 2 (3.98 g, 72.3% yield) was obtained in the same manner using 4-hydroxy-4′-cyanobiphenyl (3.00 g, 15.4 mmol) and 1,6-dibromohexane (37.5 g, 154 mmol).

2.4. *Synthesis of compound 3*

4-Hydroxy-4′-cyanobiphenyl (1.95 g, 10.0 mmol), 11-bromoundecan-1-ol (2.51 g, 10.0 mmol) and TPP (2.7 g, 10 mmol) were dissolved in chloroform (30 ml), and the mixture was cooled to 0°C. After dropwise addition of a solution of DEAD, (5.0 ml, 11 mmol) in toluene, the mixture was stirred at room temperature for 1 h. The solvent was then removed under reduced pressure. The residue was purified by column chromatography with chloroform/*n*-hexane (1/1 v/v) as eluent to afford 3 (1.94 g, 45.3% yield) as a colourless solid. ^{1}H NMR, δ (ppm, CDCl$_3$, 90 MHz): 1.1–2.0 (m, 18H), 3.40 (t, 2H), 4.01 (t, $J = 6.2$ Hz, 2H), 6.98 (d, $J = 8.8$ H , 2H), 7.52 (d, $J = 8.6$ Hz, 2H), 7.66 (s, 4H).

2.5. Synthesis of compounds **4a**–**4f**

The alcohol compounds **4a**–**4f** were prepared by etherification of compounds **1**–**3** with tri(ethylene glycol) or tetra(ethylene glycol). A typical procedure is described as follows.

Sodium hydride (60% in oil, 0.122 g, 3.05 mmol) was washed with *n*-hexane dispersed in THF (10 ml) and cooled to 0°C. Tri(ethylene glycol) (0.45 ml, 3.4 mmol) was added dropwise to the mixture. After stirring at 0°C for 1 h, a solution of **1** (0.913 g, 2.76 mmol) in THF (10 ml) was added and the mixture was then stirred at reflux for 3 h. The solvent was distilled off, and chloroform (150 ml) and water (150 ml) were added to the residue. The separated organic layer was washed by water (150 ml) seven times. The solvent was then removed under reduced pressure, and the residue purified by column chromatography with chloroform as eluent to afford **4a** (0.431 g, 39.0% yield) as a colour-less liquid. IR (neat, cm^{-1}): 3447 (–OH), 2917, 2870, 2226 (–CN), 1605 (arC=C), 1522 (w), 1495, 1474 (w), 1397 (w), 1352 (w), 1292, 1250 (arC–O–Cal st as), 1191, 1119 (CH$_2$–O–CH$_2$ st as), 8.24. ^{1}H NMR, δ (ppm, CDCl$_3$, 400 MHz): 1.80 (m, 2H), 1.89 (m, 2H), 2.61 (t, 1H), 3.55 (t, 2H), 3.60–3.63 (m, 4H), 3.66–3.70 (m, 6H), 3.71 (m, 2H), 4.40 (t, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 8.6$ Hz, 2H), 7.69 (d, $J = 8.6$ Hz, 2H). EIMS (m/z): 399 (M)$^+$, 294 (CH$_2$CH$_2$OC$_4$H$_8$OC$_{12}$H$_8$CN)$^+$, 267 (HOC$_4$H$_8$OC$_{12}$H$_8$CN)$^+$, 250 (C$_4$H$_8$OC$_{12}$H$_8$CN)$^+$, 222 (C$_2$H$_4$OC$_{12}$H$_8$CN)$^+$, 208 (CH$_2$OC$_{12}$H$_8$CN)$^+$, 205 (H(OCH$_2$CH$_2$)$_3$OC$_4$H$_8$)$^+$, 195 (HOC$_{12}$H$_8$CN)$^+$, 178 (C$_{12}$H$_8$CN)$^+$, 133 (H(OCH$_2$CH$_2$)$_3$)$^+$, 89 (H(OCH$_2$CH$_2$)$_2$)$^+$, 45 (HOCH$_2$CH$_2$)$^+$.

The remaining series members were obtained using the reagents indicated below.

Compound **4b** (0.608 g, 33.9% yield): sodium hydride (60% in oil, 0.178 g, 4.45 mmol), tetra(ethylene glycol) (0.80 ml, 4.6 mmol) and **1** (1.335 g, 4.043 mmol).

Compound **4c** (0.788 g, 44.0% yield): sodium hydride (60% in oil, 0.184 g, 4.60 mmol), tri(ethylene glycol) (0.65 ml, 4.9 mmol) and **2** (1.500 g, 4.187 mmol).

Compound **4d** (1.19 g, 60.4% yield): sodium hydride (60% in oil, 0.184 g, 4.60 mmol), tetra(ethylene glycol) (0.80 ml, 4.6 mmol) and **2** (1.501 g, 4.189 mmol).

Compound **4e** (0.66 g, 57% yield): sodium hydride (60% in oil, 0.120 g, 3.00 mmol), tri(ethylene glycol) 90.4 ml, 3 mmol) and **3** (1.005 g, 2.346 mmol).

Compound **4f** (0.795 g, 68.9% yield): sodium hydride (60% in oil, 0.094 g, 2.3 mmol), tetra(ethylene glycol) (0.52 ml, 3.0 mmol) and **3** (0.913 g, 2.13 mmol).

2.6 Synthesis of acrylate monomers having a segmented spacer chain (**5a**–**5f**)

The acrylate monomers **5a**–**5f** were prepared by esterification of compounds **4a**–**4f** with acryloyl chloride in the presence of triethylamine as a base. A typical procedure is described as follows.

Compound **4a** (0.431 g, 1.08 mmol) and TEA (0.60 ml, 4.3 mmol) were mixed in 5 ml of THF under argon, and cooled to 0°C. Acryloyl chloride (0.18 ml, 2.2 mmol) was added, and the mixture stirred with gradually increasing temperature to room temperature for 15 h. After distilling off the solvent diethyl ether (200 ml) and water (200 ml) were added and the organic layer separated. This was concentrated and purified by column chromatography with chloroform as eluent to afford **5a** (0.347 g, 70.8% yield) as a colourless liquid. IR (neat, cm^{-1}): 2948, 2870, 2226 (–CN), 1725 (ester C=O), 1636 (w, acryl C=C st), 1605 (ar C=C), 1524 (w), 1495, 1474 (w), 1406, 1352 (w), 1294, 1250 (arC–O–Cal st as), 1194, 1115 (CH$_2$–O–CH$_2$ st as), 1069 (w, C–O–C st sy), 986, 824. ^{1}H NMR, δ (ppm, CDCl$_3$, 400 MHz): 1.78 (m, 2H), 1.89 (m, 2H), 3.55 (t, 2H), 3.61 (m, 2H), 3.65 (m, 2H), 3.67 (s, 4H), 3.74 (t, 2H), 4.04 (t, 2H), 4.32 (t, 2h), 5.83 (dd, $J = 1.4, 10.4$ Hz, 1H), 6.15 (dd, $J = 10.4, 17.3$ Hz, 1H), 6.43 (dd, $J = 1.4, 17.3$ Hz, 1H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 2H), 7.69 (d, $J = 8.5$ Hz, 2H). EIMS (m/z): 453 (M)$^+$, 259 (M-OC$_{12}$H$_8$CN)$^+$, 250 (C$_4$H$_8$OC$_{12}$H$_8$CN)$^+$, 208 (CH$_2$OC$_{12}$H$_8$CN)$^+$, 195 (HOC$_{12}$H$_8$CN)$^+$, 178 (C$_{12}$H$_8$CN)$^+$, 99 (CH$_2$=CHCOOCH$_2$CH$_2$)$^+$, 55 (CH$_2$=CHCO)$^+$.

The remaining members of the series were obtained using the reagents indicated below.

Compound **5b** (0.649 g, 96.4% yield): **4b** (0.600 g, 1.35 mmol), TEA (0.75 ml, 5.4 mmol) and acryloyl chloride (0.22 ml, 2.7 mmol).

Compound **5c** (0.790 g, 98.5% yield): **4c** (0.712 g, 1.67 mmol), TEA (0.93 ml, 6.7 mmol) and acryloyl chloride (0.27 ml, 3.3 mmol).

Compound **5d** (1.153 g, 91.5% yield): **4d** (1.130 g, 2.396 mmol), TEA (1.34 ml, 9.61 mmol) and acryloyl chloride (0.39 ml, 4.8 mmol).

Compound **5e** (0.54 g, 74% yield): **4e** (0.66 g, 1.33 mmol), TEA (0.74 ml, 5.3 mmol) and acryloyl chloride (0.22 ml, 2.7 mmol).

Compound **5f** (0.746 g, 90.2% yield): **4f** (0.752 g, 1.39 mmol), TEA (0.77 ml, 5.5 mmol) and acryloyl chloride (0.23 ml, 2.8 mmol).

2.7. Synthesis of compounds **7a** and **7b**

A typical procedure is described as follows.

A mixture of tri(ethylene glycol) (75 g, 0.50 mol) and pyridine (24 ml, 0.30 mol) was cooled to 0°C; a solution of 4-toluenesulfonyl chloride (19 g, 0.10 mol) in 100 ml of diethyl ether was then added dropwise. After stirring for 12 h at room temperature, the mixture was allowed to settle and the upper ethereal layer removed. Chloroform (400 ml) was then added to the residue.

After washing with 1N hydrochloric acid aq. (400 ml) and water (400 ml) three times, the solution was dried over sodium sulphate. Salt and solvent were then removed and the residue was dried overnight at 85°C under reduced pressure to afford crude **7a** (18 g, 61% yield) as a colourless transparent liquid. ^{1}H NMR, δ (ppm, CDCl$_3$, 90 MHz): 2.23 (s, 1H), 2.44 (s, 3H), 3.5–3.7 (m, 8H), 4.1–4.2 (m, 2H), 7.33 (d, 2H), 7.80 (d, 2H).

Compound **7b** (93 g, 58% yield): was obtained in the same manner using tetra(ethylene glycol) (450 g, 2.33 mol), pyridine (185 ml, 2.44 mol) and 4-toluenesulfonyl chloride (88 g, 0.46 mol).

2.8. *Synthesis of compounds* **8a** *and* **8b**

A typical procedure is described as follows.

4-Hydroxy-4'-cyanobiphenyl (1.95 g, 10.0 mmol) and **7a** (3.04 g, 10.0 mmol) were dissolved in acetone (400 ml); potassium carbonate (1.40 g, 10.0 mmol) was added, and the mixture heated under reflux for 13 h. After distilling off the solvent chloroform (100 ml) and water (100 ml) were added and the organic layer separated off. This solution was washed with water (100 ml) seven times and dried over sodium sulphate. After removing the solvent, the residue was purified by silica gel column chromatography with chloroform as eluent to afford **8a** (1.83 g, 56.0% yield) as a pale yellow liquid. IR (neat, cm^{-1}): 3447 (broad, –OH), 2924, 2876, 2226 (–CN), 1605 (aromatic C=CH), 1522 (w), 1495, 1456 (w), 1400 (w), 1354 (w), 1292, 1252 (arC–O–Cal st as), 1182, 1123 (CH$_2$–O–CH$_2$ st as), 1063, 928, 824, 664 (w). ^{1}H NMR, δ (ppm, CDCl$_3$, 400 MHz): 2.40 (t, $J = 6.1$ Hz, 1H), 3.62–3.64 (m, 2H), 3.71–3.77 (m, 6H), 3.90 (t, 2H), 4.20 (t, 2H), 7.03 (d, $J = 8.8$ Hz, 2H), 7.53 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 8.6$ Hz, 2H), 7.69 (d, $J = 8.6$ Hz, 2H). EIMS (m/z): 327 (M)$^+$, 222 (M-H(OCH$_2$ CH$_2$)$_2$O)$^+$, 195 (HOC$_{12}$H$_8$CN)$^+$, 133 (H(OCH$_2$ CH$_2$)$_3$)$^+$, 89 (H(OCH$_2$ CH$_2$)$_2$)$^+$, 75 (HOCH$_2$ CH$_2$ OCH$_2$)$^+$, 45 (HOCH$_2$ CH$_2$)$^+$, 31 (HOCH$_2$)$^+$.

Compound **8b** (5.7 g, 76% yield) was obtained in the same manner using 4-hydroxy-4'-cyanobiphenyl (2.8 g, 14 mmol), **7b** (7.4 g, 21 mmol), and potassium carbonate (5.9 g, 43 mmol).

2.9. *Synthesis of acrylate monomers having an oligo(ethylene oxide) spacer (**9a** and **9b**)*

A typical procedure is described as follows.

Under an argon atmosphere, a solution of **8a** (0.915 g, 2.79 mmol) and TEA (1.6 g, 12 mmol) in THF (10 ml) was cooled to 0°C. Acryloyl chloride (0.45 ml, 5.5 mmol) was added and the mixture stirred for 15 h while gradually increasing the temperature from 0°C to ambient. The solvents were removed, diethyl ether and water added, and the organic layer separated off. After removing the solvent, the residue was purified by silica

gel column chromatography with chloroform as eluent to afford **9a** (0.81 g, 76% yield) as a colourless solid. IR (neat, cm^{-1}): 2922, 2876, 2226 (–CN), 1723 (ester C=O), 1638 (w, acryl C=C st), 1605 (ar C–C), 1524 (w), 1495, 1454 (w), 1408, 1354 (w), 1294, 1252 (arC–O–Cal st as), 1196, 1127 (CH$_2$–O–CH$_2$ st as), 1065, 986 (w), 826. ^{1}H NMR, δ (ppm, CDCl$_3$, 400 MHz): 3.68–3.72 (m, 2H), 3.74–3.77 (m, 4H), 3.89 (t, $J = 4.9$ Hz, 2H), 4.19 (t, $J = 4.9$ Hz, 2H), 4.33 (t, $J = 4.9$ Hz, 2H), 5.83 (dd, $J = 1.44, 10.4$ Hz, 1H), 6.15 (dd, $J = 10.4, 17.3$ Hz, 1H), 6.43 (dd, $J = 1.44, 17.3$ Hz, 1H), 7.02 (d, $J = 8.9$ Hz, 2H), 7.53 (d, $J = 8.9$ Hz, 2H), 7.64 (d, $J = 8.6$ Hz, 2H), 7.69 (d, $J = 8.6$ Hz, 2H). EIMS (m/z): 381 (M)$^+$, 309 (CH$_2$=CHOCH$_2$ CH$_2$ OCH$_2$ CH$_2$ OC$_{12}$H$_8$ CN)$^+$, 222 (CH$_2$ CH$_2$ OC$_{12}$H$_8$ CN)$^+$, 195 (HOC$_{12}$H$_8$ CN)$^+$, 99 (CH$_2$=CHCOOCH$_2$ CH$_2$)$^+$, 55 (CH$_2$=CHCO)$^+$, 27 (CH$_2$=CH)$^+$.

Compound **9b** (1.5 g, 86% yield) was obtained in the same manner using **8b** (1.6 g, 3.0 mmol), TEA (1.3 ml, 9.3 mmol) and acryloyl chloride (0.31 ml, 3.9 mmol).

2.10. *Polymerization*

Each monomer and AIBN were mixed in THF in a polymerization tube. The concentration of monomer, $[M]$, was 1.0 mol l^{-1}. The ratio of the initiator to each monomer, $[I][M]^{-1}$, was 0.025. After degassing the mixture, the tube was sealed and heated with stirring at 60°C for 18 h. The reaction mixture was then poured into an excess of methanol to precipitate the polymer product 0°C for **6a**–**6d**, **10a** and **10b**, and at room temperature for **6e** and **6f**. The polymer obtained was dried *in vacuo* at 50°C overnight. If the purification was found to be insufficient when each polymer was checked by GPC, it was dissolved in THF and reprecipitated in an excess of methanol. The molecular weight of each polyacrylate obtained is listed in table 1.

3. Results and discussion

The DSC profiles of the polyacrylate obtained are shown in figure 2. In both heating and cooling scans of

Table 1. The results of polymerizations experiments.

Compound	$M_n \times 10^{-3}$ [a]	$M_w \times 10^{-3}$ [b]	Yield/%
6a	6.20	9.77	77.5
6b	6.06	9.02	83.8
6c	6.26	9.36	77.7
6d	6.29	8.93	79.6
6e	6.34	9.44	83.0
6f	9.53	13.3	87.6
10a	6.79	10.7	79.6
10b	7.47	12.1	70.0

[a] Number-average molecular weight determined by GPC.
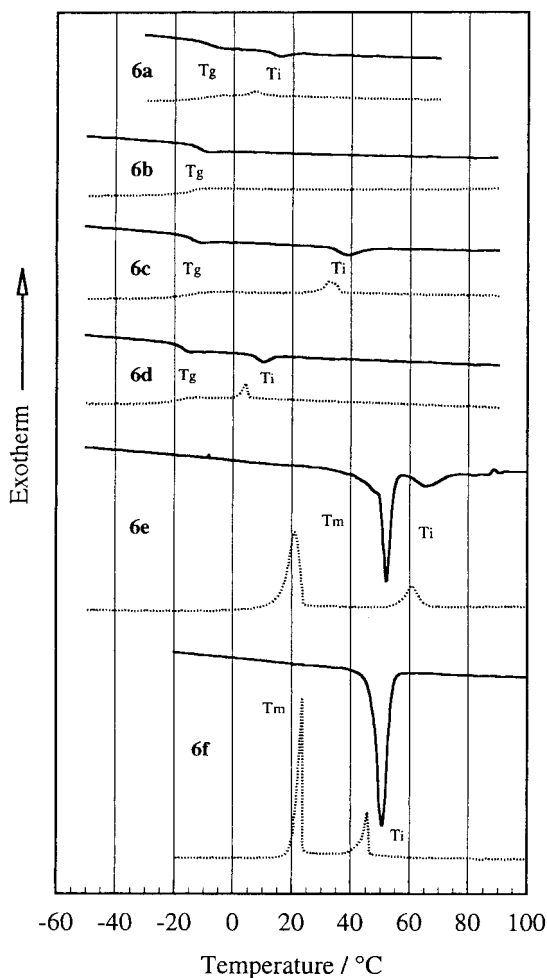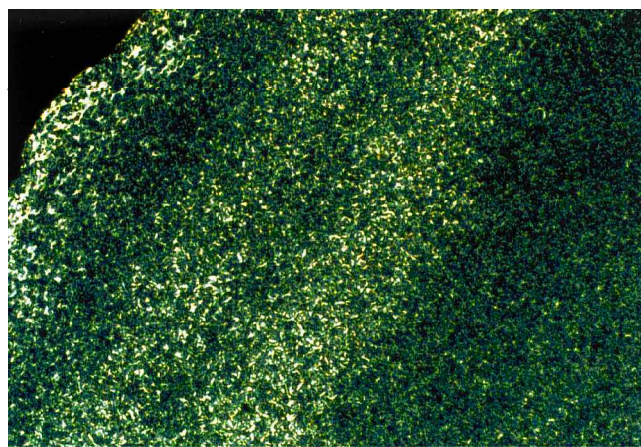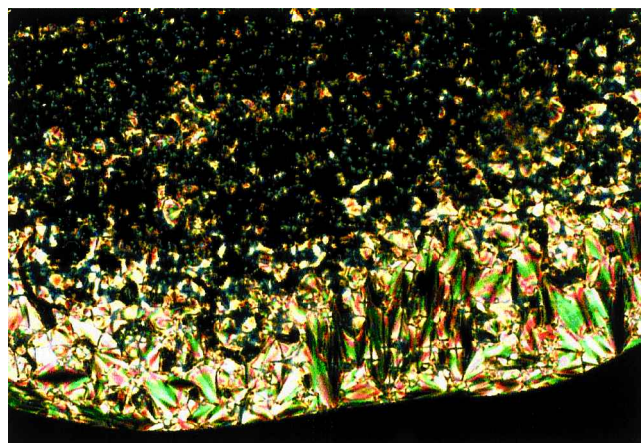[b] Weight-average molecular weight determined by GPC.

Figure 2. DSC curves for the segmented spacer type polyacrylates: solid and broken lines represent the heating and cooling DSC processes, respectively.

Figure 3. Polarizing optical micrographs of the segmented spacer type polyacrylates: (*a*) **6d** at $-0.1°C$, (*b*) **6c** at 33°C, and (*c*) **6e** at 60°C. The black areas in the fan-shaped texture of **6c** and **6e** show partially homeotropic order.

6a, **6c** and **6d**, the glass transition (T_g) and the isotropic point (T_i) clearly appeared. For **6a** and **6d**, a sanded texture was observed in the temperature region below T_i by means of POM, as shown in figure 3(*a*). For **6c**, the typical fan-shaped texture of a smectic A phase was observed as shown in figure 3(*b*). In addition, in XRD measurements, two sharp peaks in a small angle region corresponding to the smectic layer structure were observed after shearing the sample of **6c**, as shown in figure 4(*a*). Such peaks could not be detected without shearing, but a weak and broad halo near $2\theta = 5°$ and a broad halo near 20° could be seen after annealing at room temperature without shearing.
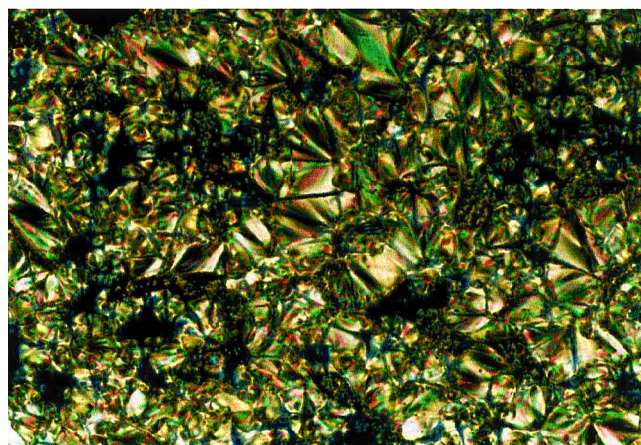
The DSC profiles of **6e** and **6f** (figure 2) suggest that they exhibit an enantiotropic and a monotropic liquid crystalline phase, respectively, and that these polymers exhibit the crystal phase in the lower temperature region. Since typical fan-shaped textures were observed from POM in the temperature region of the liquid crystalline phase, as shown in figure 3(*c*), these polymers should exhibit a smectic A phase. The XRD pattern of figure 4(*b*) at room temperature indicated a crystal phase
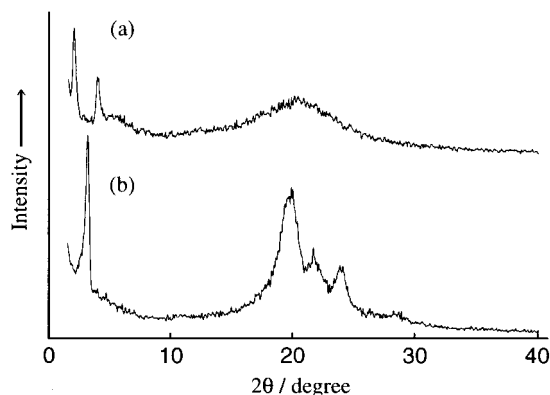
Figure 4. XRD patterns of a shear-aligned sample of **6c** (*a*), and a sample of **6e** without alignment (*b*) at 25°C.

for **6e** corresponding to the DSC results, since some sharp peaks were observed in the wide angle region (near $2\theta = 20°$). In addition, a sharp peak corresponding to a layer structure was also observed in the small angle region. This result shows that the layer structure derived from a smectic phase remains in the crystal phase. The DSC profiles of **6b** in figure 2, and for **10a** and **10b** in figure 5, suggest that these polymers exhibit no mesophases because only the T_g peak was observed.

The thermal properties of the polymers obtained are summarized in table 2. It was found that the glass transition temperature of the segmented spacer type (**6a–6d**) was unexpectedly and extremely low as compared with the reference polymers (**10a, 10b** and **11–13**). Moreover, the T_g of a polymer having the tetra(ethylene oxide) segment in the spacer part was a little lower (or almost same) as for the tri(ethylene oxide) segment, and that the introduction of a tri(ethylene oxide) segment provided the polymer with a more thermally stable LC
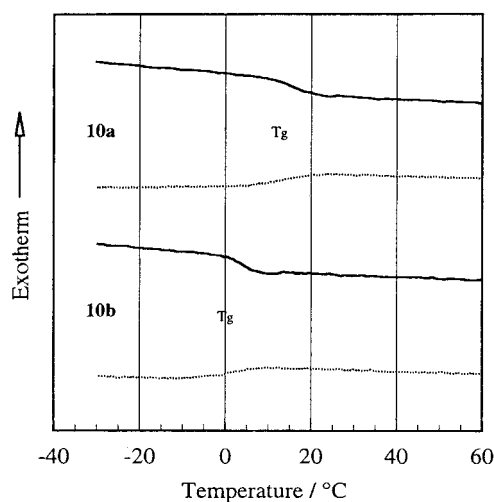
phase than in the case of tetra(ethylene oxide). It was also found that an alkylene segment in the spacer part contributed much to the appearance of a LC phase. That is, the longer alkylene segments stabilized the mesophase better. However, the polymer crystallized in the lower temperature region when the length of the alkylene segment was too large such as in **6e** and **6f**. Consequently, an optimum combination of the oligo-(ethylene oxide) segment and an alkylene segment for a certain mesogenic core is necessary, to give a very low T_g and a mesophase with a wide temperature range for a segmented spacer type SCLCP (such as **6c** in this work).

The *d*-spacings of the shear-aligned **6c** obtained from XRD were 43.7 and 22.5 Å. The sharp peak ($2\theta = 3.92°$) corresponding to 22.5 Å could be regarded as a second order reflection for the sharp peak (2.02°) corresponding to 43.7 Å. A weak and broad halo near $2\theta = 5°$ also showed coexistence of an ambiguous layer structure for a *d*-spacing of about 17 Å. From these results, a layer structure model as illustrated in figure 6 may be proposed. Before shearing, a layer structure is basically a smectic A_t-like formation, and an ordered region consists of a mesogenic core and an alkylene segment, as shown in figure 6 (*a*). However, a boundary between an ordered region and a disordered region is ambiguous, because a part of the alkylene segment is taken into a disordered region consisting of random forms of a polymer backbone and a tri(ethylene oxide) segment. After shearing,

Figure 5. DSC curves for reference polymers having the oligo-(ethylene oxide) spacer: solid and broken lines represent the heating and cooling DSC processes, respectively.
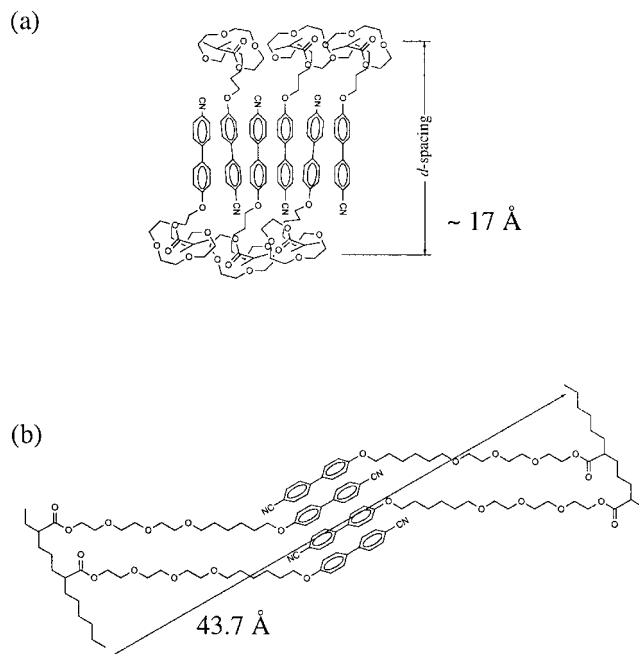

Figure 6. The layer structure model of **6c**: (*a*) the initial state in a smectic phase, (*b*) the shear-aligned region.

Table 2. Thermal properties of the polyacrylates.

Compound	Structure	Phase transition temperature[a] /°C	$\Delta H_{\text{I-S}}$ [b] /J g^{-1}
6a		$g \xrightleftharpoons[-10]{-12} M \xrightleftharpoons[7]{16} I$	− 1.8
6b		$g \xrightleftharpoons[-15]{-15} I$	—
6c		$g \xrightleftharpoons[-16]{-18} SmA \xrightleftharpoons[33]{40} I$	− 4.0
6d		$g \xrightleftharpoons[-19]{-20} M \xrightleftharpoons[4]{10} I$	− 2.5
6e		$Cr \xrightleftharpoons[21]{52} SmA \xrightleftharpoons[61]{65} I$	− 8.7
6f		$Cr \xrightarrow{51} I$; $24 \nearrow SmA \swarrow 46$	− 7.6
10a		$g \xrightleftharpoons[14]{10} I$	—
10b		$g \xrightleftharpoons[1]{1} I$	—
11[c]		g 42 N 229 I	
12[c]		g 32 N_{Re} 80 SmA 124 N 132 I	
13[d]		g 25 SmC 30 SmA 145 I	
14[e]		g − 57 I	

[a] The phase transition temperatures were determined by DSC (scan rate: ± 5°C min^{-1}): g glassy state, SmA smectic A phase, M mesophase, I isotropic liquid, Cr crystal phase, N nematic phase, N_{Re} re-entrant nematic phase, SmC smectic C phase.
[b] The enthalpy change in the phase transition from an isotropic liquid to a LC phase.
[c] Reference [8].
[d] Reference [9].
[e] Reference [10].

a polymer backbone and segmented spacer part could be drawn as extended zigzag chains. When the layer structure is a smectic A_d-like formation, as shown in figure 6(*b*), its layer spacing coincides with the *d*-spacing obtained from XRD measurement. On the other hand, a *d*-spacing of 27.9 Å was evaluated for **6e** from a sharp XRD reflection peak. Supposing 27.9 Å is the value arising from the second order reflection and a smectic A_d-like formation similar to the layer structure of **6c** is considered, the evaluated layer spacing approximates to a length of twice 27.9 Å. The reason why the smectic layer structure of **6e** without shearing is similar to that of **6c** with shearing is not understood at this stage. However, it is possible that **6e**, having a long alkylene chain such as undecamethylene in the segmented spacer, more easily forms a regular layer structure than does **6c**.

In verifying our new concept for SCLCP we found that the segmented spacer type LC polyacrylate unexpectedly showed a very low T_g. Generally speaking, the spacer introduced between a polymer backbone and a mesogenic core decouples its motions specifically, we showed in the present work that the spacer plays a delicate role in this decoupling and in the enhancement of ordering mesogenic groups. A spacer structure consisting of only a flexible chain, such as an oligo(ethylene oxide), is not enough to yield a mesophase (compounds **10a** and **10b**) and gives a T_g similar to ordinary side chain type LC polyacrylates with alkylene spacers (**11**–**13**) [8, 9]. In the case of a relatively small mesogenic core such as the 4′-cyanobiphenyl group, the alkylene segment attached directly to the mesogenic core (so-called 5OCB-like structure as typical LMMLC) would be necessary to generate a LC phase. Additionally the oligo(ethylene oxide) segment introduced between the polymer backbone and alkylene segment mainly decouples their motions. Poly(alkyl acrylates) are well-known to have very low T_g values when the length of the alkyl group is in a certain range. For example, the T_g of a poly(hexyl acrylate) is $-57°$ [10], as shown in table 2 (compound **14**). This is explained by a decrease in the interaction between polymer backbone due to the introduction of an alkyl side chain. In the same way, an oligo(ethylene oxide) segment, in the case of the segmented spacer type SCLCP in this work, would decrease the interaction between polymer backbones or between a polymer backbone and the assembled smectic layer of mesogenic side chains.

In conclusion, our segmented spacers would be useful for realization of SCLCPs having fast response to external stimuli near room temperature, as for display applications. Now, we are preparing a sequel paper in which to discuss the mobility of mesogenic groups in segmented spacer type SCLCPs using dielectric relaxation spectroscopy.

References

[1] Hsu, C.-S., 1997, *Prog. Polym. Sci.*, **22,** 829.

[2] Finkelmann, H., Ringsdorf, H., and Wendorff, J. H., 1978, *Makromol. Chem.*, **179,** 273.

[3] For example, McArdle, C. B. (editor), 1989, *Side Chain Liquid Crystal Polymers* (New York: Chapman & Hall).

[4] Engel, M., Hisgen, B., Keller, R., Kreuder, W., Reck, B., Ringsdorf, H., Schmidt, H. W., and Tschirner, P., 1985, *Pure appl. Chem.*, **57,** 1009.

[5] Akiyama, E., Matsui, N., and Nagase, Y., 1997, *Liq. Cryst.*, **23,** 425.

[6] Akiyama, E., Kawamura, K., Mihara, T., Matsui, N., Nagase, Y., Araki, K., and Koide, N., 1998, *Mol. Cryst. liq. Cryst.*, **318,** 307.

[7] Akiyama, E., Nagase, Y., Matsui, N., and Araki, K., 1998, *J. chem. Soc., Faraday Trans.*, **94,** 1995.

[8] Dubois, J. C., Decobert, G., LeBarny, P., Esselin, S., Friedrich, C., and Nöel, C., 1986, *Mol. Cryst. liq. Cryst.*, **137,** 349.

[9] Kostromin, S. G., Simitsyn, V. V., Talroze, R. V., Shibaev, V. P., and Platé, N. A., 1982, *Makromol. Chem., rapid Commun.*, **3,** 809.

[10] Rehberg, C. E., Faucette, W. A., and Fisher, C. H., 1944, *J. Am. chem. Soc.*, **66,** 1723.