A new synthetic approach to side-chain liquid crystalline polyacrylates containing siloxane spacers and their thermal behaviours

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A new synthetic approach to side-chain liquid crystalline polyacrylates containing siloxane spacers and their thermal behaviours

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The syntheses of novel side-chain liquid crystalline polyacrylates (LCPAs) containing siloxane spacers were carried out according to a convenient route by preparing alcohol compounds having a mesogenic group linked with a siloxane bond as key intermediates of the monomers. A relatively large mesogenic group was necessary to exhibit a mesophase in this system. The introduction of a siloxane spacer lowered the temperature range of mesophase of LCPAs resulting from the decrease of T_g, as compared with the corresponding LCPAs containing an alkylene spacer. It was also revealed that the chemical structure of spacer component played an important role for the assembly structure in the mesophase.

1. Introduction

In the past two decades, various and numerous types of side-chain liquid crystalline polymers (SCLCPs) have been studied for the purpose of many applications for display devices, recording media, switching devices, non-linear optical materials, and so on [1, 2]. To achieve the highly qualitative property in SCLCPs for each application, a suitable arrangement of main chain, side chain, or mesogenic and functional moieties would be a very important subject. For instance, in order to obtain a stable alignment and/or switching, many researchers have been looking for the optimized chemical structure of the backbone, spacer or mesogenic component. In particular, the spacer component, which connects the main chain to the mesogenic group, is thought to play an important role to decouple the motions of polymer backbone from the anisotropical orientations of mesogenic side chains in SCLCPs.

We have proposed SCLCPs containing a siloxane bond in the spacer component, in order to investigate the effect of the siloxane linkage on the thermal property of SCLCPs [3–9]. The introduction of a siloxane bond in the spacer (siloxane spacer) affected the phase transition behaviour and especially decreased the glass transition temperature (T_g) of the obtained polymers. As a result, the mesophase of SCLCPs containing a siloxane spacer appeared at the lower temperature range than that of SCLCPs containing an alkylene spacer with the same backbone components and mesogens [4, 6]. In our

previous studies [3–8], methacrylate-type polymers containing a siloxane spacer have been mainly prepared because of the restrict of a starting material used in the monomer synthesis via mesogenic silanol compounds, 2, as shown in scheme 1. 3-Methacryloxypropyldimethyl-chlorosilane, 3, is commercially available, and easily obtained by hydrosilylation of allyl methacrylate with dimethylchlorosilane in the presence of a platinum catalyst. However, the polymerizable group of such a chlorosilane derivative 3 is hardly changed to, for example, an acrylate moiety, because the hydrosilylation of allyl acrylate with dimethylchlorosilane gives by-products derived from the reaction between acryl and hydrosilyl groups. In addition, the intermediates, such as ethoxysilane derivative 1 and silanol derivative 2, are not generally very stable in the ordinary atmosphere, when they are purified and stored.
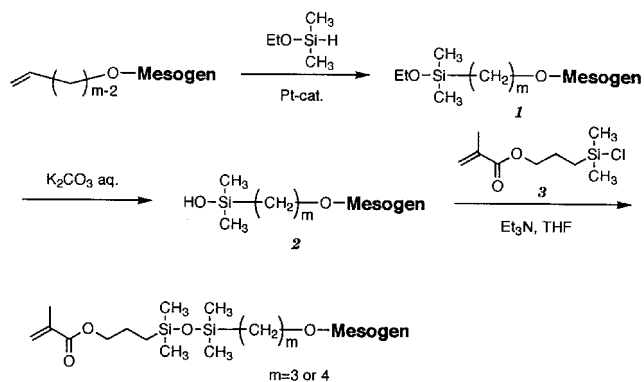
Scheme 1.

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In this paper, the convenient synthetic route of monomers of SCLCPs containing siloxane spacers is presented. The syntheses of novel acrylate-type monomers containing a siloxane spacer, which were hardly obtained by means of the previous synthetic method, were carried out by preparing novel alcohol derivatives as key intermediates, and the monomer was polymerized by the ordinary radical polymerization. Then, the thermal behaviours of the obtained polyacrylates were investigated by means of polarized optical microscopy, differential scanning calorimetry and X-ray diffractometry. In order to reveal the effect of the spacer structure, the thermal behaviours of polyacrylates containing an alkylene chain as the spacer part were also studied. Furthermore, the assembling structure of liquid-crystalline phase will be estimated from the results of X-ray diffractometry and the calculations of molecular models.

2. Experimental
2.1. *Materials*

1,1,3,3-Tetramethyldisiloxane (TMDS, Shin-etsu Chem. Ind.), 1,1,3,3,5,5-hexamethyltrisiloxane (HMDS, Chisso Corp.), diethyl azodicarboxylate (DEAD, Aldrich Chem. Co.), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Aldrich Chem. Co.) and platinum-divinyltetramethyldisiloxane complex in xylene (PDTD, Pt content: 3·0 wt %, Degussa Japan Co.) were commerically available and used as received. Triphenylphosphine (TPP, Kanto Chem. Co.) was recrystallized from ethanol, and acryloyl chloride (Tokyo Kasei Ind.) was distilled under an argon atmosphere before use. Dry tetrahydrofuran (THF) was obtained from distilling twice over calcium hydride and sodium, respectively. N,N-dimethylformamide (DMF) dehydrated for organic syntheses was purchased from Kanto Chem. Co. and used without further purification.

2.2. *Characterizations*

^{1}H NMR was conducted with Hitachi R-90H FT NMR (90 MHz) spectrometer and Bruker AM-400 FT NMR (400 MHz) spectrometer using $CDCl_3$ as the solvent. Infrared (IR) spectra were recorded on a Jasco FT IR-5300 spectrometer. Mass spectrometry was managed with a Hitachi Mass Spectrometer M-80B by the chemical ionization method (CI) using isobutane. Gel-permeation chromatography (GPC) was carried out with a Tosoh HLC-802A instrument using tetrahydrofuran as eluent, equipped with four columns of TSK gels G5000H_6, G4000H_6, G3000H_6 and G2000H_6. Standard polystyrenes were used for calibration.

Differential scanning calorimetry (DSC) was conducted by using a Seiko Electronic DSC-20 with SSC-580 thermal controller. DSC measurements of

P-1–**P-6** were carried out under an argon stream at the scanning rate of $\pm 10°C\,min^{-1}$, and those of **P7** were done at a scanning rate of $\pm 15°C\,min^{-1}$. A Nikon Microphot-UFX polarized optical microscope equipped with a Mettler FP-82 hot stage and a FP-80 central processor was used to observe the thermal transition and analyse the anisotropic texture. X-ray diffraction patterns were recorded on a MAC Science MXP[3] X-ray diffractometer.
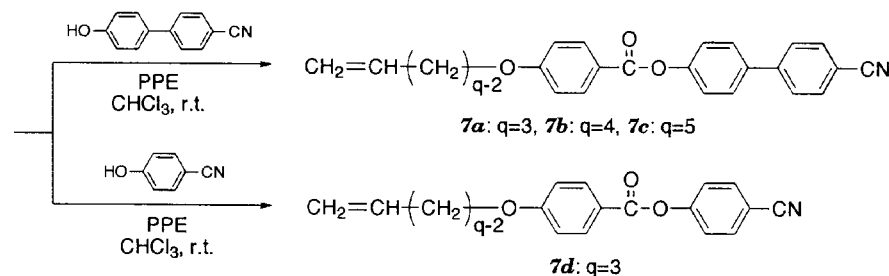
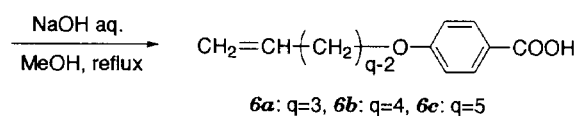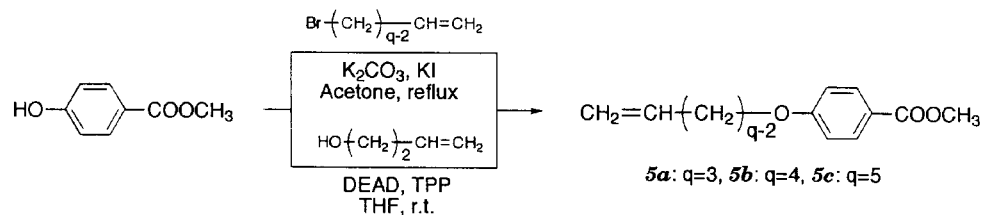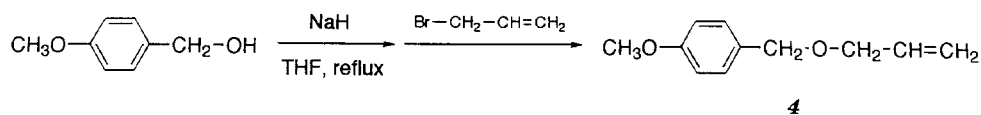### 2.3. *4-Methoxylbenzyl allyl ether (4)*

As shown in scheme 2, 4-methoxybenzyl allyl ether (**4**) was prepared through the reaction of 4-methoxybenzyl alcohol with 3-bromopentene.

Sodium hydride (87·5 mmol) was washed with 100 ml of hexane and dispersed in 100 ml of dry THF under an argon atmosphere. A solution containing 4-methoxybenzyl alcohol (10·0 g; 72·4 mmol) in 10 ml of dry THF was added dropwise to the mixture, and was heated at reflux overnight. A solution of 3-bromopropene (10·0 g; 82·7 mmol) in 20 ml of dry THF was then poured into the solution, and the mixture heated at reflux for 7 h. After the solvent was removed under reduced pressure, the residue was extracted with diethyl ether, and purified by column chromatography on silica gel with diethyl ether/*n*-hexane (1/5 vol.) as eluent to afford 12·9 g of **4** as a transparent colourless liquid. Yield: 100 per cent IR (neat, cm^{-1}): 3115 (w), 2997 (w), 2926, 2900, 2826, 1641 (w), 1608 (aromatic C=C), 1580 (w), 1508, 1460, 1298, 1241, 1169, 1077, 1031, 920, 815. ^{1}H NMR, δ ($CDCl_3$, ppm, 90 MHz): 3·80 (s, 3 H), 4·00 (dt, 2 H, $J = 1·3, 5·5$ Hz), 4·45 (s, 2 H), 5·1–5·4 (m, 2 H), 5·7–6·2 (m, 1 H), 6·87 (d, 2 H, $J = 8·6$ Hz), 7·28 (d, 2 H, $J = 8·6$ Hz).

2.4. *Methyl 4-(alkenyloxy)benzoate (5a–5c)*

These olefin compounds were prepared via a Williamson or Mitsunobu reaction according to the pathways shown in scheme 2. The typical procedures of each reaction to obtain methyl 4-(3-butenyloxy)benzoate, **5b**, are as follows:

Williamson reaction: Methyl 4-hydroxybenzoate (3·95 g; 24·7 mmol) and 4-bromobutene (5·26 g; 37·1 mmol) were dissolved in 50 ml of acetone. Potassium carbonate (3·59 g; 24·7 mmol) and potassium iodide (0·4 g) were then added to the mixture. After heating at reflux overnight, the precipitated salts were removed by filtration. The solvent was removed by distillation, and the residue purified by column chromatography on silica gel with diethyl ether/*n*-hexane (1/8 vol.) as eluent to afford 2·28 g of **5b** as a transparent pale yellow liquid. Yield: 42·6 per cent. *Mitsunobu reaction*: 3-Butenyl-1-ol (2·0 ml; 23 mmol), methyl 4-hydroxybenzoate (4·2 g; 27 mmol) and TPP (7·3 g; 28 mmol) were dissolved with

CH_3O—⟨ ⟩—CH_2-OH $\xrightarrow[\text{THF, reflux}]{\text{NaH}}$ $\xrightarrow{\text{Br—CH}_2\text{—CH=CH}_2}$ CH_3O—⟨ ⟩—CH_2·O-CH_2-CH=CH_2

4

$Br\{CH_2\}_{q-2}CH=CH_2$

HO—⟨ ⟩—$COOCH_3$ —

$\begin{array}{c}\text{K}_2\text{CO}_3\text{, KI}\\ \text{Acetone, reflux}\\ \hline \text{HO}\{CH_2\}_2\text{CH=CH}_2\end{array}$

DEAD, TPP
THF, r.t.

→ CH_2=CH$\{CH_2\}_{q-2}$-O—⟨ ⟩—$COOCH_3$

5a: q=3, *5b*: q=4, *5c*: q=5

$\xrightarrow[\text{MeOH, reflux}]{\text{NaOH aq.}}$ CH_2=CH$\{CH_2\}_{q-2}$-O—⟨ ⟩—COOH

6a: q=3, *6b*: q=4, *6c*: q=5

HO—⟨ ⟩—⟨ ⟩—CN

$\xrightarrow[\text{CHCl}_3\text{, r.t.}]{\text{PPE}}$ CH_2=CH$\{CH_2\}_{q-2}$-O—⟨ ⟩—$\overset{O}{\overset{\|}{C}}$-O—⟨ ⟩—⟨ ⟩—CN

7a: q=3, *7b*: q=4, *7c*: q=5

HO—⟨ ⟩—CN

$\xrightarrow[\text{CHCl}_3\text{, r.t.}]{\text{PPE}}$ CH_2=CH$\{CH_2\}_{q-2}$-O—⟨ ⟩—$\overset{O}{\overset{\|}{C}}$-O—⟨ ⟩—CN

7d: q=3

Scheme 2.

15 ml of dry THF at 0°C. DEAD (4·4 ml; 28 mmol) was then added dropwise to the mixture, and was stirred for 1·5 h at room temperature. The solvent was removed by distillation, and the residue purified by column chromatography on silica gel with diethyl ether/n-hexane (1/10 vol.) as eluent to afford 4·9 g of **5 b** as a transparent colourless liquid. Yield: 100 per cent. IR (neat, cm^{-1}): 3426, 3099, 3000, 2960, 2880, 2575, 2099, 1926, 1724 (C=O), 1680, 1650, 1611 (aromatic C=C), 1582, 1519, 1479, 1441, 1398, 1320, 1288, 1260, 1199, 1179, 1112, 1038, 1000, 926, 854, 788, 701, 674, 638, 520. ^{1}H NMR, δ (CDCl$_3$, ppm, 90 MHz): 2·56 (q, 2 H, $J = 6·6$ Hz), 3·88 (s, 3 H), 4·06 (t, 2 H), 5·1–5·3 (m, 2 H), 5·7–6·1 (m, 1 H), 6·90 (d, 2 H, $J = 8·8$ Hz), 7·98 (d, 2 H, $J = 9·0$ Hz).

In the above Williamson reaction, 3-bromopropene and 5-bromopentene were used instead of 4-bromobutene, to afford **5 a** (yield: 89·4 per cent) and **5 c** (yield: 97·9 per cent), respectively.

2.5. *4-(Alkenyloxy)benzoic acid (6a–6c)*

The hydrolysis of ester compounds **5 a–5 c** with sodium hydroxide was carried out to obtain the acids **6 a–6 c**, as shown in scheme 2. A typical procedure is described as follows: **5 a** (5·62 g; 29·2 mmol) was mixed in 20 ml of methanol. Sodium hydroxide (1·8 g; 44 mmol) and 5 ml of water were added to the mixture at 50°C, and it was heated at reflux for 1·5 h. The mixture was poured into 100 ml of water, and hydrochloric acid added until the mixture became acidic. The precipitated white powder was filtered, and washed with distilled water. After drying the precipitate, 5·17 g of 4-(2-propenyloxy)benzoic acid, **6 a**, was obtained as a white powder. Yield: 99·4 per cent. IR (KBr disk, cm^{-1}): 3450 (b), 2943, 2880, 2676, 2564, 2400–3200 (b), 1680 (vs, C=O), 1607 (aromatic C=C), 1580, 1510, 1462, 1429, 1369, 1319, 1306, 1290, 1252, 1175, 1128, 1107, 1019, 999, 949, 930, 851, 770, 696, 667, 637, 608, 548, 509. ^{1}H

NMR, δ (CDCl$_3$, ppm, 90 MHz): 4·61 (d, 2 H, $J = 5·1$ Hz), 5·2–5·6 (m, 2 H), 5·7–6·3 (m, 1 H), 6·96 (d, 2 H, $J = 8·8$ Hz), 8·06 (d, 2 H, $J = 9·0$ Hz). Yields of **6 b** and **6 c** obtained by the same manner from **5 b** and **5 c** instead of **5 a** were 87·8 and 91·5 per cent, respectively.

2.6. *Benzoate compounds (7 a–7 d)*

As shown in scheme 2, the benzoate compounds **7 a–7 d** were prepared by the esterification of benzoic acid derivatives **6 a–6 c** with 4-cyanophenol or 4-cyano-4′-hydroxybiphenyl in the presence of polyphosphoric ester (PPE), which was prepared according to the literature [10]. A typical procedure is described as follows:

6 a (3·27 g; 18·4 mmol) and 4-cyanophenol (2·40 g; 20·1 mmol) were mixed with PPE (40 g) under an argon atmosphere. 50 ml of chloroform was added to the mixture, and stirred for 18 h at room temperature. The solvent was evaporated under reduced pressure, and the residue was dissolved in a slight amount of acetone. The solution was poured into ice–water, and neutralized with sodium hydrogen carbonate. The obtained insoluble solid was filtered and washed with distilled water. The crude product was purified by recrystallization from ethanol to afford 4·26 g of 4-cyanophenyl 4-(2-propenyloxy)-benzoate, **7 d**, as a white crystal. Yield: 83·1 per cent. IR (KBr disk, cm^{-1}): 2960, 2230 (–CN), 1720 (C=O), 1600 (aromatic C=C), 1580, 1500, 1450, 1420, 1325, 1260, 1200, 1180, 1060, 990, 920, 880, 840, 755. ^{1}H NMR, δ (CDCl$_3$, ppm, 90 MHz): 4·63 (dt, 2 H), 5·36 (dd, 1 H), 5·45 (dd, 1 H), 5·9–6·2 (m, 1 H), 7·01 (d, 2 H), 7·34 (d, 2 H), 7·73 (d, 2 H), 8·13 (d, 2 H).

In the above reaction, 4-cyano-4′-hydroxybiphenyl was used instead of 4-cyanophenol to afford **7 a** (yield: 86·8 per cent), and **6 b** and **6 c** were used instead of **6 a** with 4-cyano-4′-hydroxybiphenyl to afford **7 b** (yield: 79·6 per cent) and **7 c** (yield: 79·5 per cent), respectively.

2.7. *Hydrosilylation (synthesis of 8 a–8 e)*

Compounds **8 a–8 e** were prepared by hydrosilylation of an excess amount of TMDS or HMDS, followed by the second hydrosilylation with compounds **7 a–7 d**, as shown in scheme 3. A typical procedure is described as follows:

4 (1·64 g; 9·28 mmol) and TMDS (32·9 ml; 186 mmol) were mixed under an argon atmosphere at 60°C. 0·12 ml (9·3 mmol) of a 3 per cent xylene solution of PDTD was then added to the mixture, and it was stirred for 1·5 h at 60°C. The solvent was removed by distillation under reduced pressure at 40°C. **7 a** (3·00 g; 8·44 mmol) in 25 ml of dry THF was added to the residue, and the mixture was stirred again for 11 h at 60°C. After the solvent was removed by distillation the residue was purifed by column chromatography on silica gel with

diethyl ether/*n*-hexane (1/5 vol.) as eluent to afford 2·34 g of 1-(4′-cyanobiphenyl-4-yloxycarbonyl-4-phenyl-3-oxypropyl)-3-(4-methoxybenzyl-3-oxypropyl)-1,1,3,3-tetramethyldisiloxane, **8 b**, as a white waxy solid. Yield 41·5 per cent. IR (neat, cm^{-1}): 2960, 2879, 2245 (–CN), 1730 (s, C=O), 1609 (aromatic C=C), 1517, 1499, 1261 (s), 1211, 1175, 1076 (bs, Si–O–Si), 1041, 849, 809, 764, 697 (w), 539 (w). ^{1}H NMR, δ (CDCl$_3$, ppm, 400 MHz): 0·07 (s, 6 H), 0·10 (s, 6 H), 0·53 (m, 2 H), 0·65 (m, 2 H), 1·63 (m, 2 H), 1·84 (m, 2 H), 3·41 (t, 2 H, $J = 7·0$ Hz), 3·79 (s, 3 H), 4·01 (t, 2 H, $J = 6·8$ Hz), 4·44 (s, 2 H), 6·87 (d, 2 H, $J = 8·7$ Hz), 6·98 (d, 2 H, $J = 9·0$ Hz), 7·27 (d, 2 H, $J = 8·7$ Hz), 7·33 (d, 2 H, $J = 8·7$ Hz), 7·64 (d, 2 H, $J = 8·7$ Hz), 7·69 (d, 2 H, $J = 8·6$ Hz), 7·74 (d, 2 H, $J = 8·6$ Hz), 8·15 (d, 2 H, $J = 9·0$ Hz).

In the above reaction, **7 d**, **7 b** and **7 c** were used instead of **7 a** to afford **8 a** (yield: 44·0 per cent), **8 d** (yield: 57·6 per cent) and **8 e** (yield: 58·4 per cent), respectively, and HMDS were used instead of TMDS to afford **8 c** (yield: 40·1 per cent).

2.8. *Oxidative cleavage (synthesis of 9 a–9 e)*

The deprotection reactions of **8 a–8 e** by oxidative cleavage of the benzyl group were carried out to obtain **9 a–9 e**, respectively, as shown in scheme 3. A typical procedure is described as follows:

8 b (2·34 g; 3·50 mmol) was dissolved in 18 ml of dichloromethane and 1 ml of water. DDQ (0·88 g; 3·9 mmol) was added to the mixture and this was stirred for 1 h at room temperature. The insoluble powder precipitated after the mixture changed colour was removed by filtration, and the filtrate concentrated. The residue was purified by column chromatography on silica gel with diethyl ether/*n*-hexane (1/5 vol.) as eluent to afford 1·14 g of 1-(4′-cyanobiphenyl-4-yloxycarbonyl-4-phenyl-3-oxypropyl)-3-(3-hydroxypropyl-1,1,3,3-tetra-methyldisiloxane, **9 b**, as a white waxy solid. Yield: 59·5 per cent. IR (neat, cm^{-1}): 3347 (b, –OH), 2953, 2938, 2876, 2228 (w, –CN), 1728 (s, C=O), 1605 (aromatic C=C), 1578 (w), 1510, 1493 (w), 1395 (w), 1256 (s), 1204 (w), 1167, 1065 (s, Si–O–Si), 1009, 845 (s), 801, 764, 735, 694, 532. ^{1}H NMR, δ (CDCl$_3$, ppm, 400 MHz): 0·09 (s, 6 H), 0·11 (s, 6 H), 0·54 (m, 2 H), 0·67 (m, 2 H), 1·43 (t, 1 H, $J = 5·5$ Hz), 1·60 (m, 2 H), 1·86 (m, 2 H), 3·61 (dd, 2 H, $J = 6·5$, 11·9 Hz), 4·03 (t, 2 H, $J = 6·8$ Hz), 6·99 (d, 2 H, $J = 8·9$ Hz), 7·33 (d, 2 H, $J = 8·7$ Hz), 7·64 (d, 2 H, $J = 8·7$ Hz), 7·69 (d, 2 H, $J = 8·6$ Hz), 7·75 (d, 2 H, $J = 8·6$ Hz), 8·17 (d, 2 H, $J = 8·9$ Hz). MS (CI using isobutane), *m/z*: 590 (M + C$_3$H$_7$)$^+$, 588 (M + C$_3$H$_5$)$^+$, 574 (M + C$_2$H$_3$)$^+$, 472, 446, 432, 414, 372, 352, 337, 311, 269, 237, 195, 166, 133, 117, 101. Elemental analysis: C$_{30}$H$_{37}$NO$_5$Si$_2$ (Mol. wt: 547·80): calculated C, 65·78; H, 6·81; N 2·56 per cent. Found, C 65·90; H 7·05; N 2·46 per cent.
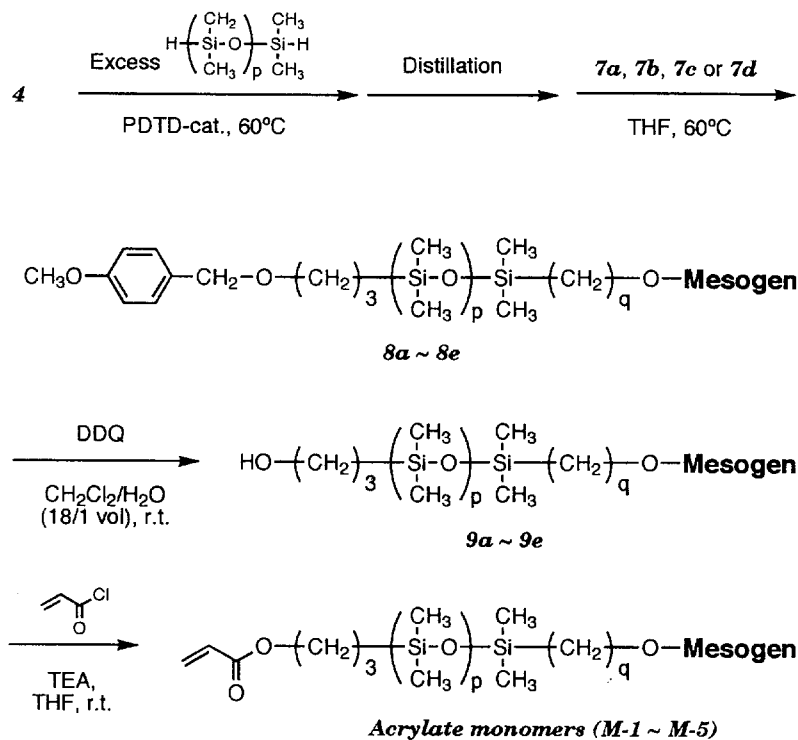
Scheme 3.

Yields of **9 a** and **9 c–9 e** obtained by the same manner by using **8 a** and **8 c–8 e** instead of **8 b** were 64·5, 78·4, 89·5 and 62·1 per cent, respectively.

2.9. *Acrylate monomers having a siloxane spacer (M-1–M-5)*

These monomers were prepared by the condensation of the alcohol derivatives **9 a–9 e** with acryloyl chloride, as shown in scheme 3. A typical procedure is described as follows:

9 b (0·41 g; 0·75 mmol) was dissolved in 10 ml of THF and 1·1 ml of TEA (7·5 mmol) was added to the mixture. Acryloyl chloride (0·31 ml; 3·7 mmol) was then added to the mixture at 0°C, and this was stirred overnight. After the solvents were removed under reduced pressure, the residue was extracted with ethyl acetate, and purified by column chromatography on silica gel with chloroform as eluent to afford 0·37 g of **M-2** as a pale yellow viscous liquid. Yield: 82·0 per cent. IR (neat, cm^{-1}): 2953, 2880, 2228 (w, –CN), 1728 (s, ester C=O), 1636 (w), 1605 (m, aromatic C=C), 1582 (w), 1510 (w), 1408 (m), 1256 (s), 1200 (m), 1167, 1067 (bs, Si–O–Si), 845 (s), 801, 764, 693, 532 (m). ^{1}H NMR, δ (CDCl$_3$, ppm, 400 MHz): 0·09 (s, 6 H), 0·11 (s, 6 H), 0·56 (m, 2 H), 0·66 (m, 2 H), 1·70 (m, 2 H), 1·85 (m, 2 H), 4·02 (t, 2 H, $J = 6·8$ Hz), 4·12 (t, 2 H, $J = 7·0$ Hz), 5·82 (dd, 1 H, $J = 1·5$, 10·4 Hz), 6·13 (dd, 1 H, $J = 10·4$, 17·3 Hz), 6·41 (dd, 1 H, $J = 1·5$, 17·3 Hz), 6·99 (d, 2 H, $J = 9·0$ Hz), 7·34 (d, 2 H, $J = 8·7$ Hz), 7·64 (d, 2 H, $J = 8·7$ Hz), 7·69 (d, 2 H, $J = 8·6$ Hz), 7·75 (d, 2 H, $J = 8·6$ Hz), 8·16 (d, 2 H, $J =$

9·0 Hz). MS (CI using isobutane), m/z: 658 $(M + C_4H_9)^+$, 644 $(M + C_3H_7)^+$, 642 $(M + C_3H_5)^+$, 630 $(M + C_2H_5)^+$, 502 $(M\text{-}CH_2\text{=}CHCOO_2H_4)^+$, 488 $(M\text{-}CH_2\text{=}CHCOOC_3H_6)^+$, 446, 432, 414 $(M\text{-}CH_2\text{=}CHCOOC_3H_6Si(CH_3)_2O)^+$, 407 $(M\text{-}OC_{12}H_8CN)^+$, 328, 316, 300, 236, 221, 203, 195, 171, 166, 133, 121. Elemental analysis: $C_{33}H_{39}NO_6Si_2$ (Mol. wt: 601·85), Calculated, C 65·86; H 6·53; N 2·33 per cent. Found, C 65·62; H 6·66; N 2·16 per cent.

Yields of **M-1** and **M-3**–**M-5** obtained by the same manner from **9 a** and **9 c**–**9 e** instead of **9 b** were 52·8, 35·1, 88·4 and 83·9 per cent, respectively.

2.10. *4-(Acryloyl-11-oxyundecyloxy)benzoic acid (12, see scheme 4)*

Methyl 4-hydroxybenzoate (11·0 g; 72·5 mmol), 11-bromoundecan-1-ol (20·0 g; 79·6 mmol) and potassium carbonate (10·0 g; 72·4 mmol) were dissolved in 100 ml of 2-butanone, and the mixture was heated at reflux for 48 h. The solution was cooled to room temperature to precipitate a white solid. The product was filtered and washed with *n*-hexane and water to afford 20·2 g of methyl 4-(11-hydroxyundecyloxy)benzoate (**10**) as a white solid. Yield: 86·7 per cent.

The obtained **10** (20·2 g; 65·6 mmol) was dissolved in a mixture of 50 ml of methanol and 50 ml acetone. To this solution, a solution of sodium hydroxide (14·0 g; 350 mmol) in 100 ml of water was added, and the mixture heated at reflux for 2 h. After the solvent was removed by distillation, the residue was dissolved in water and hydrochloric acid added until the solution became acidic whereupon a white precipitate formed. The product was filtered and washed with water to afford 19·1 g of **11** as a white solid. Yield: 98·5 per cent.

11 (4·8 g; 16 mmol), acrylic acid (50 ml), 1,4-hydroquinone and 4-toluenesulphonic acid (0·1 g) were dissolved in 100 ml of chloroform. The mixture was heated at reflux overnight with an azeotrope trap to remove the water produced. The reaction mixture was poured into 2 l of ice–water, to form a white precipitate. After the product was filtered and washed with water, it was purified by column chromatography on silica gel with chloroform/ethyl acetate (10/1 vol.) as eluent to afford 3·4 g of **12** as a white powder. Yield: 60 per cent. IR (KBr disk, cm^{-1}): 3065 (b, –OH), 2934, 2853, 2666 (b), 2562 (b), 1721 (s, ester C=O), 1680 (vs, acid C=O), 1638 (w), 1605 (s, aromatic C=C), 1578 (m), 1516 (m), 1472 (m), 1433, 1406, 1292 (s), 1264 (s), 1208 (s), 1171 (s), 1036 (m), 1013 (m), 988 (m), 960 (m), 857 (m), 646 (m). ^{1}H NMR, δ (CDCl$_3$, ppm, 90 MHz): 1·2–2·0 (m, 18 H), 4·02 (t, 2 H), 4·15 (t, 2 H), 5·8–6·4 (m, 3 H), 6·92 (d, 2 H, $J = 9·0$ Hz), 8·04 (d, 2 H, $J = 9·0$ Hz).
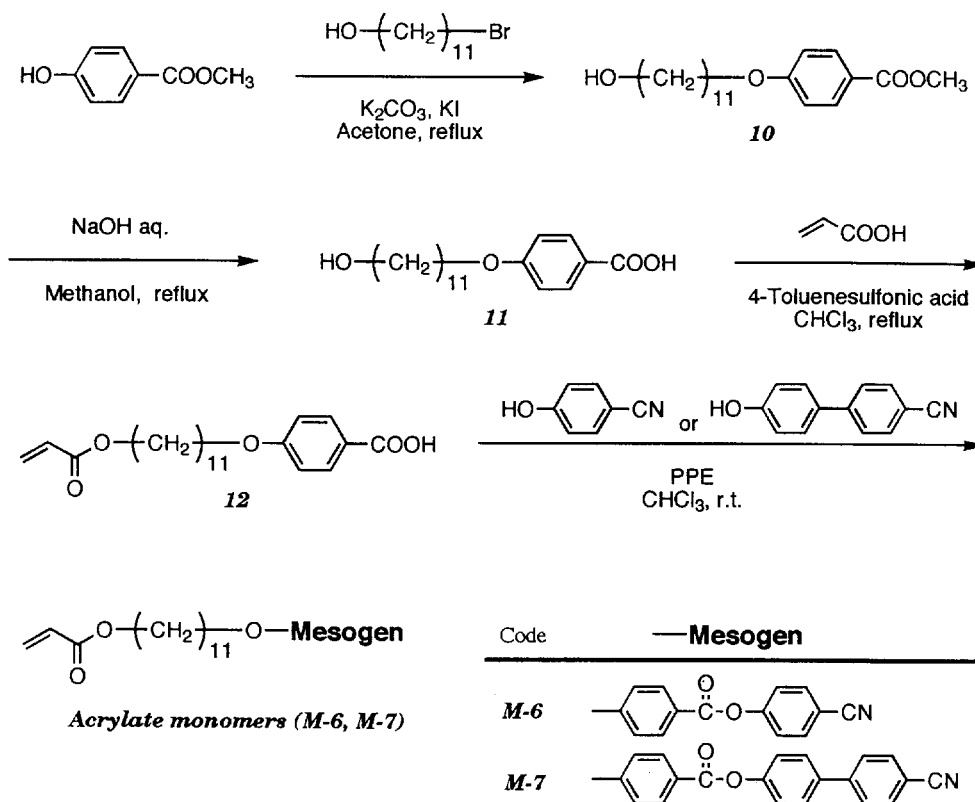
Scheme 4.

2.11. *Acrylate monomers having an alkylene spacer (M-6–M-7)*

The monomers were prepared by the esterification of the benzoic acid derivative **12** with 4-cyanophenol or 4-cyano-4′-hydroxybiphenyl in the presence of PPE, as shown in scheme 4. A typical procedure is described as follows:

12 (1·00 g; 2·76 mmol) and 4-cyanophenol (0·33 g; 2·8 mmol) were mixed with 5·9 g of PPE under an argon atmosphere. 20 ml of chloroform was added to the mixture, and this was stirred for 23 h at room temperature. The solvent was removed by distillation under reduced pressure, and the residue dissolved in a small amount of acetone. The solution was poured into 500 ml of ice–water, and sodium hydrocarbonate added until the solution became neutral. The insoluble solid formed was filtered and washed with distilled water. After drying *in vacuo*, the crude product was purified by column chromatography on silica gel with chloroform as eluent to afford 0·99 g of **M-6** as a white solid. Yield: 78 per cent. IR (KBr disk, cm^{-1}): 2924, 2853, 2228 (–CN), 1740 (vs, C=O), 1723, 1630 (w), 1603 (s, aromatic C=C), 1510, 1476, 1406, 1254 (s), 1200 (s), 1169 (s), 1059 (s), 993, 550. ^{1}H NMR, δ (CDCl$_3$, ppm, 400 MHz): 1·35 (m, 12 H), 1·48 (m, 2 H), 1·67 (m, 2 H), 1·83 (m, 2 H), 4·05 (t, 2 H, $J = 6·5$ Hz), 4·15 (t, 2 H, $J = 6·8$ Hz), 5·82 (dd, 1 H, $J = 1·5$, 10·4 Hz), 6·13 (dd, 1 H, $J = 10·4$, 17·3 Hz), 6·40 (dd, 1 H, $J = 1·5$ Hz, 17·3 Hz), 6·99 (d, 2 H, $J = 9·0$ Hz), 7·36 (d, 2 H, $J = 8·8$ Hz), 7·74 (d, 2 H, $J = 8·8$ Hz), 8·13 (d, 2 H, $J = 9·0$ Hz). Elemental analysis: C$_{28}$H$_{33}$NO$_5$ (463·57): calculated, C 72·55 H 7·18 N 3·02 per cent. Found, C 72·52 H 7·29 N 3·02 per cent.

In the above reaction, 4-cyano-4′-hydroxybiphenyl was used instead of 4-cyanophenol to afford **M-7** (yield: 71 per cent).

2.12. *Polymerizations (see scheme 5)*

Each monomer and AIBN were mixed in dry THF (for **M-1–M-3**) or DMF (for **M-4–M-7**) in a polymerization tube. The concentration of monomer, [M], was 1·0 mol l^{-1} for **M-1–M-5**, or 0·5 mol l^{-1} for **M-6** and **M-7**. The molar ratio of the initiator against 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 2-propanol to precipitate the polymer. The polymer obtained was reprecipitated from its THF solution into excess 2-propanol (for **P-1–P-5**) or diethyl ether (for **P-6, P-7**), and dried *in vacuo* for 24 h at 50°C. If the purification was not sufficient when each polymer was checked by GPC, the polymer was reprecipitated again by the same manner as mentioned above.
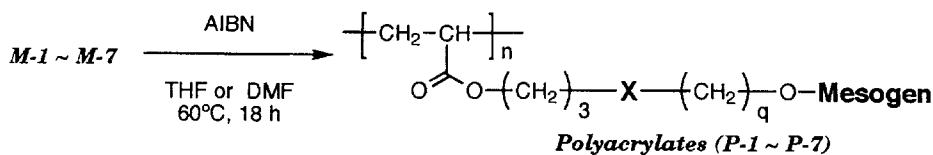
3. Results and discussion

3.1. *Synthesis of monomers*

The outline of the synthetic route of the monomers is indicated in figure 1. Both a protective group and a mesogenic group were introduced into α,ω-dihydro-oligo(dimethylsiloxane) by hydrosilylation in the presence of a platinum catalyst. The alcohol derivative containing a mesogenic group connected via a siloxane spacer was then prepared by the cleavage of the protective group. 4-Methoxybenzyl was selected as the protective group, because the deprotection step could be achieved by the oxidative cleavage in the neutral condition and the cleavage of the siloxane bond was suppressed. The alcohol derivative thus obtained can act as a key intermediate in the preparation of siloxane spacer monomers including various types of polymerizable groups, or to introduce a functional group into such siloxane compounds. In the present work, the acrylate monomers containing siloxane spacers were prepared by a condensation reaction of the alcohol derivatives with acryloyl chloride.

The olefin derivatives **5 a** and **5 c** were prepared in high yield by the Williamson etherification reaction between methyl 4-hydroxybenzoate and ω-bromoalkene in the presence of potassium carbonate base. **5 b** was obtained in a low yield by the Williamson reaction, however, the Mitsunobu reaction [11] of methyl 4-hydroxybenzoate with 2-penten-1-ol in the presence of diethyl azodicarboxylate (DEAD) and triphenylphospine (TPP) was conducted to furnish a quantitative yield of **5 b**. The compounds **5 a–5 c** thus obtained were converted to the benzoic acid derivatives **6 a–6 c** by the action of sodium hydroxide, followed by the eserification of **6 a–6 c** with 4-cyanophenol or 4-cyano-4′-hydroxy-biphenyl to afford the mesogenic olefin compounds **7 a–7 d**.

The acrylate monomers with siloxane spacers (**M-1–M-5**), were prepared according to scheme 3. Firstly, the hydrosilylation of **4** and **7 a–7 d** with TMDS or HMTS was conducted in the presence of a platinum catalyst to afford **8 a–8 e**. The first reaction between **4** and excess TMDS or HMTS was completed within 1·5 h, which was confirmed by monitoring the residual amount of **4** by thin layer chromatography. After the excess amount of TMDS or HMTS was recovered by distillation under reduced pressure, the second hydrosilylation was continued by adding a tetrahydrofuran solution of **7 a–7 d** into the residue. The main products were purified by a silica-gel chromatography to afford the compounds **8 a–8 e** (40–60 per cent yield). The starting compounds (**4** and **7 a–7 d**) were not found and the by-products could not be identified. The key intermediates, **9 a–9 e**, were then obtained by the oxidative cleavage of **8 a–8 e** according to the literature [12–14],

M-1 ~ M-7 $\xrightarrow[\text{THF or DMF} \atop 60^\circ C, 18 h]{\text{AIBN}}$ $\left[CH_2-CH \right]_n$
$O=C-O-(CH_2)_3-X-(CH_2)_q-O-$**Mesogen**

Polyacrylates (P-1 ~ P-7)

Code	—X—	q	—Mesogen
P-1	—Si-O-Si— (CH$_3$)$_2$ each	3	—⟨◯⟩—C(=O)—O—⟨◯⟩—CN
P-2	—Si-O-Si— (CH$_3$)$_2$ each	3	—⟨◯⟩—C(=O)—O—⟨◯⟩—⟨◯⟩—CN
P-3	—Si-O-Si-O-Si— (CH$_3$)$_3$ each	3	—⟨◯⟩—C(=O)—O—⟨◯⟩—⟨◯⟩—CN
P-4	—Si-O-Si— (CH$_3$)$_2$ each	4	—⟨◯⟩—C(=O)—O—⟨◯⟩—⟨◯⟩—CN
P-5	—Si-O-Si— (CH$_3$)$_2$ each	5	—⟨◯⟩—C(=O)—O—⟨◯⟩—⟨◯⟩—CN
P-6	——	8	—⟨◯⟩—C(=O)—O—⟨◯⟩—CN
P-7	——	8	—⟨◯⟩—C(=O)—O—⟨◯⟩—⟨◯⟩—CN

Scheme 5.

Figure 1. Synthetic pathway to the acrylate monomers containing a siloxane spacer.

and the acrylate monomers, **M-1–M-5**, were prepared by the esterification of **9 a–9 e** with acryloyl chloride. The acrylate monomers, **M-6** and **M-7**, which possess a methylene linked spacer, instead of the siloxane spacer of **M-1–M-5**, were prepared as a comparison to reveal the effect of the spacer structure on the thermal properties of the polymers.

3.2. *Polymerization*

The polyacrylates, **P-1–P-7**, prepared from the monomers by ordinary radical polymerization with 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The polymerizations of the monomers **M-1–M-7** were initially performed in THF, however, **M-4** and **M-5** were not polymerized (most of the starting monomers were recovered), and a small amount of oligomers were obtained from the reactions of **M-6** and **M-7**. Therefore, in the polymerizations of **M-4–M-7**, DMF was used for the solvent instead of THF, where the polymerizations proceeded successfully to furnish the high molecular weight polymers in good yields. The polymerization conditions, the molecular weights and the results of elemental analyses of the polymers are summarized in table 1. **M-6** and **M-7** were polymerized in a half
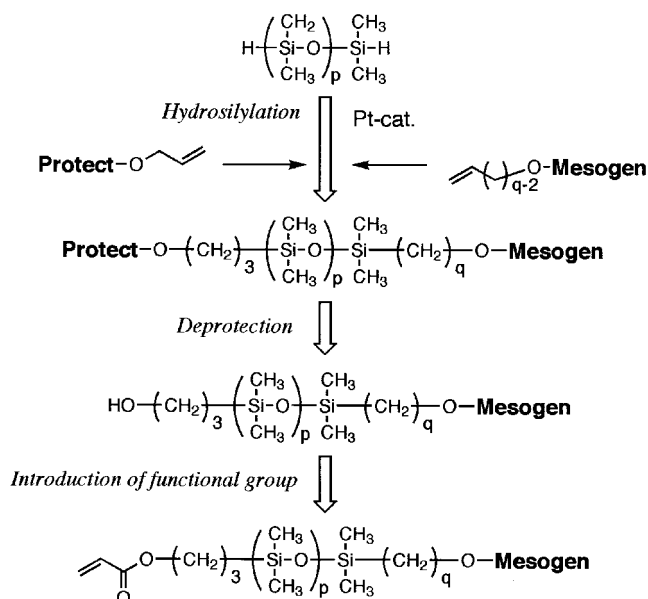
Table 1. The conditions and results of the polymerizations.

Code	Solvent	$[M]^a$/mol l^{-1}	$\bar{M}_n \times 10^{-4\,b}$	$\bar{M}_w \times 10^{-4\,c}$	Calcd.: C	H	N	Found: C	H	N
					Elemental analysis/per cent					
P-1	THF	1·0	1·9	3·8	61·68	6·71	2·66	61·41	6·81	2·42
P-2	THF	1·0	1·9	2·6	65·86	6·53	2·33	65·85	6·65	2·31
P-3	THF	1·0	1·3	1·7	62·19	6·71	2·07	62·27	6·81	1·92
P-4	DMF	1·0	3·1	6·4	66·31	6·71	2·27	66·11	6·80	2·21
P-5	DMF	1·0	3·6	6·5	66·74	6·88	2·22	66·46	7·13	2·11
P-6	DMF	0·5	2·8	4·6	72·55	7·18	3·02	72·29	7·40	2·88
P-7	DMF	0·5	1·4	1·7	75·67	6·91	2·60	75·63	6·98	2·51

[a] Concentrations of each monomer in the polymerization.
[b] Number-average molecular weight determined by GPC.
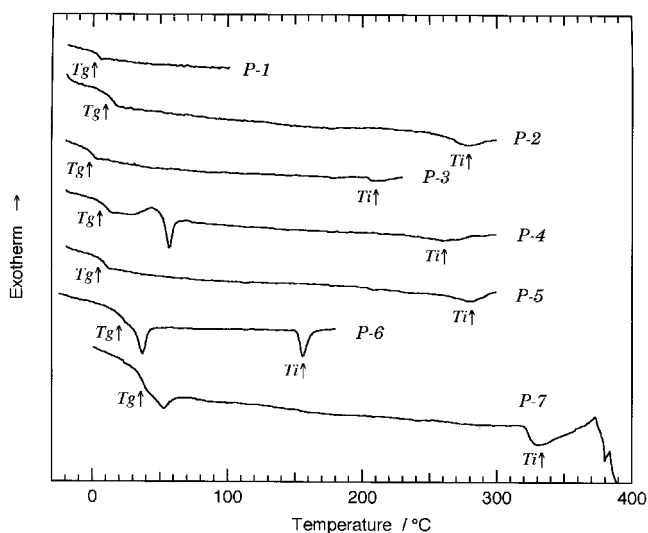[c] Weight-average molecular weight determined by GPC.

Figure 2. DSC thermograms of **P-1**–**P-7** on heating under an Ar stream.

concentration compared to the other homologues, because of the relatively poor solubility of these monomers. The molecular weights of the polymers were greater than ten thousand. In addition, the observed elemental contents of the polymers were in good agreement with the theoretical values.

3.3. *Thermal behaviours of the polymers*

Typical DSC thermograms of all the polymers on the 2nd heating scan are shown in figure 2. In the DSC curve of **P-1**, only the glass transition (T_g) was observed at 2°C, but no other endothermic nor exothermic peaks appeared. In addition, the phase in the temperature range above the T_g was confirmed as an isotropic phase by polarized optical microscopy. Therefore, it was found that a mesogenic rigid core of two phenylene rings such as phenyl benzoate was too small to stabilize a mesophase in this system, because the bulky siloxane

moiety would prevent the liquid crystalline order of the mesogenic side chains [4].

On the contrary, mesophases were observed above T_g in the cases of **P-2**, **P-4** and **P-5**, which possess the disiloxane group in the spacer and the biphenyl benzoate group (three phenylene rings) as the mesogen. The T_gs of **P-2**, **P-4** and **P-5** were observed at 5–10°C, and became slightly lower with increasing length of the alkylene side chain. Furthermore, the introduction of the trisiloxane group in the spacer brought about the greatest decrease of T_g, which was observed at −2°C (**P-3**). **P-2** and **P-5** were found to exhibit a smectic phase by polarized optical microscopy, where the typical fan-shaped texture of a smectic A phase was observed, as shown in figure 3 (*a*). **P-3** also exhibited a smectic A phase, since its optical texture was similar to that of **P-2** and **P-5** in the high temperature region. In the low temperature region below about 150°C, a striated fan-shaped texture of **P-3** was observed as shown in figure 3 (*b*), but the corresponding distinct phase transition peak was not detected in the DSC curves on both heating and cooling. **P-4** also showed a smectic A phase, the optical texture of which was very similar to the pattern of figure 3 (*a*), however, the exothermal peak owing to its crystallization and the endothermal peak of melting were observed at 30–70°C. In the polarized optical microscopy of **P-4**, the fan-shaped texture remained over 1 week when it was cooled from the isotropic phase to room temperature, whereas, on heating, the texture was broken at about 50°C and the typical fan-shaped texture appeared again above about 60°C. This behaviour is in agreement with the result of the DSC study of **P-4**, which indicated that the crystallization and melting processes appeared only in the heating scan.

The polymers **P-6** and **P-7**, with undecamethylene spacers, showed two distinct mesophases according to their DSC curves as shown in figure 2. The T_gs of **P-6**
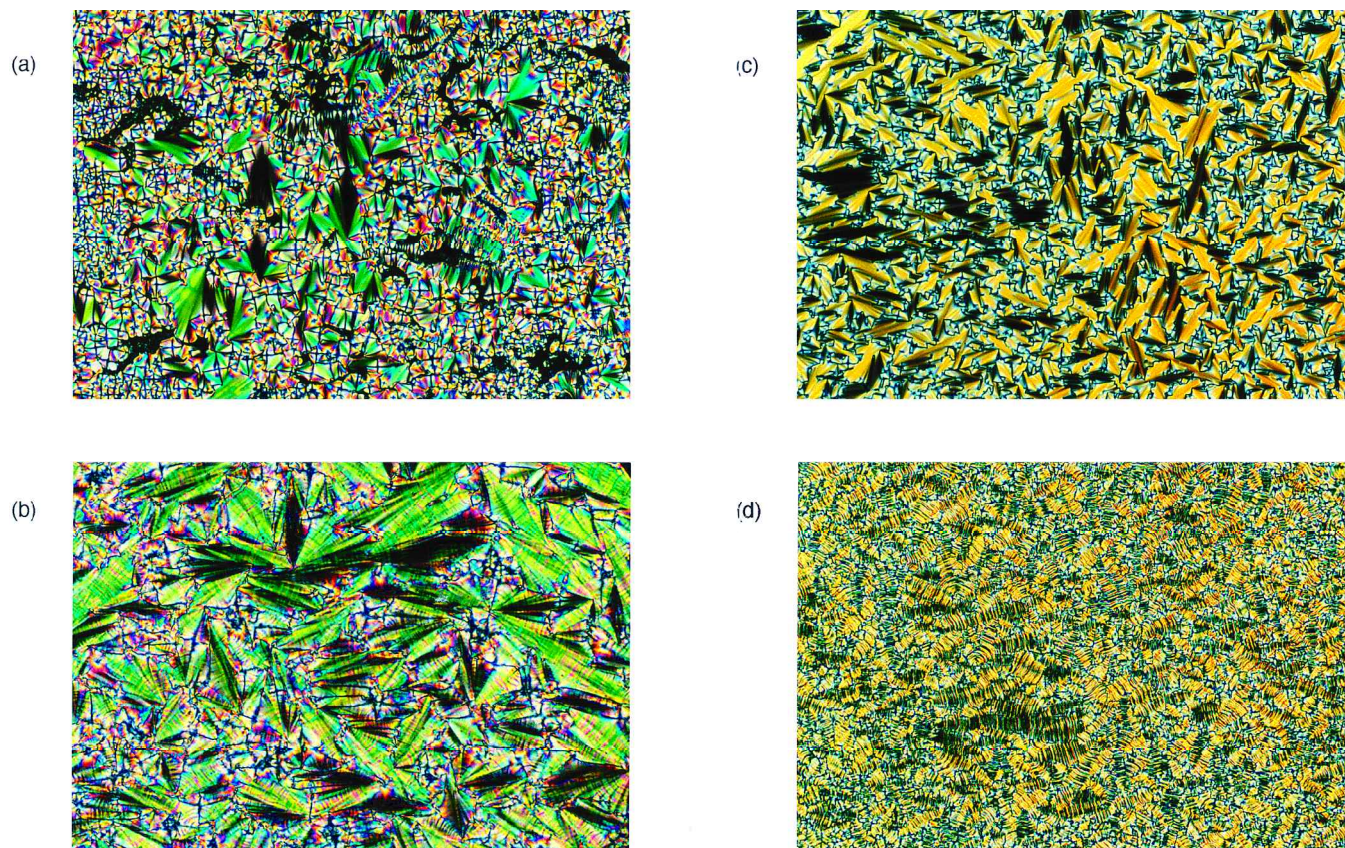
Figure 3.   Typical polarized optical micrographs of the LCPAs. (*a*) Fan-shaped texture of **P-2** at 220°C. (*b*) Striated fan-shaped texture of **P-3** at 120°C. (*c*) Broken fan-shaped texture of **P-6** at 145°C. (*d*) Banded texture of **P-6** at room temperature.
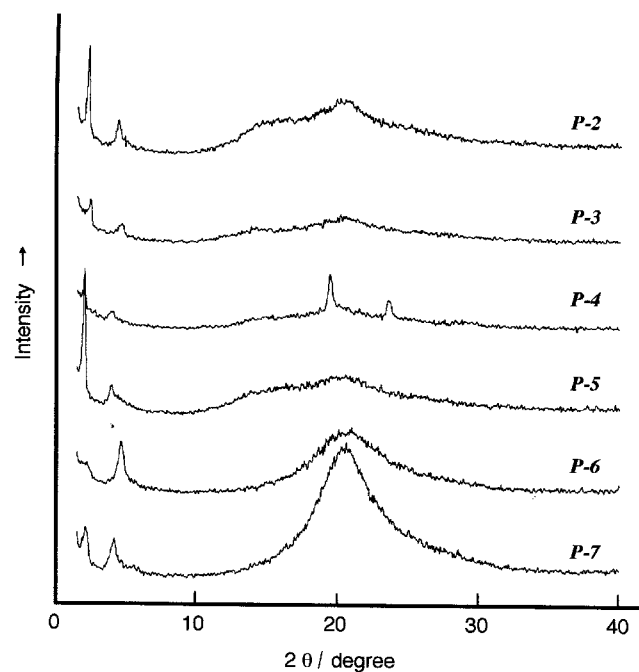

Figure 4.   X-ray powder diffraction diagrams of the LCPAs (**P-2**–**P-7**) at room temperature.

and **P-7** were observed at 20°C and 35°C, respectively. A typical broken fan-shaped texture of a smectic C phase was observed in the high temperature range (and below the isotropization temperature (T_i)) of **P-6** as shown in figure 3 (*c*). The optical texture showed a rapid and reversible change above and below the transition at about 40°C, where the banded texture (see figure 3 (*d*)) was observed at the phase transition point. In the case of **P-7**, however, the mesophases could not be identified because of the obscure optical texture although birefringence and fluidity was observed.

The thermal behaviours of the obtained polyacrylates are summarized in table 2. These polyacrylates containing a siloxane spacer with a 4′-cyanobiphenyl-4-yl benzoate mesogen, **P-2**–**P-5**, showed smectic mesophases with a wide range of phase stability. The introduction of the siloxane spacer was effective in decreasing the T_g of the polymers, in comparison with the methylene-linked polymers with the same backbone component and mesogens (**P-6** and **P-7**). Furthermore, in some cases, it is possible that the flexible siloxane spacer might enhance the anisotropic orientation of the mesogenic side chain, since crystallization of the polyacrylate was observed in a certain structure of the side chain (**P-4**).
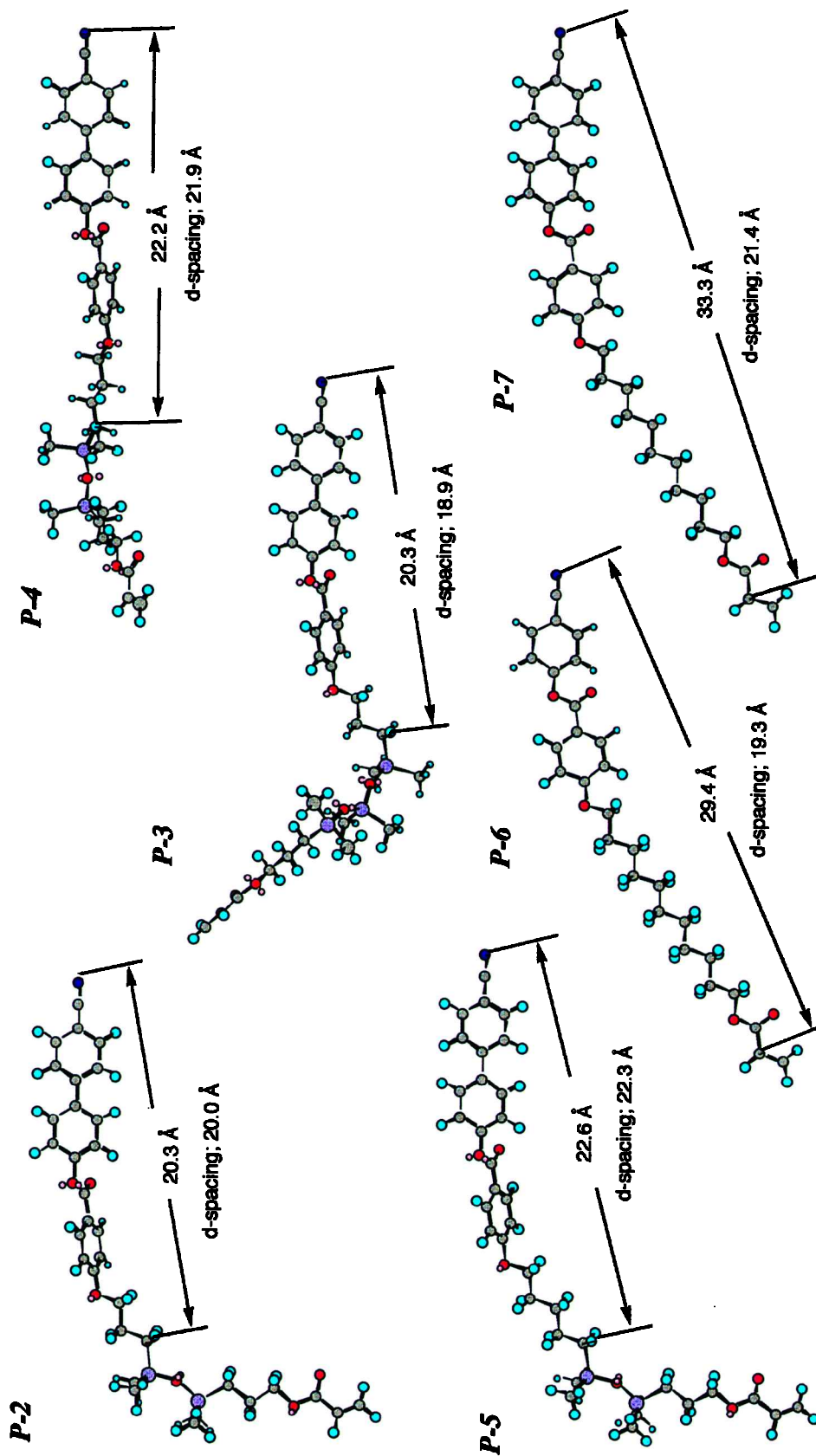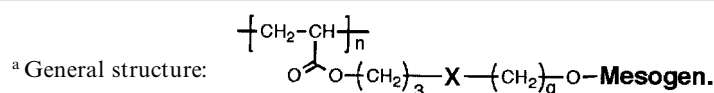
Figure 5. Molecular models of the monomer units of **P-2–P-7**, optimized by the MM2 forcefield method.

Table 2. Thermal behaviours of the polymers.

Code	$-X-$[a]	q[a]	$-$Mesogen[a]	Phase transition behaviour[b]/°C
P-1	Si-O-Si (CH₃ groups)	3	(mesogen structure)	Glassy 2 Isotropic
P-2	Si-O-Si (CH₃ groups)	3	(mesogen structure)	Glassy 10 Smectic A 278 Isotropic
P-3	Si-O-Si-O-Si (CH₃ groups)	3	(mesogen structure)	Glassy -2 Smectic C (*ca.* 150)[c] Smectic A 210 Isotropic
P-4	Si-O-Si (CH₃ groups)	4	(mesogen structure)	Glassy 8 (44 Cr)[d] 57 Smectic A 260 Isotropic
P-5	Si-O-Si (CH₃ groups)	5	(mesogen structure)	Glassy 5 Smectic A 281 Isotropic
P-6	—	8	(mesogen structure)	Glassy 20 Smectic X₁[e] 37 Smectic C 156 Isotropic
P-7	—	8	(mesogen structure)	Glassy 35 Smectic X₂[e] 53 Smectic X₃[f] 331 Isotropic (373 decomp.)[g]

[a] General structure:

$$+CH_2-CH+_n \quad O=C-O-(CH_2)_3-X-(CH_2)_q-O-\textbf{Mesogen.}$$

[b] Phase transition temperatures were determined by DSC on the 2nd heating scan ($10°C\,min^{-1}$) under an Ar stream except for **P-7**.
[c] This peak was not detected by means of DSC.
[d] Recrystallization.
[e] Smectic X_1, X_2 were not identified, but are highly ordered smectic phases.
[f] Smectic X_3 was not identified, but may be a smectic C phase.
[g] Phase transition temperatures of **P-7** were determined from the 1st heating scan ($15°C\,min^{-1}$) of the DSC because of the decomposition above the isotropic temperature.

However, from another point of view, the disiloxane or trisiloxane unit in the spacer would be regarded as a bulky moiety, and prevent the anisotropical ordering of the side chain. Therefore, a sufficiently effective mesogenic moiety such as 4′-cyanobiphenyl-4-yl benzoate group was necessary to stabilize the mesophase, whereas the polymer **P-1** with a relatively compact mesogen (such as 4-cyanophenyl benzoate) was not liquid cystalline. A series of polymethacrylates indicated the similar tendency for the effect of the siloxane spacer [3–7], however, the T_gs of polyacrylates in this study were lower than the polymethacrylates with the same side chain structure.

3.4. *X-ray diffractometry*

The assembly structures of the liquid crystalline polymers were investigated by means of powder X-ray diffraction at room temperature. The X-ray diffraction diagrams of **P-2–P-7** are shown in figure 4. In the case of **P-2**, two sharp peaks and two broad reflections were observed in the small and wide angle regions, respectively, where two sharp peaks ($2\theta = 2\cdot28$, $4\cdot42$) corresponded to the layer spacing ($d = 38\cdot7$ Å, $20\cdot0$ Å) of a smectic phase. To compare the observed layer spacing with the calculated side chain length, molecular models of the monomer units of **P-2–P-7** were minimized on the basis of the MM2 forcefield method [15–17] using CS Chem3D Pro™, version $3\cdot2$ (produced by Cambridge Soft Corporation, Inc.) as a software. The optimized molecular models of the monomer units of **P-2–P-7** are shown in figure 5. The shapes of the molecular models of **P-2**, **P-3** and **P-5** are similarly bent in the vicinity of the siloxane spacer, whereas those of **P-4**, **P-6** and **P-7** are almost linear. The layer spacing of the smectic phase
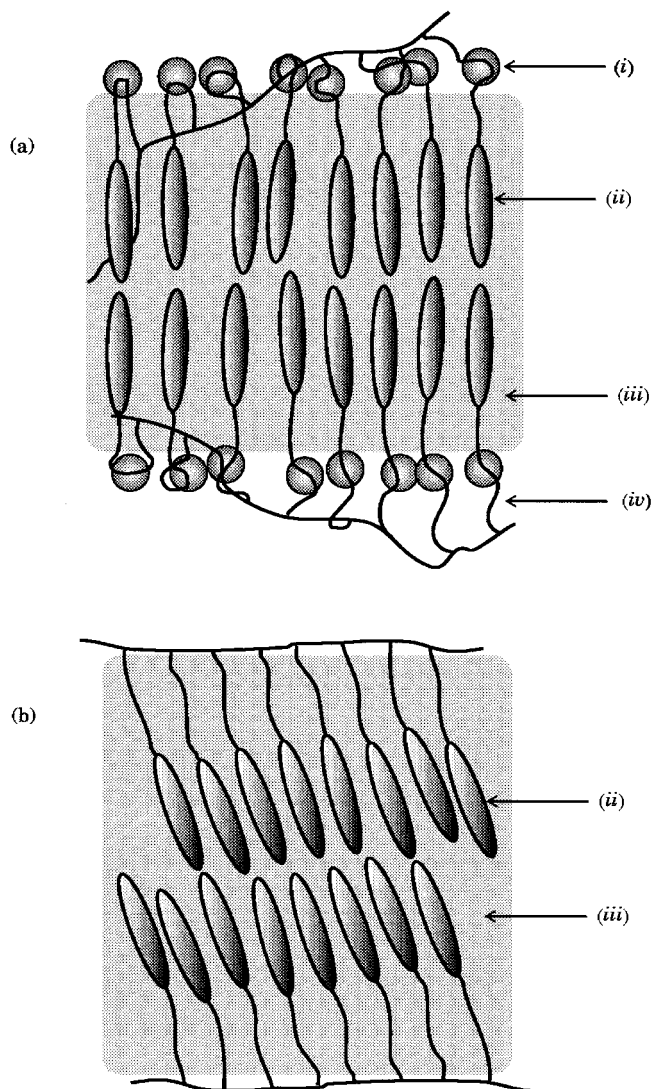
(a)

(b)

Figure 6. Schematic illustrations of the assembly structures of the LCPAs containing (*a*) a siloxane spacer and (*b*) an alkylene spacer: (*i*) bulky and flexible siloxane moiety in the spacer part, (*ii*) mesogen, (*iii*) ordered part (grey area), (*iv*) disordered part.

of **P-2** ($d = 20.0$ Å) should correspond to the length of a certain part of the side chain of **P-2**, because the aligned mesogens should be perpendicular to the smectic layer in the smectic A phase. Actually, in the cases of **P-2, P-4** and **P-5** which exhibited a smectic A phase at room temperature, the layer spacing estimated from the second reflection peak were in good agreement with the calculated length of the anisotropically ordered part, as shown in figure 5. In addition, an unidentified smectic phase of **P-3** with a striated fan-shaped texture between -2°C and about 150°C might be a tilted smectic C phase, because the observed layer spacing was shorter than the calculated length. On the other hand, the X-ray diffraction pattern of **P-4** suggested partial crystallization

of the side chain with sharp peaks in the wide angle region, although the optical texture of **P-4** was the typical fan-shaped texture of a smectic A phase at room temperature and the crystallization peak was observed above 30°C in DSC. The crystallization of **P-4** would probably arise from the increase of the linearity and freedom with the extended side chain, which is estimated from such a linear molecular model of **P-4** in figure 5. From the X-ray diffraction patterns and the molecular models of **P-6** and **P-7**, the aligned side chains of these polyacrylates were inclined at 49° and 50°, respectively, against the smectic layer. Therefore, **P-6** and **P-7** might show a highly ordered smectic phase such as smectic I or smectic F in the low temperature range above T_g.

The assembly structures of these polyacrylates were suggested as illustrated in figure 6. In the cases of **P-2–P-5** having a siloxane spacer (see figure 6(*a*)), it is assumed that a certain part of the side chain (the mesogenic group beyond the siloxane unit) relates to an anisotropical orientation. On the other hand, for **P-6** and **P-7** having an alkylene spacer, the whole side chain relates to an anisotropic order such as the ordinary orientation of a general liquid crystal. It is also evaluated that two broad reflections observed in the X-ray diffraction patterns of **P-2–P-5** would be due to the two kinds of density dispersion with a lateral direction of anisotropically ordered mesogens and an amorphous region around polymer backbones involving siloxane units.

4. Conclusion

In this paper, a novel and convenient synthetic route of the side chain liquid crystalline polyacrylates (LCPAs) containing a siloxane spacer was presented. The intermediates of the monomers, i.e. the alcohol compounds **9 a–9 e**, should be useful for the syntheses of various polymers containing siloxane spacers or the introduction of a functional group into a siloxane compound. It was found that the introduction of a relatively large mesogenic group was necessary to promote liquid crystallinity in the case of LCPA containing a siloxane spacer. In addition, as compared with the corresponding LCPA containing an alkylene spacer, the introduction of a siloxane spacer was effective to decrease the T_g of LCPA. Furthermore, the T_gs of the LCPAs containing a siloxane spacer were lower than those of the polymethacrylates having the same side chain structure. It was also revealed that the assembly structures of LCPAs were affected by the chemical structures of the spacer components.

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