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Side-chain liquid crystalline homo- and copolymethacrylates with a carbonate linkage between the benzylideneaniline mesogen and ethylene chain

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New liquid crystalline (LC) homo- and copolymethacrylates having a carbonate linkage between a benzylideneaniline mesogen and ethylene chain in the side chain were prepared by free radical polymerization of methacrylate derivatives comprising 4-cyano- and/or 4-methoxybenzylideneaniline units using AIBN as an initiator. The structures of the polymers were characterized by FTIR, ^{1}H NMR, and elemental analyses. The LC properties were evaluated by differential scanning calorimetry (DSC), polarizing microscopic observation of textures and X-ray diffraction. These measurements showed that all the homo- and copolymers form nematic phases. The isotropization temperatures on composition exhibited a negative deviation from a linear relationship between them predicted by the Schroeder–Van Laar equation. This phenomenon might be caused mainly by an unusual geometry arising from a smaller bond angle in the carbonate linkage.

1. Introduction

In general, side-chain liquid crystalline (LC) polymers composed of acrylate, methacrylate and siloxane linkages in the main chain have both rigid rod-like mesogens, for example, biphenyl and azomethine, and flexible spacers, like aliphatic and siloxane chains, to decouple the motion of the polymer backbone from that of the anisotropically oriented mesogenic unit in the side chain [1, 2]. There is a relationship between spacer length, type of spacer chain and interconnecting group attaching the mesogen to the flexible side branch and LC property [1]. Direct attachment of the mesogen to the backbone results in steric hindrance in the packing of the mesogen and the absence of LC phase in some cases [1, 2]. The majority of the interconnecting groups linking the mesogen and the spacer are either ether or ester linkages [3–5]. Only a few studies of the influence of a carbonate linkage have been reported [6, 7].

Our previous paper described preparation and thermal properties of homo- and copolymethacrylates having a carbonate linkage between an ethylene segment and mesogenic unit in the side chain. The copolymers containing both 4-cyanobiphenyl and 4′-methoxybenzylideneaniline mesogens were found to have no thermotropic LC phases; nevertheless the homopolymer composed of the 4′-methoxybenzylideneaniline and ethylene chain formed a LC phase [6]. Teyssié *et al.* [7] reported that side-chain polyallylcarbonates having the carbonate linkage in the spacer between the polymer backbone and diphenylester mesogen exhibited LC states (smectic and nematic), although polyvinylcarbonates composed of the mesogen attaching directly to the backbone showed no LC phases.

In this work, new homo- and copolymethacrylates having the interconnecting carbonate linkage between the mesogen and ethylene segment were prepared by free radical polymerization of methacrylate derivatives comprising electron-withdrawing 4-cyano- and/or electron-donating 4′-methoxybenzylideneaniline mesogens for the purpose of evaluating the relationship between polymer structure and mesogenic property. Introduction of the interconnecting carbonate linkage in the side chain was expected to affect potential LC phase formation and phase transition temperatures in the copolymers (**4**) having both the electron-withdrawing and the electron-donating groups because of the smaller bond angle of the carbonate link than those of the ether and ester groups [8].

2. Experimental

2.1. *Materials*

[(2-Methacryloyloxy)ethyloxy]carbonyl chloride (**1**) was kindly supplied by Nippon Oil and Fats Co. Ltd. and

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was purified by vacuum distillation before use. 4′-Cyanobenzylidene-4-hydroxyaniline (**2 a**) was prepared from 4-aminophenol and 4-cyanobenzaldehyde in the presence of *p*-toluenesulphonic acid and recrystallized from methanol. Yield 70 per cent, m.p. = 186–188°C ([9] m.p. = 181°C). 4′-Methoxybenzylidene-4-hydroxyaniline (**2 b**) was commercially available and used after recrystallization from methanol.

2.2. *4′-Cyanobenzylidene-[4-(2-methacryloyloxy)ethyleneoxycarbonyloxy]aniline* (**3 a**)

4′-Cyanobenzylidene-4-hydroxyaniline (**2 a**) (0·011 mol, 2·4 g), triethylamine (0·011 mol, 1·1 g) and hydroquinone (0·01 g) as a radical inhibitor were dissolved in tetrahydrofuran (THF) (10 ml). The chloroformate (**1**) (0·01 mol, 1·9 g) was added dropwise into the THF solution at room temperature and the reaction mixture was stirred for 24 h. After the reaction, chloroform (80 ml) was added into the mixture and by-product was removed by shaking with water. The organic layer was separated, dried over $MgSO_4$ and evaporated to dryness under vacuum. The residual product was recrystallized from a mixture of chloroform/*n*-hexane (= 1/4 (v/v)) three times. Yield 55 per cent, m.p. = 129–130°C. FTIR (cm^{-1}) (KBr method): 2959 (CH stretching). 2224 (CN), 1767 (carbonate C=O), 1721 (ester C=O). 1624 (azomethine), 1597 (C=C), 1265 (ether). ^{1}H NMR (ppm) (in $CDCl_3$): 1·98 (CH_3, 3 H), 4·44–4·55 (–CH_2CH_2–, 4 H), 5·63, 6·19 (C=CH_2, 2 H), 7·25, 7·78, 7·99 (aromatic, 8 H), 8·49 (N = CH, 1 H). Elemental analysis ($C_{21}H_{18}N_2O_5$) (378·4), calculated: C 66·70, H 4·80, N 7·40; found: C 66·42, H 4·86, N 7·45.

2.3. *4′-Methoxybenzylidene-[4-(2-methacryloyloxy)-ethyleneoxycarbonyloxy]aniline* (**3 b**)

This was prepared from the chloroformate (**1**) and 4′-methoxybenzylidene-4-hydroxyaniline (**2 b**) according to our previously described method [6]. The crude product was recrystallized from *n*-hexane three times. Yield 49 per cent, m.p. = 73–74°C ([6] m.p. = 72·5–74°C). The FTIR and ^{1}H NMR spectra agreed with our previously reported data [6].

2.4. *Homopolymers* **4 a** *and* **4 f**

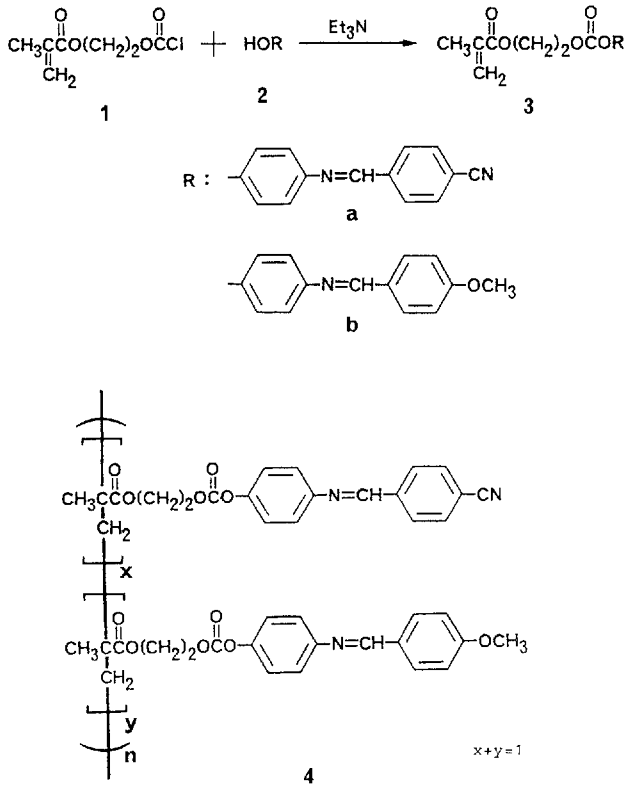
Typical polymerization method for the homopolymer **4 a** is described. The monomer **3 a** (1 mmol, 0·378 g) in THF (1 ml) in the presence of AIBN (1 mol % based on monomer) as an initiator was polymerized at 60°C for 30 h in oxygen-free nitrogen. After the polymerization, the resulting polymer solution was poured into a large excess of methanol to reprecipitate the polymer **4 a**. The product was then dissolved in THF and reprecipitated into methanol again. The polymer was dried at 40°C for one day under reduced pressure. Yield 88 per cent. FTIR (cm^{-1}) (KBr method): 2959 (CH stretching), 2228 (CN), 1763 (carbonate C=O), 1730 (ester C=O), 1628 (azomethine), 1257 (ether). ^{1}H NMR (ppm) (in $CDCl_3$): 1·05 (–C$\underline{H}_2$C(CH_3)(C=O)–, 2 H), 1·95 (CH_3, 3 H), 4·36–4·46 (–CH_2CH_2–, 4 H), 7·24, 7·76, 7·94 (aromatic, 8 H), 8·48 (N = CH, 1 H). Elemental analysis $(C_{21}H_{18}N_2O_6)_n$ (378·4)*n*, calculated C 66·70, H 4·80, N 7·40; found C 65·67, H 4·74, N 7·05.

2.5. *Copolymers* (**4 b–4 e**)

These were polymerized by the method described for the homopolymers **4 a** and **4 f**. The compositions were determined from ^{1}H NMR spectrum data.

2.6. *Measurements*

The ^{1}H NMR spectra were obtained by a JEOL LNM-GSX 270N spectrometer. The FTIR spectra were recorded with a Jasco FTIR 5300 spectrometer by the KBr disk method. The differential scanning calorimetry (DSC) measurements were conducted with a Shimadzu DSC-50 calorimeter at a heating and a cooling rate of 10°C min^{-1} in nitrogen. The optical textures were observed with an Olympus Model (POM) polarizing microscope equipped with a hot stage (magnification × 400). The temperature-changeable wide-angle X-ray analysis was performed with a Rigaku Denki RINT-2200 generator equipped with a temperature controller with CuK_α irradiation.



Scheme.

3. Results and discussion

3.1. *Preparation of monomers* 3 *and polymers* 4

Synthetic route of the monomers **3** and the polymers **4** is presented in the scheme. The monomers **3** were synthesized by the Schotten–Baumann reaction from the chloroformate **1** and hydroxy derivatives of the benzylideneaniline **2** in THF in the presence of triethylamine at room temperature. The monomers **3** showed a normal melting process. Next, we tried to polymerize these monomers in the presence of AIBN in benzene, chlorobenzene, toluene, *N,N*-dimethylformamide (DMF) and THF as polymerization solvents. The polymerization proceeded in only DMF and THF. Yield and inherent viscosity of the polymer prepared in DMF were low, so all the homo- and copolymers in the present work were prepared in THF. Synthetic results of the polymers **4** are shown in table 1. These polymers **4** with inherent viscosities of 0·20–0·32 dl g^{-1} in THF were obtained at yields more than 85 per cent. In the FTIR spectra of the homo- and copolymers **4** characteristic absorption bands of the carbonate C=O, ester C=O, C–O–C, CN and N=CH were observed, respectively, and those of the vinyl group at 1597 and 1638 cm^{-1} detected in the monomers **3** disappeared. In addition, ^{1}H NMR spectra described that signals of $-C\underline{H}_2C(CH_3)(C{=}O)-$ were observed at 1·05–1·10 ppm in the polymers **4** instead of those for the vinyl protons at 5·60–6·19 ppm in the monomers **3**. The elemental analysis values for the polymers **4** were in agreement with the calculated data.

3.2. *Thermal and mesomorphic properties of polymers* 4

In our previous work [6], only the homopolymethacrylate having a carbonate linkage between 4-methoxybenzylideneaniline and ethylene segment possessed a thermotropic nematic phase, although homopolymer from 4-cyanobiphenyl and copolymers composed of both the 4-cyanobiphenyl and the 4-methoxybenzylideneaniline formed no LC states. This was explained by an unusual geometry of the interconnecting carbonate linkage depressing effective orientation of the mesogens and due to the coexistence of the side-chain 4-cyanobiphenyl with a lower aspect ratio. In the present work the homo- and copolymers **4**, which are composed of both the 4-methoxy- and 4-cyanobenzylideneaniline units with a higher aspect ratio instead of the 4-cyanobiphenyl unit, might have thermotropic LC phases.

Thermal and mesomorphic properties of the side-chain polymers **4** were evaluated by DSC, polarizing microscopic observation of textures and temperature-changeable wide-angle X-ray analyses. The DSC curves of the polymers 4 on the second heating runs exhibited two endotherms, melting (120–127°C) and isotropization (136–161°C) in addition to glass transition steps (T_g) at 78–82°C. The phase transition data are listed in table 2. The homopolymer **4 a** with the 4-cyanobenzylideneaniline mesogen exhibits a nematic (N) schlieren texture between the melting and the isotropization transitions. For the polymers **4** with the carbonate linkage, the higher aspect ratio and more rigid rod-like structure of the 4-cyanobenzylideneaniline are still responsible for the formation of a LC phase in comparison with the 4-cyanobiphenyl unit [6].

The nematic phase was confirmed by the temperature-changeable wide-angle X-ray analyses. The X-ray patterns show no reflections at small angles, and some weak reflections are observed at around $2\theta = 20°$ at room temperature. In the LC states the reflections were broad indicating that the LC phase is nematic. It is enantiotropically nematic and maintained below the T_g step on cooling. The homopolymer **4 a** has higher transition temperatures and a wider LC temperature range than the homopolymer **4 f** owing to the higher dipole moment and anisotropy of molecular polarizability arising from the cyano group at the 4-position of the benzene ring [10].

Very recently, it was reported that the similar polymethacrylate (PM6CN) having hexamethyleneoxy spacer

Table 1. Synthetic results for the polymers **4**.

Polymer	Polymer composition† $x{:}y$	Yield/per cent	η_{inh}/dl g^{-1}‡	Solubility§ CHCl$_3$	DMF‖	THF‖
4 a	1:0	88	0·29	±	+ +	+ +
4 b	0·82:0·18	85	0·22	±	+ +	+ +
4 c	0·56:0·44	87	0·20	±	+ +	+ +
4 d	0·33:0·67	94	0·32	±	+ +	+ +
4 e	0·15:0·85	96	0·27	±	+ +	+ +
4 f	0:1	96	0·30	±	+ +	+ +

† Calculated from ^{1}H NMR spectral data.

‡ Measured at a concentration of 0·2 g dl^{-1} at 30°C in THF.

§ + + : Soluble at room temperature, ± : partly soluble or swelling.

‖ DMF: *N,N*-dimethylformamide, THF: tetrahydrofuran.

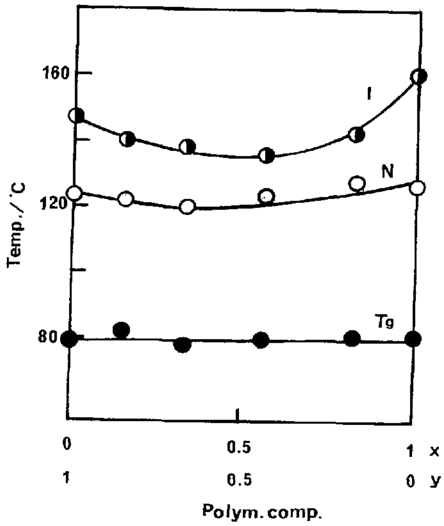
Table 2. Phase transition data for the polymers 4.

Polymer	T_g/°C	N/°C	ΔH_m/J mol^{-1}	I/°C	ΔH_I/J mol^{-1}	ΔT/°C
4a	81	127	257	161	<3·78	34
4b	81	128	307	143	<3·79	15
4c	80	124	83·7	136	<3·81	12
4d	78	120	153	138	3·82	18
4e	82	122	176	140	<3·83	18
4f	79	123	268	147	3·83	24
PM6CN‡	53	Smectic		146	1420	93
PM6NO$_2$‡	45	Nematic		111	370	66
PM6OCH$_3$‡	56	Nematic		123	580	67

† T_g: Glass transition, N: Nematic, ΔH_m: transition enthalpy for nematic phase, I: isotropization, ΔH_I: transition enthalpy for isotropization, ΔT: LC temperature range.

‡ Thermodynamic data for similar polymethacrylate containing a benzylideneaniline unit reported by Kosaka *et al.* [11].

(–C(O)OC$_6$H$_{12}$O–) between the polymer backbone and the 4-cyanobenzylideneaniline moiety exhibits a smectic phase between the T_g step and the isotropization temperature (T_g 56°C S 146°C I) and the transition enthalpy for the isotropization (ΔH_I) is 1·42 KJ mol^{-1} [11]. The others containing the benzylideneaniline unit with terminal groups such as NO$_2$ (PM6NO$_2$) (T_g 45°C N 111°C I) and OCH$_3$ (PM6OCH$_3$) (T_g 56°C N 123°C I) formed nematic phases, whose transition enthalpies of the isotropization (ΔH_I) are 0·37–0·58 KJ mol^{-1} [11]. In addition, the polymethacrylate with an ester linkage attached without a spacer between the polymer backbone and ethoxy-group substituted benzylideneaniline mesogen [12] showed a smectic phase and had higher transition temperatures (T_g 160°C S 213°C I) than the homopolymers **4a** and **4f**. A comparison of the thermodynamic data of the polymers **4a** and **4f** with these analogous polymers indicates that the transition temperatures and the isotropization enthalpies of polymers **4a** and **4f** are considerably lower and smaller. These analogous polymers had more stable LC states than the homopolymers **4a** and **4f**. Interactions between the mesogenic side groups in the homopolymers **4a** and **4f** were probably weak.



Relationship between copolymer composition and phase transition temperatures for the polymers 4.

The copolymers **4b–4e** also showed a nematic phase. The temperature-changeable X-ray analysis data support the appearance of nematic phase. The melting and the isotropization temperatures of the copolymers **4b–4e** varied with the polymer composition and a downward curvature was exhibited. The isotropization temperatures were lower than those estimated by the Schroeder–Van Laar equation, which predicts a linear dependence of the isotropization temperature on polymer composition for nematic copolymers [13–15], and a eutectic point is detected at around the composition of **4a**:**4f** = 1 : 1. The LC temperature ranges and the transition enthalpies of isotropization (ΔH_I) are 12–18°C and <3·83 J mol^{-1}, respectively. The T_g values of the copolymers (**4b–4e**) were constant and independent of the polymer composition. In the figure the relationship between the polymer composition and the phase transition temperatures for the polymers **4** is presented.

Imrie *et al.* [16, 17], reported that copolystyrenes having both electron-donating 4-methoxyazobenzene and electron-withdrawing 4-nitroazobenzene units linked through a flexible spacer show stable smectic phases by charge-transfer interactions which result in a positive deviation of isotropization temperatures on polymer composition. Kosaka *et al.* [11], found that for copolymers containing an electron-donating carbazoyl group and an electron-accepting 4-nitro- or 4-cyanobenzylideneaniline group, the appearance of a smectic phase and the enhancement in thermal stability are caused by electron donor–acceptor complexation. Unexpectedly for the copolymers **4b–4e**, such a phenomenon was not observed and a negative deviation from the isotropization temperatures predicted by the Schroeder–Van Laar equation was shown in spite of the emergence of a nematic phase.

From the thermodynamic data in table 2, which show that the isotropization enthalpies (ΔH_{I}) ($< 3{\cdot}83\,\mathrm{J\,mol^{-1}}$) for the polymers **4** are not only very small, but also 0·006 times as high as those ($0{\cdot}64$–$1{\cdot}28\,\mathrm{KJ\,mol^{-1}}$) of the copolymers by Kosaka *et al.* [11]; it is suggested that there are no interactions between both the benzylideneaniline units and difficulties in the effective packing and alignment of the side-chain mesogens in our homo- and copolymers **4**. This could be explained by the assumption that an unusual geometry of the carbonate linkage in the polymers **4** disturbs effective alignment of mesogens, because the bond angle in the carbonate linkage is smaller than that in the ester or ether linkage, and the carbonate groups are considered not to show a pseudo-*trans* conformation [8, 18]. Thus, for the polymers **4** nematic mesophases were formed without the appearance of a layered smectic phase.

4. Conclusions

The side-chain LC homo- and copolymethacrylates having an interconnecting carbonate linkage between the 4-cyano- and/or 4-methoxybenzylideneaniline mesogens and an ethylene segment formed a nematic phase. The nematic–isotropization temperatures of these copolymers exhibited a negative deviation from a linear dependence of the transition temperatures predicted by the Schroeder–Van Laar equation. Unexpectedly, enhancement in the thermal stability of the LC phase by electron donor–acceptor interaction was not observed. This might be due to prevention of effective alignment of mesogens by the carbonate linkage, which has an unusual geometry arising from a smaller bond angle than the ester or ether linkage.

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