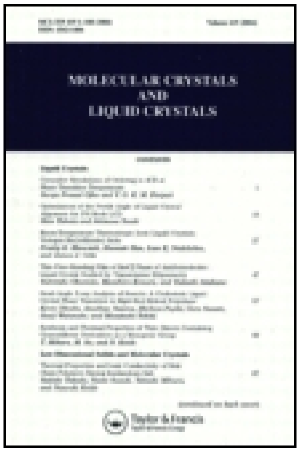

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Influence of the Spacer Structure on Liquid-Crystallinity and Dielectric Behavior of Polyacrylates Having p-Cyanophenyl Benzoate Group in the Side-Chain

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To cite this article: Eiichi Akiyama, Kenji Kawamura, Takashi Mihara, Norihiro Matsui, Yu Nagase, Kazuo Araki & Naoyuki Koide (1998): Influence of the Spacer Structure on Liquid-Crystallinity and Dielectric Behavior of Polyacrylates Having p-Cyanophenyl Benzoate Group in the Side-Chain, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 318:1, 307-324

To link to this article: http://dx.doi.org/10.1080/10587259808045392

Mol. Cryst. Liq. Cryst., Vol. 318, pp. 307–323
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Influence of the Spacer Structure on Liquid-Crystallinity and Dielectric Behavior of Polyacrylates Having p-Cyanophenyl Benzoate Group in the Side-Chain.

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The three kinds of polyacrylates having the same mesogenic group of p-cyanophenyl benzoate were prepared, which consisted of the different spacer chain; alkylene- (AS), siloxane- (SS) and oligo(ethylene oxide)-spacer (EOS). AS showed two smectic phases, however both SS and EOS exhibited no mesophase. Dielectric relaxation measurements of these polymers were carried out, and the obtained data of dielectric loss was mainly analyzed using *Fuoss-Kirkwood* function. As the result, it was suggested that the siloxane-spacer and the oligo(ethylene oxide)-spacer were more flexible chains than the ordinary alkylene-spacer, and it would be due to the high flexibility of the spacer chain that no mesophase appeared in SS and EOS.

Keywords: Side-chain liquid-crystalline polymer; alkylene-spacer; siloxane-spacer; oligo(ethylene oxide)-spacer; dielectric relaxation spectroscopy; *Fuoss-Kirkwood* function

INTRODUCTION

Side-chain liquid-crystalline polymers (SCLCP) are very interesting materials for the various applications, for example, optical data storage, non-linear optics, conducting material, stationary phase for gas chromatography, liquid crystal display (LCD) and so on[1]. We have tried to develop the SCLCP, which is able to vary the anisotropic order against a change of an external field, because the SCLCP still has the possibility of acquiring both the advantages of fast responsible low molar mass liquid crystal (LMMLC) and of good processable polymer. In order to apply a SCLCP to display device, two problems should be solved. That is, in general, SCLCP shows a high glass transition temperature (T_g) and a high viscosity.

SCLCP has been investigated by numerous researchers since H. Finkelmann *et al.* announced the guide to synthesis of SCLCP in 1978[2]. With respect to synthetic approach of the composition of SCLCP, the influences of chemical structure of polymer backbone, mesogenic group and flexible spacer group, which links mesogenic group to backbone, on the thermal behaviors or physical properties have been mainly studied[3]. In general, it is thought that a flexible spacer part plays an important role to decouple the motions of a polymer backbone and a mesogenic group. It is considered that the introduction of more flexible spacer chain would be necessary to maintain the higher mobility of the mesogenic side-chain at a room temperature, such as a LMMLC.

Then, we proposed the introduction of a siloxane bond into the flexible spacer chain, in order to enhance the mobility of a mesogenic group, because it is well-known to be one of the most flexible linkages. In our previous work, the side-chain liquid-crystalline polyacrylates having a siloxane-spacer and a corresponding ordinary alkylene-spacer were prepared and their thermal properties were investigated in detail[4]. It was found that the introduction of siloxane bond into the spacer chain lowered T_g of polymers compared with the ordinary alkylene spacer, and that the relatively large mesogenic core (more than three phenylene rings) was necessary to exhibit a liquid-crystalline phase. This result would suggest that dimethylsiloxane unit prevents the mesogenic groups from anisotropically ordering because of its bulkiness.

On the other hand, p-cyanophenyl benzoate group is well-known as one of the ordinary mesogenic groups[2]. The siloxane-spacer type polyacrylate having p-cyanophenyl benzoate group as a mesogenic core (SS in Fig. 1) shows

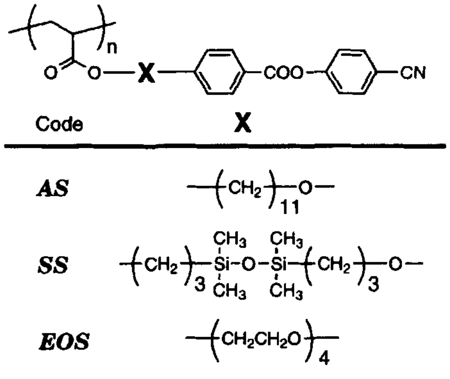


FIGURE 1 The chemical structures of the polyacrylates

no mesophase. The spacer chain length of SS is the almost same as that of undecamethylene unit in AS. In addition, we took an interest in an oligo(ethylene oxide)-spacer as another flexible chain instead of a siloxane-spacer, considering that oligo(ethylene oxide)-spacer is unbulky to the contrary of the siloxane-spacer. In order to make the spacer chain the same length, we chose a tetra(ethylene oxide)-spacer (EOS), as illustrated in Fig. 1. In this paper, the thermal properties of three kinds of polyacrylates having a different spacer structure (AS, SS and EOS) will be described. Furthermore, the dielectric behavior of these polyacrylates will be also discussed. From these results, we would like to clear the influence of the chemical structure of a spacer chain on the appearance of a liquid crystalline phase and on the mobility of a mesogenic side-chain.

EXPERIMENT

Materials

Methyl 4-hydroxybenzoate, 4-cyanophenol, 4-toluenesulfonic acid, dicyclohexylcarbodiimide (DCC) and 4-N,N-dimethylaminopyridine were purchased from Tokyo Chemical Ind. Co., Ltd., and used without further purification. Tetra(ethylene oxide) and 2,2'-azobis(isobutyronitrile) (AIBN) were from Kanto Chemical Co., Inc. and Wako Pure Chemical Ind., Ltd., respectively, and used without further purification. 4-Toluenesulfonyl chloride and acryloyl chloride were used after purifications by recrystallization from hexane and by distillation in argon stream, respectively. Tetrahydrofuran (THF) used as the solvent was distilled over sodium. All other chemicals were of reagent and commercially obtained.

Characterizations

^{1}H-NMR was conducted with JEOL JNM-PMX60 NMR (60 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 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 were carried out in the scanning-rate of ±5 °C/min.

Synthesis

Syntheses of AS and SS have already reported in our previous paper[4]. EOS was prepared according to the pathways shown in Fig. 2.

Tetra(ethylene glycol) mono tosylate: *1*

Tetra(ethylene glycol) (450 g, 2.33 mol) and pyridine (185 mL, 2.44 mol) were

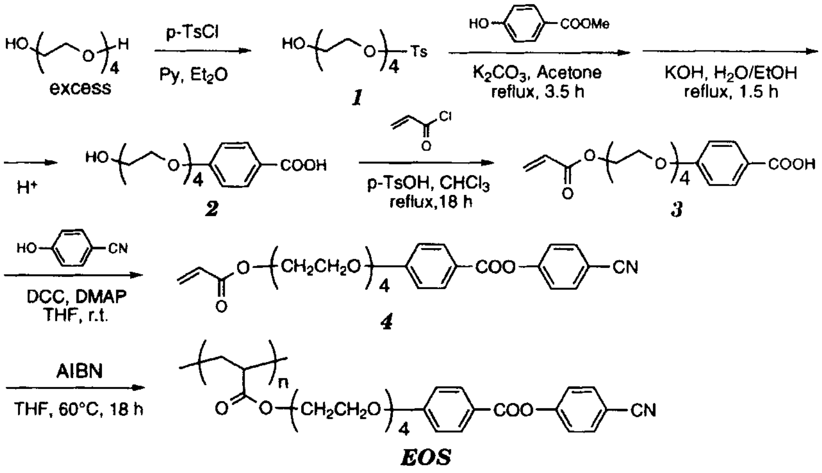


FIGURE 2 Synthesis of polyacrylate having an oligo(ethylene oxide)-spacer.

mixed and cooled to 0 °C. The solution of p-toluenesulfonyl chloride (88 g, 0.46 mol) in 400 mL of ethyl ether was added dropwise to the mixture, and the reaction mixture was stirred for 13 h at room temperature. Then, it was permitted to stand until separating to two layers. The layer of ethyl ether was removed, and 700 mL of chloroform was added to the rest. The extraction with chloroform was washed with dilute hydrochloric acid and water. After the solution was concentrated, the residue was dried at 85 °C under reduced pressure overnight to afford 93 g of ***1*** as colorless transparent liquid. Yield: 58 %
^{1}H-NMR (60 MHz, $CDCl_3$, ppm): 2.51 (s, 3H), 3.12 (broad s, 1H), 3.6-4.0 (m, 14H), 4.33 (t, 2H), 7.62 (d, 2H), 8.12 (d, 2H).

4-(11-hydroxy-3,6,9-trioxyundecyloxy)benzoic acid: *2*

Methyl 4-hydroxybenzoate (48.7 g, 320 mmol), ***1*** (93 g, 267 mmol) and potassium carbonate (111 g, 803 mmol) were mixed in 600 mL of acetone, and the mixture was stirred for 3.5 h at reflux temperature. After the salts and the solvent were removed, the residue was extracted with chloroform and washed with water to afford 50 g of crude methyl 4-(11-hydroxy-3,6,9-trioxyundecyloxy)benzoate as a pale yellow liquid.

This crude production (50 g) was dissolved with 400 mL of ethanol, then the solution of potassium hydroxide (13.0 g, 232 mmol) in 100 mL of water was added dropwise. After the mixture was stirred for 1.5 h at reflux temperature, this was acidified by addition of dilute hydrochloric acid, and stirred for 30 min. at reflux temperature. The solvents were removed under reduced pressure, then the residue was extracted with ethyl acetate. The extraction was purified by recrystallization from the solvents of acetone and hexane (1/2 vol. ratio) to afford 34.3 g of **2** as a colorless solid. Yield: 40.9 %
IR (KBr, cm^{-1}): 3454 (broad, -OH), 2873, 1598 (aromatic C=C), 1452, 1356, 1292, 1248 (arC-O-Cal st as), 1176, 1124 (CH_2-O-CH_2 st as), 1097, 1070, 1018, 924, 818, 758, 665, 584, 555.
^{1}H-NMR (60 MHz, $CDCl_3$, ppm): 3.52-3.95 (m, 14H), 4.19 (m, 2H), 6.92 (d, 2H), 7.99 (d, 2H).

4-(11-Acryloyloxy-3,6,9-trioxyundecyloxy)benzoic acid: *3*

2 (13.2 g, 40.2 mmol), acrylic acid (150 mL, 2.19 mol), p-hydroquinone (6.0 g, 55 mmol), p-toluenesulfonic acid (catalytic amount, 0.2 g) and 600 mL of chloroform were mixed in the reactor with azeotropic trap, and stirred for 18 h at relfux temperature. After the solvents were removed under reduced pressure, the residue was purified by column chromatography on silica gel with ethyl acetate/n-hexane (1/3 vol.) as eluent to afford 11.7 g of ***3*** as a colorless solid. Yield: 76.2 %

IR (KBr, cm^{-1}): 3429 (broad, carboxylic acid -OH), 2895, 2669, 2565, 1724 (ester C=O), 1687 (carboxylic acid C=O), 1635 (acryl C=C), 1608 (aromatic C=C), 1512 (w), 1427, 1412, 1323, 1298, 1257 (arC-O-Cal st as), 1198, 1173, 1142, 1124 (CH_2-O-CH_2 st as), 1109, 1057, 985 (w), 957 (w),852, 812 (w), 773, 650 (w).

^{1}H-NMR (60 MHz, $CDCl_3$, ppm): 3.7-4.1 (m, 12H), 4.1-4.7 (m, 4H), 5.7-6.5 (m, 3H), 7.01 (d, 2H), 8.09 (d, 2H).

11-(4-Cyanophenoxy-4-carbonylphenoxy)-3,6,9-trioxyundecyl acrylate: *4*

3 (5.0 g, 13 mmol), 4-cyanophenol (1.4 g, 12 mmol) and 4-N,N-dimethylaminopyridine (0.2 g, 2 mmol) were dissolved in 140 mL of THF, and the solution of 3.71 g of DCC in 50 mL of THF was slowly added dropwise. After the mixture was stirred at room temperature overnight, the precipitate was filtered off. The filtrate was purified by column chromatography on silica gel with ethyl acetate/n-hexane (1/4 vol.) as eluent to afford 1.4 g of ***4*** as a colorless transparent liquid. Yield: 24 %

IR (cast, cm^{-1}): 2874, 2230 (-CN), 1730 (broad, ester C=O), 1638 (w, acryl C=C st), 1603 (ar C=C), 1510, 1453 (w), 1408, 1354 (w), 1260 (arC-O-Cal st as), 1209, 1167, 1130 (broad, CH_2-O-CH_2 st as), 1057, 849 (w), 812 (w), 762 (w).

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 3.67 (s, 4H), 3.70 (m, 2H), 3.74 (m, 4H), 3.90 (t, 2H), 4.23 (t, 2H), 4.32 (t, 2H), 5.83 (dd, 1H, J=1.4, 10.4Hz), 6.15 (dd, 1H, J=10.4, 17.3Hz), 6.43 (dd, 1H, J=1.4, 17.3Hz), 7.01 (d, 2H, J=9.0Hz), 7.36 (d, 2H, J=8.79Hz), 7.73 (d, 2H, J=8.79Hz), 8.13 (d, 2H, J=9.0Hz).

CI-MS (Isobutane, m/z): 512 $(M + 43)^+$, 510 $(M + 41)^+$, 351 $(M - OC_6H_4CN)^+$, 310 $(M - CH_2{=}CHCOOCH_2CH_2OCH_2CH_2O)^+$, 266 $(M - CH_2{=}CHCOOCH_2CH_2O)^+$, 99 $(CH_2{=}CHCOOCH_2CH_2)^+$.

Polymerizations

The monomer and AIBN were mixed in dry THF in a polymerization tube. The concentration of monomer [M] was 1.0 mol·L^{-1}. The mole ratio of initiator against a monomer [I]·[M]$^{-1}$ was 0.025. After degassing the mixture, the tube was sealed and heated with stirring at 60 °C for 18 hours. The reaction mixture was then poured into excess methanol to precipitate the polymer.

Dielectric relaxation measurements

Dielectric relaxation measurements were carried out over the frequency range from 10^2 to 10^6 Hz using a computer controlled YHP 4284A Precision LRC Meter. The sample for dielectric measurement was prepared as a thin film of 1.0 cm diameter and 100 μm thickness. The thin film of the polymer was directly sandwiched between two metal electrodes. To keep a constant thickness of 100 μm, Teflon™ ring spacer was used. And dielectric measurements were made above a room temperature with no treatment for alignment. The dielectric loss, ε'', was calculated and mainly analyzed by means of *Fuoss-Kirkwood* function, using G/ω ($=\varepsilon'' C_0$) obtained from the measurement, where G, ω and C_0 are the equivalent parallel conductance of a sample, the angular frequency and the interelectrode capacitance, respectively.

RESULTS AND DISCUSSION

The results of GPC measurements of the obtained polymers were listed in Table I. These polymers were used for studying thermal properties and dielectric behaviors. Because EOS exhibited high wettability, the wet sample of EOS was prepared to investigate the effect of absorbed water on the thermal and dielectric properties. EOS was kept wettish in 83 % of humidity for 70 h at room temperature in the sample cell for DSC to absorb 2.8 wt% (76.2 mol%/unit) of water,

TABLE I Molecular weight of each polyacrylate

Code	$Mn\times10^4$ [a]	$Mw\times10^4$ [b]
AS	2.8	4.6
SS	1.9	3.8
EOS	1.0	1.6

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

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

and then DSC was carried out. On the other hand, after keeping in 83 % of humidity for 48 h at room temperature on the one side of the metal electrode, the sample of wet EOS was prepared by sandwiching between this and the opposite electrode. Dielectric relaxation spectroscopy, DRS, was then conducted.

Thermal properties

DSC curves of heating process of the polyacrylates were illustrated in Fig. 3. AS and SS showed glass transition at 20 and 2 °C, respectively. AS showed smectic phases, but for SS no mesophase was observed as described in the previous paper[4]. Unfortunately, EOS also showed no mesophase. The glass transition of EOS was only observed at 10 °C, and it was the isotropic liquid above the T_g. The T_g of wet EOS was lower than that of dry EOS. The wet EOS also showed no mesophase, and released the absorbed water above 106 °C as observed in the DSC profile.

The oligo(ethylene oxide)-spacer had been reported by M. Engel *et al.* in 1985[5]. They prepared the polyacrylates having di- or tri(ethylene oxide) as a spacer chain. It was found that this series of polymers showed no mesophase

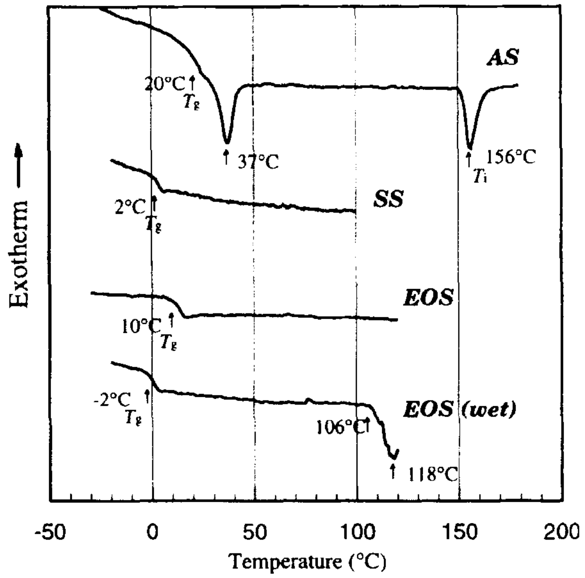


FIGURE 3 DSC Curves of the polyacrylates.

TABLE II Phase transition behaviors of polyacrylates

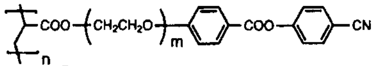
Code	Phase transition temperature (°C) [a]
AS	G 20 Sm X[b] 37 Sm C 156 Iso
SS	G 2 Iso
EOS	G 10 Iso
EOS (wet) [c]	G -2 Iso
m = 2 [d]	G 46 Iso
m = 3 [d]	G -5 Iso

[a] Results of DSC in 2nd heating scan of 10°C/min. except for ***EOS***, which was measured in 5°C/min.
G: glassy, Sm: smectic, Iso: isotropic liquid.

[b] Unknown highly ordered smectic phase.

[c] After keeping in 83 % of humidity for 70 h at room temperature.

[d] General chemical structure is:



cf. reference 5.

regardless of the repeating number of ethylene oxide unit, and that the odd-even effect of the repeating number for the T_g was recognized, as shown in Table II.

Temperature dependence of dielectric loss

Temperature dependence of dielectric loss of each polymer at 10 kHz was illustrated in Fig. 4. For AS, SS, EOS and wet EOS, only one peak was observed. In all cases, the δ-relaxation was mainly observed, therefore, the weak α-relaxation was hindered with the strong δ-relaxation as described later. It was indicated from Fig. 4 that the siloxane-

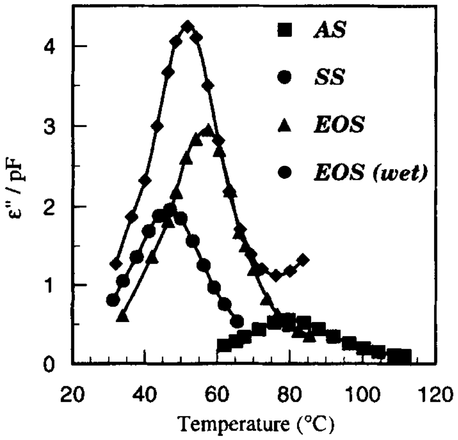


FIGURE 4 The temperature dependences of dielectric loss in 10 kHz.

spacer and the oligo(ethylene oxide)-spacer enhanced the motion of the side-chain group compared with the alkylene-spacer, and that the introduction of the more flexible spacer chain achieved the possibility of the response against the change of an external field in the lower temperature region.

Analysis of dielectric loss curve by *Fuoss-Kirkwood* function

In general, *Fuoss-Kirkwood* function[6] well presents the dielectric loss of the experimental data in one relaxation process. In fact, the data was fitted by using the equation (1), which consisted in dc conductivity (σ) term and one or two *Fuoss-Kirkwood* function corresponding to δ- and/or α-relaxations as shown in equation (1).

$$\varepsilon'' = (\sigma / 2\pi f \varepsilon_0) + \sum_{i=\delta,\alpha} \varepsilon''_{mi} \operatorname{sech}[2.303\beta_i \log(f / f_{mi})] \quad (1)$$

where, ε_0 and ε''_m are the permittivity at limiting low frequency and dielectric loss at critical relaxation frequency, respectively; f is the frequency and equals to $\omega/2\pi$; f_{mi} is the critical relaxation frequency in δ- and/or α-relaxations; β is the empirical distribution parameter. β lies between 0 and 1, and a dielectric behavior in a certain relaxation mode follows Debye-type when β equals to 1.

The only δ-relaxation was supposed to exsist from Fig. 4 as described above. But in the all cases, it was found that α-relaxation also existed in the higher frequency region of the dielectric loss peak of δ-relaxation from the result of curve fitting by means of eq. (1) as illustrated in Fig. 5 for instances.

The temperature dependence of the values of β obtained from the data fitting with *Fuoss-Kirkwood* function (1) was shown in Fig. 6. The values of β_δ (closed symbols) in all cases were similar and almost constant, and slightly increased with increase of temperature. On the contrary, the β_α (open symbols) showed the different tendency though the β_α increased with increase of temperature in all cases. For SS showing no mesophase, β_α increased from about 0.5 to about 0.9 and finally became similar to the value of β_δ. For EOS and wet EOS, the temperature dependences of β_α showed the similar tendencies to the case of SS. However, for AS showing a smectic C phase, β_α was about 0.4 in maximum. Therefore, the polymer-backbone of an isotropic polymer such as

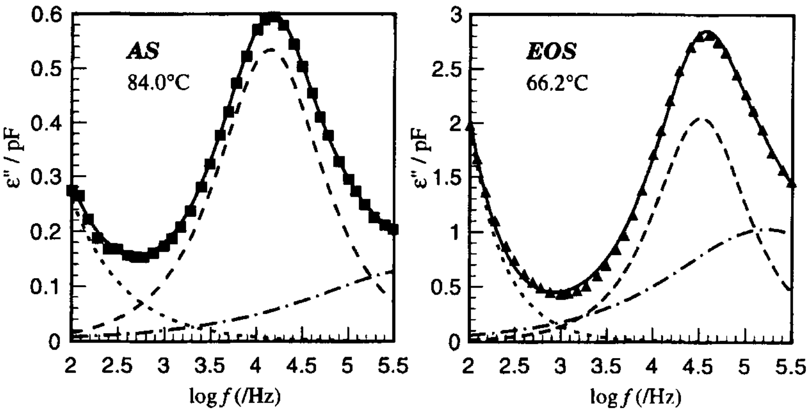


FIGURE 5 The instances of the results of curve-fitting using *Fuoss-Kirkwood* function; ——— : fitted curve, ····· : conductivity, – – – – : δ-relaxation, —·—· : α-relaxation.

SS and EOS would have the more ideal motion than that of AS, which exists in the assembling layer structure of a smectic phase.

It is reasonable that the mobility of a polymer-backbone or a side-chain group increases with increase of temperature without regard to showing a mesophase or no mesophase. The increase of the value of β would be interpreted as the increase of decoupling motions between a polymer-backbone and a side-chain group. In view of the dielectric relaxation behavior, the mobilities of the mesogenic side-chains of the polyacrylates having p-cyanophenyl benzoate as a mesogenic core were similar each other. In addition, it was seemed that the mobilities of the polymer-backbone affected if a liquid-crystalline phase was revealed or not. In this paper, each polyacrylate consists of the same chemical structures of a polymer-backbone and a mesogenic core, but the different structure of a spacer chain. In the case of such a relatively small mesogenic core, we propose two hypotheses as follows;

At first, in order to exhibit a liquid-crystalline phase, not only a mesogenic core but also a spacer chain must be ordered anisotropically because the excluded volume effect is not very strong in the two phenylene rings system. Therefore, the excessively flexible spacer chain prevents a mesogenic core from anisotropically ordering. Secondly, a polyacrylate-backbone basically has the ability of anisotropically ordering of a mesogenic side-chain. So that, the excessively flexible spacer chain can not transmit the ordering power to a mesogenic core. Otherwise, a mesophase of a polymer might appear on the basis of both hypotheses.

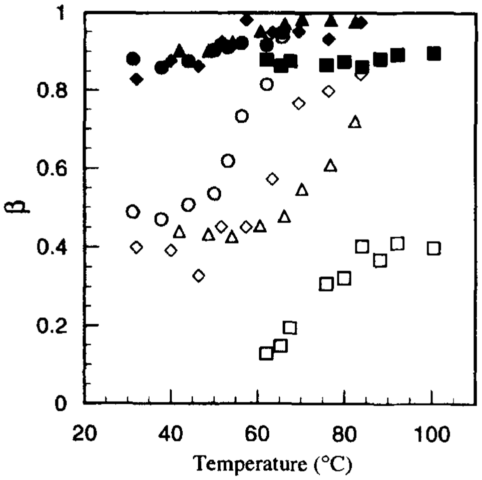


FIGURE 6. The temperature dependence of values of β in *Fuoss-Kirkwood* function (eq.1.): ■ and □: AS, ● and O: SS, ▲ and Δ: EOS, ● and ◇: EOS (wet); Closed symbol and open symbol represent δ- and α-relaxations, respectively.

Relaxation time evaluated from dielectric loss curves

The comparative values of the relaxation time, τ_m (= $(2\pi f_m)^{-1}$), were managed with the normalized dielectric loss curves illustrated in Fig. 7. It was assumed that the value calculated from the peak top of a loss curve approximately coincided with the τ_m of δ-relaxation. At the same absolute temperature, T_{ab} (≈ 66 °C), SS showed the shortest relaxation time (Fig. 7 (A)). The lower macroscopic viscosity in an isotropic phase than a smectic phase probably cause this result. However, the decrease of the rotation viscosity around the short axis of a mesogenic group (or the decrease of the resistance against the flip-flop motion) arising from the decrease of the glass transition temperature might also contribute to this result (AS: T_g = 20 °C, SS: T_g = 2 °C). Consequently, SS and EOS have a possibility for the application to response against the change of an external field at the lower temperature compared with AS, although SS and EOS exhibited no mesophase as a matter of fact.

In order to compare the mobilities of the polyacrylates with the different glass transition temperatures, the normalized dielectric loss curves at the same reduced temperature, T_{red} (≈ 1.2), were shown in Fig. 7 (B). T_{red} is defined as T_{ab} (K) / T_g (K). The relaxation times of AS and SS approximately coincided with that of wet EOS and EOS, respectively. It was expected that wet EOS would

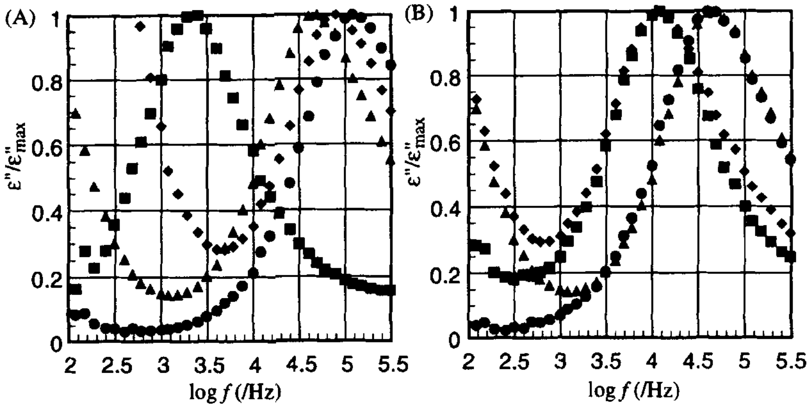


FIGURE 7 The normalized dielectric loss curves of the polyacrylates: (A) at the same absolute temperature ≈ 66°C; (B) at the same reduced temperature (T/T_g) = 1.2, ■: AS, ●: SS, ▲: EOS, ◆: EOS (wet).

exhibit the shorter relaxation time at the same T_{red} than dry EOS, because wet EOS had the lower glass transition temperature than dry EOS (EOS: T_g = 10 °C, wet EOS: T_g = -2 °C). But the contrary result was obtained in fact. The amount of water in the sample for DSC must be different from that for DRS. Therefore, the result at the same T_{red} is not very precise in regard to wet EOS. By the way, EOS and SS showed the almost same τ_m at the same T_{red}. This result suggests that the oligo(ethylene oxide)-spacer enhances the mobility of a mesogenic side-chain rather than the alkylene-spacer, and has the same influence as the siloxane-spacer.

Arrhenius plots

The *Arrhenius* plots of f_m obtained from *Fuoss-Kirkwood* fitting were illustrated in Fig. 8. In general, it is well-known that δ- and α-relaxation processes follow the *Williams-Landel-Ferry*, or *Vogel-Fulcher* equations[7, 8]. That is, a glassy behavior contributes very much to δ- and α-relaxation processes. Therefore, the profiles of the *Arrhenius* plots is not strictly linear in usual. As shown in Fig. 8, the profiles of δ- and α-relaxations of each polyacrylate slightly bent. The apparent activation energies, E_{ap}, were evaluated from the *Arrhenius* plots, and summarized in Table III.

TABLE III The apparent activation energies evaluated from *Arrhenius* plots in δ- and α-relaxations.

Code	δ-relaxation (kJ·mol^{-1})	α-relaxation (kJ·mol^{-1})
AS	103.9	77.4
SS	114.1	105.0
EOS	123.8	111.4
EOS (wet)	122.4	149.3

AS showing a smectic C phase seems to have the highest mobilities of the mesogenic side-chain and the polymer-backbone in this work, because the value of E_{ap} of AS is the lowest in the the both processes. However, the investigation of the analyses about δ- and α-relaxations in regard to the dielectric behavior of a none-liquid-crystalline polymer having a mesogenic side-chain was reported very little. Therefore, it is difficult to explain that the values of E_{ap} of δ- and α-relaxations for SS, EOS and wet EOS were relatively large compared with the case of AS. On the other hand, wet EOS showed the similar value of E_{ap} of δ-relaxation to EOS, and the larger

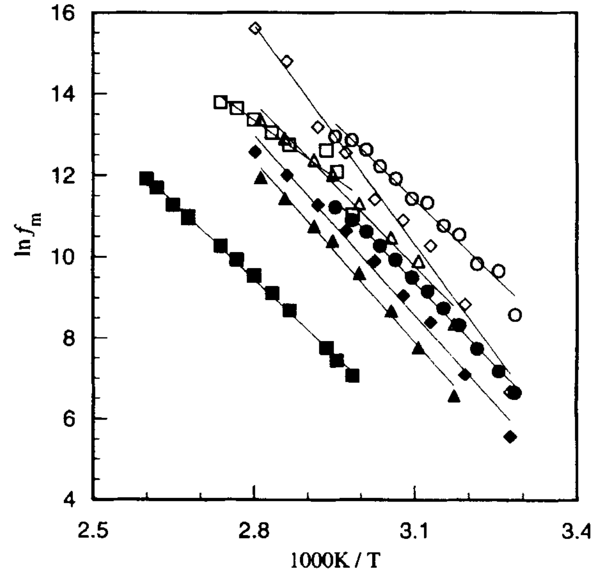


FIGURE 8 Arrhenius plots of the polyacrylates: ■ and □: AS, ● and ○: SS, ▲ and △: EOS, ◆ and ◇: EOS (wet); Closed symbol and open symbol represent δ- and α-relaxation processes, respectively.

value of E_{ap} of α-relaxation than EOS. This result suggests that the absorbed water mainly affects the mobility of the polymer-backbone. Thus, though the glass transition temperature of EOS decreased due to absorbing the water, the mobility of the mesogenic group hardly changed.

CONCLUSION

The three kinds of polyacrylates having the different spacer chain, *i.e.* the ordinary alkylene-spacer (AS), the siloxane-spacer (SS) and the oligo(ethylene oxide)-spacer (EOS), and having the same mesogenic group of p-cyanophenyl benzoate were prepared, and their thermal and the dielectric behaviors were investigated. EOS was highly hygroscopic. AS showed two smectic phases, however both SS and EOS exhibited no mesophase.

The results of the analyses of the obtained dielectric loss data would produce the followings:

The siloxane-spacer and the oligo(ethylene oxide)-spacer is more flexible chain than the alkylene-spacer. Properly speaking, the siloxane-spacer and the oligo(ethylene oxide)-spacer effectively enhance the motion of a mesogenic group owing to decrease of the glass trânsition temperature of a polymer. In addition, these flexible spacer chain effectively decouple the motions of a polymer-backbone and a mesogenic group compared with the ordinary alkylene-spacer from the comparative values of β of *Fuoss-Kirkwood* function. On the other hand, in this system of the two phenylene rings as a mesogenic core, the spacer chain does not only play a role for decoupling the motion of a polymer-backbone and a mesogenic group, but also a role for anisotropically ordering a mesogenic group. What does the ordering power, as we mentioned above, arise from? We can not yet conclude this problem. In our previous work, we reported the liquid-crystallinity of the polyethers derived from p'-substituted biphenyl glycidyl ether or p-alkoxyphenyl glycidyl ether[9, 10]. It was suggested that the polyether-backbone played an important role for the assembling structure in a liquid-crystalline state. Considering the results about the polyethers and the present work, it is possible that a polymer-backbone get a mesogenic group ordered anisotropically, and particularly situated in a smectic liquid-crystalline state. This ordering power of a polymer-backbone would be easily transmitted to a mesogenic group by the alkylene-spacer. Furthermore, a spacer chain has the ability of anisotropically ordering a mesogenic group, as characteristics of the alkylene-spacer. An excessively flexible spacer chain such as the siloxane-spacer or the oligo(ethylene oxide)-spacer can not adjust the interaction between mesogenic groups very well. As an exception, J. M. Rodriguez-Prada *et al.* had reported the liquid-crystallinity of the polymethacrylates and poly(propenyl ether)s having p'-methoxybiphenyl as a mesogenic group and di- or tri(ethylene oxide) as a spacer chain, but the thermal behavior was not satisfyingly revealed in detail[11]. R. Duran had also reported the synthesis of the similar poly(meth)acrylates, but did not show the data of the thermal properties[12].

Now, we are preparing the paper about the dielectric behavior of smectic polyacrylates having the different spacer structure and the three phenylene rings as a mesogenic group. The comparative dielectric relaxation behavior in the same state of liquid crystalline phase would give us the some informations about the motions of a polymer-backbone and a mesogenic side-chain.

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