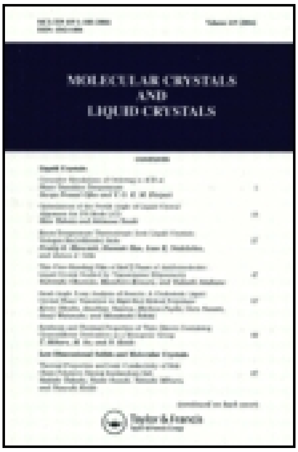

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Molecular Dynamics of Smectic Liquid Crystalline Side-Chain Polymers as Studied by Dielectric Relaxation Spectroscopy

Kazuo Araki [a] , Maki Yamaguchi [a] , Seiji Ujiie [b] & Kazuyoshi Iimura [b]
[a] Department of Materials Science and Technology, Science of Tokyo, Yamaguchi College, Daigaku-dori, Onodashi, Yamaguchi, 756, Japan
[b] Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162, Japan

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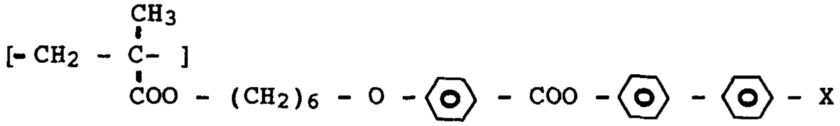
MOLECULAR DYNAMICS OF SMECTIC LIQUID CRYSTALLINE SIDE-CHAIN POLYMERS AS STUDIED BY DIELECTRIC RELAXATION SPECTROSCOPY

KAZUO ARAKI and MAKI YAMAGUCHI
Department of Materials Science and Technology,Science of Tokyo, Yamaguchi College, Daigaku-dori, Onodashi, Yamaguchi 756 Japan
SEIJI UJIIE and KAZUYOSHI IIMURA
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

Abstruct The dielectric properties of the liquid crystallline polymethacylates with side chain containing a terminal alkyloxy chain have been over wide ranges of frequency and temperature. The temperatures corresponding to the peak of the dielectric loss tangent for PM6BP and PM6BP5 in its temperature dependence agreed well with those phase transition. The activation energies at low temperature agreed with δ-relaxation which is $\varepsilon_{//}$ -relaxation by rotation of mesogenic gruop around the backbone chain. The dipole moment have been calculated by using the Frohlich modification of Onsager's equation. The alignment of both materials in the present of an a.c.electric field are also discussed.

INTRODUCTION

Liquid crystalline side chain polymers represent a novel class of hybrid materials with electro- and magneto-optic properties simillar to those observed in low molar mass mesogens, and which possess the good film-forming properties characteristic of high molar mass polymers[1,2] . Nowdays, a number of liquid crystalline side chain polymers have been synthesized and these polymers may form nematic,smectic, or cholesteric phases, dependent on chemical structure. The phase behavior of these polymers is well-known to be influenced by the length and the chemical constitution of the side chain spacer and mesogenic units[1-3] . Thus, recently we have been reported on the preparation and phase transition of the polymethacrylates with side chain containing a terminal alkyoxy chain[4]. In our work we have been discussed the influence of the length of a terminal alkyloxy chain for the phase transition of liquid crystalline polymers having the following structure:



where X = H (PM6BP), and X = O - $(CH_2)_mH$ and m=1-8.

The materials using in this work are X=H (PM6BP) and m=5 (PM6BP5). The thermal properties of PM6BP and PM6BP5 are summerized in Table I.

TABLE I Phase transition temperatures

Sample	Mn	Phase transition temp./°C
PM6BP	42000	G 65 SmA 162 N 180 I
PM6BP5	34000	G 70 SmC 198 N 249 I

G; glassy state: Sm; smectic phase: N; nematic phase: I; isotropic phase.

As mentioned above, the chemical structure constitute of side chain in liquid crystalline polymers is considered to be effectiv for the physicochemical features. Generally, dielectric relaxation behavior reflects the orientation of the constutuent group of materials, i.e. that of side chain in this study. Therefore, dielectric relaxation studies provide us new information on relationship between structure and physical properties in materials. Furthermore, most studies using aligning electric fields report the formation of homeotropically aligned materials, but it is possible to obtain planerly aligned material using high frequency electric fields. Tha dielectric absorption changes remakably on alignment of the material such as the δ-relaxation process and then the variation of dielectric properties shown to depend on the dipole components and the director order parameter Sd for the direction alignment[5]. In ths present study we describe the effect of a terminal alkyloxy chain in side chain and changes for the aligned and unaligned mesophases of a smectic side chain in the liquid crystalline side chain of polymethacrylates .

EXPERIMENTAL

The materials (PM6BP and PM6BP5) studied have the structures and physical properties as mentioned above. The dielectric loss and capacitance data were acquired over the frequency range 150 Hz to 1.5×10^7 Hz with a computer controlled YHP 4697A Impedance Analyzer, and made in temperature range 50 to 180°C. The sample for dielectric measurements was prepared as a thin film of about 1.0 cm diameter sandwiched between two metal electlodes whose surfaces were not pre-treated in any way. Constant sample dimensions were maintained by means of a teflon ring spacer of about 100 μm thickness. Aligned specimens were prepared by cooling the sample from the isotropic phase at a rate of about 0.5°C/min.

RESULTS AND DISCUSSION

The variations of the amplitude of dielectric loss tangent (tan δ) with tempeatre for PM6BP and PM6BP5 are illustrated in Figures 1

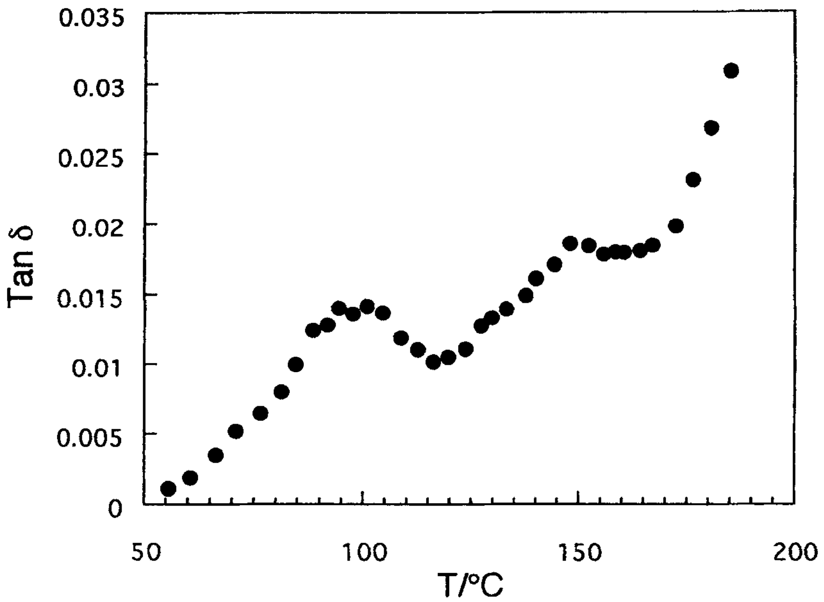


FIGURE 1 Temperature dependence of the dielectric loss tangent at 10 kHz for PM6BP.

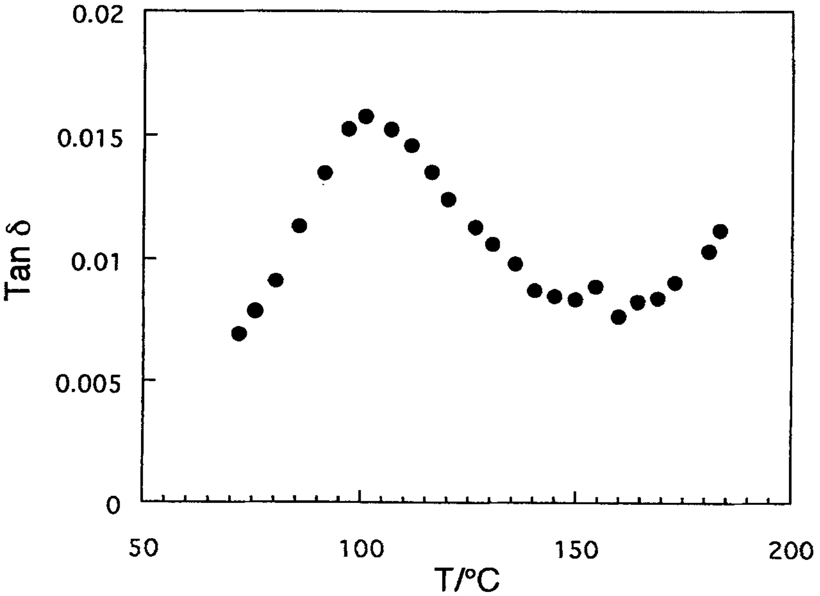


FIGURE 2 Temperature dependence of the dielectric loss tangent at 10kHz for PM6BP5.

and 2. As shown in Figure 1, the peaks of tan δ were obtained for PM6BP at apploximatly 80 and 150°C, respectively. However, that of PM6BP5 at high temperature was absent. The peaks of tan δ peaks obtained at low temperature would be caused by phase transition of these materials as seen in Table I. Cosequently, we considered that this transition phenomena closely related to the orientation of the side chain. Figure 3 shows Arrhenius plots of PM6BP and PM6BP5, respectively. The activation energies obtained from Arrhenius plots for PM6BP are 146.3 and 230.6 kJ/mol for low and high temperature, respectively, and that of PM6BP5 was the same value for low temperature. It agreed closely with that the values for low and high temperature compare with those of δ- and α- relaxation reported by R.Zentel et al.[6] and W.Haase et al.[7] The δ- relaxation reflects the orientational jumps of the long axis of the mesogenic side chain. The observation indicates that the phase transition occures by the incorporation as an additional factor an abrupt change in the state of motion.

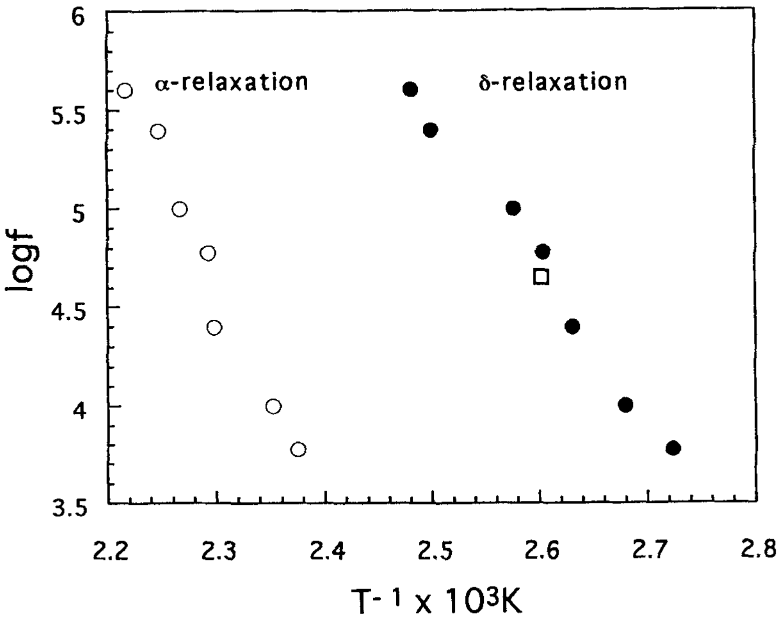


FIGURE 3 Arrhenius plots of α- and δ- relaxations of PM6BP, and PM6BP5. (●): overlapping, (□): PM6BP5.

We are interesting in the estimation of dipole moment for PM6BP and PM6BP5. Figures 4 and 5 show the Cole-Cole plots for the δ -relaxation in PM6BP and PM6BP5, respectively. The values of the relaxed low frequency dielectric constant (ε_r), unrelaxed high frequency dielectric constant (ε_u) is found from Cole-Cole plots (Figures 4 and 5). These values are shown in Table II. The dipole moments of the δ-relaxation in PM6BP and Pm6BP5 are calculated using the Frohlich modification of Onsager's equation[8]:

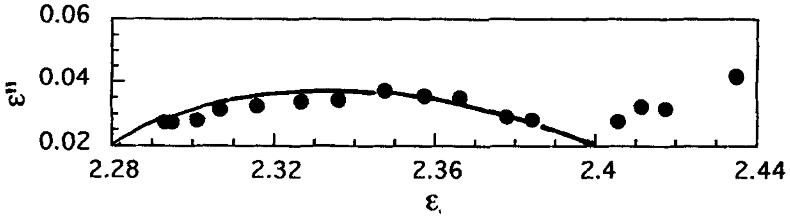


FIGURE 4 Cole-Cole plots for δ-relaxation in PM6BP at 108.7°C.

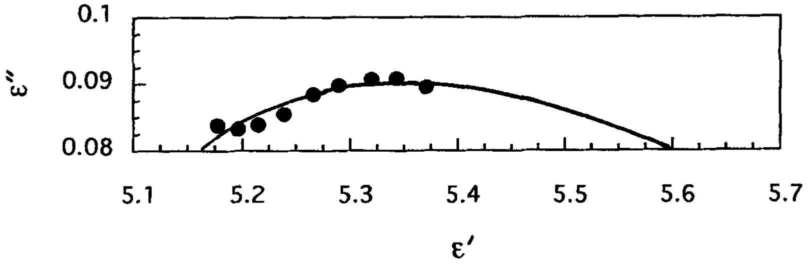


FIGURE 5 Cole-Cole plots for δ-relaxation in PM6BP5 at 106.6°C

$$\mu^2 = \frac{3\kappa T}{4\pi N g}(\varepsilon_r - \varepsilon_u)\left(\frac{2\varepsilon_r + \varepsilon_u}{3\varepsilon_r}\right)\left(\frac{3}{\varepsilon_u + 2}\right)^2 \qquad (1)$$

where μ is diole moment (D), κ Boltzmann's constant, T absolute temperature, N the concentration of dipoles (mol/cm^3), and g the

Kirkwood's factor. The value of N is computed by dividing the density (0.23g/cm^3) by molecular weight of the repeating unit. The g factor is assumed to be unity in this work. These values are summmerized in Table II. As shown in Table II, the dipole moment of PM6BP is about 2.4 D and that of PM6BP5 is about 3.0 D, respectively. The dipole moments for the side chain varied between 3.1 and 4.1 D which consists of a sum of group moment in the side chain.[9] The dipole moment of PM6BP is slightly lower than that of PM6BP5. It suggests that the terminal alkoxy chain would be contributed to the dipole moment.

TABLE II Data of δ-relaxation in PM6BP and PM6BP5.

Materials	T/°C	ε_r	ε_u	μ/D
PM6BP	108.7	2.400	2.280	2.43
	127.3	2.340	2.215	2.23
	160.6	1.930	1.835	2.39
PM6BP5	106.6	5.600	5.150	2.78
	135.5	5.500	5.000	2.95
	164.2	5.325	4.800	3.15

As described above, alignment may be achieved using directing magnetic or electric fields, or by surface force, in conjuction with thermal treatment. In the case of electric field incluced alignment, the response of the materials is dependent on the dielectric anisotropy of materials. This frequency-dependent quantity may be positive or negative as a result of dielectric relaxation of the principle permittivities parallel and perpendicular to the direction axis, respectively. Thus homeotropic or planer alignment may be achieved for liquid crystalline polymers by choice of the frequency of the directing electric field.[10,11] Thus the behavior of liquid crystalline polymers in directing electric fields has its origin in the anisotropic motions of the dipolar groups in the mesophase, which give arise to the dielectric relaxation properties, In this fact, if the homeotropically aligned mesophase is perfect, the director order parameter, Sd is unity, and that of planarly perfect aligned masophase is -0.5. The evaluation of Sd is calculatted using the following equation:[12]

$$Sd = (1/2)\ [(\varepsilon_m'')_{PA,\delta} / (\varepsilon_m'')_{U,\delta} - 1] \qquad (2)$$

where $(\varepsilon_m'')_{PA,\delta}$ and $(\varepsilon_m'')_{U,\delta}$ are maximum dielectric loss factor of partial aligned and unaligned mesophase of δ-relaxation in liquid crystalline polymers. the director order parameter, Sd obtained from Eq.(2) shows as a function of frequency of the aligning field at 100 and 300 volts (rms) for PM6BP and PM6BP5. As seen in Figure 6, the

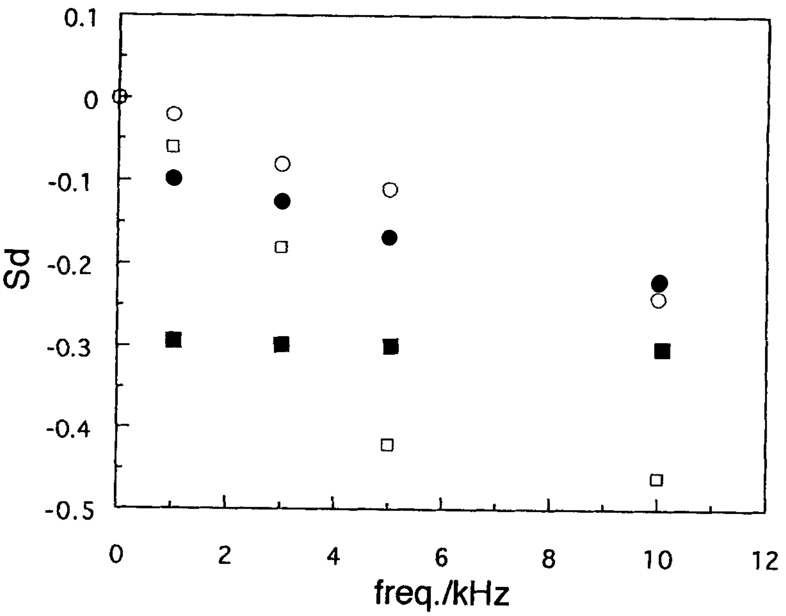


FIGURE 6 The director order parameter,Sd plots as function of frequency of the aligning field.
PM6BP: (○): 100 Vrms; (□): 300 Vrms;
PM6BP5: (●): 100 Vrms; (■): 300 Vrms.

values of Sd for both PM6BP and PM6BP5 are smaller than unity. Consequently, the alignments of both PM6BP and PM6BP5 are changed to partial planer. The alignment of PM6BP changes rapidly to partial planer with 300 V/5kHz and that of PM6BP5 changes rapidly to partial planar with 300 V/1kHz and becomes flatter with more 1kHz. When it is cooled from the melt in the present an a.c. electric field, it may be conclude that the alignments of both materials are planar, in spite of the difference on phase properties in both materials, i.e. SmA , layer spacing= 2.88nm and tilt angle=0° for PM6BP, and SmC, layer spacing=4.65nm and tilt angle 60° for PM6BP5[4],respectively.

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