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

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Version of record first published: 24 Sep 2006

To cite this article: Naoyuki Koide & Kenji Kawamura (2000): Thermal Properties and Ionic Conductivity of Side Chain Type Polyethers with Alkali Metal Salts, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 352:1, 417-427

To link to this article: http://dx.doi.org/10.1080/10587250008023200

Mol. Cryst. and Liq. Cryst., 2000, Vol. 352, pp. 417-427
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Thermal Properties and Ionic Conductivity of Side Chain Type Polyethers with Alkali Metal Salts

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Side chain type polyethers were synthesized by ring opening polymerization of glycidyl ether with p-alkoxyphenyl moiety. A liquid crystalline phase was found at the alkoxy chain length of below 12. A smectic phase was induced for the mixture of the non-mesomorphic polyethers with alkali metal salt, and the mesomorphic temperature range for the mixed system of the polyethers became wider with increasing amounts of alkali metal salt. These mixtures had ionic conductivity. The ionic conductivity of the mesomorphic polyethers with alkali metal salt was larger than that of the non-mesomorphic polyethers with same alkali metal concentration in the whole measured temperature range. Activation energy of the smectic phase region was larger than that of the isotropic phase region. The ionic conductivity of the liquid crystalline polyether with $LiClO_4$ was $5.3\ 8\times10^{-6}Scm^{-1}$ and that of the non-mesomorphic polyether was $4.57\times10^{-7}Scm^{-1}$ at 100°C.

Keywords: ionic conductivity; side chain type polyether; liquid crystalline polymer; alkali metal salt; smectic phase

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INTRODUCTION

Recently, many kinds of ion-conductive polymers have been investigated in view of their theoretical and technical potentialities such as polymer battery, fuel cells, and chemical sensors[1]. The factors influencing ionic conductivity of ion-conductive polymer are configuration of host polymer, ion-dipole interaction, orientation behavior of one direction[2], and dissolving state of ion in its complex. On these backgrounds, series of poly (ethylene oxide) with alkali metal salts were investigated for polymer electrolytes expected for new solid electrolytes[3-5]. These mixtures showed high ionic conductivity and new possibility for the electrochemical reaction [6].

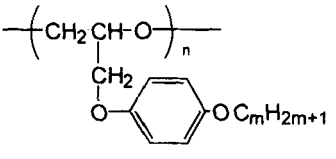
The introduction of ions into polymeric materials is a useful way to establish the supramolecular structure of polymers. Consequently ion- containing polymers produce various changes of physical properties. For example, poly(ethylene oxide) containing ionic species showed ionic conductivity of 10^{-5} Scm^{-1} in the temperature range from 45 to 50°C at the amorphous state. As liquid crystals have both anisotropy and fluidity properties, then, it is anticipated that ion-containing liquid crystalline polymers would enable the conductivity to be enhanced in one direction, possibly by providing channels for ionic conduction, and then anisotropic ionic conduction would exhibit high ion conductivity.

The side chain type liquid crystalline polyethers are considered as a candidate for ion conductive polymers based on their structure of polymer backbone, because their chemical structure of polymer backbone is similar to that of poly(ethylene oxide). The liquid crystallinity and self-assembly behavior of the polyethers with no mesogenic group and no spacer chain are produced by an extra amphiphilic effect [7]. The amphiphilic organization would provide ion channels for ionic conduction in one direction.

We have synthesized non-mesogenic side chain type polyethers without spacer, and complexation of the polyether with alkali metal salt could

induce a mesophase and enhance the thermal stability of the mesophase. The polyethers with p-alkoxyphenyl moiety exhibited a smectic A phase. We have described the mesomorphic behavior and the physical properties of the resulting polyethers complexed with alkali metal salt in a previous publication[8].

The polyethers with p-alkoxyphenyl moiety formed a liquid crystalline phase at the length of the alkoxy chain below 12. The non-mesomorphic polyethers with p-alkoxyphenyl moiety induced a clear smectic phase after adding an alkali metal salt, and these mixtures had ionic conductivity. So in order to clarify the relationship between ionic conductivity and mesomorphic property of the mixtures of side chain type polyethers, as shown in Fig. 1, with various kinds of alkali metal salts, we have carried out AC-impedance measurements, Differential Scanning Calorimetry (DSC) measurements and X-ray diffraction analysis.



PEm (m=2~16)

FIGURE 1 Structure of side chain type polyether

EXPERIMENTAL SECTION

Poly [oxy-1-(4-alkoxyoxyphenoxymethylene) ethylene], PEm (m=2~16), was prepared by ring opening polymerization with a solution of boron trifluoride diethyl ether complex in dichloroethane at -20°C for 16 hour stirring. Then, the mixture was poured into excess methanol to precipitate the polyether. The metal salt used here was lithium perchlorate ($LiClO_4$). The metal salt was used without further purification. Mixture was prepared by drying of mixed solution (acetone and tetrahydrofuran) with the polyether and $LiClO_4$. Ionic conductivities of the mixture were measured using an AC-impedance measurements with the sealed cell by IMPEDANCE / GAIN-PHASE ANALYZER SI 1260 produced by Solartron. X-ray diffraction measurements were conducted on capillary

quartz tube using Rigaku RINT-2500 x-ray diffractometer with Nickel filtered CuKα radiation at 40 kV/ 200 mA.

RESULTS AND DISCUSSION

The monomers of glycidyl ethers didn't show any kind of mesophase. The polyethers having alkoxy chain length between 4 and 12 show a smectic phase and their isotropization temperatures increase and mesomorphic temperature range becomes narrow with increasing alkoxy chain length. However, a smectic phase generated in the non-mesomorphic polyethers having a longer alkoxy chain by adding an alkali metal salt.

In this paper, we discuss two types of polyethers, mesomorphic polyether (PE6, the number denotes the alkoxy chain length for p-position of the benzene ring) and non-mesomorphic polyether (PE16). Degree of polymerization for the obtained polyethers was about 10.

On the thermal property of side chain type polyethers with lithium perchlorate, the transition temperature increases with increasing amounts of $LiClO_4$ for PE6-$LiClO_4$ as shown in Table I. The mesomorphic temperature range for PE6-$LiClO_4$ system is wider than that of PE6. However their textures are the same as PE6.

The phase transition behavior of the PE16-$LiClO_4$ system shows three kinds of

TABLE I Phase transition temperatures of PE16-$LiClO_4$

Ratio of $LiClO_4$ to polymer repeat unit	Phase transition temperatures / °C
0	Cr $\underset{72}{\overset{76}{\rightleftharpoons}}$ I
0.11	Cr $\underset{24}{\overset{35}{\rightleftharpoons}}$ M' $\underset{58}{\overset{64}{\rightleftharpoons}}$ M" $\underset{}{\overset{69}{\rightleftharpoons}}$ Sm $\underset{91}{\overset{91}{\rightleftharpoons}}$ I
0.25	g $\underset{12}{\overset{46}{\rightleftharpoons}}$ M' $\underset{35}{\overset{54}{\rightleftharpoons}}$ M" $\underset{39}{\overset{}{\rightleftharpoons}}$ Sm $\underset{82}{\overset{89}{\rightleftharpoons}}$ I
0.33	g $\underset{28}{\overset{36}{\rightleftharpoons}}$ M' $\underset{49}{\overset{56}{\rightleftharpoons}}$ M" $\underset{65}{\overset{71}{\rightleftharpoons}}$ Sm $\underset{94}{\overset{101}{\rightleftharpoons}}$ I
0.43	g $\underset{25}{\overset{33}{\rightleftharpoons}}$ M' $\underset{37}{\overset{45}{\rightleftharpoons}}$ M" $\underset{51}{\overset{56}{\rightleftharpoons}}$ Sm $\underset{95}{\overset{100}{\rightleftharpoons}}$ I
0.54	g $\underset{27}{\overset{31}{\rightleftharpoons}}$ M' $\underset{38}{\overset{44}{\rightleftharpoons}}$ M" $\underset{49}{\overset{54}{\rightleftharpoons}}$ Sm $\underset{110}{\overset{121}{\rightleftharpoons}}$ I
0.67	g $\underset{26}{\overset{31}{\rightleftharpoons}}$ M' $\underset{39}{\overset{45}{\rightleftharpoons}}$ M" $\underset{49}{\overset{54}{\rightleftharpoons}}$ Sm $\underset{117}{\overset{120}{\rightleftharpoons}}$ I
1.00	g $\underset{30}{\overset{25}{\rightleftharpoons}}$ M' $\underset{40}{\overset{49}{\rightleftharpoons}}$ M" $\underset{48}{\overset{52}{\rightleftharpoons}}$ Sm $\underset{116}{\overset{127}{\rightleftharpoons}}$ I

Cr, solid; g, glassy; M', M": mesophase; Sm, smectic; I, isotropic

mesophase, that is, one phase at higher temperature is exactly assigned to a smectic A phase based upon the focal conic texture, and the others can not be determined exactly with their optical microscopic measurements. Crystal phase is observed at the ratio of $LiClO_4$ to PE16 repeat unit between 0.11 and 0.25, while a glassy phase is observed with increasing ratio of $LiClO_4$ to PE16 above 0.33. The behavior of the transition temperature from glass transition temperature to mesophase for PE16-$LiClO_4$ is different from that for PE6-$LiClO_4$. These differences would result from consuming of $LiClO_4$ in order to form the liquid crystalline phase for the non-mesomorphic polyether (PE16). The distinction of the phase temperatures for PE6-$LiClO_4$ and for PE16-$LiClO_4$ would arise from the difference of the mesomorphic capability for two kinds of the polyethers itself, because the neat PE6 shows a smectic phase, while neat PE16 do not show any mesophase.

X-ray diffraction patterns of PE16-$LiClO_4$ (0.67) at heating cycle are shown in Fig. 2. Upper diffraction pattern was measured at 20°C, and lower one was measured at 140°C with each intervals of 10°C. All diffraction patterns show a characteristic smectic phase with a sharp peak in the small angle region around 2° and with a broad peak at the wide angle region around 20°. However, the sharp peak at the small angle region is shifted to the wide angle side on heating cycle. In the same way, the sharp peak in the small angle region is shifted to the small angle region on cooling cycle.

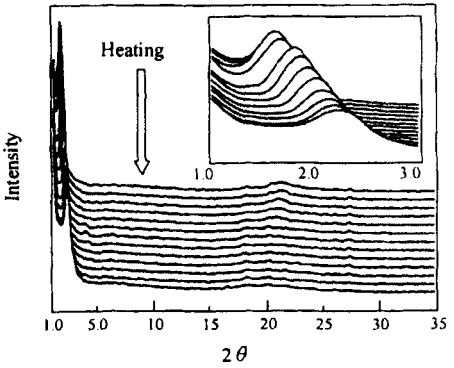


FIGURE 2 X-ray diffraction patterns of PE16-$LiClO_4$(0.67)

Fig. 3 shows a d-spacing of the sharp peak in the small angle region

at different temperatures. The d-spacing at the smectic A phase decreases from 55 Å to 41 Å on heating, and increases from 40 Å to 52 Å on cooling. It is clear that a d-spacing of ~55 Å at the lower temperature is approximately twice the length of the side chain in its most extended conformation as calculated by assuming standard bond lengths, angles and van der Waals radii. These results are consistent with the formation of a "bilayer" smectic A phase. This phenomenon is induced by adding the lithium perchlorate and is also related to the mesomorphic property.

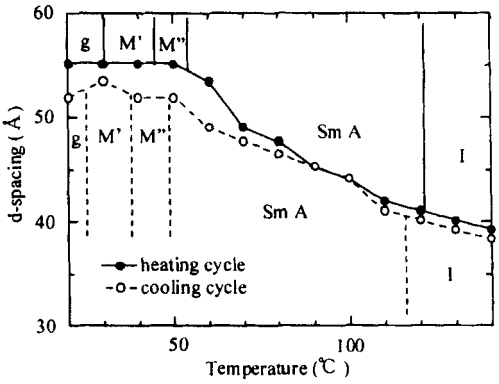


FIGURE 3 Temperature dependence of layer spacing for PE16-$LiClO_4$ from X-ray diffraction patterns

The self-assembly of the bilayer structure for these mixtures can arise from the interaction of the hydrophilic layer (polyether backbone) and the hydrophobic layer (p-alkoxyphenyl group) like a lyotropic liquid crystal. So PE6 shows a smectic phase without a mesogen group, and PE16 shows an induced smectic phase by adding alkali metal salts. Influence of adding alkali metal salt to PE16 to give rise to mesophase is also supported by change of the order of methylene chain in the side chain from thermal variable Raman spectroscopy measurements[8].

The significant shortening of d-spacing with decreasing temperature would be interpreted by the interdigitation of alkyl chains. However M' and M" phase could not be assigned to the characteristic mesophase because of the unclear texture at this temperature range.

Surprisingly, the sharp peak in the small angle region do not disappear even at the isotropic phase at X-ray diffraction of the mixture for PE16 and lithium perchlorate. The results of the sharp diffraction pattern at the isotropic phase would be interpreted by the phase separation of the hydrophilic layer and the hydrophobic layer, consisting of liquid state at the isotropic phase. However, this mixture does not show any texture by polarized optical microscopic measurements beyond the clearing temperature at 121°C. This clearing temperature is determined by DSC measurements.

Ionic conductivity of the four mixtures was determined by curve fitting of the complex impedance diagram and AC-impedance measurements with thermo-controlled. Ionic conductivity of polymer electrolytes is sensitive to temperature, because one of the origins of ionic conductivity is one of the mass transfers, such as transportation of the cation and the anion of the salt.

With the possible exception of some of the data for these mixed systems, plots of the log σ against reciprocal temperature are curved, and the data can not be described by the Arrhenius equation. The results are more accurately represented by the empirical Vogel-Tamman-Fulcher(VTF) equation(1)

$$\sigma(T) = AT^{-1/2} \exp [-B/(T-T_0)] \quad (1)$$

where A is a constant, B is a constant, but has been regarded

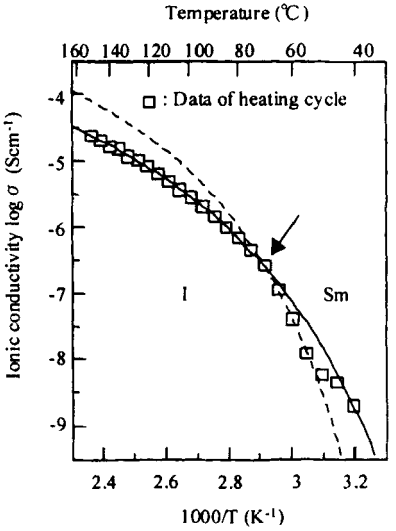


FIGURE 4 Best-fit VTF curve for the temperature dependence of the ionic conductivity for PE6-$LiClO_4$(0.11)
solid line : best-fit curve for isotropic phase
broken line : best-fit curve for smectic phase

as being related to an apparent activation energy, and T_0 can be taken as the temperature at which the configuration entropy in the system approaches zero[9-11]. The data were analyzed in terms of WLF equation(2)[13]:

$$\log_{10}[\sigma(T)/\sigma(T_g)]=[C_1(T-T_g)] / [C_2+(T-T_g)]. \qquad (2)$$

The values of C_1 and/or C_2 are closed to universal values of 17.4 and 51.6. The data were analyzed via the VTF equation (1) which is analytically identical to the WLF equation with

$T'_0 = T_g - C_2$, $E'_a = 2.303C_1C_2$, and $\ln A' = 2.303C_1 + \ln\sigma(T_g)$.

The VTF equation parameters were obtained from nonlinear fits by substitution these values to the equation (1)[14]. Although T_0 is not accessible experimentally it is normally assumed to have a value of ~50K below Tg. Alternatively one can use an experimental Tg as an approximation for T_0.

Ionic conductivity of the mixture of the mesomorphic polyether (PE6) with lithium perchlorate (0.11) is shown in Fig. 4. Open-squares are ion-conductivity data from AC-impedance measurements at the 1st heating cycle, and the solid line is the best-fit VTF curve for isotropic phase, and broken line is best-fit VTF curve for the smectic phase. At the isotropic phase, heating data is in good agreement with the VTF equation, but heating data of the smectic phase differs with the VTF equation of the isotropic phase. This phe-

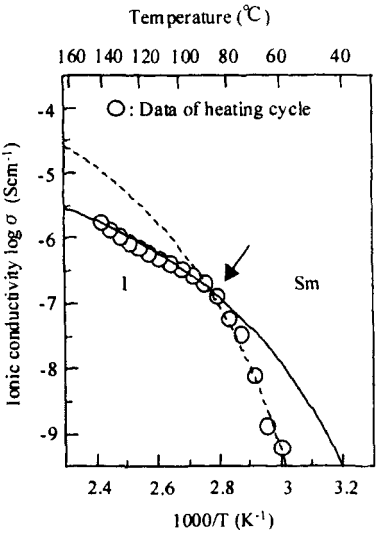


FIGURE 5 Best-fit VTF curve for the temperature dependence of the ionic conductivity for PE16-$LiClO_4$(0.11)
solid line : best-fit curve for isotropic phase
broken line : best-fit curve for smectic phase

nomenon would demonstrate that the ionic conductivity of the smectic phase do not perfectly follow ionic conductivity due to the VTF equation. Therefore, the best-fit VTF parameters of both phases are different from each other, and both slopes for the measured data are different from the transition temperature from the smectic phase to the isotropic phase determined by DSC measurements, suggested by an arrow in the Fig.4.

The ionic conductivity of PE16-$LiClO_4$ (0.11) was measured for the same salt concentration as for the mixture of the non-mesomorphic polyether with lithium perchlorate as shown in Fig. 5. Open-circles are ion-conductivity data from AC-impedance measurements for the 1st heating cycle, and the solid line is the best-fit VTF curve for the isotropic phase and the broken line is the best-fit VTF curve for the smectic phase. For PE16-$LiClO_4$ (0.11), the heating data of the isotropic phase and the smectic phase do not coincide with the VTF equation of the isotropic phase of PE6-$LiClO_4$ (0.11). This behavior of the measured data resembles an ionic conductivity of crystals at high temperature based on the change of slope at the phase transition[12]. Thus the VTF parameters of the smectic phase are different in the isotropic phase for PE16-$LiClO_4$ (0.11). The change of slope is clear as shown in Fig. 5, and this change coincides with the clearing temperature determined by DSC measurements.

The relevant VTF parameters are gathered in Table II, where Ea is the activation energy. For both of the mixtures, activation energies of the smectic phase are larger than those of the isotropic phase. This could mean that the layer-structure of the smectic phase plays an important effect on the ion transport. The difference of the activation energy of PE16-$LiClO_4$ (0.11) is larger than that of the activation energy of PE6-$LiClO_4$ (0.11), and the results are supported by the distinction in density of the ion conductive part in a matrix. T_0 is found to be about ~44°C below Tg determined by DSC measurements in all cases.

TABLE II Best-fit VTF parameters of PE6-$LiClO_4$(0.11) and PE16-$LiClO_4$(0.11)

Sample		A	Ea/eV	T_0/K	Tg/K
PE6-$LiClO_4$ (0.11)	whole	0.0721	7.05E-2	259.08	
	Isotropic phase	0.0680	6.90E-2	260.71	303
	Smectic phase	0.4269	7.09E-2	270.81	
PE16-$LiClO_4$ (0.11)	whole	0.0088	7.00E-2	269.37	
	Isotropic phase	0.0036	6.12E-2	260.22	296
	Smectic phase	0.1495	7.48E-2	280.55	

CONCLUSION

Non-mesomorphic polyethers with alkali metal salts exhibited the smectic A phase, and their thermal stabilities of the mesophase are enhanced. The layer spacing of the smectic phase decreased with heating from 55 Å to 41 Å, and increased with cooling. Ionic conductivity of the mesomorphic polyethers with alkali metal salt was larger than that of nonmesomorphic polyether with the same salt concentration in whole measured temperature range. Activation energy of the smectic phase region was larger than that of the isotropic phase region in all mixtures. The calculated T_0 was found to be about ~44°C below the *Tg* determined by DSC measurements in the all cases.

Acknowledgments

This work was supported partly by a Grant-in-Aid for Scientific Research on Priority Areas of the Ministry of Education, Science, Sports and Culture, Japan (No 10650872)

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