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: 04 Oct 2006

To cite this article: Kenji Kawamura, Tadahiro Kikuchi & Naoyuki Koide (1998): Mesomorphic Properties of Side Chain Type Polyethers Containing Metal Salts, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 318:1, 87-100

To link to this article: http://dx.doi.org/10.1080/10587259808045377

Mol. Cryst. Liq. Cryst., Vol. 318, pp. 87–100
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Mesomorphic Properties of Side Chain Type Polyethers Containing Metal Salts

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Polyethers with p-alkoxyphenyl groups in the side chain (PEn) were prepared by ring opening polymerization of the corresponding glycidyl ether derivatives. These polyethers exhibited highly ordered smectic phase depending upon the alkoxy chain length. A liquid crystalline phase was formed at the alkoxy chain length of below 12. The mesomorphic properties for the mixed system were originated from adding an alkali metal salt into the non-mesomorphic side chain type polyethers. The mesomorphic temperature range for the mixed system was wider with increasing amount of alkali metal salt. The occurrence of the complexed the side chain type polyethers with the alkali metal salt was confirmed by Raman spectroscopy and X-ray photoelectron spectroscopy measurements (XPS).

Keywords: side chain type polyether, alkali metal salt, smectic phase, Raman spectroscopy, X-ray photoelectron spectroscopy

INTRODUCTION

Generally, side chain type liquid crystalline polymers (SLCPs) compose with polymer backbone, spacer and mesogen. The role of spacer, such as alkyl chain, siloxane or ethylene oxide to be considered is that the molecular mobility between the

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mesogenic group and polymer backbone can be minimanized. Consequently, the mesogenic groups in the side chain of the polymer acts like a similar orientational behavior to the low molecular weight liquid crystal compounds and then, SLCPs would be considered as a candidate of high functional polymers. The spacer length and the end group of the mesogen play an important role in the stability of the oriented state of the liquid crystalline phase. However, in our previous paper, although a series of polyethers consisted for poly(glycidyl ether)s having p'-substituted –biphenyl or phenyl moieties did not contain a flexible spacer in the side-chain, the polyether exhibited a highly ordered smectic phase[1-2]. This result shows that the molecular mobility of the polymer backbone and selected mesogenic group are important factors to arise the mesophase for the SLCP[3].

Moreover, the polyethers with nonmesogenic p-alkoxyphenyl group in the side-chain exhibited a smectic A phase with structure of bilyer, and a liquid crystalline phase was formed at the alkoxy chain length of below 12. The self-assembly of bilayer structures can be arisen from the interaction of hydrophilic layer (polyether backbone) and hydrophobic layer (p-alkoxyphenyl group) like a lyotropic liquid crystal.

On the other hand, many kinds of ion conductive polymers have been investigated in view of their theoretical and technical potentialities such as polymer battery. Most of ion conductive polymers have a polyether structure, and ion conduction is attributed to highly dissociative alkali metal salts in the matrix[4]. The side-chain type liquid crystalline polyethers are also considered as a candidate for ion conductive polymers based on the their chemical structure of polymer backbone.

Surprisingly, non-mesogenic polyethers having the alkoxy chain length of

beyond 12, a smectic phase was arisen from adding a metal salt, and the complexed mesomorphic polyethers show high ionic conductivity[4]. With origination the mesophase, it can be considered that complexation of polyether with alkali metal salts can yield a moderate chain mobility of the polymer backbone and then complexed polyether would be easily formed a self-assembly layer structure. This behavior was also demonstrated by the recent publication on polyethylene oxide with flexible side chain groups which show a induced smectic lamellar mesophase by complexation of polymer backbone with $LiClO_4$[5].

In this paper, we describe the mesomorphic behavior and the physical properties of the resulting polyethers complexed with the alkali metal based on polarized optical microscopy, differential scanning calorimetry, FT-Raman spectroscopy and XPS measurements.

EXPERIMENTAL SECTION

Characterization

^{1}H-NMR was performed with a JEOL JNM-PMX60 spectrometer using $CDCl_3$ as the solvent. Infrared spectra were recorded on a JEOL JIR-100 spectrometer. Spectra were collected at 4cm^{-1} resolution. DSC measurements were conducted with a Perkin Elmer DSC 7 instrument equipped with DEC 325C personal workstation at rate of 5°C/min, employing a flow of dry nitrogen as a purge gas for the sample and reference cells. Gel permeation chromatography (GPC) was carried out with a Tosoh HLC-8020 instrument using chloroform as the eluent. The instrument was calibrated with a polystyrene standard. Optical microscopy was performed on a

Nikon polarizing optical microscopy equipped with a Mettler FP80 controller and a FP82 hot stage. The preparation of the sample cell was carefully sealed with epoxy resin in order to prevent the moisture.

FT-Raman spectroscopy and XPS measurements

The spectra of the mixed system of PE6 or PE16 with alkali metal salts were measured at $2cm^{-1}$ resolution with a JEOL JIR-7000FT-IR RSU-200 Raman spectrometer equipped with an InGaAs detector at variable temperature. Excitation radiation of a cw Nd:YAG laser ($1064cm^{-1}$) was used. The excitation laser power was controlled to fit on the sample during a spectral measurement. For XPS measurements, the photoelectron takes-off direction was normal to the sample surface and then the pass energy was 20eV. XPS analysis with MgK α X-ray(1253.3eV) excitation was the AXIS-HS (Shimadzu KRATOS) system.

Synthesis of intermediates

4-Benzyloxy-4'-hexadecanoxyphenyl

A mixture of 1-bromohexadecane (17g, 56mmol), 4-benzyloxyphenol (9.2g, 46mmol), KOHaq (4.2g, 75mmol) and a small amount of potassium iodide in THF (150ml) was refluxed for 18h. The solvents were distilled off with rotary-evaporator, and then the residue was washed with water and with ethanol at twice. Yield 18.3g (94%).

^{1}H-NMR ($CDCl_3$) : δ 7.5, 7.0(d, 9H, Ar-H), 5.1(s, 2H, -OCH_2-Ar), 4.0(t, 2H, -OCH_2-CH_2-), 1.3(s, 28H, -CH_2-), 0.9(t, 3H, -CH_3)

4-Hexadecanoxyphenol

4-Bezyloxy-4'-hexadecanoxyphenyl (18g, 54mmol) and 10% Pd-C(3.5g) with THF(150ml), ethanol(80ml) and a small amount of HClaq was stirred in three neck round-bottom flask under H_2-atmosphere for 4h. The reaction mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure. The residue was purified by recrystallization with hexane to give 17.2g (95%) of 4-hexadecanoxyphenol as white plates.

^{1}H-NMR ($CDCl_3$) : δ 6.8(s, 4H, Ar-H), 4.7(s, 1H, -OH), 3.9(t, 2H, -OCH_2-), 1.3(m, 28H, -CH_2-), 0.9(t, 3H, -CH_3)

Synthesis of glycidyl ether monomer (GEn, n denotes alkoxy chain length)

Each of the glycidyl ether monomers was prepared from the corresponding p-substituted alkoxyphenol derivative and excess epichlorohydrin with sodium hydroxide as base. Epichlorohydrin was mixed with 4-hexyloxyphenol(10g, 51mmol). Sodium hydroxide (4.4g, 110mmol) was added to the mixture. Then the reaction mixture, alkoxyphenol, sodium hydroxide, epichlorohydrin and THF was refluxed at 100℃ for 3h. The solvent and excess epichrolohydrin were distilled off. The residure was purified by column chromatography on silica gel with chloroform as eluent to afford 9.0g (70%) of GE6.

GE6: ^{1}H-NMR ($CDCl_3$) : δ 6.8(s, 4H, Ar-H), 4.3-3.8(m, 4H, -CH_2O-), 3.3(m, 1H, -CH(O-)-), 3.0-2.7(m, 2H, (CH_2-O)-), 1.8-1.2(m, 8H, -CH_2-), 0.9(t, 3H, -CH_3)
IR (KBr disk) : 2950, 2930, 2855, 1510, 1285, 1240, 1110, 1030, 912cm^{-1}

GE16: ^{1}H-NMR ($CDCl_3$) : δ 6.9(s, 4H, Ar-H), 4.2-3.8(m, 4H, -CH_2O-), 3.3(m, 1H, -CH(O-)-), 3.0-2.7(m, 2H, (CH_2-O)-), 1.8-1.2(m, 28H, -CH_2-), 0.9(t, 3H, -

CH_3)

IR (KBr disk) : 2954, 2818,2848, 1514, 1290, 1243, 1113, 1036, 912cm^{-1}

Polymerization

The polymer was prepared by polymerization of the monomer 1.0g(1.0eq) in a three-neck round-bottom flask under the N_2 atmosphere. GE6 was dissolved in 10ml of dry 1,2-dichloroethane under a nitrogen atmosphere. In the case of GE16, the monomer was dissolved in dry dichloromethane. Cooling the flask to become -20°C, finally, boron trifluoride ethyl ether complex (0.01eq) diluted with solvents was added, and the mixture was stirred at -20°C for 16 hours. Then the mixture was poured into c.a.300ml of methanol to precipitate the polymer. The polymer was dissolved in THF and reprecipitated with methanol by two times. The polymer was dried under vacuum.

RESULTS AND DISCUSSION

The monomers of glycidyl ethers didn't show any kind of mesophase, while the polyethers having alkoxy chain length between 4 and 12 showed a smectic phase and their isotropization temperatures increased and mesomorphic temperature range became narrow with increasing alkoxy chain length. However, a smectic phase was arisen in nonmesogenic polyethers having a longer alkoxy chain by adding an alkali metal salt.

In this paper, we discuss the two types of polyethers, mesomorphic polyether (PE6) and nonmesomorphic polyether (PE16). The obtained polyethers were

oligomer whose degree of polymerization of about 10.

Thermal properties of PEn · $LiClO_4$ system

The typical polarized optical micrographs of PE16-$LiClO_4$ (0.43) are shown in Fig.1. A focal conic texture characteristic of a smectic A phase was observed at 81℃, as shown in Fig.1(a). The texture was changed to obscure texture with cooling as shown in Figs.1(b) and 1(c), respectively. And the mesomorphic state was preserved at room temperature.

A typical DSC curve is shown in Fig.2. The mesomorphic properties for PE6-$LiClO_4$ were detected between glass transition temperature and isotropic temperature, as shown in Fig.2 (a), whereas there were three kinds of mesophases for PE16-$LiClO_4$ in Fig.2 (b).

FIGURE 1 Optical micrograph of PE16-$LiClO_4$(0.43)

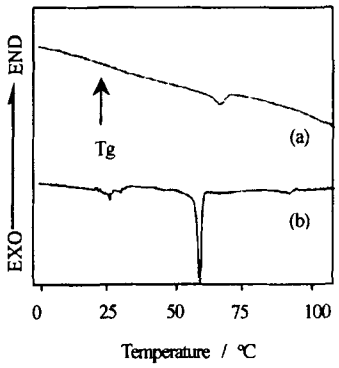

FIGURE2 DSC curves of PEn with $LiClO_4$ on cooling run (a) PE6-$LiClO_4$(0.11) (b) PE16-$LiClO_4$(0.11)

The transition temperature increased with increasing amounts of $LiClO_4$ for PE6-$LiClO_4$(0.2), whereas that from a smectic to isotropic fluid increased with increasing amounts of mesomorphic temperature range for PE6-$LiClO_4$ system was

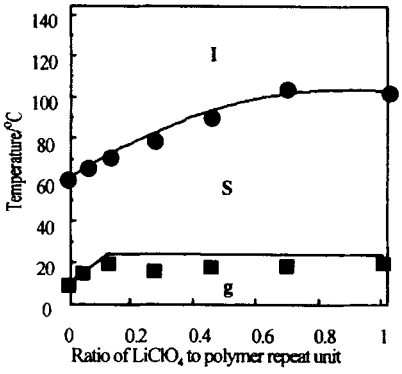

FIGURE 3 Phase transition diagram of PE6-$LiClO_4$ by DSC measurement.
I:isotropic, S:smectic, M:mesophase, g:glassy, K:crystal

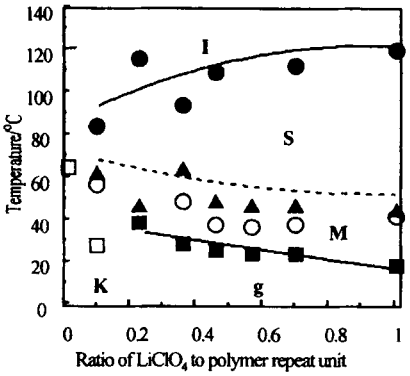

FIGURE 4 Phase transition diagram of PE16-$LiClO_4$ by DSC measurement.
●:T_{S-I} ■:T_{g-M} ▲:T_{M-S} ○:$T_{M-M'}$, □:T_{K-I},T_{K-M}

wider than that of PE6. However the optical texture of PE6-$LiClO_4$ was the same as PE6.

The phase transition behavior of the PE16-$LiClO_4$ system is shown in Fig.4. As shown in Fig.4, there were three kinds of mesophase, one phase at higher temperature range was exactly assigned to a smectic A phase based upon the focal conic texture, the others could not determined exactly the phase with their optical microscopic measurements. A crystalline phase was observed at the ratio of $LiClO_4$ to PE16 repeat unit between 0.11 and 0.25, while a glassy phase was observed with increasing ratio of $LiClO_4$ to PE16 above 0.33. The behavior of the transition temperature from a glassy to a mesophase for PE16-$LiClO_4$ was different from that

for PE6-$LiClO_4$, as shown in Figs.3 and 4, respectively. These differences would result from consuming $LiClO_4$ in order to form the liquid crystalline phase for nonmesogenic polyether derivatives of PE16. We thought that the difference of PE6-$LiClO_4$ and PE16-$LiClO_4$ for transition temperature would be arisen from the difference of two kinds of polyether itself, because the neat PE6 showed a smectic phase, while neat PE16 did not show a mesophase.

Raman and XPS measurements

We have investigated the PEn-$LiClO_4$ system at elevated temperature by Raman spectra and XPS in order to clarify the origin of the formation of the mesophase for the mixed system and degree of ion association situation of the salt in the polymer. The symmetric stretching modes of perchlorate anion were chosen for a detail investigation. The spectra for $LiClO_4$, PE6, and PE6-$LiClO_4$ contents are displayed in Figs.5 and 6, respectively. The symmetric stretching mode for the anions in the polyether complexed with lithium perchlorate at an ether oxygen of alkali metal have been studied as a function of polyether and lithium perchlorate ratio using Raman spectroscopy. As shown in Fig.5, two components band analysis led to the identification of a mode in the lithium complex at 940cm^{-1} due to the vibration of free perchlorate anion and another mode

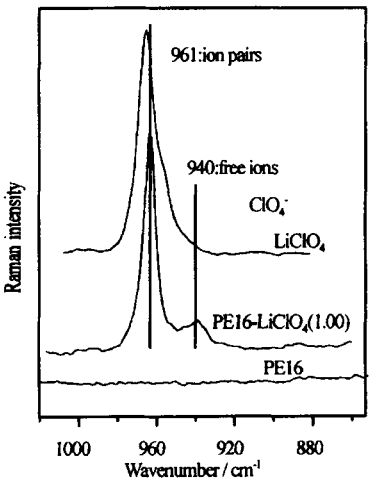

FIGURE 5 Raman spectra of $LiClO_4$, PE16-$LiClO_4$ and PE16 on room temperature.

of 961cm^{-1} due to contact ion pairs of lithium cation and perchlorate for PE16-$LiClO_4$ system. However, with comparing the intensity ratio of a perchlorate anion mode at 940cm^{-1} and an anion ion pair mode for 961 cm^{-1} between PE6-$LiClO_4$ and PE16-$LiClO_4$, the intensity of ion pairs for PE16-$LiClO_4$ is larger than that for PE6-$LiClO_4$. These difference would be explained that most of the lithium cation combines with polyether backbone for PE16 in order to arise the polyethylene oxide sodium cation

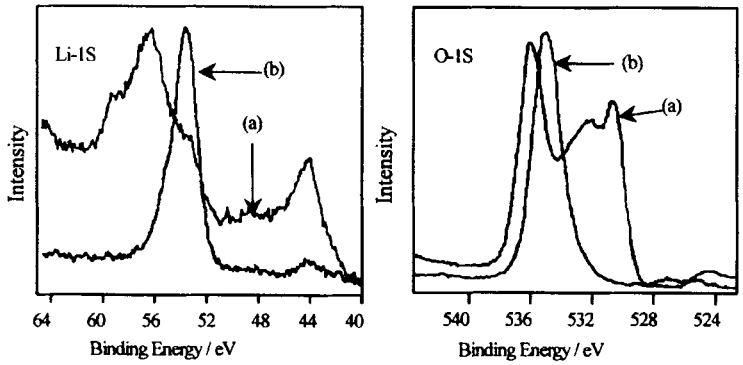

FIGURE 6 XPS spectra of PE6-$LiClO_4$ (a) $LiClO_4$ only (b) PE6-$LiClO_4$ (1.00)

helix[6], and then the self-assembly can be formed in the complexed polyethers.

The shift of the peaks for Li-1S and O-1S was observed in the PEn-$LiClO_4$ by XPS measurements, as shown in Fig.6. This shift to the lower binding energy for Li-1S and O-1S was occurred the dissociation of lithium perchlorate and complexation polyether backbone with lithium ion. Changes in the environment of hydrocarbon chains of the polyether derivatives gave strong effects on the C-H stretching vibration region of the Raman spectra.

Thus, we thought that the appearance of the liquid crystalline phase for PE16-

$LiClO_4$ was also related to the ordered methylene chain of alkoxy groups in the side chain similar to the lyotropic liquid crystals. So we have examined the order of the

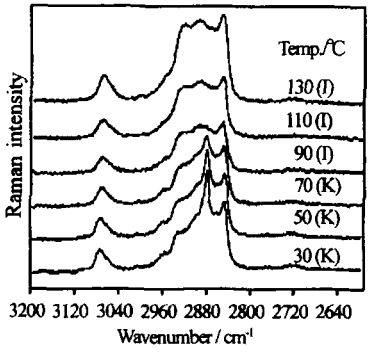

FIGURE 7 Thermal variable Raman spectra of PE16 on heating.

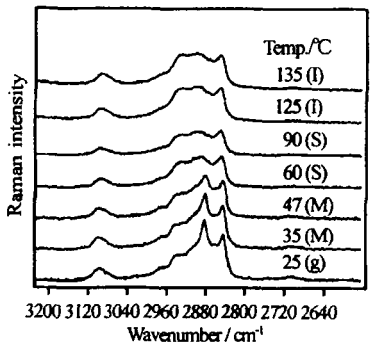

FIGURE 8 Thermal variable Raman spectra of PE16-$LiClO_4$ on heating.

methylene chain by thermal variable Raman spectroscopy. In order to clarify the conformation of the methylene chains in the mesopahse, the Raman spectra for 2640 to 3200cm^{-1} regions were measured with temperature dependence as shown in Fig.7. In the solid state there are two dominating peaks at 2885cm^{-1} and 2850cm^{-1}, however, in the isotropic phase the peak at 2885cm^{-1} disappears. After adding the lithium perchlorate to PE16, the spectrum pattern is similar to that of PE6 which exhibited smectic phase without alkali metal salts.

Raman spectra of PE16 and the PE16-$LiClO_4$ on a heating scan from room temperature to isotropic phase is shown in Fig.8. In thermal variable Raman spectra of PE16, the sharp peak was observed nearby 2885cm^{-1} on the crystal state, but this peak was broad on isotropic phase. In the case of PE16-$LiClO_4$, the peak of nearby 2885cm^{-1} was sharp at the lower two mesophases until 47°C, whereas with the high temperature region about 60°C corresponding a smectic phase, the peak of 2885cm^{-1}

was broad. Although the sharp peak of 2885cm^{-1} was changed to a broadness with different peak positions between mesophase and isotropic state, then we can demonstrate that an appearance of the mesophase for PE16 is deeply dependent upon the disordered state of methylene chian supported by conventional lyotropic liquid crystals[7].

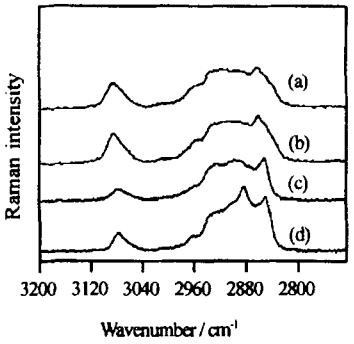

FIGURE 9 Raman spectra of PE6, PE16 and complex mixtures.
(a): PE6-$LiClO_4$(0.67) (Smectic)
(b):PE6 only (Smectic)
(c): PE16-$LiClO_4$ (0.67) (Smectic)
(d):PE16 only (glassy)

To clarify about the correlation for state in ordered methylene chain between liquid crystalline phase of PE6 and PE16, we have compared Raman spectrum in liquid crystalline phase of PE6 with PE16, as shown in Fig.9. The peak of 2885cm^{-1} was broad for the PE6 independent of addition of lithium perchlorate in PE6. While for the PE16, the sharp peak was observed at 2885cm^{-1}. However the peak was broad by addition of lithium perchlorate. These results would be supported that appearance of the liquid crystalline phase for the PE6 and the PE16 can be related to the state in disorder of methylene chain, as already disscussed in the enviornment of hydrocarbon chains of lipid molecules[7].

The complex polyethers are sensitive to the moisture as shown in Fig.10. The time dependence of the Raman spectra of free perchlorate anion and lithium complex band intensity was a dramatic change with the saturation in the moisture atmosphere. We have found that the ion paired anion and the free perchlorate anion can be easily

detected by Raman spectroscopy. However, the peak intensity of 961cm^{-1} decreased with time in the moisture atmosphere, while that of 940cm^{-1} increased. So, it was necessary to carry out for these polyethers in the absence of water in order to clarify an amount of the two detected species.

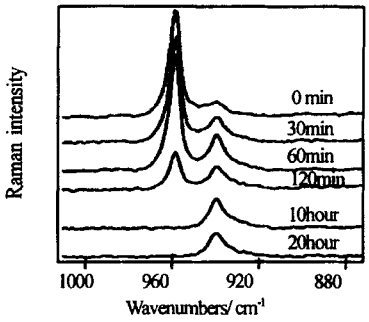

FIGURE10 Time dependence of Raman spectar for PE16-$LiClO_4$ in the moisture atomosphere

CONCLUSION

Polyethers with p-alkoxyphenyl group in the side chain exhibited a smectic A phase which formes a bilayer structure. A liquid crystal phase was formed at the length of alkoxy chain below 12. For nonmesogenic polyethers having alkoxy chain length beyond 12, a smectic phase was induced by adding an alkali metal salt. An induced smectic lamella mesophase can be explained by the complexation of the polyether with the alkali metal salt based upon Raman and X-ray photoelectron spectroscopy.

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