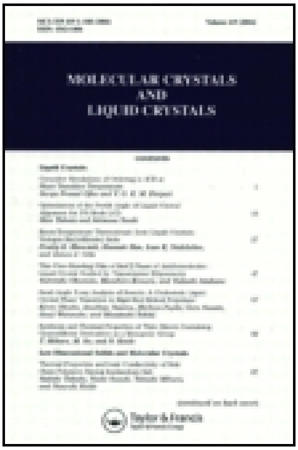

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Thermal and Ionic-Conductive Behaviors of Main Chain Type Liquid Crystalline Polymers with Lithium Salt

Yosuke Akachi [a] & Naoyuki Koide [a]

[a] Department of Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, JAPAN

Version of record first published: 27 Oct 2006

To cite this article: Yosuke Akachi & Naoyuki Koide (2001): Thermal and Ionic-Conductive Behaviors of Main Chain Type Liquid Crystalline Polymers with Lithium Salt, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 427-437

To link to this article: http://dx.doi.org/10.1080/10587250108025322

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 427-437
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Thermal and Ionic-Conductive Behaviors of Main Chain Type Liquid Crystalline Polymers with Lithium Salt

YOSUKE AKACHI and NAOYUKI KOIDE*

Department of Chemistry, Faculty of Science, Science University of Tokyo 1–3 Kagurazaka, Shinjuku-ku, Tokyo 162–8601, JAPAN

Two types of the main chain type liquid crystalline polymer were synthesized and measured ionic conductivity. One of the polymers exhibited a smectic phase. The mixture with lithium salt at the ratio of 0.04 per repeating unit also exhibited a smectic phase. However, the mixture with lithium salt (0.11) showed a nematic phase. Ionic conductivity of the mixture with lithium salt (0.11) was larger than that of the mixture with lithium salt (0.04).

The trans type polymer exhibited a liquid crystalline phase, while the cis type polymer didn't show. We found that the ionic conductivity of the trans type polymer with lithium salt mixture (0.11) was larger than that of the cis type polymer with lithium salt mixture (0.11) Moreover, the ionic conductivity of the ceramic-polymer with lithium salt composite was larger than that of the ceramic-free polymer with lithium salt.

The other polymer showed a nematic phase. The mixture with lithium salt (0.04) or (0.11) also exhibited a nematic phase. Ionic conductivity of the polymer with lithium salt mixture (0.11) was smaller than that of the polymer with lithium salt mixture (0.04).

Keywords: ionic conductivity; liquid crystalline polymer; nematic phase; smectic phase; cis-trans isomerization

---

* To whom correspondence should be addressed.

INTRODUCTION

Ionic conductive polymers are expected to be applied to a polymer battery and a paper battery as prominent materials of solid polymer electrolytes.[1-4] Ionic conductive polymers have a structure of soft materials dissolve alkali metal salts and dissociated ions in the matrix. Consequently, ionic conductive polymers generally require low glass transition temperature (T_g) and high polar amorphous structure to transfer dissociated ions.[5] In particular, poly (ethylene oxide) (PEO) is well known as an ionic conductive polymer. The ionic conductivity of the mixtures for PEO with alkali metal salt has been studied intensively to ascertain the origin and the mechanism of their high ionic conductivities.[6-8]

On the other hand, a liquid crystal phase exists between a crystal state and a liquid state like an amorphous state. By bonding a mesogenic group to the polymer backbone for the ionic conductive polymer, we can succeed in the ionic conductive polymer with a liquid crystalline phase.

In the previous work, we investigated about the relationship between the liquid crystallinity and the ionic conductivity for the mixtures of the side chain type polyethers-alkali metal salt.[9] Consequently, we found that ionic conductive behavior of the liquid crystalline polymer is different from that of polymer in the vitreous state.

However, the ionic conductive behavior in the liquid crystal region is not yet fully understood. It is important to accumulate a fundamental data of the ionic conductivity in the liquid crystal region.

In this study, we prepared the two kinds of main chain type liquid crystalline polymers having ethylene oxide chain in the repeating unit (MCLCP-1), (MCLCP-2), as shown in Figure 1 and 2, respectively. The MCLCP-1 exhibited only a smectic phase. However, the

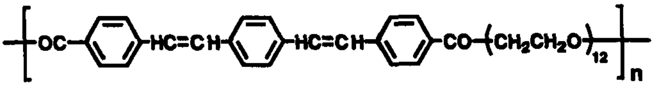

FIGURE 1 Structure of main chain type polymer-1 (MCLCP-1)

mesomorphic phase of the MCLCP-1/$LiClO_4$ mixture deeply depend on the content of $LiClO_4$. The mixture with $LiClO_4$ at the ratio of 0.04 per polymer repeating unit exhibited a smectic phase and the mixture with $LiClO_4$ at the ratio of 0.11 showed a nematic phase.

In short, this mixture shows the different liquid crystal phases with changing the salt concentration. Therefore, we can investigate the relationship between a liquid crystal phase structure and ionic conductive behavior.

The other characteristic of this polymer is to occur cis-trans isomerization by I_2 or UV irradiation, because the mesogenic unit has a bisstyrylbenzene group. The trans type polymer exhibited a liquid crystalline phase, while the cis type polymer showed only glass transition temperature. Therefore, we can investigate how ionic conductivity in the liquid crystal state is different from that in the vitreous state.

On the other hand, introducing ceramic powders with nanometer-sized grains to a polymer electrolyte would improve mechanical strength, conductivity, and interfacial properties.[10-12] In particular, it has recently shown ionic conductivity of a PEO/$LiClO_4$/ceramic composite electrolyte was larger than that of a ceramic-free PEO/$LiClO_4$ electrolyte.[13, 14] Therefore, we have also prepared the MCLCP-1/$LiClO_4$ mixture adding ceramic powder to improve the conductivity in the liquid crystalline state.

The MCLCP-2 exhibited only a nematic phase. The mixture with lithium salt at the ratio of 0.04 or 0.11 per polymer repeating unit also exhibited a nematic phase. We investigated about ionic conductivity in the liquid crystalline state same method as MCLCP-1/$LiClO_4$ mixtures.

The liquid crystallinity and the ionic conductivity for the mixtures of the main chain type polymer with lithium salt are described using X-ray

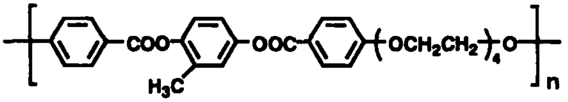

FIGURE 2 Structure of main chain type polymer-2 (MCLCP-2)

diffraction, DSC and AC-impedance measurements.

EXPERIMENTAL

Characterization

The polymers were characterized by DSC and GPC (polystyrene equivalent molar mass). Polarized microscopy and X-ray diffractometer were used to examine the mesophase structure. Bulk ionic conductivities were measured by ac-impedance spectroscopy in the frequency range 100Hz to 10MHz. The liquid crystalline polymers with lithium salt were pressed between the stainless steel or ITO glass blocking electrodes with a PTFE spacer (0.25cm^2 in a surface area of the electrode, 160μm in thickness of the spacer).

Preparation of MCLCP-1

p-Xylylene bis (triphenyl phosphonium chloride)

The mixture of p-xylylene dichloride (15.0g, 86mmol) and triphenylphosphyne (34.7g, 170mmol) in DMF (175ml) was refluxed for 3 hours, and cooled to room temperature. The reaction mixture was filtered and washed with DMF and with diethylether. Yield 28.2g (87%).

1,4-bis (4-ethoxy carbonyl styryl) benzene

p-Xylylene bis (triphenyl phosphonium chloride) (20g, 53mmol) with ethanol and terephthalaldehydic acid methyl ester (10.5g, 64mmol) and lithiumethylate solvent (0.3 mol/l) previously prepared by adding lithium (0.65g) to ethanol (300ml) was stirred in a three-neck round-bottom flask for 2 days. The reaction mixtures were filtered, and then the filtrate washed with water, and extracted with hot methanol. Yield 12.3g (67%)

^{1}H-NMR ($CDCl_3$) : δ 8.0-6.5 (m, 16H, Ar-$\underline{H}$, -C$\underline{H}$=C), 4.4 (m, 4H, -C$\underline{H}_2$-), 1.4 (t, 6H, -C$\underline{H}_3$)

Polymerization

The polymer was prepared by polycondensation of 1,4-bis (4-ethoxy carbonyl styryl) benzene (1.0g 1eq) and polyethylene glycol (Mw.600) (1.49g, 1.05eq) in a three-neck round-bottom flask. After lead acetate was added to the reaction mixtures, the mixtures were stirred at 170 ^{0}C for 4 hour under the N_2 atmosphere. In addition, tin oxide (IV) was added and the mixtures were stirred at 220 ^{0}C for 8 hour under vacuum. Then the product was dissolved in chloroform and reprecipitated with ethanol by two times. The polymer was dried under vacuum. The resulting polymer was dissolved in benzene and a small amount of iodine was added to the solution. The solvents were distilled off with rotary-evaporator, and then the residue was dissolved in chloroform, and reprecipitated with methanol to precipitate polymer. In this way, we obtained the all trans type polymer.

Preparation of MCLCP-2

Tetraethyleneglycol ditosylate

After p-toluenesulfonyl chloride (18.5g, 97mmol) was added to tetraethyleneglycol (9.5g, 49mmol) in pyridine. The mixture was stirred at 0^0C for 3 hour. In addition, water was added, the reaction mixtures were stirred for 5 hour. Then, the product was extracted with chloroform and the solvent was removed by evaporator. The residue was purified by column chromatography on silica gel with the mixed solvent of acetone: chloroform (1: 20). Yield 18.1g (73%).

^{1}H-NMR ($CDCl_3$) : δ 8.0, 7.5 (d, 8H, Ar-H), 4.2-3.5 (t, 16H, -CH_2O-), 2.5 (s, 6H, Ar-CH_3)

Tetraethyleneglycol bis (4-carboxyphenyl)ether

A mixture of methyl 4-hydroxybenzoate (4.9g, 32mmol), tetraethyleneglycol ditosylate (7.9g, 16mmol) and K_2CO_3 in acetone was refluxed for 15 hour. The solvents were distilled off with rotary-evaporator. The residue was extracted with chloroform and the solvent was removed by evaporator. Next, KOH_{aq} and ethanol were added the resulting product. The reaction mixtures were refluxed for 5

minutes and acidified with HCl_{aq}. The precipitate was filtered and the filtrate was washed with hot water and dried under vacuum. The residue was purified by recrystallization with THF. Yield 5.2g 80%
^{1}H-NMR (DMSO-d) : δ 12.5 (s, 2H, -COO<u>H</u>), 8.0, 7.0 (d, 8H, Ar-<u>H</u>), 4.2-3.5 (t, 16H, -$C\underline{H_2}O$-)

Polymerization

p-Toluenesulfonyl chloride (1.27g, 6.7mmol) and N, N-dimethylformamide (0.11g, 1.5mmol) was stirred in three-neck round-bottom flask at room temperature for 30 minutes. Tetraethyleneglycol bis (4-carboxyphenyl) ether (1.0g, 1eq) in pyridine was added to the mixture. The reaction mixture was stirred at room temperature for 10 minutes, and then stirred at 120 ^{0}C for 10 minutes. In addition, methylhydroquinone (0.3g, 1.0eq) in pyridine was added to the mixture and refluxed for 3 hour. Then, the mixture was poured into c.a. 200ml of methanol to precipitate the polymer. The polymer was dissolved in chloroform and reprecipitated with hot methanol by two times. The polymer was dried under vacuum.

<u>Preparation of polymer-lithium salt mixtures</u>

The polymer-lithium salt mixtures were obtained by mixing the polymer dissolved in tetrahydrofuran and lithium salt ($LiClO_4$) dissolved in acetone. The solvent was removed by evaporator at room temperature, and then the mixtures were dried in vacuum at 80℃.

RESULTS AND DISCUSSION

The MCLCP-1 exhibited a smectic phase, and the MCLCP-1 with lithium salt ($LiClO_4$) at the ratio of 0.04 per polymer repeating unit (MCLCP-1/$LiClO_4$=0.04) also exhibited a smectic phase. However, the MCLCP-1/$LiClO_4$ (0.11) showed a nematic phase. These liquid crystalline phase structures were determined by X-ray diffraction measurements, as shown in Figure 3 (a) and (b), respectively. The

X-ray diffraction pattern of the MCLCP-1/$LiClO_4$ (0.04) (Figure 3 (a)) showed the sharp diffraction peak in the small angle region characteristic of a smectic phase. However, the diffraction peak in the small angle region disappeared with increasing salt concentration. We investigated the ionic conductivity in these different liquid crystal phases. As a result, the ionic conductivity of both the MCLCP-1/$LiClO_4$ (0.04) and (0.11) increased with increasing temperature. The ionic conductivity of the MCLCP-1/$LiClO_4$ (0.04) is 10^{-4}S/cm in a smectic phase (80℃), while that of the MCLCP-1/$LiClO_4$ (0.11) is 10^{-3}S/cm in a nematic phase (80℃), as shown in Figure 4. Consequently, we found that the ionic conductivity of the mixture in a nematic phase is larger than that of the mixture in a smectic phase. This tendency can be explained that the fluidity in a nematic phase is larger than that in a smectic phase.

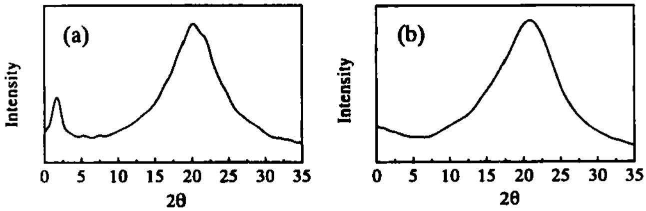

FIGURE 3 X-ray diffraction pattern of MCLCP-1/$LiClO_4$
(a) MCLCP-1/$LiClO_4$ (0.04) (b) MCLCP-1/$LiClO_4$ (0.11)

On the other hand, the MCLCP-1 occurs cis-trans isomerization by I_2 and UV irradiation, because its chemical structure has bisstyrylbenzene unit. The trans type MCLCP-1 exhibited a liquid crystalline phase, while the cis type MCLCP-1 showed only glass transition temperature. The DSC curve for these polymers were shown in Figure 5 (a) and (b), respectively. Usually, the virgin MCLCP-1 shows a cis type configuration. We obtained all trans type polymer by adding iodine. In this report we compared the ionic conductivity of the trans type MCLCP-1/$LiClO_4$ (0.11) with that of the cis type MCLCP-1/$LiClO_4$ (0.11). The ionic conductivity of the trans type MCLCP-1/$LiClO_4$

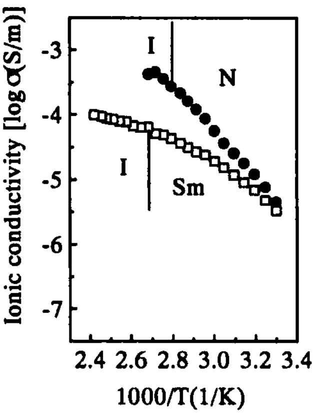

FIGURE 4 Temperature dependence of ionic conductivities for MCLCP-1/LiClO$_4$

☐ :MCLCP-1/LiClO$_4$ (0.04) ● :MCLCP-1/LiClO$_4$(0.11)

Sm: Smectic N: Nematic I: Isotropic

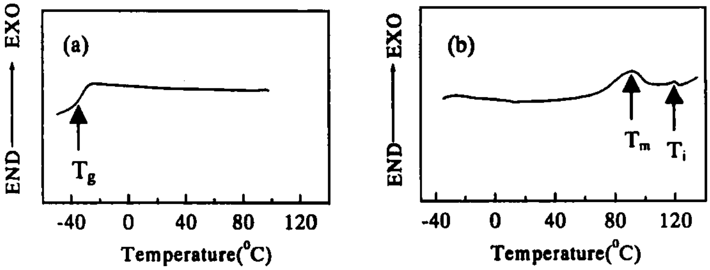

FIGURE 5 DSC cooling curves of cis & trans type MCLCP-1/ LiClO$_4$ (0.11)

(a) cis type (b) trans type

(0.11) is larger than that of the cis type MCLCP-1/LiClO$_4$ (0.11), as shown in Figure 6. It demonstrates that the ionic mobility deeply correlates with the orientational order in the liquid crystalline phase.

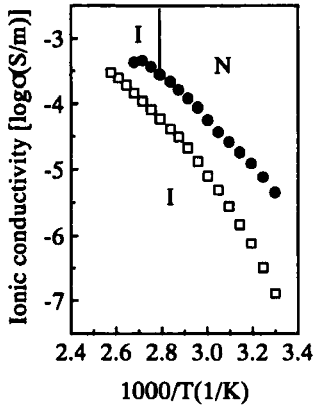

FIGURE 6 Temperature dependence of ionic conductivities for MCLCP-1/$LiClO_4$ (0.11)
N:nematic, I:isotropic □:cis-type, ●:trans-type

Next, ceramic powder was added to the MCLCP-1/$LiClO_4$ (0.11) mixture in order to improve the ionic conductivity. Titanium (IV) oxide was used as a ceramic powder. Figure 7 compares the ionic conductivity of a ceramic-free MCLCP-1/$LiClO_4$ (0.11) with the MCLCP-1/$LiClO_4$ (0.11) to which titanium (IV) oxide (TiO_2) has been added. Consequently, a dramatic improvement in the ionic conductivity is evident. However, the enhancement of the ionic conductivity in the presence of the ceramic powder is not yet fully understood.

In addition, we investigated about the ionic conductivity in the liquid crystalline state for MCLCP-2/$LiClO_4$ mixture. The MCLCP-2 exhibited a nematic phase. The mixtures with lithium salt at the ratio of 0.04 or 0.11 per polymer repeating unit also exhibited a nematic phase. The ionic conductivity of the MCLCP-2/$LiClO_4$ (0.11) mixture was smaller than that of the MCLCP-2/$LiClO_4$ (0.04) mixture, as shown in Figure 8. It is considered that the decrease in the ionic conductivity is most likeable due to crystallization by increasing salt concentration.

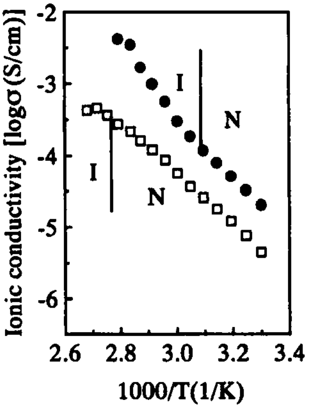

FIGURE 7 Temperature dependence of ionic conductivities for ceramic-free MCLCP-1/$LiClO_4$ & MCLCP-1/$LiClO_4$/TiO_2 mixture
N:nematic, I:isotropic □:ceramic-free, ●: TiO_2 (10w%) mixture

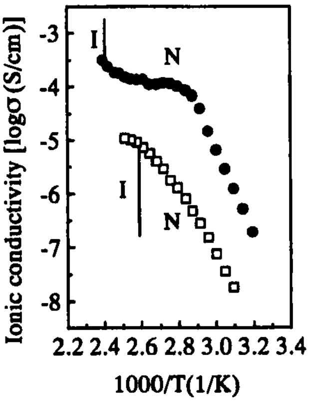

FIGURE 8 Temperature dependence of ionic conductivities for MCLCP-2/ $LiClO_4$
N:nematic I:isotropic ● :MCLCP-2/ $LiClO_4$ (0.04)
□:MCLCP-2/ $LiClO_4$ (0.11)

CONCLUSION

In order to clarify the ionic conductivity in the liquid crystalline phase we prepared two kinds of the main chain type liquid crystalline polymers. The ionic conductivity of the MCLCP-1/$LiClO_4$ in a nematic phase is larger than that of the MCLCP-1/$LiClO_4$ in a smectic phase. And then, the ionic conductivity of the trans type MCLCP-1/$LiClO_4$ is larger than that of the cis type MCLCP-1/$LiClO_4$. Furthermore, the ionic conductivity of the MCLCP-1/$LiClO_4$ mixture was improved by adding titanium (IV) oxide.

On the other hand, the ionic conductivity of the MCLCP-2/$LiClO_4$ (0.11) mixture was smaller than that of the MCLCP-2/$LiClO_4$ (0.04) mixture.

References

[1] P.V. Wright, *J. Poly. Sci. Poly. Phys. ed.*, 1976; **14**:955.
[2] K. Ono, *Kobunshi*, 1985; **34**:766.
[3] N. Ogata, *Doudensei Koubunsi*, 1990; Koudansha Scientific, Tokyo.
[4] A. Hooper, J.M. North, *Solid State Ionics*, 1983; **9&10**:1161.
[5] C.C. Lee, P.V. Wright, *Polymer*, 1982; **23**:681.
[6] M.Z.A. Munshi, B.B. Owens, S. Nguyen, *Polym. J.*, 1988; **20**:597.
[7] J.E. Weston, B.C.H. Steele, *Solid State Ionics*, 1982; **7**:81.
[8] Y. Chatani, S. Okumura, *Polymer*, 1987; **28**:1815.
[9] K. Kawamura, N. Koide, *Kobunshi Ronbunsyu*, 1999; **56**:240.
[10] B. Kumar, L.G. Scanlon, *J. Power Sources*, 1994; **52**:261.
[11] G.B. Appetecchi, F. Croce, G. Dautzenberg, M. Mastragostino, F. Ronci, B. Scrosati, F. Soavi, A. Zanelli, F. Alessandri, and P. P. Prosini, *J. Electrochem. Soc.*, 1998; **145**:4126.
[12] G.B. Appetecchi, F. Croce, M. Mastragostino, B. Scrosati, F. Soavi, and A. Zanelli, *J. Electrochem. Soc.*, 1998; **1454**133.
[13] G.B. Appetecchi, F. Croce, L. Persi, and B. Scrosati, *Nature*, 1998; **394**:456.
[14] R. Curini, F. Croce, A. Martinelli, L. Persi, B. Scrosati, and R. Caminiti, *J. Phys. Chem. B*, 1999; **103**:10632.