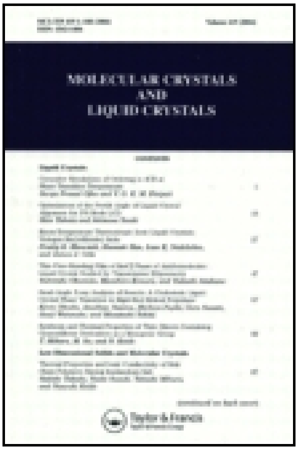

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Thermal Properties and Ionic Conductivity of Side Chain Polymers Having Imidazolium Salt

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THERMAL PROPERTIES AND IONIC CONDUCTIVITY OF SIDE CHAIN POLYMERS HAVING IMIDAZOLIUM SALT

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We synthesized polymethacrylate containing imidazolium salts via three aromatic rings in the side chain. A smectic phase is shown for the polymer having imidazolium salts with Br anion. Temperature dependence of ionic conductivity for the polymers is observed. The ionic conductivity of the polymers increased with increasing temperature. The ionic conductivity of the polymersis about 10^{-9}–10^{-8} *Scm*$^{-1}$ *near room temperature. The highest ionic conductivity of the polymers is about* 10^{-5} *Scm*$^{-1}$ *at 130°C.*

Keywords: ionic liquid; imidazolium salt; liquid crystalline polymer

INTRODUCTION

The ionic conductivity of the mixtures of poly(ethylene oxide) (PEO) with an alkali metal salt has been studied intensively to ascertain the mechanism of their high ionic conductivity [1].

The conductivity of polymer electrolytes in the amorphous phase above glass transition temperature has received much attention, because polymer chain motion in the amorphous phase creates a dynamic, disordered environment for facilitating ion transport. However, recently Gadjourova et al. [2] reported that the ionic conductivity in the static, ordered environment of the crystalline phase was greater than that in the equivalent amorphous material above glass transition temperature. This behavior indicated that the ionic conductivity would be expected to be favored in the static and ordered environment where permanent pathways for ion transport were present.

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We considered that liquid crystalline properties consisting of order and anisotropy would improve the conductivity of the ionic conductive polymers. Ionic conductive liquid crystalline polymer (LCPs) would be obtained by introducing a mesogenic group into the polymer backbone of the ionic conductive polymer such as PEO. The liquid crystal (LC) electrolytes would combine the segmental motion of the ethylene oxides and formation of ionic channel originated in LC phases. Then we have created the ionic conductive polymer with a LC phase [3–5].

Although many ionic conductive polymers are known, the ionic conductivity of ionic polymer itself is very low. Therefore, many researchers are searching for new ionic conductive materials substituted for PEO. Ionic liquids are intensively investigated based on their properties of nonvolatility, incombustibility, chemical stability, high ionic conductivity, etc. [6–11]. The imidazolium salts are especially well known as ionic liquids, and their physical properties and application to a solvent have been investigated by many researchers [12–16]. Furthermore, the ionic conductivity of polymers having imidazolium salts was reported by Hirao et al. [17], and Ohno [18].

From the standpoint of LC materials, ammonium salts, pyridinium salts, or imidazolium salts with long alkyl chain would easily display a smectic phase [19–22]. Furthermore, the organic salts have a possibility to be an ionic conductive material without mixing a salt as an alkali metal salt [23,24]. However, these low molecular mass organic salts have a poor mechanical property and processability. In order to overcome the weak points of the ionic liquids, the organic salts were introduced into the side chain LCPs [25]. The polymers having organic salts in the side chain would have a possibility to be an ionic conductive LCP. We can expect that the ionic conductive LCPs would have both the ionic conductive and self-assembly properties and that they would have ionic conductive path formed by their self-assembly properties. In this report, we described thermal properties and temperature dependence of the ionic conductivity of side-chain polymers having the imidazolium salt.

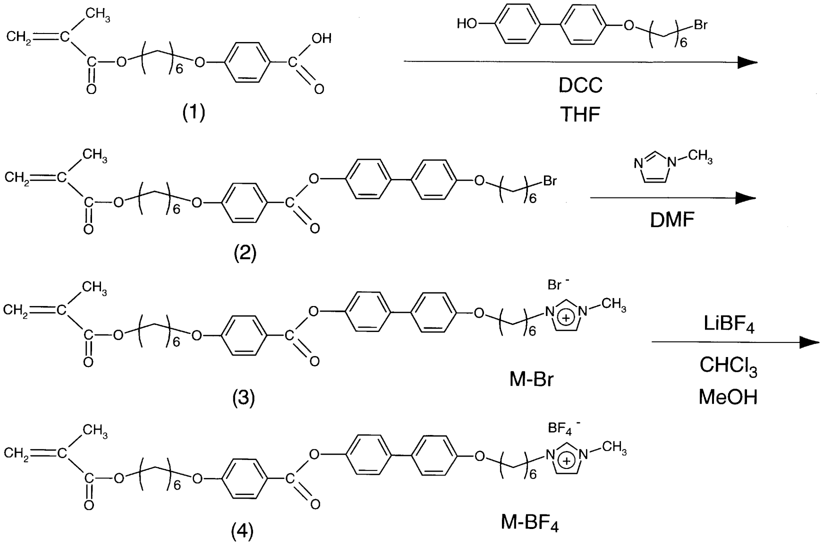
EXPERIMENTAL

Materials

A monomer having the imidazolium salt was prepared as shown in Scheme 1. The intermediates (compounds (1) and (2)) were synthesized according to the conventional synthetic methods of side-chain LCPs [26].

Imidazolium Salt Monomer with Br Anion (3: M-Br)

N-methylimidazole (3.1 g, 37.8 mmol) and the compound (2) (6.8 g, 12.6 mmol) were dissolved in dimethylformamide (DMF) (20 ml). After



SCHEME 1 Synthesis of monomers having imidazolium salt.

the DMF solution was stirred for 3 days at 50°C, the DMF solution was poured into diethyl ether. The product precipitated was collected by filtration. The product was purified by recrystallization from methanol. The white solid was obtained in a 76% yield (4.5 g).

^{1}H-NMR ($CDCl_3$), δ ppm): 1.41–1.56 (m, 8H, CH_2), 1.71–1.86 (m, 8H, CH_2), 1.95 (s, 3H, CH_3), 3.99 (t, 3H, CH_2–N), 4.00 (t, 2H, CH_2–O), 4.08 (s, 3H, N–CH_3), 4.17 (t, 2H, CH_2–O), 4.33 (t, 2H, CH_2–O), 5.56 (s, 1H, CH_2 =), 6.10 (s, 1H, CH_2=), 6.96 (m, 4H, Ar), 7.23 (d, 2H, Ar), 7.35 (s, 1H, imidazolyl ring), 7.36 (s, 1H, imidazolyl ring), 7.50 (d, 2H, Ar), 7.56 (d, 2H, Ar), 8.15 (d, 2H, Ar), 10.50 (d, 1H, 2-position in imidazolyl ring).

IR (KBr, cm^{-1}): 3062 (CH, imidazolium cation), 2941, 2854 (CH_2), 1732, 1708 (COO), 1635 (CH_2=C(CH_3)), 1608, 1498 (Ar).

Imidazolium Salt Monomer with BF_4 Anion (4: M-BR_4)

A methanol solution of $LiBF_4$ (1.8 g, 3.2 mmol) was added to a chloroform solution of the compound (3) (1.0 g, 1.6 mmol). Then the reaction mixture was stirred for 12 h at room temperature. After the methanol and chloroform were evaporated, the residue was washed with water to remove produced LiBr salt. The product was obtained in a 74.4% yield (0.75 g).

^{1}H-NMR ($CDCl_3$), δ ppm): 1.41–1.56 (m, 8H, CH_2), 1.71–1.86 (m, 8H, CH_2), 1.95 (s, 3H, CH_3), 3.93 (t, 3H, CH_3–N), 3.99 (t, 2H, CH_2–N), 4.05

(t, 2H, O–CH_3), 4.17 (m, 4H, CH_2–O), 5.56 (s, 1H, CH_2=), 6.10 (s, 1H, CH_2=), 6.96 (m, 4H, Ar), 7.23 (m, 4H, Ar, imidazolyl ring), 7.50 (d, 2H, Ar), 7.56 (d, 2H, Ar), 8.16 (d, 2H, Ar), 8.90 (s, 1H, 2-position in imidazolyl ring).

IR (KBr, cm^{-1}): 3062 (CH, imidazolium cation), 2943, 2854 (CH_2), 1732, 1709 (COO), 1633 (CH_2=C(CH_3)), 1608, 1498 (Ar).

Radical Polymerization

Each polymer was prepared by radical polymerization in a sealed ampoule with 1.0 mol% of α, α′-azobisisobutyronitrile in anhydrous chloroform at 60°C for 48 h. The product was obtained by reprecipitation with methanol and washed with methanol several times. It was dried at 40°C under vacuum. The product was obtained in about a 54–70% yield.

Polymer with Br Anion (P-Br)

IR (KBr, cm^{-1}): 3068 (CH, imidazolium cation), 2939, 2860 (CH_2), 1728 (COO), 1604, 1497 (Ar).

Polymer with BF_4 Anion (P-BF_4)

IR (KBr, cm^{-1}): 3068 (CH, imidazolium cation), 2939, 2861 (CH_2), 1728, (COO), 1606, 1497 (Ar).

Characterization

^{1}H-NMR was carried out with a JEOL JNM-LA 400 spectrometer using $CDCl_3$ as the solvent. Infrared spectra was recorded on a JEOL JIR 7000 spectrometer. Spectra were collected at 4 cm^{-1} resolution. DSC measurements were conducted with a Mettler DSC821^e. Polarized optical microscopy measurements were performed on a Nikon polarizing optical microscope, OPTIPHOTO-POL, equipped with a Mettler FP80 controller and a FP82 hot stage. Thermal properties of polymers were investigated by polarized optical microscopy and differential scanning calorimetry (DSC) measurements. X-ray diffraction patterns were recorded with a RIGAKU RINT2500 with Ni-filtered CuKα radiation. The sample in quartz capillary (diameter 1 mm) was held in a temperature-controlled cell (RIGAKU LC high-temperature controller). The structure of mesophase for the polymers having the imidazolium salt was investigated by X-ray measurements. The ionic conductivity of the polymers was measured with an AC impedance analyzer (Solartron Co. Impedance/Gain-Phase Analyzer SI 1260) over a frequency range of 10–10^6 Hz. The cell used in the conductive measurements was made by pressing the sample between the indium tin oxide (ITO) glass blocking electrodes with polytetrafluoroethylene (PTFE) spacer (0.25 cm^2 in a surface area of the electrode, 160 μm in the thickness of the spacer).

RESULTS AND DISCUSSION

Figure 1 shows the chemical structures of polymers that have a mesogenic group and an imidazolium salt in the side chain. In order to investigate the effect of counter anion on the ionic conductivity, we prepared two polymers with different counter anions by radical polymerization.

Thermal properties of the monomers and side-chain polymers are summarized in Table 1. The melting points of both monomers are observed near 80–90°C. Above these melting points, birefringence is shown for these monomers: however, optical textures characteristic of LC phases are not observed for these monomers. When these monomers are further heated above the melting points, thermal polymerization occurs near 155°C based upon the exothermic peak near 155°C in the DSC curve on the heating scan.

A shift of the baseline is observed in the DSC curve of the polymers. The shift is attributed to glass transition temperature of the polymers. When the polymers are further heated, thermal decomposition of the polymers occurs before the isotropic liquid. Birefringence is observed for the polymers above glass transition temperature. Figure 2 shows the X-ray patterns of the polymers above glass transition temperature. A sharp peak in the small-angle region and a broad peak in the wide-angle region are observed in the X-ray pattern of P-Br at 140°C. The d-spacing is 63.0 Å based on the sharp peak in the small-angle region, while the calculated length of the side chain is about 34 Å. Therefore, P-Br would exhibit a bilayer smectic phase. Although the value is related to the length between the imidazolium and mesogenic groups, we cannot clarify the assignment of the small peak at 6.0° (14.6 Å).

On the other hand, a broad peak is observed in the wide-angle region of the X-ray pattern of P-Br_4 at 150°C. Although the X-ray pattern of P-BF_4 is similar to that of a nematic liquid crystal, we conclude that P-BF_4 exhibits a mesophase, because an optical texture characteristic of a nematic phase is not shown for P-BF_4. The small peak at 6.3° (14.0 Å) is also detected in the

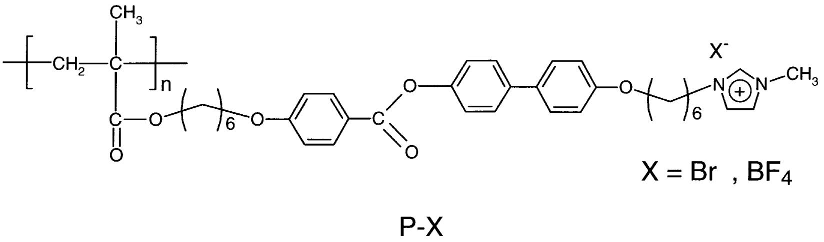


FIGURE 1 Chemical structure of polymers containing imidazolium salt.

TABLE 1 Phase Transition Temperatures of Monomers and Polymers

Compounds	Phase transition temperatures (°C)
M-Br	$\mathrm{Cr} \xrightarrow{80} \mathrm{M}$
M-BF$_4$	$\mathrm{Cr} \xrightarrow{88} \mathrm{M}$
P-Br	$\mathrm{g} \xrightarrow{28} \mathrm{Sm} \xrightarrow{240} \mathrm{Decom.}$
P-BF$_4$	$\mathrm{g} \xrightarrow{8} \mathrm{M} \xrightarrow{260} \mathrm{Decom.}$

g, glassy; Cr, crystal; M, mesophase; Sm, smectic phase; Decom., thermal decompostion.

X-ray pattern of P-BF$_4$. The assignment of the small peak is not clarified at the present time.

Temperature dependence of the ionic conductivity for the monomers is shown in Figure 3. Temperature dependence of the ionic conductivity of M-BF$_4$ is similar to that of M-Br. A rapid increase in the ionic conductivity is observed near 70°C for both monomers. The remarkable change in the ionic conductivity would be related to the melting points of the monomers. The

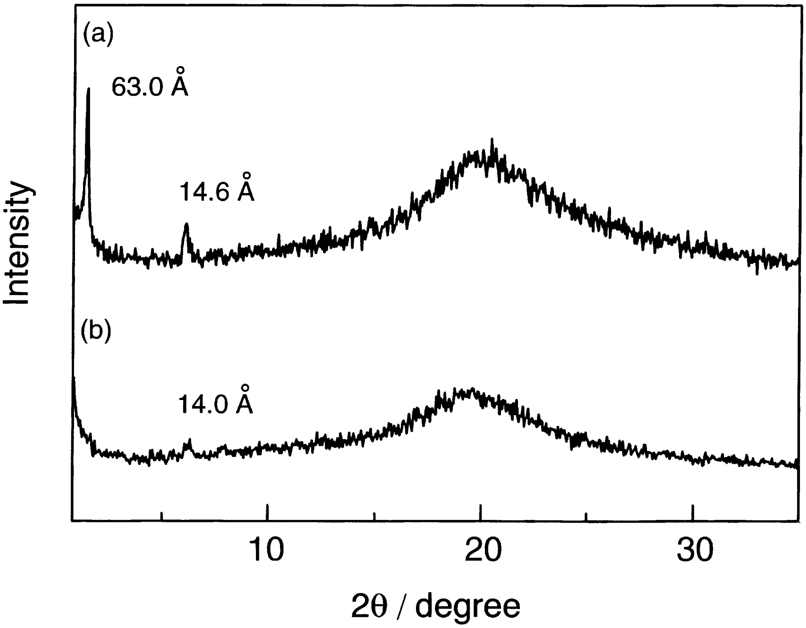


FIGURE 2 X-ray patterns of polymers, (a) P-Br at 140°C and (b) P-BF$_4$ at 150°C.

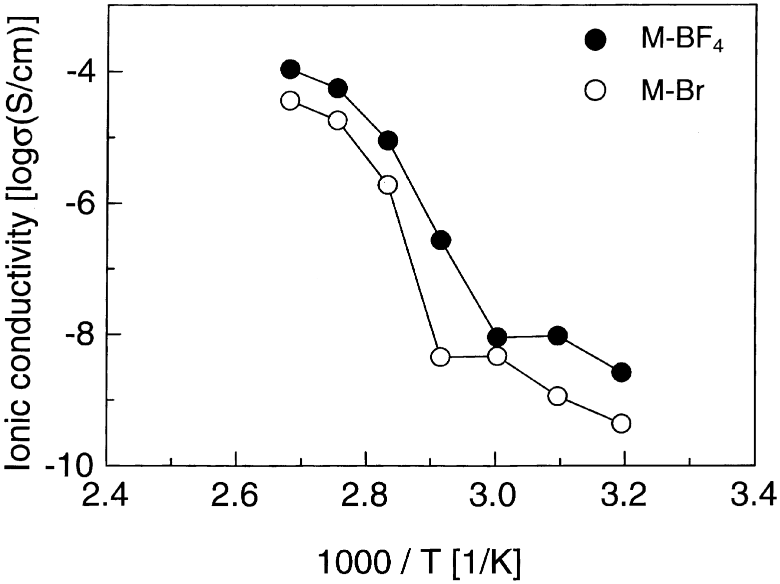


FIGURE 3 Temperature dependence of ionic conductivity of monomers having imidazolium salt.

ionic conductivity of M-BF_4 is higher than that of M-Br, despite measurement temperature.

Temperature dependence of the ionic conductivity for the polymers is shown in Figure 4. Temperature dependence of the ionic conductivity for P-BF_4 is similar to that of P-Br. The ionic conductivity of P-BF_4 is higher than that of P-Br. This behavior related to the ionic conductivity for the polymers is the same as that of the monomers. The ionic conductivity of P-BF_4 is higher than that of P-Br. The difference in the ionic conductivity between P-BF_4 and P-Br would arise from the difference in the size of the counter anion or in the structure of mesophase for the polymers. However, at the present time we cannot discuss the reason why the difference in the ionic conductivity of the polymers is generated because we cannot measure the molecular weight, the distribution of molecular weight, and so on of the ionic polymers by conventional GPC measurements. The ionic conductivities of P-Br and P-BF_4 are about 10^{-9} and about 10^{-8} Scm^{-1} near room temperature, respectively.

The ionic conductivity of polymers having imidazolium salts via alkylene or ethylene oxide spacer is reported by Yoshizawa and Ohno [27]. The ionic conductivity of the polymers without phenylene rings is about 10^{-4} Scm^{-1} at 30°C. This result indicates that the three phenylene rings as a mesogenic group in P-Br and P-BF_4 would depress the ionic conductivity of them,

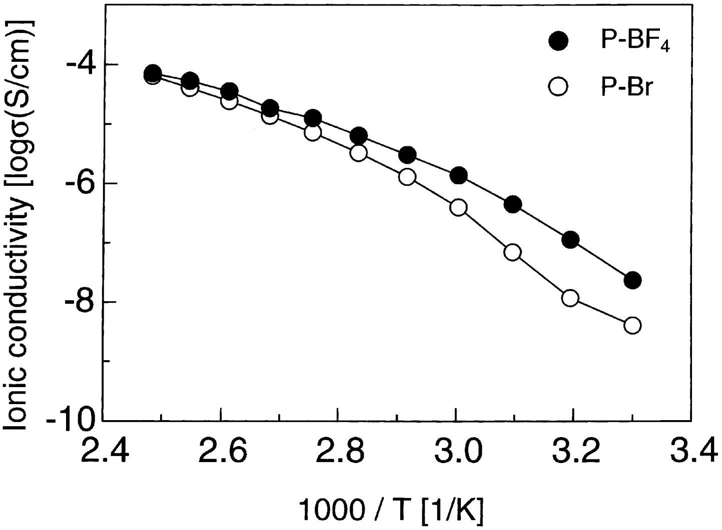


FIGURE 4 Temperature dependence of ionic conductivity of polymers having imidazolium salt.

although we cannot discuss the difference in the ionic conductivity in detail because the counter anion of the polymers without phenylene rings is bis(trifluoromethanesulfonyl) imide anion (TFSI$^-$). The viscosity and glass transition temperature for P-BR and P-BF$_4$ would be higher than those of the polymers without phenylene rings. Consequently, the ionic conductivity of P-Br and P-BF$_4$ would become low compared with that of the polymers without phenlene rings.

Yoshio et al. [24] reported the anisotropic ion conduction in the mixture of calamitic liquid crystal and ionic liquid (imidazolium salt). To measure the anisotropic ion conduction in P-Br and P-BF$_4$, we try to obtain the sample with the oriented monodomain by imposing shear strain. However, we cannot obtain the sample with the oriented monodomain because of high viscosity of the polymers. The ionic interaction would be formed between the imidazolium salts in the polymers. Therefore, the viscosity of P-Br and P-BF$_4$ would be higher than that of conventional LCPs without ionic groups.

REFERENCES

[1] MacCallum, J. R. & Vincent, C. A. (Eds.). (1987, 1989). *Polymer Electrolyte Review I and 2* (London: Elsevier).

[2] Gadjourova, Z., Andreev, Y. G., Tunstall, D. P., & Bruce, P. G. (2001). *Nature*, *412*, 520–523.

[3] Kawamura, K., Kikuchi, T., & Koide, N. (1998). *Mol. Cryst. Liq. Cryst*, *318*, 87–100.
[4] Kawamura, K. & Koide, N. (1999). *Koubunshi Ronbunshu*, *56*, 240–246.
[5] Akachi, Y., Kawamura, K., & Koide, N. (2001). *Polym. Adv. Tech.*, *12*, 422–426.
[6] Welton, T. (1999). *Chem. Rev.*, *99*, 2071–2083.
[7] Huddleston, J. G., Willauer, H. D., Swatloski, R. P., Visser, A. E., & Rogers, R. D. (1998). *Chem. Commun.*, 1765–1766.
[8] Koch, V. R., Nanjundiah, C., Appetecchi, G. B., & Scrosati, B. (1995). *J. Electrochem. Soc.*, *142*, L116–L118.
[9] Papageorgiou, N., Athanassov, Y., Armand, M., Bonhôte, P., Petterson, H., Azam, A., & Grätzel, M. (1996). *J. Electrochem. Soc.*, *143*, 3099–3108.
[10] Matsumoto, H., Matsuda, T., Tsuda, T., Hagiwara, R., Ito, Y., & Miyazaki, Y. (2001). *Chem. Lett.*, 26–27.
[11] Doyle, M., Choi, S. K., & Proulx, G. (2000). *J. Electrochem. Soc.*, *147*, 34–37.
[12] Bonhôte, P., Dias, A-P., Papageorgiou, N., Kalyanasundaram, K., & Grätzel, M. (1996). *Inorg. Chem*, *35*, 1168–1178.
[13] MacFarlane, D. R., Huang, J., & Forsyth, M. (1999). *Nature, 402*, 792–794.
[14] MacFarlane, D. R., Sun, J., Golding, J., Meakin, P., & Forsyth, M. (2000). *Electrochim. Acta. 45*, 1271–1278.
[15] Hagiwara, R. (2002). *Electrochemistry, 70*, 130–136.
[16] Olivier-Bourbigou, H. & Magna, L. (2002). *J. Mol. Catal. A*, 182–183, 419–437.
[17] Hirao, M., Ito-Akita, K., & Ohno, H. (2000). *Polym. Adv. Technol.*, *11*, 534–538.
[18] Ohno, H. (2001). *Electrochim. Acta.*, *46*, 1407–1411.
[19] Bowlas, C. J., Bruce, D. W. & Seddon, K. R. (1996). *Chem. Commun.*, 1625–1626.
[20] Lee, K. M., Lee, C. K., & Lin, I. J. B. (1997). *Chem. Commun.*, 899–900.
[21] Holbrey, J. D. & Seddon, K. R. (1999). *J. Chem. Soc., Dalton Trans.*, 2133–2139.
[22] Bradley, A. E., Hardacre, C., Holbrey, J. D., Johnston, S., McMath, S. E. J., & Nieuwenhuyzen, N. (2002). *Chem. Mater*, *14*, 629–635.
[23] Yoshio, M., Mukai, T., Kanie, K., Yoshizawa, M., Ohno, H., & Kato, T. (2002). *Chem. Lett.*, 320–321.
[24] Yoshio, M., Mukai, T., Kanie, K., Yoshizawa, M., Ohno, H., & Kato, T. (2002). *Adv. Mater.*, *14*, 351–354.
[25] Takada, S., Suzuki, N., Mihara, T., & Koide, N. (2002). *Polym. Prep., Japan, 51*, 737.
[26] McArdle, C. B. (Ed.) (1989). *Side Chain Liquid Crystal Polymers* (Glasgow, Blackie, and New York: Chapman and Hall).
[27] Yoshizawa, M. & Ohno, H. (2001). *Electrochim. Acta, 46*, 1723–1728.