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Preparation and properties of solid electrolytes on the basis of alkali metal salts and poly(2,2-dimethyltrimethylene carbonate)-block-poly(ethylene oxide)-block-poly(2,2-dimethyltrimethylene carbonate)

Martin Melchiors, Helmut Keul and Hartwig Höcker*
Lehrstuhl für Textilchemie und Makromolekulare Chemie der Rheinisch-Westfälischen Technischen Hochschule Aachen, Worringerweg 1, 52056 Aachen, Germany

The dissolution of alkali metal salts, e.g. $LiClO_4$, $LiCF_3SO_3$, NaSCN, NaI, $NaCF_3SO_3$ and KSCN in poly(2,2-dimethyltrimethylene carbonate)-block-poly(ethylene oxide)-block-poly(2,2-dimethyltrimethylene carbonate) (PDTC-*b*-PEO-*b*-PDTC) results in solid polymeric electrolytes. Depending on the nature of the salt, differential scanning calorimetry (d.s.c.) measurements of the polymer/salt systems reveal that crystalline complexes are obtained with NaI, NaSCN, and $LiCF_3SO_3$. These complexes exhibit characteristic infra-red (i.r.) bands, e.g. at 1106 and 1080 cm^{-1} for the complex with NaI. X-ray powder diagrams of the polymer/salt complexes show that the original patterns of the salt and the crystalline PEO phase have disappeared in favour of a new pattern for the complex; however, reflections attributed to the crystalline PDTC phase are found to be unchanged. Complexation takes place mainly with the PEO segments of the block copolymer, thus causing a change in the secondary structure of the original PEO helix. The stoichiometry of the polymer/salt complexes is 3/1 (EO repeating units/metal cation). The highest value of the alternating current conductivity was obtained for $LiCF_3SO_3$ as the salt component, with values of $\sigma = 10^{-4}\ S\,cm^{-1}$ at 60°C being obtained at concentrations of 5 to 10 mol% (based on the EO repeat units). From temperature dependent conductivity measurements it was concluded that above the glass transition temperature the ionic conductivity of the sodium salt systems follows an Arrhenius behaviour, while the lithium and potassium salt systems follow a Vogel–Tammann–Fulcher behaviour. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Much interest has been focused on ion-containing polymers, because of the need for a fundamental understanding of the ion transport in polymers and because of their potential application as solid electrolytes in batteries[1–3]. These ion containing polymers—so called 'solid polymer electrolytes'—are formed by the dissolution of salts in polymers containing donor atoms such as oxygen, nitrogen or sulfur. Interaction of the cations of the salt with the heteroatoms of the polymeric matrix may lead to crystalline complexes (with considerably higher melting points than the melting point of the polymeric matrix) or to amorphous polymer/salt solutions. Most of the knowledge of PEO/salt systems is based on the initial work of Wright[4,5] and Armand[6]. Thus with Na and Li cations PEO forms a 7_2-helix in which the cations are situated in the helix axis and stabilized by the oxygen atoms directed to the helix centre[7–10]. In this way stoichiometric polymer/salt complexes are formed in which the molar ratio of the EO repeat unit to the cation is 3/1. Poly(propylene oxide) behaves in a similar way as PEO; the difference, however, is that the polymer/salt complex which is formed is amorphous[3]. As the conductivity pathway is believed to be through the disordered part of the polymer matrix[11], assisted by large-amplitude segmental motion, it is advantageous to reduce the crystalline order and to create an amorphous system with a low glass transition temperature. Possible ways for achieving this goal are: (i) selection of alkali metal salts with large, monovalent anions which have the advantage of being polarizable and having a low lattice energy[1,12] e.g. I^-, SCN^-, ClO_4^- or $CF_3SO_3^-$, and (ii) the use of poly(ethylene oxide) (PEO), which has been the most favoured solvating medium because of the high density of complexing donor atoms (oxygen atoms) and their corresponding spatial coordinates for ion–dipole interactions[3]. There are, however, several disadvantages for using such a system, with the major one being that PEO tends to crystallize or to form crystalline complexes. Replacement of PEO by a

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* To whom correspondence should be addressed

Dedicated to Professor Dr W. Borchard on the occasion of his 60th birthday, with best wishes block copolymer comprising PEO may improve the situation or remove this disadvantage.

In this present communication we present our results on polymer/salt systems in which the PEO moiety is the B block of an A–B–A triblock copolymer with poly(2,2-dimethyltrimethylene carbonate) as the A block. We have chosen a polycarbonate as the A block to enhance the mechanical and thermal properties and in addition to investigate the influence of this block on the ionic conductivity.

EXPERIMENTAL

Materials

2,2-Dimethyltrimethylene carbonate (DTC, from Bayer AG) was recrystallized from ethyl acetate and dried for 4 h at room temperature *in vacuo* before use. The hydroxytelechelic poly(ethylene oxide)s (PEO 8000, PEO 3400 and PEO 1000 from Aldrich) were dried for 2 days *in vacuo* before use. Determination of M_n (of the PEO used) by end-group analysis[13,14] (concentration of hydroxyl groups, [OH]) revealed for $([OH]/[C_2H_4O]) \times 10^2$ values of 1.12 (for PEO 8000), 2.35 (for PEO 3400) and 9.36 (for PEO 1000), which is in good agreement with the M_n values given by the supplier. sec-Butyllithium (1.4 M solution in cyclohexane/isopentane, from Aldrich) was used for the preparation of the telechelic lithium alcoholates of the PEOs.

The salts used for the preparation of solid electrolytes, namely $LiClO_4$, $LiCF_3SO_3$, NaSCN, NaI, $NaCF_3SO_3$, and KSCN (from Aldrich), were dried *in vacuo* for 4 days and then stored in a nitrogen atmosphere. Toluene and tetrahydrofuran (THF) were freshly distilled from solutions of sec-butyllithium and sodium naphthalene, respectively, before use. Nitrogen (from Linde) was passed over molecular sieve (4 Å), finely distributed potassium on aluminium oxide and BTS catalyst (from BASF AG) for purification.

Measurements

^1H and ^{13}C nuclear magnetic resonance n.m.r. spectra were recorded with a Varian VXR 300 spectrometer, operating at 300 and 75.4 MHz, respectively. Deuterochloroform was used as a solvent and tetramethylsilane as an internal standard. Infra-red spectra were recorded on a Nicolet 60SXR spectrometer using the photoacoustic spectroscopy technique.

Gel permeation chromatography (g.p.c.) analyses were carried out by using an ERC HPLC 64 pump with an ERMA 7515 A refractive index detector. For the separation a combination of two columns was employed (Jordi gel, length 500 mm, diameter 8 mm, pore width 10^4 and 10^5 Å, respectively). Chloroform was used as the eluting solvent, at a flow rate of 1.0 ml min^{-1}; calibration was achieved with polystyrene standards.

Differential scanning calorimetry (d.s.c.) was performed with a Perkin Elmer DSC-7 apparatus, at a heating rate of 20 K min^{-1}. The melting temperature (T_m) and melting enthalpy (ΔH_m) values were taken from the first heating run. X-ray diffraction patterns were obtained with an automatic Siemens D-5000 powder diffractometer (CuKα radiation of $\lambda = 1.54$ Å) in the range $1° < 2\Theta < 35°$.

Alternating current conductivity measurements (impedance measurements, dielectric spectroscopy) were performed at the Max Planck Institut für Polymerforschung, Mainz, using an impedance spectrometer, consisting of a Schlumberger SI 1260 impedance gain phase apparatus, a dielectric Chelsea interface and a Hewlett Packard 4192A impedance analyser. The impedance was measured over the frequency range 0.1–10^5 Hz for the temperature range $-100 < T < +60°C$. The samples were pressed into pellets of 1 mm thickness and were sandwiched between gilded stainless steel electrodes of 40 mm diameter. The glass transition temperatures of the samples were determined from these impedance measurements.

Synthesis of poly(2,2-dimethyltrimethylene carbonate)-block-poly(ethylene oxide)-block-poly-(2,2-dimethyltrimethylene carbonate)

Hydroxytelechelic PEO in toluene (6 wt%) was treated with an equimolar amount of sec-butyllithium (with respect to [OH]) and stirred for 15 min at room temperature. The yellow solution was cooled to 0°C and DTC dissolved in toluene (17 wt%) was added with vigorous stirring. After 5 min the polymerization was stopped by the addition of phosphoric acid in methanol (5 wt%). The copolymer was precipitated in methanol, filtrated and dried; copolymer yields of 75–98% were obtained. The ^1H and ^{13}C n.m.r. spectra obtained for the products correspond to those reported in the literature[15]. Details of further characterization of the copolymers are given in *Table 1*.

Dissolution of salts in poly(2,2-dimethyltrimethylene carbonate)-block-poly(ethylene oxide)-block-poly-(2,2-dimethyltrimethylene carbonate)

To a solution of 1 g of PDTC-*b*-PEO-*b*-PDTC in 20 ml of THF, a calculated amount of the chosen salt ($LiClO_4$,

Table 1 Compositions, molecular weights and molecular-weight distributions of the PDTC-*b*-PEO-*b*-PDTC copolymers

No.	M_n of PEO block[a]	Amount of DTC used (mol%)[a]	Amount of DTC used (wt%)[a]	M_n of PDTC block[a]	M_n of block copolymer[b]	M_w/M_n of block copolymer[b]
1a	8000	24.3	48.8	3 800	10 400	1.9
1b	8000	33.9	60.3	6 100	19 800	2.4
1c	8000	40.8	67.1	8 100	26 500	1.8
1d	8000	49.7	74.6	11 800	32 000	1.9
1e	8000	67.2	85.8	24 200	46 300	2.1
1f	3400	50.3	75.0	5 100	15 000	2.4
1g	1000	44.7	70.6	1 200	3 300	1.9

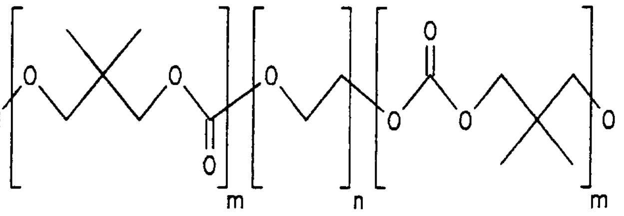
[a] Determined by ^1H n.m.r. spectroscopy

[b] Determined by g.p.c. measurements in $CHCl_3$ using polystyrene standards

$LiCF_3SO_3$, NaSCN, NaI, $NaCF_3SO_3$, or KSCN) was added. The mixture was heated gently to 40–50°C to form a clear solution, and stirring was continued for up to 4 h at room temperature. The solvent was then removed *in vacuo* at 0°C, the samples were dried *in vacuo* for 2 days and the residue then kept under dry inert gas. The salt content in the solid polymer electrolytes is given in mol% with respect to the EO repeat units.

RESULTS AND DISCUSSION

In order to obtain reproducible results the procedure described in the Experimental section was always used for dissolution of the salts in the polymeric matrix, PDTC-*b*-PEO-*b*-PDTC (**1**).



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The salt was added to the copolymer solution in THF. After a short time an increase in the viscosity was observed, and for NaI and NaSCN a gel was formed. From this increase in viscosity during dissolution of the salt an interaction of the salt with the polymer chains is to be concluded. The residual amount of solvent was constant at a low level. Characterization of the solid polymer/salt solutions was achieved by d.s.c. measurements, Fourier transform infra-red (*FT*i.r.) spectroscopy and X-ray diffraction. In addition, the ionic conductivities of the samples were measured by impedance spectroscopy.

Differential scanning calorimetry measurements

Figure 1 shows the d.s.c. curves of solid solutions of sodium iodide (NaI) in PDTC-*b*-PEO-*b*-PDTC (**1b**). With increasing amounts of NaI the crystallinity of the PEO phase decreases as compared to the salt-free copolymer **1b**. At a salt concentration of ~10 mol% the crystalline PEO phase disappears and at the same time a new endotherm appears at higher temperatures. This endotherm is attributed to the formation of the PEO/NaI complex, which the former becoming more prominent at higher salt concentrations. The melting point T_m approaches a plateau value at 170 to 180°C and the melting enthalpy shows a maximum (cf. below). The crystalline PDTC phase is hardly modified at all, but the endotherm becomes broader due to defects in the crystalline structure of this phase. *Figure 2* shows quantitative results with respect to the melting points and melting enthalpies of the PEO and PDTC phases, and the PEO/NaI complex. The appearance of the polymer/salt complex coincides with the disappearance of the crystalline PEO phase at ~10 mol% of salt. The melting point of the polymer/salt complex reaches its plateau value at ~17 mol% of salt; the melting enthalpy of the melting endotherm, however, reaches a maximum at 25 mol% of salt, after which a slow decrease is observed. The maximum of the melting enthalpy corresponds to a molar ratio of EO repeat units to metal cations of 3/1. These results suggest that the sodium ions form a complex with the EO repeat units; below a concentration of NaI of ~10 mol% a polymer/salt solution is obtained, while above this concentration the polymer/salt complex is formed. The stoichiometry of 3/1, however, does not allow any conclusion to be reached concerning the coordination number of sodium by oxygen atoms since counterions may also participate

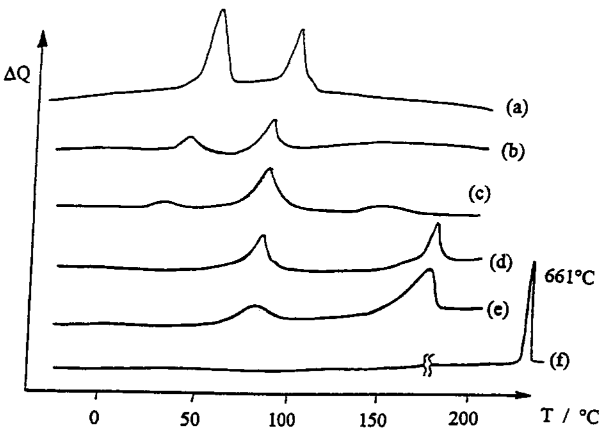

Figure 1 D.s.c. curves of the system PDTC-*b*-PEO-*b*-PDTC (**1b**)/NaI: (a) pure copolymer **1b**; (b) [NaI] = 4.8 mol%; (c) [NaI] = 9.1 mol%; (d) [NaI] = 16.7 mol%; (e) [NaI] = 25 mol%; (f) pure NaI

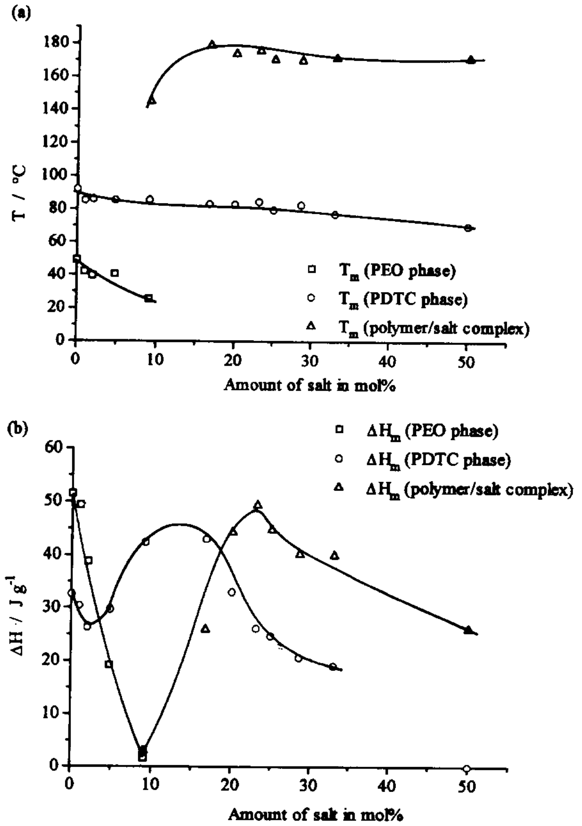

Figure 2 Thermal characteristics of the PEO, PDTC, and the polymer/salt complex phases in the system PDTC-*b*-PEO-*b*-PDTC (**1b**)/NaI as a function of salt concentration: (a) melting points; (b) melting enthalpies (obtained from d.s.c. measurements)

in the coordination of the cation. The stoichiometry of 3/1 and the participation of the counterions in the coordination sphere of the cations are discussed in the literature for the systems PEO/NaI[16] and PEO/NaSCN[8–10]. These authors propose polymer/salt complex structures in which the ions form a zigzag chain in the centre of a PEO helix or a PEO double helix, respectively.

The decrease of the melting enthalpy of the complex beyond a salt content of ~25 mol% can be explained by a solubilization of the salt by the polymer at the expense of the stoichiometric polymer/salt complex.

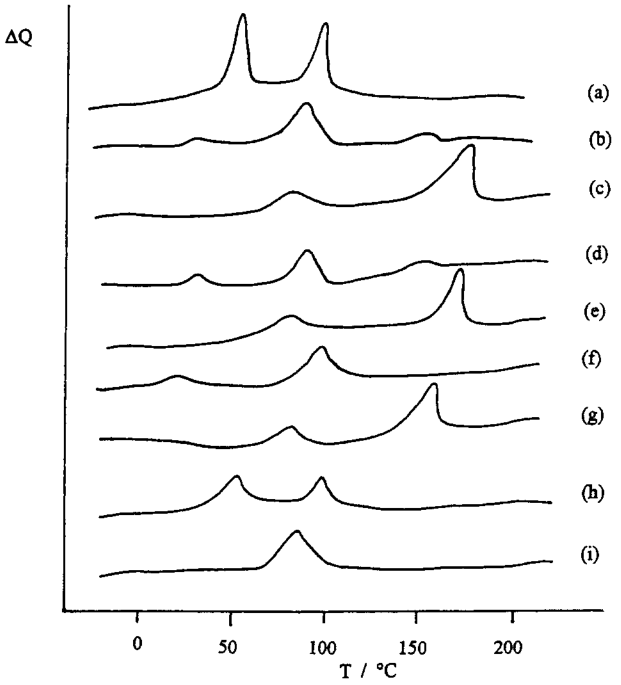

Figure 3 D.s.c. curves of the system PDTC-*b*-PEO-*b*-PDTC (**1b**) with different salts: (a) pure copolymer **1b**; (b) [NaI] = 9.1 mol%; (c) [NaI]= 25 mol%; (d) [NaSCN] = 9.1 mol%; (e) [NaSCN] = 25 mol%; (f) [$LiCF_3SO_3$] = 9.1 mol%; (g) [$LiCF_3SO_3$] = 25 mol%; (h) [$LiClO_4$] = 9.1 mol%; (i) [$LiClO_4$] = 25 mol%

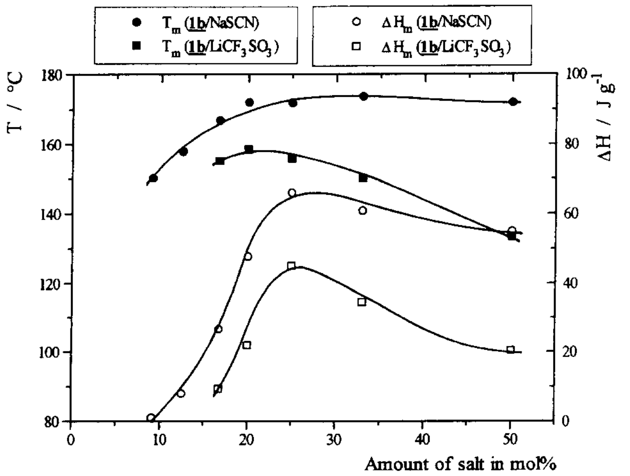

Figure 4 Melting points and melting enthalpies of the polymer/salt complexes obtained by dissolution of NaSCN and $LiCF_3SO_3$ in PDTC-*b*-PEO-*b*-PDTC (**1b**) as a function of salt concentration; data obtained from d.s.c. measurements (first heating run at 20 K/min^{-1})

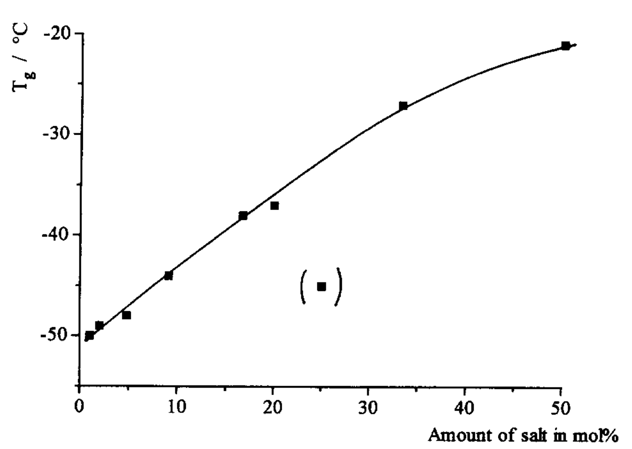

Figure 5 Dependence of the glass transition temperature of the system PDTC-*b*-PEO-*b*-PDTC (**1b**)/$LiClO_4$ on the molar salt concentration (with respect to the EO repeat units), with data obtained from conductivity measurements

A comparison of the d.s.c. thermograms of solutions of NaI, NaSCN, $LiCF_3SO_3$ and $LiClO_4$ (9.1 mol% ($M^+/EO = 1/10$) and 25 mol% ($M^+/EO = 1/3$)) in PDTC-*b*-PEO-*b*-PDTC (**1b**) (*Figure 3*) reveals three different cases: (i) with $LiClO_4$ no crystalline polymer complex is detected in the d.s.c. thermogram, but the crystallinity, however, of the PEO phase decreases to zero; (ii) NaI and NaSCN behave identically, and a crystalline polymer/salt complex is formed with a melting point of ~170°C; (iii) with $LiCF_3SO_3$ a crystalline polymer/salt complex is also formed, but, the melting point, however, is only ~155°C. This leads to the conclusion that the structure of the Li^+/EO complex differs from that of the Na^+/EO complex. The melting points and melting enthalpies of the systems containing polymer **1b**/NaSCN and polymer **1b**/$LiCF_3SO_3$ as a function of salt concentration are shown in *Figure 4*. The maximum melting enthalpy in both cases is obtained for a salt content of 25 mol% and corresponds to a stoichiometry of $M^+/EO = 1/3$.

For all three types of polymer/salt systems the behaviour of the PDTC phase is very similar. A broadening and a shift to lower temperatures is observed for the endothermic peak characteristic of the PDTC phase. An indication of interaction of the salt with the amorphous polymer phase arises from the increase in T_g with increasing salt content (*Figure 5* shows the effect for the system $LiClO_4$/**1b**). This effect has been extensively discussed for PEO/salt systems[17–19], and reflects the loss of chain mobility in the amorphous phase which results from the interaction with the cations of the salt (without formation of a crystalline structure).

I.r. characterization

I.r. spectroscopy is a useful tool for studying the interactions of inorganic electrolytes with polymeric matrices. For these present systems the diagnostic bands for complexation are the carbonate carbonyl stretching frequency (1741 cm^{-1}), the carbonate C–O stretching frequency (1275 cm^{-1}) and the C–O–C ether stretching frequency (1113 cm^{-1}). For the characteristic frequencies of the carbonate unit no significant changes were observed (other than a broadening of the bands) while, however, significant changes were observed for the characteristic absorption bands of the ether. The pure copolymer shows a major sharp band at 1113 cm^{-1}, associated with two smaller bands at 1146 and 1060 cm^{-1} (*Figure 6*). With increasing salt concentration in the system NaI/**1b**, a broadening of the bands is first observed and, at a molar ratio of EO/Na$^+$ of 3/1 two new bands show up at 1105 and 1080 cm^{-1}. These bands are attributed to the C–O–C ether group complexed with Na$^+$ in analogy to the system poly(ethylene oxide)/NaI.

For different salts dissolved in PDTC-*b*-PEO-*b*-PDTC the i.r. spectra show characteristic differences (*Figure 7*). First, for **1b**/NaI and **1b**/NaSCN the spectra are identical in the ether region, thus suggesting the same complex geometry and isomorphic crystal structures. Secondly, the spectrum of LiCF$_3$SO$_3$/**1b** suggests also the existence of a polymer/salt complex of a well-defined structure and stoichiometry. In addition to the slightly shifted PEO band (1110 cm^{-1}), two new bands appear at 1162 cm^{-1} and 1045 cm^{-1}, thus indicating a complex geometry different from that mentioned above. If the band at 1110 cm^{-1} is attributed to the uncomplexed C–O–C stretching frequency (due to the small shift of the band) the new band at 1162 cm^{-1} should be attributed to a C–O–C group involved in the complexation of the Li$^+$. However, a definite interpretation of these bands is somewhat more difficult. According to Schantz and coworkers[20], the symmetric S–O frequency of CF$_3$SO$_3^-$ may be shifted from 1032 to 1046 cm^{-1} when ion clusters are formed, as a result of the increasing anion concentration. The frequency observed at 1045 cm^{-1} in the spectrum might be attributed to such ion clusters. Thirdly in the i.r. spectrum of the LiClO$_4$/**1b** system no sharp bands are observed in this ether region. The band centred at 1099 cm^{-1} indicates an interaction between salt and matrix (the band is shifted to a lower value) but, however, a well-defined complex geometry does not seem to be established.

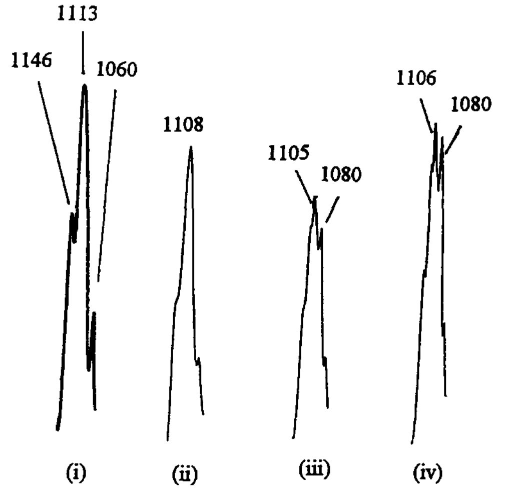

Figure 6 I.r. spectra of the system PDTC-*b*-PEO-*b*-PDTC (**1b**)/NaI as a function of salt concentration (region of the C–O–C frequency): (i) pure copolymer (**1b**); (ii) [NaI] = 4.8 mol%; (iii) [NaI] = 16.7 mol%; (iv) [NaI] = 28.6 mol% (recorded using the *FT*i.r. photoacoustic spectroscopy technique)

X-ray analysis

A direct investigation of the microstructures of polymer/salt mixtures is usually hampered by the multiphase behaviour of such systems. However, some stoichiometric complexes are crystalline and can be studied by X-ray diffraction techniques. The X-ray powder patterns of the polymer/salt complexes **1a**/NaSCN and **1a**/LiCF$_3$SO$_3$ (EO/M$^+$ = 3/1), are compared with the patterns of pure copolymer **1a** and of PEO in *Figure 8*. The first point to be noted is that the crystallinity of the PEO block in the copolymer is clearly lower than the crystallinity of the pure PEO, while in the polymer/salt complexes the crystallinity is reduced even further.

The pure PEO shows characteristic reflections at 2Θ values of 19.2 and 23.2° which appear at the same values in the block copolymer **1a**. This finding supports the results obtained from d.s.c. measurements on the formation of microphases in the block copolymer. The block

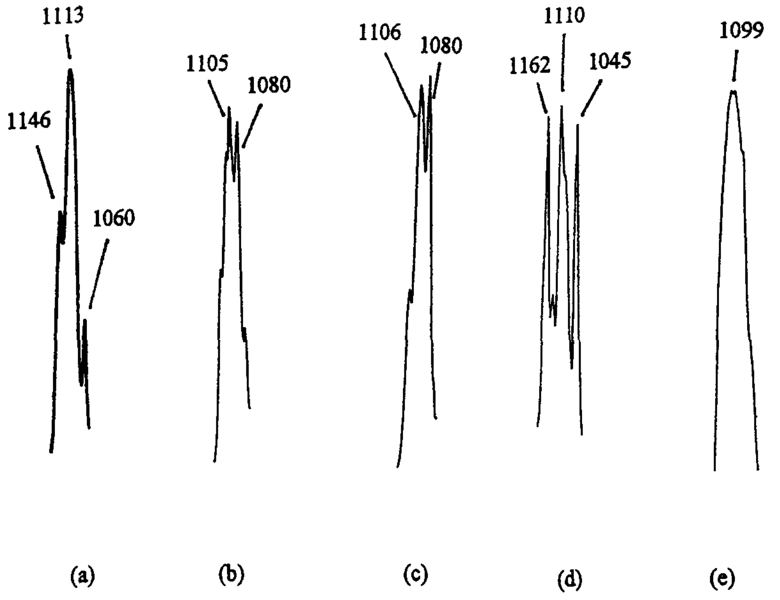

Figure 7 I.r. spectra of the system PDTC-*b*-PEO-*b*-PDTC (**1b**) with different salts ([salt] = 25 mol%): (a) pure copolymer **1b**; (b) **1b**/NaI; (c) **1b**/NaSCN; (d) **1b**/LiCF$_3$SO$_3$; (e) **1b**/LiClO$_4$

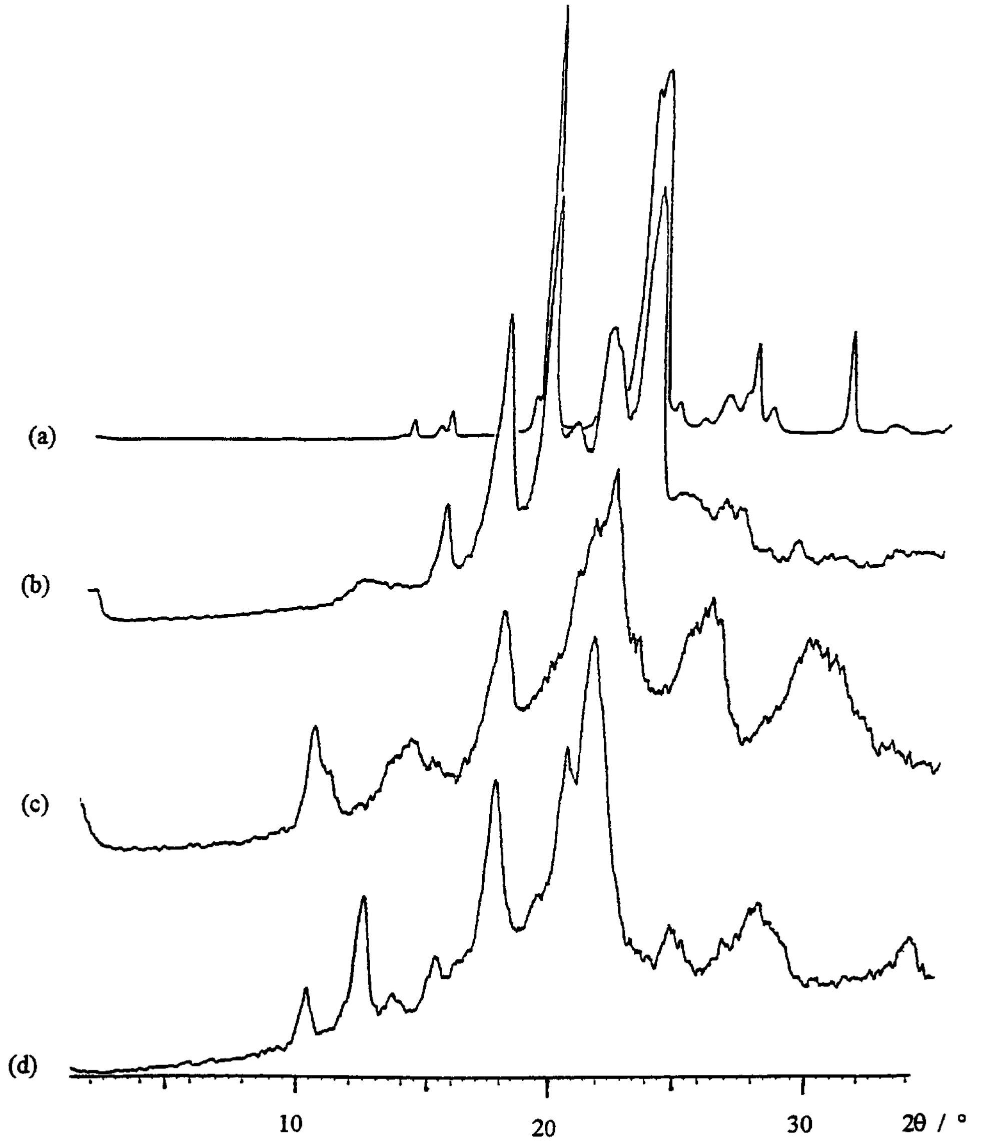

Figure 8 X-ray powder diagrams of polymer/salt systems: (a) pure PEO; (b) PDTC-*b*-PEO-*b*-PDTC (**1a**); (c) **1a**/NaSCN (25 mol%); (d) **1a**/$LiCF_3SO_3$ (25 mol%)

copolymer shows additional reflections at $2\Theta = 14.9$, 17.3, and 21.6°, which can be attributed to the PDTC phase.

The X-ray powder patterns of the polymer/salt complexes differ significantly from the pattern of the block copolymer. In no case were reflections observed from the original salt. In the system **1a**/NaSCN the reflections attributed to the PDTC phase are found to be unchanged; thus salt is not incorporated in the crystalline PDTC phase. In contrast, the reflections characteristic of the PEO phase (19.2 and 23.2°) are not found; thus no crystalline PEO is present. Instead, new reflections are found at $2\Theta = 10.1$, 13.7, 20.8, 25.5, and 29.5°. This new crystalline phase is attributed to the polymer/salt complex.

Since this new phase is built up by insertion of the salt into the helical PEO segment of the copolymer and crystalline PEO or PEO/salt complexes are known to prefer helices as their secondary structures, it is likely that the two characteristic reflections of pure PEO are just shifted upon insertion of the salt and that the two prominent new reflections of the polymer salt complex at $2\Theta = 20.8$ and 25.5° correspond to the original PEO peaks at $2\Theta = 19.2$ and 23.2. Due to Bragg's law, a shift to larger reflection angles corresponds to a decrease in the respective lattice spacings. Structural changes such as these can be attributed to a contraction of the original 7_2 PEO helix, as has been observed in the analogous PEO/NaSCN system[2,10].

In the case of the **1a**/$LiCF_3SO_3$ system, the unshifted PDTC reflections at 17.5 and 21.6° show that there is no relevant interaction between the crystalline PDTC phase and this salt. However, the X-ray diffraction pattern of this system differs significantly from the pattern of pure PEO, as well as from the pattern of the **1a**/NaSCN complex. This result suggests the formation of a new crystalline structure in the **1a**/$LiCF_3SO_3$ system, which is different from that of the **1a**/NaSCN complex.

Ionic conductivity of the polymer/salt systems

The ionic conductivities of solid polymer electrolyte systems depend primarily on the morphology of the system being considered: in an amorphous polymeric medium ionic motion occurs predominantly and most easily, whereas crystallinity impairs the ion transport in polymers. We have studied the ionic conductivity of the block copolymers 1 with a variety of dissolved salts as a function of salt concentration and temperature. As the analytical method, dielectric spetroscopy was applied in the range of 0.1 to 10^5 Hz, at temperatures from -100 to $+60$°C.

Dependence of the conductivity on the nature and concentration of the salt. In the microscopic picture the magnitude of ionic conductivity depends on the amount (n_i), charge (q_i), and mobility (μ_i) of each kind of charge carrier (i) present in the system, with $\sigma = \Sigma n_i \mu_i q_i$.

The dependence of the ionic conductivity on the salt concentration gives information on specific interactions between the salt and polymeric matrix (*Figure 9*). For the three systems studied here, namely **1b**/$LiClO_4$, **1b**/NaSCN and **1c**/$LiCF_3SO_3$, up to a level of ~10 mol% of salt the conductivity increases with increasing salt content. This behaviour was expected since at low salt concentration all of the ions contribute to the charge transport in the electric field. The higher the number of charge carriers then the higher will be the conductivity. For the system **1b**/$LiClO_4$ a slow increase of conductivity is observed up to ~20 mol%, when a maximum value is reached. A higher salt concentration leads to a decrease in conductivity. This behaviour was explained by aggregation of the ions at higher ion concentrations leading to the formation of ion clusters[21]; thus the number of charge carriers and their mobility is decreased. In addition, at high ion concentrations the polarity of the medium increases, which reduces the ion mobility and thus the conductivity. As a conclusion, the dependence of the conductivity on the concentration of $LiClO_4$ arises from two opposite effects: (i) an increase in conductivity due to a higher number of charge carriers (predominant at low concentrations) and (ii) a decrease in conductivity due to aggregation and an increase in the polarity of the medium (predominant at higher concentrations). These two effects lead to a maximum in conductivity at ~20 mol% $LiClO_4$.

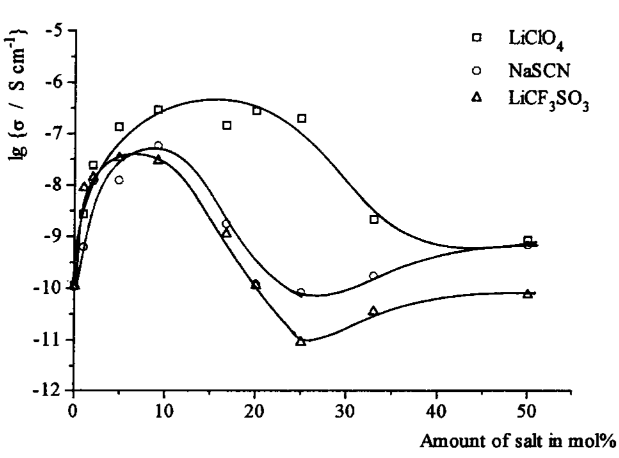

Figure 9 Dependence of the ionic conductivity on the nature and concentration of the salt in the system PDTC-*b*-PEO-*b*-PDTC/salt: (□) **1b**/$LiClO_4$; (○) **1b**/NaSCN; (Δ) **1c**/$LiCF_3SO_3$

For the systems **1b**/NaSCN and **1c**/$LiCF_3SO_3$ the dependence of the conductivity on the salt concentration is more complex. After an initial increase in conductivity, the conductivity then decreases, beginning at a salt concentration of 10 mol%; the minimum conductivity is achieved at ~25 mol%, after which the conductivity increases again, reaching the same level as for $LiClO_4$ at 50 mol% salt. This behaviour for the conductivity can be explained if an additional effect is considered, namely the formation of a crystalline polymer/salt complex in the case of NaSCN and $LiCF_3SO_3$. The minimum in the conductivity corresponds to a molar ratio EO/M^+ of 3/1, which was previously observed as a specific value in d.s.c. and i.r. spectroscopic investigations. At this composition, nearly all of the charge carriers are fixed in the crystalline lattice of the polymer/salt complex and cannot contribute to the conductivity. Additional salt will dissolve in the amorphous PEO phase or in the PDTC phase (less probable) and will thus increase the conductivity. At salt concentrations between 5 and 10 mol%, ionic conductivities of 10^{-6} to 10^{-4} S cm^{-1} at 60°C were measured in the polymer/salt systems studied here, with the lithium systems showing slightly higher values compared to the sodium or potassium systems.

Temperature dependence of the conductivity of polymer/salt systems. The temperature dependence of the ionic conductivity gives information on the mechanism of

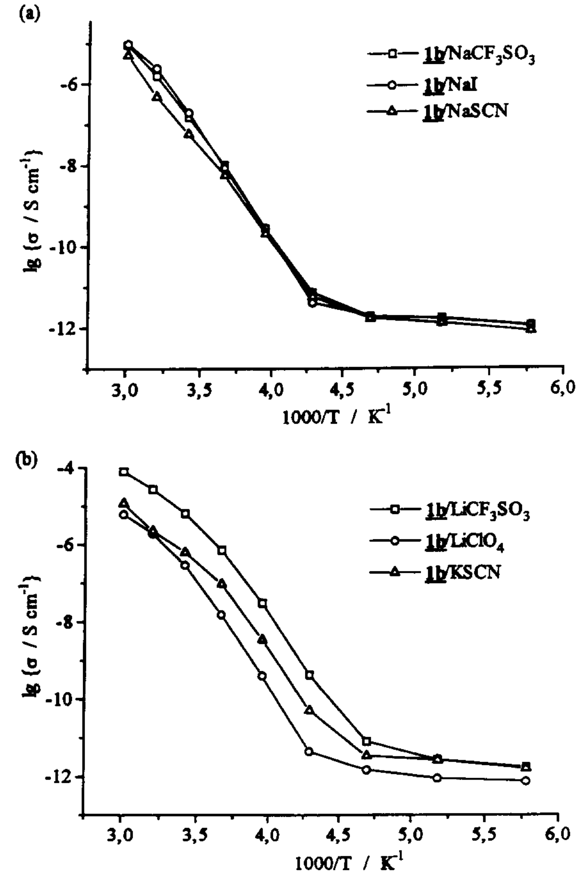

Figure 10 Arrhenius plot of the conductivity σ of PDTC-*b*-PEO-*b*-PDTC (**1b**)/salt systems ([salt] = 9.1 mol%); (a) Na^+X^- ($X^- = CF_3SO_3^-$, I^-, and SCN^-); (b) Li^+X^- ($X^- = CF_3SO_3^-$, and ClO_4^-). Data for the **1b**/KSCN system are also shown

ion transport through the polymeric matrix[22]. Crystalline polymer/salt systems show mainly an Arrhenius-type behaviour, i.e. ionic conductivity is determined by the activation energy necessary to overcome the polymer/salt interaction and to remove the cation from its coordination sphere. Amorphous polymer/salt systems show a Vogel–Tammann–Fulcher (VTF) behaviour[23–25], i.e. chain segment mobility determines the conductivity.

The polymer/salt systems studied in this work show both types of temperature dependence of the conductivity, depending on the nature of the salt used.

A plot of $\log\sigma$ *versus* T^{-1}, where σ is the conductivity and T is the absolute temperature (*Figure 10*), confirms an Arrhenius-type behaviour of the conductivity for the respective systems. The two different slopes characterize the system below and above its glass transition temperature (T_g). Thus the systems **1b**/$NaCF_3SO_3$, **1b**/NaI, and **1b**/NaSCN show an Arrhenius-type behaviour, while for the systems **1b**/$LiCF_3SO_3$, **1b**/$LiClO_4$, and **1b**/KSCN the $\log\sigma$ *versus* T^{-1} representation shows a slightly positive curvature which is characteristic of a VTF behaviour. A plot of $\log(\sigma T^{1/2})$ *versus* $(T - T_0)^{-1}$ (*Figure 11*), which corresponds to the VTF equation, i.e.

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

(where A and B are semiempirical constants and $T_0 \sim T_g - 50\,\mathrm{K}$ is the equilibrium glass transition temperature) results in linear relationships for the systems **1b**/$LiCF_3SO_3$, **1b**/$LiClO_4$, and **1b**/KSCN at temperatures above the T_g, whereas the data for the system **1b**/NaSCN, typical of an Arrhenius-type behaviour (in comparison), show a negative curvature.

The different behaviours of the polymer/salt systems with respect to their conductivities and conductivity mechanisms are in full agreement with the results obtained by d.s.c., i.r. spectroscopy and X-ray diffraction. From the Arrhenius-type behaviour for the conductivity of the polymer/Na salt systems it is concluded that the conductivity is determined by the interaction energy between the polymer matrix and the cation. From the d.s.c., i.r. spectroscopic and X-ray diffraction data the complexes **1**/NaSCN and **1**/NaI are found to be particularly strong and correspondingly the conductivity at a given temperature is low. The conductivities of the lithium and potassium salt systems show, in accordance with their VTF-type behaviour, that the mobility of the ions is less determined by the enthalpic term (interaction of M^+ with the polymeric matrix) but rather by the entropic term which is related to the free volume distribution in the polymeric matrix ('free volume model')[26] or the local chain segment mobility ('configurational entropy model')[27,28]. For Li^+ and K^+ the coordination with PEO is weak, and this is reflected by the absence ($LiClO_4$ and KSCN systems) or low stability ($LiCF_3SO_3$ system) of a crystalline complex.

For the polymer/salt systems represented in *Figure 10* the ionic conductivities just above the glass transition temperatures reveal an Arrhenius-type behaviour, while at higher temperatures the VTF-type behaviour becomes evident.

Influence of the relative block length on the thermal properties and the ionic conductivity of the polymer/salt systems

Two series of PDTC-*b*-PEO-*b*-PDTC were studied: (i) the PEO block was varied (PEO 1000, PEO 3400, and PEO 8000) with the weight fraction of DTC in the copolymer remaining constant (**1d**, **1f**, and **1g**), and (ii) the PEO block length was kept constant (PEO 8000) while the block length of the PDTC block was varied from 48.8 to 85.8 wt% (**1a**–**e**).

For the polymer/salt system containing 25 mol% NaSCN both T_m of the PDTC phase and T_m of the complex increase with increasing PEO block length (*Figure 12*). For PEO 8000 a plateau value of T_m (~175°C) is reached. In accordance with our result, Lee and Wright[29] found a dependence of T_m on the molecular weight of PEO for the PEO/NaSCN and PEO/NaI systems; a plateau value of T_m was reached with PEO 6000. ΔH_m shows a maximum for PEO 3400, and since this parameter is directly related to the crystallinity of the sample one may conclude that the crystallinity is at a maximum for relatively low molecular weights of PEO. The decrease of crystallinity at higher molecular weights may be related to chain entanglements which decrease the chain mobility and, as a consequence, on addition of salt the PEO chains cannot adopt the

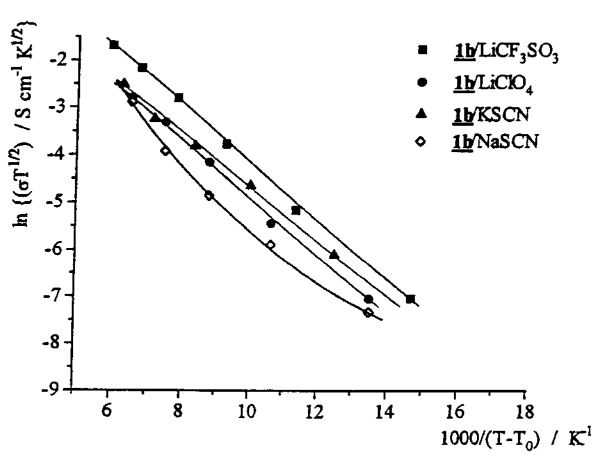

Figure 11 Dependence of the ionic conductivity on temperature for PDTC-*b*-PEO-*b*-PDTC (**1b**)/salt systems (according to the VTF equation), with salt concentrations = 9.1 mol%

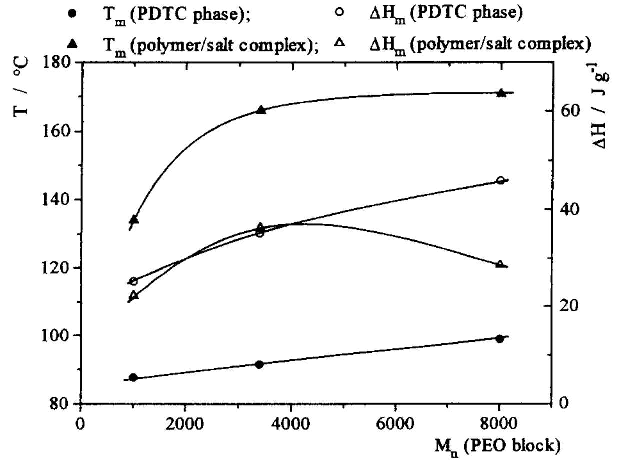

Figure 12 Dependence of the melting points and melting enthalpies on the PEO-block length in PDTC-*b*-PEO-*b*-PDTC (**1d**, **1f**, and **1g**)/NaSCN systems with [NaSCN] = 25 mol%

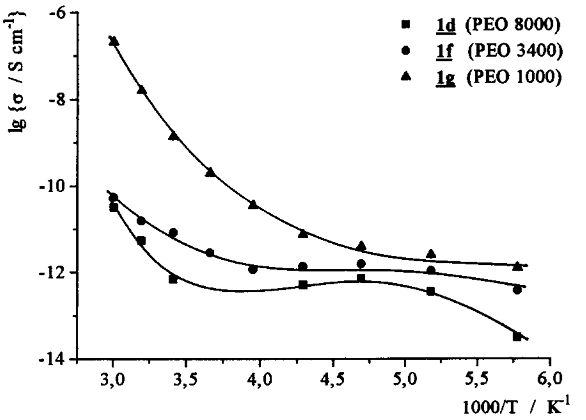

Figure 13 Dependence of the ionic conductivity on the PEO-block length in PDTC-*b*-PEO-*b*-PDTC (**1d**, **1f**, and **1g**)/NaSCN systems, with [NaSCN] = 25 mol%

conformation necessary to develop an ideal structure for the polymer/salt complex. The distinctly lower T_m and ΔH_m values of the polymer/salt complexes containing PEO 1000 show that M_n (PEO block) ~1000 (= 20 EO repeat units) represents the lowest limit for the formation of crystalline polymer/salt complexes.

The degree of crystallinity of a polymer/salt system is also reflected by the conductivity of the system, i.e. a decrease in crystallinity leads to an increase in conductivity (*Figure 13*). This effect is especially pronounced in the molecular-weight range from 1000 to 3400 for the PEO block; the polymer/salt complexes containing PEO 3400 blocks show the highest crystallinity values, whereas in systems containing PEO 1000 blocks the crystallinity is significantly lower.

The set of copolymer/salt systems containing a PEO 8000 middle block and PDTC side blocks of increasing molecular weight showed no significant changes with composition in their thermal properties or conductivities.

CONCLUSIONS

The results obtained from d.s.c., i.r. spectroscopic and X-ray diffraction investigations of polymer/salt solutions, with PDTC-*b*-PEO-*b*-PDTC as the polymeric matrix and alkali metal salts with large, monovalent anions, reveal two classes of materials, depending on the nature of the salt:

1. Solid solutions of the salt in the polymeric matrix (one-phase system). These solutions are stable over a large compositional range, and the PEO phase is considered to be the solvent for the salt. A typical example is the $LiClO_4$ system.
2. Crystalline polymer/salt complexes with a stoichiometry of 3/1 (EO repeat units/metal cation). Below and above this stoichiometry the polymer/salt system behaves like a two-phase system with salt present in both the crystalline and the amorphous phase. The complex of the salt with the PEO segments of the polymer leads to a change in the PEO helix. The structure of the complexes differ with the nature of the salt. Thus the polymer/NaSCN and polymer/NaI complexes have a melting point of 170–175°C, while for the $LiCF_3SO_3$/polymer complex a melting point of ~155°C was found. Ionic conductivity measurements can be interpreted in the same way: the formation of a crystalline complex reduces the conductivity by three orders of magnitude. Since the complex will not form below salt concentrations of 8 to 10 mol%, the highest ionic conductivities are obtained below salt concentrations of 8 mol%.

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