Macromol. Symp. **2006**, 235, 57–63 DOI: 10.1002/masy.200650308

Solid Polymer Electrolytes Studied by NMR Spectroscopy and DFT Calculations

Jiří Spěváček, Jiří Brus, Jiří Dybal*

Summary: Results obtained recently on polymer electrolytes poly(ethylene oxide) (PEO)/$LiCF_3SO_3$ and poly(2-ethyl-2-oxazoline) (POZ)/$AgCF_3SO_3$ by a combination of solid-state ^{13}C and ^{1}H NMR spectroscopy and DFT quantum-chemical calculations are discussed. Essentially the same local structure was found for the amorphous and crystalline phases of semicrystalline PEO/$LiCF_3SO_3$ polymer electrolyte. The amorphous POZ/$AgCF_3SO_3$ complex has a defined stoichiometry with two POZ monomeric units per one $AgCF_3SO_3$. A close contact between the metal salt and polymer was determined for both investigated systems from the Lee-Goldburg cross-polarization $^{1}H \rightarrow {}^{13}C$ dynamics.

Keywords: calculations; NMR; poly(2-ethyl-2-oxazoline)/$AgCF_3SO_3$; poly(ethylene oxide)/$LiCF_3SO_3$; solid polymer electrolyte

Introduction

It is well known that by incorporating a metal salt into a polar polymer matrix the system becomes ionically conductive, i.e., a solid polymer electrolyte is formed. Typical example is molecular complexes of poly(ethylene oxide) (PEO) with alkali metal salts; an application of these systems in electrochemical devices like solid-state batteries has been suggested.[1,2] The PEO/$LiCF_3SO_3$ complex (stoichiometry three PEO monomeric units per one $LiCF_3SO_3$) is one of the most investigated systems and its crystal structure was determined by X-ray diffraction.[3] Correlating NMR results and conductivity measurements, it was concluded that due to high mobility, the amorphous phase of the polymer electrolyte is primarily responsible for the ionic conductivity.[4] Recently the results were published[5,6] showing that ionic conductivity in the crystalline phase can be greater than in equivalent amorphous material; however, the opposite conclusion was also published.[7] In contrast to the crystalline phase, virtually no structural information is available for the amorphous phase and the only information in this respect was based on infrared spectra measured above the melting point from which the authors concluded the structural similarity of the crystalline and amorphous phase in PEO/$LiCF_3SO_3$ complex.[8]

Another type of solid polymer electrolytes is polymer-silver salt complexes, such as, e.g., poly(2-ethyl-2-oxazoline) (POZ)/$AgCF_3SO_3$ complex. These systems showed high separation performance for alkene/alkane mixtures and they are investigated as promising membrane materials.[9,10] Wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) have shown that POZ/$AgCF_3SO_3$ polymer electrolytes are completely amorphous.[11,12] IR spectroscopy indicated that the stoichiometry of the POZ/$AgCF_3SO_3$ complex might be close to 1/1.[13]

Among other methods, solid-state NMR spectroscopy (in particular ^{7}Li and ^{23}Na NMR) has been also used to study polymer electrolytes based on PEO (mainly their phase composition and ionic mobility).[2,14] It has been shown that solid-state ^{13}C NMR

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic
Fax: +420 296809410
E-mail: spevacek@imc.cas.cz

is another suitable method for structural characterization of PEO-based polymer electrolytes.[15–17] The present paper provides an overview of our recent NMR studies of semicrystalline PEO/LiCF$_3$SO$_3$ and amorphous POZ/AgCF$_3$SO$_3$ polymer electrolytes.[17–20] In these studies we have found useful a combination of solid-state ^{13}C and ^{1}H NMR spectroscopy on real system and density functional theory (DFT) quantum-chemical calculations on model systems.

Table 1.
^{13}C and ^{1}H NMR chemical shifts of PEO in the PEO/LiCF$_3$SO$_3$ complex and in neat PEO.[19]

Sample	phase	δ (ppm)	
		^{13}C	^{1}H
PEO	crystalline	72.0	3.60
	amorphous	70.8	3.59
PEO/LiCF$_3$SO$_3$ complex	crystalline	68.9	3.93
	amorphous	68.9 (−1.9[a)])	3.98 (0.39[a)])

[a)] In parentheses are values of the difference $\Delta = \delta_{PEO/LiCF3SO3} - \delta_{PEO}$.

Polymer Electrolyte PEO/LiCF$_3$SO$_3$

We have chosen ^{13}C and ^{1}H NMR chemical shifts of PEO nuclei to characterize interactions and local structure separately in the crystalline and amorphous phases of the PEO/LiCF$_3$SO$_3$ semicrystalline polymer electrolyte with the aim to contribute to fill the existing gap concerning the structural characterization of the amorphous phase in the PEO-based polymer electrolytes.[19] We investigated a stoichiometric sample of the PEO ($M_w = 6000$)/LiCF$_3$SO$_3$ complex (i.e., PEO monomeric unit/LiCF$_3$SO$_3$ = 3/1). Sample of the neat PEO 6000 was also studied. Both the PEO/LiCF$_3$SO$_3$ complex and the neat PEO were highly crystalline (degree of crystallinity ≈90%). Due to high degree of crystallinity there is a dominant contribution of the crystalline phase to the PEO signal in solid-state ^{13}C CP/MAS (cross polarization/magic angle spinning) and ^{1}H CRAMPS (combined rotation and multipulse spectroscopy) NMR spectra. On the other hand only amorphous phase contributes to the narrow component in the ^{1}H MAS NMR spectra measured with spinning frequency 5 kHz and to the PEO signal in ^{13}C MAS NMR spectra measured without CP with a short pulse repetition time of 1 s. In the latter case this is a consequence of the fact that spin-lattice relaxation times T_1 of crystalline PEO carbons in the PEO/LiCF$_3$SO$_3$ complex and in the neat PEO are 15.6 and 10 s, respectively, while for amorphous PEO carbons it holds $T_1 < 1$ s in both cases.[17,21] ^{13}C and ^{1}H NMR chemical shifts of PEO in the crystalline and amorphous phase of the complex are shown in Table 1, together with the respective values in the neat PEO. A higher shielding of PEO carbons and lower shielding of PEO protons was found for the PEO/LiCF$_3$SO$_3$ complex in comparison with neat PEO; a similar behavior was found also for PEO nuclei in PEO/hydroxybenzene complexes stabilized by hydrogen bonds.[18,21] From Table 1 it further follows that ^{13}C PEO chemical shifts are identical in the crystalline and amorphous phase of PEO/LiCF$_3$SO$_3$, and also ^{1}H PEO chemical shifts are virtually the same for both phases. This result confirms the same interaction (i.e., the coordination of ether oxygens to the Li$^+$ cation) in both phases and shows the same or at least very similar local structure in the crystalline and amorphous phase of PEO/LiCF$_3$SO$_3$ polymer electrolyte.

The experimental NMR results are corroborated by quantum-chemical DFT calculations on a model complex of diglyme CH$_3$O(CH$_2$CH$_2$O)$_2$CH$_3$ and LiCF$_3$SO$_3$.[19] The optimized geometry of this model complex is shown in Figue 1. The presented structure of the model complex, indicating coordination of the Li$^+$ cation by the three diglyme oxygens and the two oxygens of the anions, simulates well the X-ray crystal structure of the PEO/LiCF$_3$SO$_3$ complex.[3] ^{13}C and ^{1}H NMR chemical shifts were calculated both for diglyme/LiCF$_3$SO$_3$ model complex and uncoordinated diglyme. The values of difference of the respective chemical shifts, defined as $\Delta = \delta_{diglyme/LiCF3SO3} - \delta_{diglyme}$, are shown for diglyme carbons and protons (with exception of

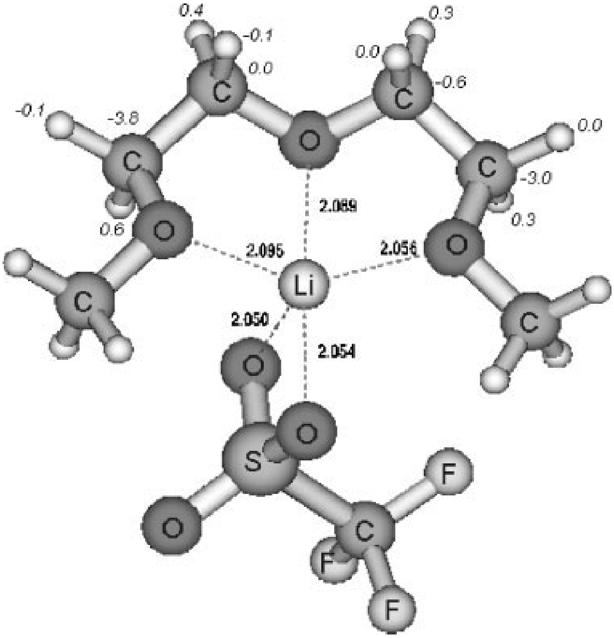

Figure 1.
Optimized geometry of the model complex of diglyme $CH_3O(CH_2CH_2O)_2CH_3$ and $LiCF_3SO_3$ as obtained from DFT calculations. The values of the difference Δ of the respective chemical shifts $\Delta = \delta_{diglyme/LiCF3SO3} - \delta_{diglyme}$ are shown for various diglyme carbons and protons directly in the figure (values for protons are in italics). At dotted lines the respective distances are given in Å.[19]

CH_3 end groups) directly in Figure 1 (values for protons are in italics). In accord with experimental results these calculations have shown a higher shielding of diglyme carbons and lower shielding of diglyme protons (those at the rear side of the structure presented in Figure 1) in the model complex in comparison with uncoordinated diglyme. The averaged values of the difference Δ as found for diglyme carbons and protons (at the rear side of the structure in Figure 1), $\Delta(^{13}C) = -1.9$ ppm and $\Delta(^{1}H) = 0.4$ ppm, agree well with the respective experimental values (cf. Table 1), so supporting the idea that local structures in crystalline and amorphous phases are virtually the same.

To obtain information on the geometrical structure of the $PEO/LiCF_3SO_3$ polymer electrolyte, we attempted to determine the effective distance r_{eff} between $LiCF_3SO_3$ carbon and its nearest PEO protons. Two types of the approach were used for this purpose. First, from the measurement of the CP dynamics the distance $r_{eff} = 0.36$ nm was determined.[17] However, in this case the resulting value might be affected by proton spin diffusion. Therefore we applied also a method based on the measurements of the dynamics of the Lee-Goldburg (LG) CP $^{1}H \rightarrow {}^{13}C$.[22] The homonuclear proton dipolar interactions are averaged-out and proton spin diffusion is effectively supressed during LG irradiation of protons. Using this method, for the effective distance between the $LiCF_3SO_3$ carbon and its nearest PEO protons we obtained the value $r_{eff} = 0.33$ nm.[19] This value is in accord with distances 0.31–0.34 nm[17] between the $LiCF_3SO_3$ carbon and the nearest PEO hydrogens calculated by using refined atomic parameters of the crystal structure of the $PEO/LiCF_3SO_3$ polymer electrolyte.[3]

Polymer Electrolyte $POZ/AgCF_3SO_3$

We investigated samples of $POZ/AgCF_3SO_3$ polymer electrolytes with molar ratio of both components in the range 10/1–1/1; samples of the neat POZ and $AgCF_3SO_3$ were also studied for comparison.[20] As mentioned in Introduction, both POZ/$AgCF_3SO_3$ blends and neat POZ were completely amorphous.[11] Similarly as for PEO/$LiCF_3SO_3$ polymer electrolyte,[17,19] also for all POZ/$AgCF_3SO_3$ blends with various molar ratios of both components, in ^{13}C CP/MAS NMR spectra in addition to POZ resonances also the signal of $AgCF_3SO_3$ carbons was detected. Because in CP/MAS spectra ^{13}C lines originate from dipolar-coupled protons, the existence of the signal of $AgCF_3SO_3$ carbons confirms that in all blends both components are in contact forming the molecular complex; the distance between $AgCF_3SO_3$ carbon and nearest POZ protons in the complex has to be smaller than $\approx$0.5 nm. Some changes of POZ resonances (shape and chemical shifts) in POZ/$AgCF_3SO_3$ samples in comparison with the neat POZ were also visible in ^{13}C CP/MAS NMR spectra. The largest changes of chemical shifts were found for carbonyl carbons (cf. further text). Smaller changes (downfield shift 0.5 ppm) were found for the line of adjacent side-chain methylene carbons, while the chemical shifts of main-chain POZ carbons and side-chain methyl carbons were the same in POZ/$AgCF_3SO_3$ blends and in the neat POZ. These results show that the dominant interaction in the POZ/$AgCF_3SO_3$ complex is the coordination between silver cations and carbonyl oxygens.

The carbonyl region in ^{13}C CP/MAS NMR spectra is shown in Figure 2a. From this figure it follows that in blends containing $AgCF_3SO_3$ a new carbonyl signal exists with $\approx$4 ppm larger chemical shift in comparison with the carbonyl resonance in the neat POZ. From Figure 2a it also follows that with the increasing amount of silver salt in POZ/$AgCF_3SO_3$ blend the relative intensity of the new carbonyl line increases (up to molar ratio POZ/$AgCF_3SO_3 = 2/1$) and that both for 2/1 and 1/1 POZ/$AgCF_3SO_3$ mixing ratios no signal of the neat uncomplexed POZ was detected. For remaining POZ/$AgCF_3SO_3$ mixing ratios a deconvolution of the carbonyl region into two components is shown in Figure 2b. The new carbonyl signal with larger chemical shift evidently corresponds to carbonyls in the POZ/$AgCF_3SO_3$ complex. From the fact that no signal of the neat uncomplexed POZ was detected for the mixing ratio POZ/$AgCF_3SO_3 = 2/1$ as well as from the ratios of the intensities of the carbonyl line in the complex and the line of the uncomplexed POZ as a function of the mixing ratios of POZ and $AgCF_3SO_3$ (cf. Figure 2b) it results that the complex has the defined molar stoichiometry POZ/$AgCF_3SO_3 =$ 2/1. This is also in accord with the shape of the signal of $AgCF_3SO_3$ carbons which for mixing ratio POZ/$AgCF_3SO_3 = 1/1$ shows the existence of the excessive uncomplexed $AgCF_3SO_3$.[20]

Quantum-chemical DFT calculations were also used to study interaction of "monomeric" model ($CH_3CH_2N(COCH_2CH_3)CH_3$) and "dimeric" model ($CH_3CH_2N(COCH_2CH_3)CH_2CH_2N(COCH_2CH_3)CH_2CH_3$) of POZ with $AgCF_3SO_3$. Resulting structure as obtained for "dimeric" model complex that is in accord with 2/1 stoichiometry determined for the POZ/$AgCF_3SO_3$ complex from ^{13}C CP/MAS NMR spectra, is depicted in Figure 3. In this structure the silver cation is coordinated to both carbonyl oxygens. In accord with experimental NMR results, DFT calculations have shown lower shielding of carbonyl carbons and adjacent side-chain methylene carbons in model complexes in comparison with "neat" models of POZ. Concerning the absolute values of the difference $\Delta = \delta_{POZ/AgCF3SO3} - \delta_{POZ}$ (for calculated chemical shifts, POZ should be replaced by either the "monomeric" or "dimeric" model of POZ), contrary to PEO/$LiCF_3SO_3$ polymer electrolyte where the experimental values of the difference Δ were in excellent agreement with values obtained by DFT calculations, for the POZ/$AgCF_3SO_3$ system the difference of the respective chemical shifts Δ calculated for carbonyl carbons in model complexes was

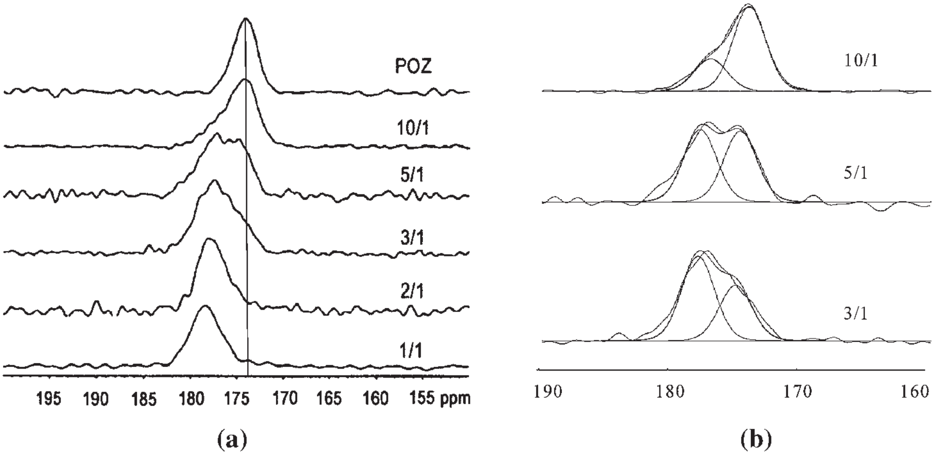

Figure 2.
(a) Carbonyl region in ^{13}C CP/MAS NMR spectra of POZ/$AgCF_3SO_3$ polymer electrolytes with various molar mixing ratios of POZ and $AgCF_3SO_3$. (b) Deconvolution of the carbonyl region into two components.[20]

more than twice larger than the experimental value $\Delta = 3.9$ ppm found for the stoichiometric POZ/$AgCF_3SO_3 = 2/1$ complex. For the adjacent side-chain methylene carbons the value of the difference Δ calculated for the "dimeric" model complex ($\Delta = 1.2$ ppm) is much closer to experimental value ($\Delta = 0.5$ ppm) than the value calculated for the "monomeric" model complex ($\Delta = 3.2$ ppm).[20]

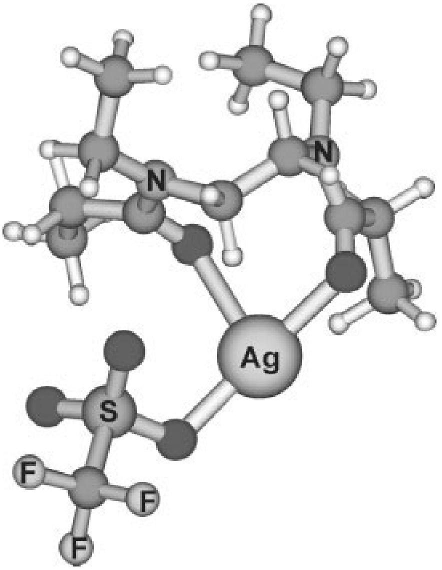

Figure 3.
Structure obtained from DFT calculations for "dimeric" model of POZ interacting with $AgCF_3SO_3$.[20]

Measurements of ^{13}C spin-lattice relaxation times T_1 have shown that T_1 values in the stoichiometric polymer electrolyte POZ/$AgCF_3SO_3 = 2/1$ are significantly shorter in comparison with the neat POZ.[20] The fact that that the temperature of the glass transition $T_g = 360$ K found for this sample is by 16 K higher than in the neat POZ[12] contradicts the explanation that shorter T_1 values in the POZ/$AgCF_3SO_3$ complex might indicate a higher segmental mobility, as found for neat POZ from T_1 measurements at variable temperatures. We assume that shorter T_1 values found for the POZ/$AgCF_3SO_3$ sample are due to the paramagnetic contribution to the relaxation mechanism. The source for this contribution is evidently atoms of neutral silver (Ag^0) that can be formed in small amount in this system.[23] From the fact that the paramagnetic contribution to the total relaxation is roughly comparable with the contribution from the dipolar coupling between carbons and directly bonded protons it follows that relative amount of the atoms of neutral silver in the studied POZ/$AgCF_3SO_3$ complex is $\sim 0.1\%$.[20]

To obtain information on the geometrical structure of the POZ/$AgCF_3SO_3$

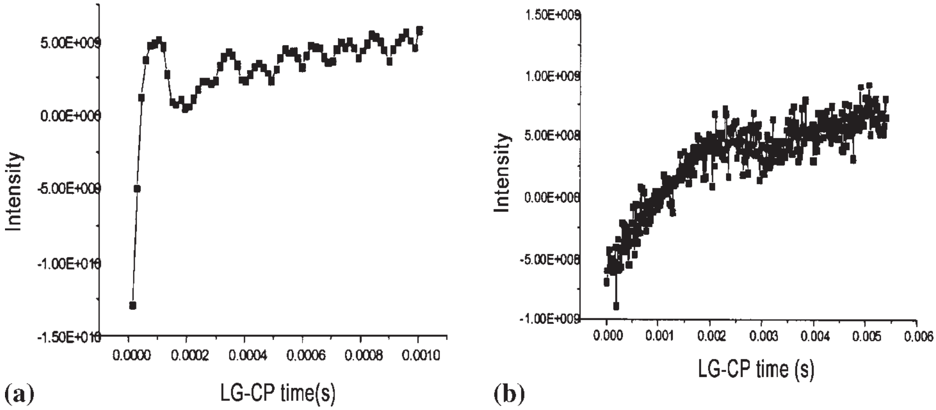

Figure 4.
LG-CP dynamics (integrated intensity vs. contact time) for POZ NCH_2 (a) and $AgCF_3SO_3$ (b) carbons in the POZ/$AgCF_3SO_3 = 2/1$ polymer electrolyte.[20]

complex, we determined the effective distance r_{eff} between $AgCF_3SO_3$ carbon and its nearest POZ protons using a method based on the measurements of the dynamics of LG CP $^1H \rightarrow {}^{13}C$, similarly as mentioned above for PEO/$LiCF_3SO_3$ polymer electrolyte. Figure 4 shows for illustration the integrated intensities of POZ NCH_2 and $AgCF_3SO_3$ signals in ^{13}C CP/MAS NMR spectra of the stoichiometric POZ/$AgCF_3SO_3 = 2/1$ complex, measured with LG irradiation of protons, as a function of LG-CP time. The Fourier transforms of LG-CP curves yield the respective ^{13}C-^1H dipolar couplings $\Delta\omega/2\pi$, equal to 10 and 0.78 kHz for NCH_2 POZ carbons and $AgCF_3SO_3$ carbons, respectively.[20] The value obtained for NCH_2 carbons shows that system is not completely rigid; for CH_2 carbons in the crystalline PEO/$LiCF_3SO_3$ complex we obtained $\Delta\omega/2\pi = 12.2$ kHz.[18,19] After the correction for the rigid system and using the formula for the internuclear distance r_{CH} (in nm)[22], $r_{CH} = 2.586(\Delta\omega/2\pi)^{-1/3}$, for the effective distance of $AgCF_3SO_3$ carbon and its nearest POZ protons we obtained $r_{\mathrm{eff}} = 0.26$ nm, showing a very close contact between both components.

Conclusion

Solid-state NMR spectra and quantum-chemical DFT calculations confirmed that dominant interaction in the PEO/$LiCF_3SO_3$ and POZ/$AgCF_3SO_3$ polymer electrolytes is coordination between respective cation (Li^+ or Ag^+) and ether or carbonyl oxygens of PEO and POZ, respectively. A close contact between interacting components was determined from the LG CP $^1H \rightarrow {}^{13}C$ dynamics for both systems. Higher shielding of PEO carbons and lower shielding of PEO protons was found for PEO/$LiCF_3SO_3$ polymer electrolyte compared with the neat PEO both experimentally from NMR spectra and from DFT calculations on a model complex of diglyme and $LiCF_3SO_3$. ^{13}C and ^1H NMR chemical shifts are the same in amorphous and crystalline phases of PEO/$LiCF_3SO_3$ polymer electrolyte, showing essentially the same local structure in both phases. Therefore, the important factors affecting the ionic conductivity might be either a higher mobility of the amorphous phase or a regular long-distance conformational arrangement of the crystalline phase. Solid-state ^{13}C NMR spectra (carbonyl region) evidence that the POZ/$AgCF_3SO_3$ complex has a defined stoichiometry: two POZ monomeric units per one $AgCF_3SO_3$. The shorter ^{13}C spin-lattice relaxation times in the stoichiometric POZ/$AgCF_3SO_3$ sample in comparison with neat POZ indicate a formation of small amount (~0.1%) of paramagnetic neutral silver.

Acknowledgment: Financial support of the Academy of Sciences of the Czech Republic (grant No. AVOZ 40500505) and Grant Agency of the Czech Republic (grant No. 525/05/0273) is gratefully acknowledged.

[1] M. B. Armand, in: "*Polymer Electrolyte Reviews-1*", J. R. MacCallum, C. A. Vincent, Eds., Elsevier, London 1987, Chapter 1.
[2] V. Chandrasekhar, *Adv. Polym. Sci* **1998**, *135*, 139.
[3] P. Lightfoot, M. A. Mehta, P. G. Bruce, *Science* **1993**, *262*, 883.
[4] C. Berthier, W. Gorecki, M. Minier, M. B. Armand, J. M. Chabagno, P. Rigaud, *Solid State Ionics* **1983**, *11*, 91.
[5] Z. Gadjourova, Y. G. Andreev, D. P. Tunstall, P. G. Bruce, *Nature* **2001**, *412*, 520.
[6] Z. Stoeva, I. Martin-Litas, E. Staunton, Y. G. Andreev, P. G. Bruce, *J. Am. Chem. Soc.* **2003**, *125*, 4619.
[7] W. A. Henderson, S. Passerini, *Electrochem. Commun.* **2003**, *5*, 575.
[8] R. Frech, S. Chintapalli, P. G. Bruce, C. A. Vincent, *Chem. Commun.* **1997**, 157.
[9] Y. Yoon, J. Won, Y. S. Kang, *Macromolecules* **2000**, *33*, 3185.
[10] J. H. Kim, Y. S. Kang, J. Won, *Macromol. Res.* **2004**, *12*, 145.
[11] S. Choi, J. H. Kim, Y. S. Kang, *Macromolecules* **2001**, *34*, 9087.
[12] J. H. Kim, B. R. Min, J. Won, Y. S. Kang, *J. Phys. Chem. B* **2003**, *107*, 5901.
[13] J. H. Jin, S. U. Hong, J. Won, Y. S. Kang, *Macromolecules* **2000**, *33*, 4932.
[14] A. V. Chadvick, M. R. Worboys, in: "*Polymer Electrolyte Reviews-1*", J. R. MacCallum, C. A. Vincent, Eds., Elsevier, London 1987, Chapter 9.
[15] J. F. O'Gara, G. Nazri, D. M. MacArthur, *Solid State Ionics* **1991**, *47*, 87.
[16] A. Asano, K. Takegoshi, K. Hikichi, *Polym. J.* **1999**, *31*, 602.
[17] J. Spěváček, J. Dybal, *Macromol. Rapid Commun.* **1999**, *20*, 435.
[18] J. Spěváček, J. Brus, *Macromol. Symp.* **2003**, *203*, 111.
[19] J. Spěváček, J. Brus, J. Dybal, *Solid State Ionics* **2005**, *176*, 163.
[20] J. Spěváček, J. Brus, J. Dybal, Y. S. Kang, *Macromolecules* **2005**, *38*, 5083.
[21] J. Spěváček, L. Paternostre, P. Damman, A. C. Draye, M. Dosiere, *Macromolecules* **1998**, *31*, 3612.
[22] B.-J. van Rossum, C. P. de Groot, V. Ladizhansky, S. Vega, H. J. M. de Groot, *J. Am. Chem. Soc.* **2000**, *122*, 3465.
[23] J. H. Kim, B. R. Min, H. S. Kim, J. Won, Y. S. Kang, *J. Membr. Sci.* **2003**, *212*, 283.