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Solid-State ^{13}C NMR and DFT Quantum-Chemical Study of Polymer Electrolyte Poly(2-ethyl-2-oxazoline)/$AgCF_3SO_3$

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ABSTRACT: Solid-state ^{13}C NMR spectra and DFT calculations confirmed that dominant interaction in POZ/$AgCF_3SO_3$ polymer electrolyte is coordination between carbonyl groups and silver cation. Lower shielding of POZ carbonyl carbons and to a smaller extent also adjacent methylene carbons was found for the POZ/$AgCF_3SO_3$ complex in comparison with neat POZ, both in ^{13}C NMR spectra and by DFT calculations on model systems. The POZ/$AgCF_3SO_3$ complex has a defined stoichiometry: two POZ monomeric units per one $AgCF_3SO_3$. A close contact between both components was determined from the Lee−Goldburg cross-polarization $^{1}H \rightarrow {}^{13}C$ dynamics. 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.

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. The conductive properties of polymer electrolytes have led them to be intensively studied for potential applications in electrochemical devices like solid-state batteries; systems based on molecular complexes of poly(ethylene oxide) (PEO) and alkali metal salts are typical representatives of this category.[1] Recently, solid polymer electrolytes containing silver salts were investigated as promising membrane materials because they showed high separation performance for alkene/alkane mixtures; polymer electrolyte poly(2-ethyl-2-oxazoline) (POZ)/$AgCF_3SO_3$ is of this type.[2−5] Wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) have shown that POZ/$AgCF_3SO_3$ systems are completely amorphous.[6,7] Infrared (IR) spectroscopy (the carbonyl region) and density functional theory (DFT) calculations on a "monomeric" model system (*N*-methyl-*N*-ethylpropionamide) confirmed complex formation between silver cations and carbonyl oxygens of POZ.[8,9] IR spectroscopic results also indicated that the stoichiometry of the POZ/$AgCF_3SO_3$ complex might be close to 1/1.[8] On the other hand, the intersegmental distances, *d* spacings, as determined by WAXS, as well as glass transition temperatures T_g suggest that optimal interaction between POZ chains and $AgCF_3SO_3$ appears for the molar ratio POZ/$AgCF_3SO_3$ = 3/1.[6,7] To our knowledge, no solid-state NMR studies exist for the POZ/$AgCF_3SO_3$ polymer electrolyte.

In our recent studies of semicrystalline PEO/$LiCF_3SO_3$ polymer electrolyte we have found useful a combination of solid-state NMR spectroscopy on real system and quantum-chemical calculations on model systems.[10,11] We used also this approach in the present paper where we applied a combination of solid-state ^{13}C NMR and DFT calculations to characterize interactions and structure in the amorphous POZ/$AgCF_3SO_3$ polymer electrolyte. Some experimental NMR results (chemical shifts) were compared with those obtained by DFT quantum-chemical calculations on model systems.

Experimental Section

Samples. POZ ($M_w = 5 \times 10^5$) and $AgCF_3SO_3$ were purchased from Aldrich. Samples of POZ/$AgCF_3SO_3$ films with molar ratio of both components in the range 10/1−1/1 were prepared from mixed methanol solutions cast on a glass plate and then dried for 2 h under a N_2 environment. The films were further dried for 1 day in a vacuum at room temperature to remove residual solvent. Samples of the neat POZ and $AgCF_3SO_3$ were also studied for comparison.

NMR Measurements. Solid-state ^{13}C NMR spectra were measured on Bruker Avance 500 spectrometer at 125.8 MHz. Samples were measured in 4 mm ZrO_2 rotors with spinning frequency 8−11 kHz. ^{13}C RAMP/CP/MAS (ramped amplitude/cross-polarization/magic angle spinning) NMR spectra were measured with a contact time 1 ms (neat POZ) or 5 ms (POZ/$AgCF_3SO_3$ blends). In the latter case a sufficiently long contact time 5 ms should make it possible to detect also a signal of $AgCF_3SO_3$ and allow a quantitative analysis of the carbonyl region of POZ.[12,13] ^{13}C MAS NMR spectra (without CP) were also measured. Chemical shifts in the ^{13}C NMR spectra were referred to the carbonyl band of glycine (with a signal at 176.0 ppm) by sample replacement. Spin−lattice relaxation times T_1 of POZ carbons were measured with CP by the method of Torchia.[14] The magnitude of $^{13}C-^{1}H$ couplings was determined using a method[15] based on the measurements of the dynamics of the Lee−Goldburg (LG) CP $^{1}H \rightarrow {}^{13}C$.

DFT Calculations. The calculations were done using the Gaussian 98 program package.[16] Molecular geometry was optimized at the B3LYP level,[17] the basis set being of 6-31+G(d) quality. For silver atom, the LANL2DZ basis set was used.[18] The gauge-including atomic orbitals (GIAO)[19,20] method was employed to calculate absolute shielding constants (σ, in ppm) for tetramethylsilane (TMS), "monomeric" model of POZ, "dimeric" model of POZ, "monomeric" model of POZ/$AgCF_3SO_3$, and "dimeric" model of POZ/$AgCF_3SO_3$ structures. Subtraction gave the calculated ^{13}C chemical shifts (δ, in ppm) of the structures relative to TMS. The basis set of

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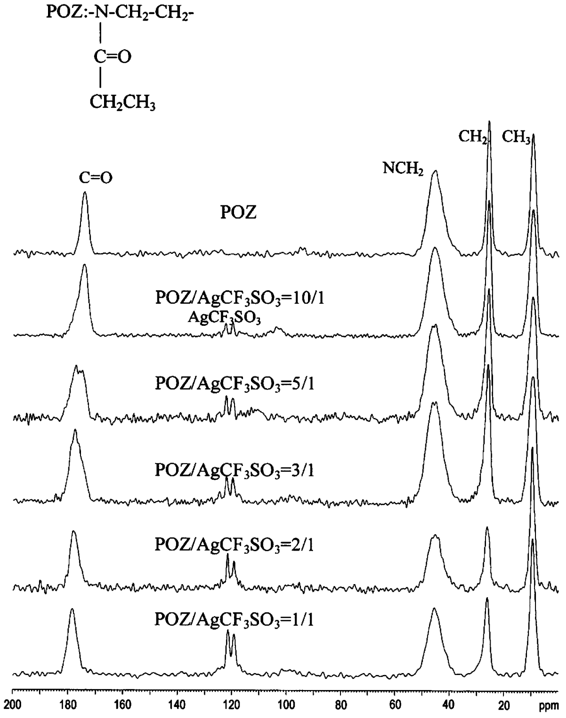

Figure 1. ^{13}C CP/MAS NMR spectra of POZ/AgCF$_3$SO$_3$ polymer electrolytes with various molar ratios of both components and neat POZ. Spectra were measured with the contact time 5 ms (POZ/AgCF$_3$SO$_3$ blends) or 1 ms (neat POZ) at ambient temperature.

6-311+G(2d,p) quality was used in computation of the ^{13}C NMR shifts.

Results and Discussion

^{13}C CP/MAS NMR spectra of the neat POZ and POZ/AgCF$_3$SO$_3$ blends with various molar ratios of both components are shown in Figure 1. The assignment of resonances to various types of carbons of POZ and AgCF$_3$SO$_3$ is shown directly in this figure. For all samples of POZ/AgCF$_3$SO$_3$ polymer electrolytes, in addition to POZ resonances also the signal of AgCF$_3$SO$_3$ carbons was detected; only internal components of the quartet due to the ^{13}C$-^{19}$F spin−spin coupling (coupling constant 285 Hz) are clearly revealed in the spectra. Because in CP/MAS spectra ^{13}C lines originate from dipolar-coupled protons, the existence of the signal of AgCF$_3$SO$_3$ carbons confirms that in all blends both components are in contact forming the molecular complex; the distance between AgCF$_3$SO$_3$ carbon and nearest POZ protons in the complex has to be smaller than ≈0.5 nm. Some changes of POZ resonances (shape and chemical shifts) in POZ/AgCF$_3$SO$_3$ samples in comparison with the neat POZ are also shown in these spectra. The largest changes were found for carbonyl carbons (cf. further text) and 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 as well as side-chain methyl carbons are the same in POZ/AgCF$_3$SO$_3$ blends and in the neat POZ. These results support the former results of IR spectroscopy[8] that the dominant interaction in the POZ/AgCF$_3$SO$_3$ complex is the coordination between silver cations and carbonyl oxygens.

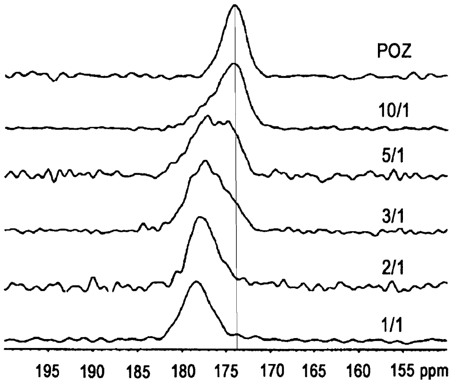

Figure 2. Carbonyl region in ^{13}C CP/MAS NMR spectra of POZ/AgCF$_3$SO$_3$ polymer electrolytes with various molar mixing ratios of POZ and AgCF$_3$SO$_3$ and neat POZ.

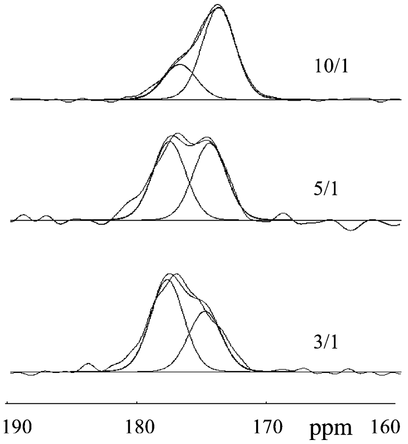

Figure 3. Deconvolution of the carbonyl region in ^{13}C CP/MAS NMR spectra into two components for POZ/AgCF$_3$SO$_3$ polymer electrolytes with mixing ratios 10/1, 5/1, and 3/1.

The carbonyl region in ^{13}C CP/MAS NMR spectra is shown in detail in Figure 2. From this figure it follows that in systems containing AgCF$_3$SO$_3$ a new carbonyl signal exists with ≈4 ppm larger chemical shift in comparison with the carbonyl resonance in the neat POZ. For selected sample with the mixing ratio POZ/AgCF$_3$SO$_3$ = 5/1, the line shape of the carbonyl region identical with that shown in Figure 2 was detected in ^{13}C MAS NMR spectrum measured without CP with relaxation delay 20 s. This confirms that ^{13}C CP/MAS NMR spectra measured with the contact time 5 ms show correctly the intensities of both carbonyl signals and hence can be used in quantitative analysis. With increasing amount of silver salt in POZ/AgCF$_3$SO$_3$ blend the relative intensity of the new carbonyl line increases (up to molar ratio POZ/AgCF$_3$SO$_3$ = 2/1). From Figure 2 it also follows that both for 2/1 and 1/1 POZ/AgCF$_3$SO$_3$ mixing ratios no signal of the neat (uncomplexed) POZ was detected. For remaining POZ/AgCF$_3$SO$_3$ mixing ratios a deconvolution of the carbonyl region into two components is shown in Figure 3. We assumed the same line widths of both components in these deconvolutions as a consequence of the finding that a small amount of paramagnetic neutral silver (Ag^0) exists in POZ/AgCF$_3$SO$_3$ samples (this result is discussed hereafter in the text). The new carbonyl line with larger chemical shift evidently corresponds to carbonyls in the POZ/AgCF$_3$SO$_3$ complex. From the fact that no signal of the neat uncomplexed POZ was detected for the mixing ratio POZ/AgCF$_3$SO$_3$ = 2/1 as well as from the ratios of the intensities of the carbonyl

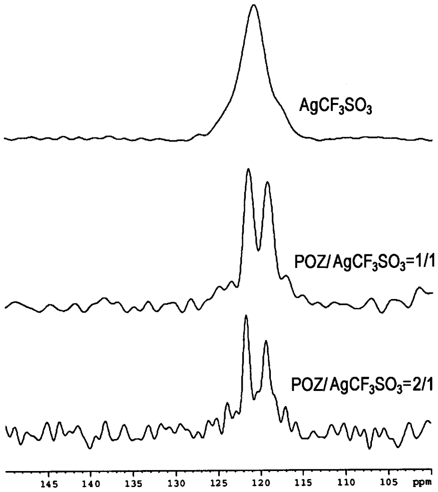

Figure 4. Signal of $AgCF_3SO_3$ carbons in ^{13}C NMR spectra of POZ/$AgCF_3SO_3$ polymer electrolytes (CP/MAS spectra with contact time 5 ms) and neat $AgCF_3SO_3$ (spectrum without CP).

line in the POZ/$AgCF_3SO_3$ complex and the line of the uncomplexed POZ as a function of the mixing ratios of POZ and $AgCF_3SO_3$ (cf. Figure 3), it results that the complex has the defined molar stoichiometry POZ/$AgCF_3SO_3$ = 2/1 (two POZ monomeric units per one $AgCF_3SO_3$). This is also in accord with the shape of the signal of $AgCF_3SO_3$ carbons which for polymer electrolyte POZ/$AgCF_3SO_3$ = 1/1 shows a certain amount of the broad component evidently corresponding to excessive uncomplexed $AgCF_3SO_3$ which manifests itself by the line shape found for neat $AgCF_3SO_3$ (Figure 4).

From Figures 2 and 3 it also follows that the chemical shift of carbonyl carbons in the POZ/$AgCF_3SO_3$ complex slightly depends on the blend composition. Its value increases with increasing amount of $AgCF_3SO_3$ in the POZ/$AgCF_3SO_3$ blend; for the blend POZ/$AgCF_3SO_3$ = 1/1 its value is by 0.9 ppm larger than for the POZ/$AgCF_3SO_3$ = 5/1 blend. We assume that this fact might be in connection with possible changes of the conformational structure of the side-chain ethyl group in complexes formed in POZ/$AgCF_3SO_3$ blends with various mixing ratios of both components. Such an idea is corroborated by results of DFT quantum-chemical calculations done on a "monomeric" model of POZ, $CH_3CH_2N(COCH_2CH_3)CH_3$ (Figure 5). As follows from Figure 5, the chemical shifts of carbonyl carbons in model structures that differ by the conformation of the adjacent ethyl group might differ by 1.5 ppm.

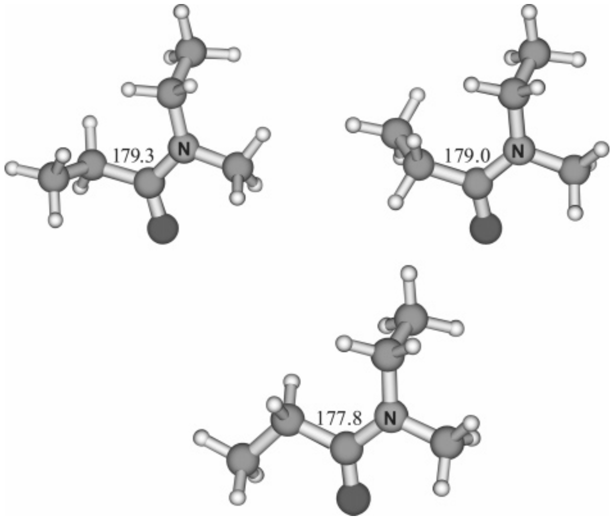

Figure 5. DFT calculations on "monomeric" model of POZ: effect of conformational structure of side-chain ethyl group on chemical shift of carbonyl carbons. The calculated values of chemical shift are shown directly with the structures.

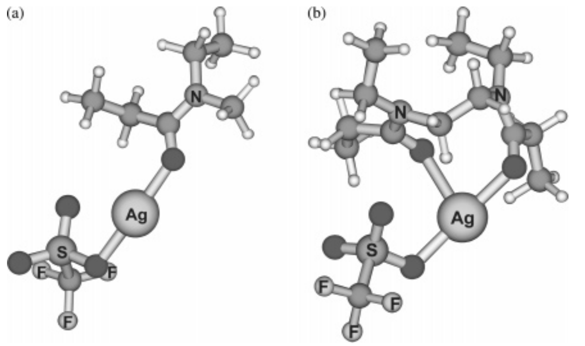

Figure 6. Structures obtained from DFT calculations for "monomeric" (a) and "dimeric" (b) models of POZ interacting with $AgCF_3SO_3$.

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 structures of model complexes are depicted in Figure 6. In the obtained DFT structures the silver cation is coordinated to carbonyl oxygen (for the "monomeric" model complex) or to both carbonyl oxygens (for the "dimeric" model complex). The stabilization energies −29.04 and −31.57 kcal/mol were obtained for the "monomeric" and "dimeric" model complex, respectively. For the comparison of experimental results and results of DFT calculations of chemical shifts, we used the values of the difference of chemical shifts $\Delta = \delta_{POZ/AgCF_3SO_3} - \delta_{POZ}$ (for calculated chemical shifts, POZ should be replaced by either the "monomeric" or "dimeric" model of POZ). In accord with experimental NMR results, DFT calculations have shown lower shielding of carbonyl carbons and adjacent side-chain CH_2 carbons in model complexes in comparison with "neat" models of POZ (both experimental and calculated values of the difference Δ were positive). Concerning the absolute values of the difference Δ, 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,[11] for the POZ/$AgCF_3SO_3$ system the difference of the respective calculated chemical shifts Δ was for carbonyl carbons Δ = 9.6 and 9.4 ppm for the "monomeric" and "dimeric" model complex, respectively, i.e., more than twice larger than the experimental value Δ = 3.9 ppm found for the stoichiometric POZ/$AgCF_3SO_3$ = 2/1 complex. For the adjacent side-chain CH_2 carbons the value of the difference Δ calculated for the "dimeric" model complex (Δ = 1.2 ppm) is much closer to experimental value (Δ = 0.5 ppm) than the value calculated for the "monomeric" model complex (Δ = 3.2 ppm). The "dimeric" model complex is also in accord with the 2/1 stoichiometry determined experimentally for the POZ/$AgCF_3SO_3$ complex by NMR spectra.

Measurements of ^{13}C spin−lattice relaxation times T_1 of POZ carbons have shown that T_1 values in the stoichiometric sample of the polymer electrolyte POZ/$AgCF_3SO_3$ = 2/1 are significantly shorter in comparison with the neat POZ (Table 1). The fact that the temperature of the glass transition T_g = 360 K found for the

Table 1. ^{13}C Spin−Lattice Relaxation Times of POZ Carbons in Neat POZ and Polymer Electrolyte POZ/$AgCF_3SO_3$ = 2/1

sample	temp (K)	T_1 (s)			
		C=O	NCH_2	CH_2	CH_3
POZ	306	39.4	21.2	6.7	2.8
	323	25.4	10.4	4.2	2.9
POZ/$AgCF_3SO_3$ = 2/1	306	26.9	12.8 (1.66^a)	2.5 (2.68^a)	1.9 (1.50^a)

[a] $\eta = (T_1^{-1})_{POZ/AgCF_3SO_3}/(T_1^{-1})_{POZ}$.

sample POZ/$AgCF_3SO_3$ = 2/1 is by 16 K higher than in the neat POZ (T_g = 344 K)[7] 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 (cf. Table 1). This discrepancy suggests that in the POZ/$AgCF_3SO_3$ complex an additional relaxation mechanism is effective, in addition to $^{13}C-^{1}H$ dipolar interactions. Recently, it was shown that a small amount of neutral silver (Ag^0) can be formed in POZ/silver salt polymer electrolytes under UV−vis light or heat by the reduction of silver ions and participation of the trace of water.[21] The mechanism of this reduction might be similar as suggested for the reduction of silver ions by *N,N*-dimethylformamide in water.[22] Neutral silver is paramagnetic, and interaction with the unpaired electron spin provides an efficient way for nuclear spin relaxation. 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. For POZ carbon types with directly bonded hydrogens (dipolar coupling between carbons and directly bonded hydrogens represents a dominant relaxation contribution for these carbons in the neat POZ), the values of the enhancement of the relaxation rate η in the PEO/$AgCF_3SO_3$ complex defined as $\eta = (T_1^{-1})_{POZ/AgCF_3SO_3}/(T_1^{-1})_{POZ}$ are also shown in Table 1. The largest value of the enhancement was found for the side-chain CH_2 carbons, again indicating that atoms of neutral silver are located in the vicinity of the carbonyl group. From the values of the enhancement η which show that the paramagnetic contribution to the total relaxation is roughly comparable with the contribution from the dipolar coupling with directly bonded protons, one can estimate the relative amount of the atoms of neutral silver in the studied POZ/$AgCF_3SO_3$ system. Taking into account that the relaxation rate is proportional to the term γ_x^2/r^6, where γ_x is either the gyromagnetic constant γ_e for electrons (for paramagnetic relaxation contribution) or the gyromagnetic constant γ_H for protons (for dipolar $^{13}C-^{1}H$ relaxation contribution) and the r is the respective internuclear distance ($^{13}C-Ag^0$ or $^{13}C-^{1}H$), and furthermore that γ_e is 658 times larger than γ_H and assuming that the distance carbon−silver is about 3−3.5 times larger than the length of CH bond, then the found values of the relaxation enhancement η indicate that the relative amount of the atoms of neutral silver in the studied POZ/$AgCF_3SO_3$ complex is of the order 10^{-3}, i.e., ~0.1%.

To obtain information on the geometrical structure of the POZ/$AgCF_3SO_3$ complex, we attempted to determine the effective distance r_{eff} between $AgCF_3SO_3$ carbon and its nearest POZ protons using a method[15] based on the measurements of the dynamics of the Lee−Goldburg (LG) cross-polarization $^{1}H \rightarrow {}^{13}C$. Figure 7 shows the integrated intensities of POZ NCH_2 and $AgCF_3SO_3$ signals in ^{13}C CP/MAS NMR spectra (spinning frequency 11 kHz) of the 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 $^{13}C-^{1}H$ dipolar couplings $\Delta\omega/2\pi$, equal to 10 and 0.78 kHz for NCH_2 POZ carbons and $AgCF_3SO_3$ carbons, respectively. The value obtained for NCH_2 carbons shows that the system is not completely rigid, probably in connection with the fact that the real temperature in the sample during MAS with spinning frequency 11 kHz is around 310 K,[23] i.e., only 50 K below the respective T_g. For CH_2 carbons in the crystalline PEO/$LiCF_3SO_3$ complex we obtained $\Delta\omega/2\pi$ = 12.2 kHz.[11] After the correction for the rigid system (assuming that the internal mobility affects the dipolar couplings of NCH_2 carbons and $AgCF_3SO_3$ carbons in the same way) and using the formula for the internuclear distance r_{CH} (in nm),[15] $r_{CH} = 2.586(\Delta\omega/2\pi)^{-1/3}$, for the effective distance of $AgCF_3SO_3$ carbon and its nearest POZ protons we obtained r_{eff} = 0.26 nm. This value shows a very close contact between both components; for comparison, using the same method, for the distance between $LiCF_3SO_3$ carbon and its nearest protons in the PEO/$LiCF_3SO_3$ complex we obtained r_{eff} = 0.33 nm.[11]

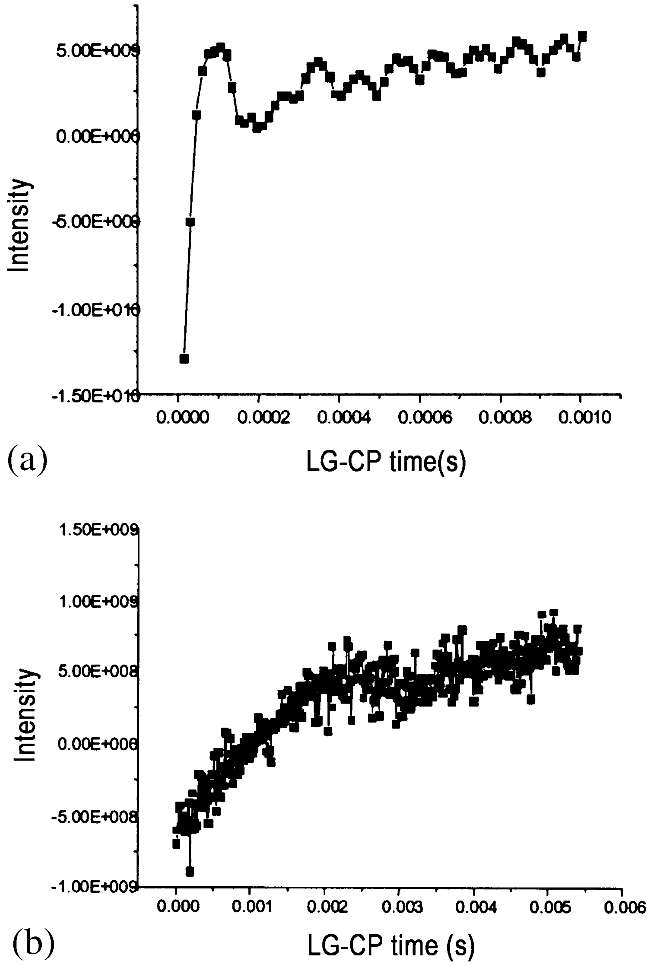

Figure 7. LG−CP dynamics (integrated intensity vs contact time) for POZ NCH_2 (a) and $AgCF_3SO_3$ (b) carbons in the POZ/$AgCF_3SO_3$ = 2/1 polymer electrolyte.

Conclusions

Solid-state ^{13}C NMR spectra and DFT quantum-chemical calculations confirmed that dominant interaction in the amorphous POZ/$AgCF_3SO_3$ polymer electrolyte is coordination between carbonyl groups and silver cation. Lower shielding of POZ carbonyl carbons and in smaller extent also adjacent side-chain methylene carbons was found for the POZ/AgCF$_3$SO$_3$ complex in comparison with neat POZ, both experimentally in ^{13}C NMR spectra and by DFT calculations on model systems. Integrated intensities of the lines corresponding to carbonyl carbons in the POZ/AgCF$_3$SO$_3$ complex and in uncomplexed POZ as a function of the composition of POZ/AgCF$_3$SO$_3$ blends evidence that the POZ/AgCF$_3$SO$_3$ complex has a defined stoichiometry: two POZ monomeric units per one AgCF$_3$SO$_3$. The shorter ^{13}C T_1 values found for the stoichiometric POZ/AgCF$_3$SO$_3$ sample in comparison with the neat POZ are probably due to the paramagnetic contribution to the relaxation mechanism; the source is evidently atoms of neutral silver that can be formed in a small amount (~0.1%) in this system. The effective distance between AgCF$_3$SO$_3$ carbon and its nearest POZ protons in the POZ/AgCF$_3$SO$_3$ complex, $r_{\mathrm{eff}} = 0.26$ nm, was determined from the LG−CP ^{1}H → ^{13}C dynamics.

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