Macromol. Symp. **2003**, *203,* 111-121

Solid State NMR Study of Intercalate Complexes of Poly(ethylene oxide) and Small Molecules

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Summary: From solid state NMR spectra, a lower shielding of poly(ethylene oxide) (PEO) protons, in contrast to higher shielding of PEO carbons, has been found for PEO/hydroxybenzene and PEO/$LiCF_3SO_3$ complexes in comparison with neat PEO. The same PEO chemical shifts were found both for crystalline and amorphous phase of PEO/$LiCF_3SO_3$ polymer electrolyte, confirming the same interaction in both phases. Measurements of 2D ^1H CRAMPS exchange NMR spectra have been used to characterize proton distances in complexes of PEO and benzene derivatives. A close contact (~ 0.3 nm) between aromatic and PEO protons was detected in some cases. From the measurements of the cross polarization $^1H \rightarrow {}^{13}C$, using Lee-Goldburg irradiation of ^1H nuclei, the distance between $LiCF_3SO_3$ carbon and the nearest PEO protons in the PEO/$LiCF_3SO_3$ complex was determined.

Keywords: 2D ^1H CRAMPS exchange NMR spectra; intercalate complexes; poly(ethylene oxide); solid polymer electrolyte; solid state NMR

Introduction

It is well known that poly(ethylene oxide) (PEO) can form crystalline molecular complexes with small organic or inorganic molecules. Intercalate complexes of PEO with benzene derivatives, such as hydroxybenzenes (resorcinol (RES), 2-methylresorcinol (2MR), hydroquinone (HYD), 4-nitrophenol (4NP)), which are capable of forming hydrogen bonds with PEO, or PEO complexes with para-disubstituted benzenes (e.g., 1,4-dichlorobenzene), which are stabilized by weak van der Waals interactions, are one type.[1,2] In addition to other methods, interactions, conformational structure and molecular dynamics in these complexes were also investigated by solid state ^{13}C NMR spectroscopy.[3-9] Another type is PEO/alkali metal salts intercalate complexes; they exhibit high ionic conductivity and are known as solid

DOI: 10.1002/masy.200351309

polymer electrolytes.[10] The PEO/$LiCF_3SO_3$ complex is one of the most investigated systems and its crystal structure was determined by X-ray diffraction.[11] Recently we studied polymer electrolyte PEO/$LiCF_3SO_3$ by combining solid state ^{13}C NMR and *ab initio* quantum-chemical calculations.[12,13]

The main aim of the present work was to characterize structure and interactions in complexes of PEO with benzene derivatives and in PEO/$LiCF_3SO_3$ complex by methods of high-resolution solid state ^1H NMR spectroscopy, in the latter case also in combination with ^{13}C NMR methods.

Experimental Part

Samples: PEO of molecular weight 6000 and 4000 were used in this study. Stoichiometric samples of complexes of PEO 6000 with hydroxybenzenes or $LiCF_3SO_3$ were studied. The stoichiometric ratio of PEO monomeric units and the respective hydroxybenzene was 2:1 in PEO/RES, PEO/HYD and PEO/2MR-β complexes, ~ 7:2 in the PEO/2MR-α complex (two complexes, α and β, exist in the PEO/2MR system[2,7]), 3:2 in the PEO/4NP complex and 3:1 in the PEO/$LiCF_3SO_3$ complex. Stoichiometric sample of the complex of PEO 4000 and 1,4-dichlorobenzene (molar stoichiometry 10:3) was also studied. Both the PEO complexes of interest and neat PEO samples were highly crystalline (degree of crystallinity $\geq$ 85 % for PEO complexes with benzene derivatives[7] and $\geq$ 77 % for PEO/$LiCF_3SO_3$ complex[13]).

NMR measurements: Solid state ^{13}C CP/MAS (cross polarization/magic angle spinning) NMR spectra, a part of one-dimensional (1D) ^1H CRAMPS (combined rotation and multipulse spectroscopy) NMR spectra and most of two-dimensional (2D) ^1H CRAMPS exchange NMR spectra were measured at 50.3 MHz (^{13}C) and 200.1 MHz (^1H) using a Bruker Avance DSX-200 spectrometer. In ^1H CRAMPS measurements, the BR24 pulse sequence[14] was used with a 90° pulse length of 1.8 μs, long and short delays of 3.8 and 1.0 μs, respectively, and spinning frequency 2 kHz. The ^1H scale was calibrated using external standards, glycine and adipic acid. 2D ^1H CRAMPS exchange spectra were measured with 64 scans, 256 increments and relaxation delay 4 s. ^1H CRAMPS spectra of PEO/hydroxybenzene complexes were also measured at 400 MHz. 500 MHz ^1H MAS NMR spectra of some samples were also recorded, using a Bruker Avance-500 spectrometer. All spectra were measured at 300 K.

Results and Discussion

Crystalline Intercalate Complexes of PEO and Benzene Derivatives

^{1}H CRAMPS NMR spectra of several PEO/hydroxybenzene complexes are shown in Figure 1. Neat PEO and neat hydroxybenzenes were also measured for comparison. The ^{1}H chemical shifts of PEO were correlated with the hydrogen bond strength as characterized by infrared (IR) spectra (OH stretching band), which have shown that the hydrogen bond strength increases in the order PEO/2MR-α < PEO/HYD, PEO/2MR-β < PEO/RES < PEO/4NP.[7] From ^{1}H CRAMPS NMR spectra it follows that chemical shift δ of PEO protons in the complex differs from that in the neat PEO ($\delta = 3.6$ ppm) only for complexes PEO/RES and in particular PEO/4NP with stronger hydrogen bonds ($\delta = 3.8$ and 4.3 ppm, respectively). Correlation between PEO chemical shift and the hydrogen bond strength has been previously found also from ^{13}C NMR spectra,[7] but there the increasing hydrogen bond strength resulted in higher

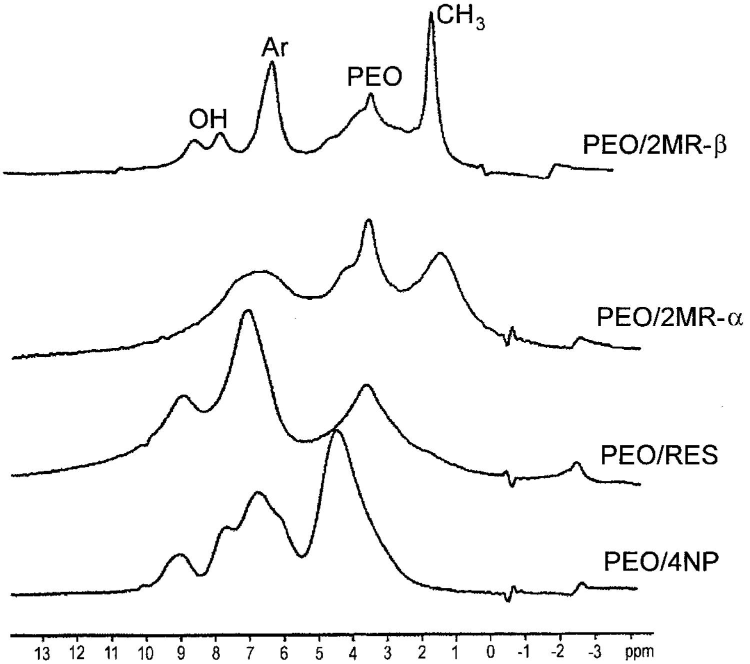

Fig. 1. 400 MHz ^{1}H CRAMPS NMR spectra of PEO/hydroxybenzene complexes.

shielding of PEO carbons, in contrast to lower shielding of PEO protons. On the other hand, in PEO/RES, PEO/2MR (α and β) and PEO/HYD complexes, where hydrogen bonds are weaker in comparison with the respective neat hydroxybenzenes (as shown by OH stretching band in IR spectra), aromatic protons are less shielded than in the respective hydroxybenzene. For the PEO/4NP complex, where hydrogen bonds are stronger in comparison with the neat 4NP, the chemical shifts of aromatic protons are the same as those in the neat 4NP.

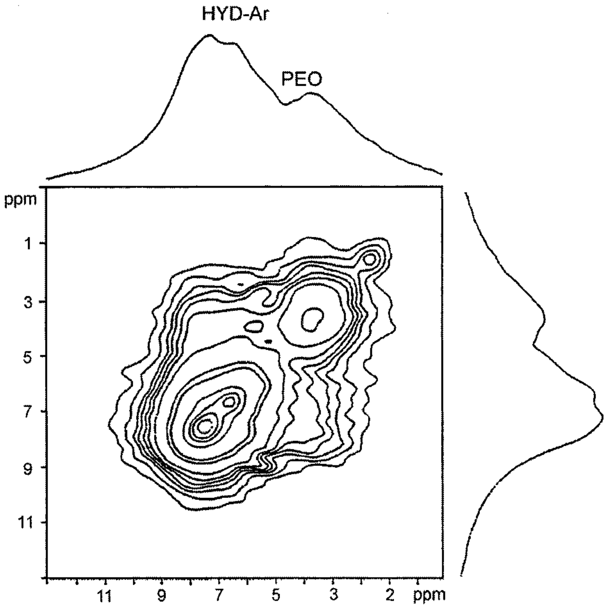

Fig. 2. 2D ^{1}H CRAMPS exchange NMR spectrum of PEO/HYD complex measured at 200.1 MHz with $\tau_m = 100\ \mu s$.

Measurements of 2D ^{1}H CRAMPS exchange spectra as function of the mixing time have been used to characterize proton distances. In 2D ^{1}H exchange spectra, originally proposed for investigation of polymer blends,[15] protons coupled by sufficiently strong dipolar interactions (in the distance shorter than ca. 0.5 nm) produce off-diagonal crosspeaks. The dependence of the crosspeak intensity on mixing time τ_m reflects the interproton distance. We tried to find out the shortest mixing time where the "well defined" crosspeaks between resonances of PEO and benzene derivative were detected. As a "well defined" crosspeak we considered a crosspeak with the relative intensity amounting to ~ 40 % of its equilibrium intensity. For PEO/HYD complex (Figure 2), such crosspeak was detected with $\tau_m = 100$ μs. Similar situation was found also for the PEO/2MR-α complex and, as already reported by Belfiore et al.[3], for the PEO/RES complex. On the other hand, for the PEO/2MR-β (Figure 3), PEO/4NP and PEO/1,4-dichlorobenzene (Figure 4) complexes, "well defined" crosspeaks between resonances of PEO and aromatic protons of benzene derivative could be detected already with $\tau_m = 50$ μs, indicating a closer contact between respective protons.

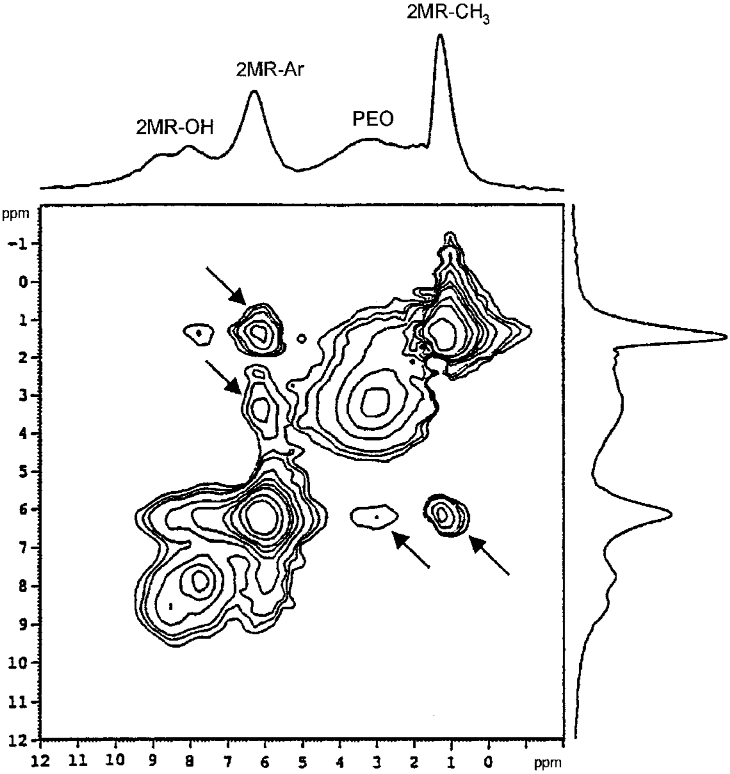

Fig. 3. 2D ^{1}H CRAMPS exchange NMR spectrum of PEO/2MR-β complex measured at 200.1 MHz with $\tau_m = 50$ μs. Crosspeaks discussed in text are marked by arrows.

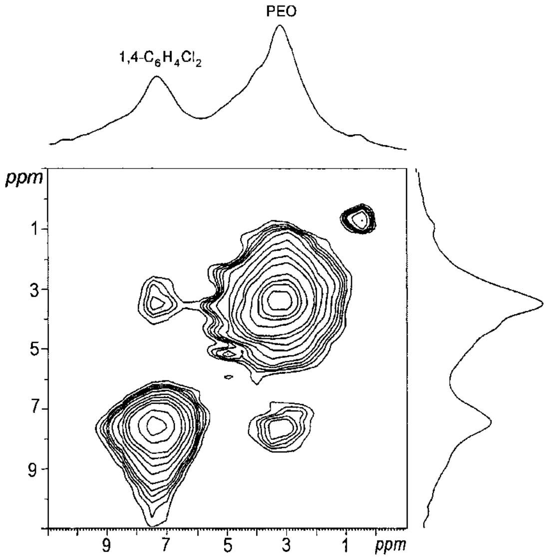

Fig. 4. 2D ^1H CRAMPS exchange NMR spectrum of PEO/1,4-dichlorobenzene complex measured at 200.1 MHz with τ_m = 50 μ.

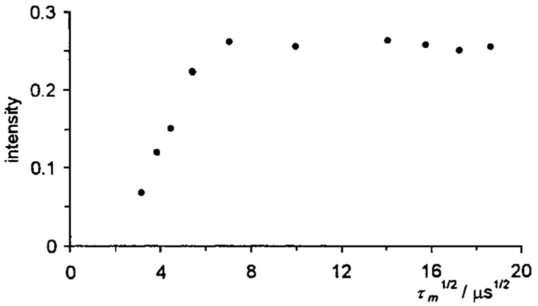

Fig. 5. Dependence of intensity of the crosspeak between nonequivalent CH_2 protons in 2D ^1H CRAMPS exchange NMR spectrum of glycine on square root of mixing time.

For quantitative analysis we used the approach based on comparison of 2D ^1H CRAMPS exchange NMR spectra of PEO complexes and glycine, where the distance between nonequivalent CH_2 protons is known (0.18 nm). For glycine, the dependence of the intensity of the respective crosspeak on mixing time is shown in Figure 5. From this figure it follows that the crosspeak between nonequivalent CH_2 protons with the relative intensity 40 % is developed using $\tau_m = 15$ μs. Based on the simple formula for the maximum diffusive path length $L = (6Dt)^{1/2}$, where D is spin-diffusion coefficient and t is a time (in our case the mixing time τ_m), the interproton distance r (in nm) in the PEO/benzene derivative complex can be obtained from the relation

$$(r/0.18) = (\tau_{mc}/\tau_{mg})^{1/2} \qquad (1)$$

where τ_{mc} and τ_{mg} are mixing times necessary to develop the crosspeaks of the same relative intensity in the PEO complex and glycine, respectively (both the PEO complexes and glycine are crystalline, and therefore an implicit assumption in Eq. (1) of the same diffusion coefficient D is well justified). From Eq. (1) it follows that for the PEO/HYD complex (crosspeak of the relative intensity 35 % developed with $\tau_m = 100$ μs, cf. Figure 2), and similarly also for PEO/2MR-α and PEO/RES complexes, the distance between PEO and aromatic protons is ~ 0.48 nm. For the PEO/2MR-β complex (crosspeak of relative intensity 48 % developed with $\tau_m = 50$ μs, cf. Figure 3), and similarly for the PEO/4NP complex, a much closer contact, 0.32 nm, between aromatic and PEO protons was detected. This result together with ^{13}C NMR spectra (splitting of aromatic hydroxybenzene resonances[6]) indicates that interactions of other functional groups of 4NP or 2MR with PEO can be important in these complexes, in addition to hydrogen bonds. 2D ^1H CRAMPS exchange spectra (a crosspeak of relative intensity 35 % developed with $\tau_m = 50$ μs) also evidence a close contact (proton distance 0.34 nm) between both components in the PEO/1,4-dichlorobenzene intercalate complex (Figure 4). This is not surprising for the complex stabilized by weak van der Waals interactions which assume a good steric fit of both components.

For the PEO/2MR-β complex (Figure 3), an intensive crosspeak between CH_3 and aromatic 2MR protons should be also briefly discussed. Its relative intensity (40 %) obtained with $\tau_m = 50$ μs suggests the proton distance ~ 0.33 nm, while the respective distance within 2MR molecule is ~ 0.5 nm. The intermolecular origin of the respective crosspeak is in accord with the recent suggestion of the crystal structure of this complex[16], where in the orthorhombic unit cell always two 2MR molecules have the same orientation.

$PEO/LiCF_3SO_3$ Complex (Polymer Electrolyte)

In addition to ^1H CRAMPS NMR spectra, with dominating crystalline phase, ^1H MAS NMR spectra with spinning frequncy 5-15 kHz were also measured for the $PEO/LiCF_3SO_3$ complex and neat PEO; only the amorphous phase contributes to the narrow component of the ^1H MAS NMR spectrum. ^1H chemical shifts of PEO, together with ^{13}C chemical shifts, are shown in Table 1 (only amorphous PEO is detected in ^{13}C MAS NMR spectra measured without CP with a short pulse repetition time of 1 s[13]). Similarly to PEO/hydroxybenzene complexes, also for the $PEO/LiCF_3SO_3$ complex, a lower shielding of PEO protons and a higher shielding of PEO carbons, was found in comparison with neat PEO. From Table 1 it follows that both ^1H and ^{13}C PEO chemical shifts in crystalline and amorphous phase of $PEO/LiCF_3SO_3$ are virtually the same, thus confirming the existence of the same interaction (coordination of ether oxygens to the Li^+ cation) in both phases.

Table 1. ^1H and ^{13}C NMR chemical shifts of PEO in the $PEO/LiCF_3SO_3$ complex and in neat PEO.

Material	Phase	δ (ppm)	
		^1H	^{13}C
PEO	crystalline	3.60	72.0
	amorphous	3.59	70.8
$PEO/LiCF_3SO_3$	crystalline	3.93	68.9
	amorphous	3.98	68.9

To determine the effective distance between $LiCF_3SO_3$ carbon and its nearest PEO protons, we used the method based on the measurements of ^{13}C CP/MAS NMR spectra (spinning frequency 8 kHz) with Lee-Goldburg (LG) irradiation of protons. This method[17] is a new tool for measuring heteronuclear ^{13}C-^1H distances and, to our best knowledge, our case is probably its first application to systems containing ^{13}C nuclei in natural abundance. Figure 6 shows the intensities of signals of PEO and $LiCF_3SO_3$ carbons in spectra measured with LG-CP as function of LG-CP time. Typical oscillatory character of both curves is clearly shown. Their Fourier transforms yield the respective heteronuclear ^{13}C-^1H dipolar couplings $\Delta\omega/2\pi$, equal to 12.2 kHz and 0.5 kHz for PEO carbons (with directly bonded protons) and $LiCF_3SO_3$ carbon, respectively. The $\Delta\omega/2\pi$ values are related to ^{13}C-^1H internuclear distance r_{CH} (in nm)[17]

$r_{CH} = 2.586\,(\Delta\omega/2\pi)^{-1/3}$. For PEO carbons in the PEO/$LiCF_3SO_3$ complex, we obtained $r_{CH} = 0.112$ nm, which is virtually the C-H bond length, while for the effective distance of $LiCF_3SO_3$ carbon and its nearest PEO protons R, we obtained $R = 0.33$ nm. This value is in accord with $R = 0.36$ nm as obtained from comparison of CP dynamics of PEO and $LiCF_3SO_3$ carbons,[13] and with distances 0.31–0.34 nm[13] between the $LiCF_3SO_3$ carbon and the nearest PEO hydrogens calculated by using refined atomic parameters of the crystal structure of the PEO/$LiCF_3SO_3$ complex.[11]

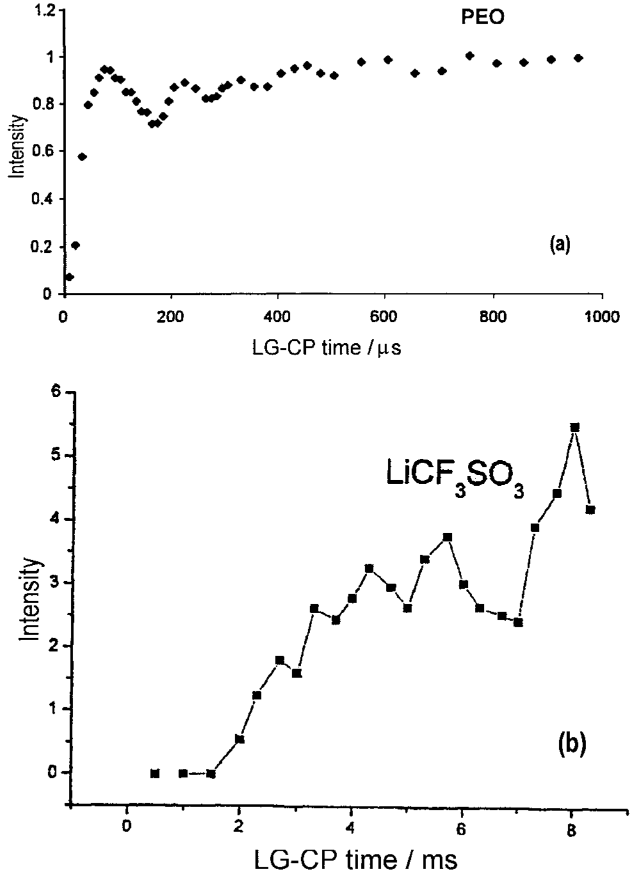

Fig. 6. LG-CP curves for PEO (a) and $LiCF_3SO_3$ (b) carbons in the PEO/$LiCF_3SO_3$ complex.

Conclusions

High-resolution solid state NMR spectra show, in comparison with neat PEO, a lower shielding of PEO protons and a higher shielding of PEO carbons in PEO/hydroxybenzene complexes stabilized by hydrogen bonds, and in the PEO/$LiCF_3SO_3$ polymer electrolyte where the dominant interaction is the coordination of ether oxygens to the Li^+ cation. For the PEO/$LiCF_3SO_3$ complex, the virtually same values of ^1H or ^{13}C chemical shifts were found for PEO in crystalline and amorphous phase, confirming the same interaction in both phases. Measurements of 2D ^1H CRAMPS exchange spectra as function of the mixing time were used to characterize proton distances in complexes with benzene derivatives. For all the complexes studied, a close contact (proton distance 0.48 nm) between both components was found. For the PEO/4NP, PEO/2MR-β and PEO/1,4-dichlorobenzene complexes, even a closer contact (~ 0.32 nm) between aromatic and PEO protons was detected. Measurements of the polarization transfer $^1H \rightarrow {}^{13}C$, using the Lee-Goldburg irradiation of protons, were used to determine the effective distance R between the $LiCF_3SO_3$ carbon and its nearest PEO protons in the PEO/$LiCF_3SO_3$ complex. The obtained value $R = 0.33$ nm is in agreement with the published X-ray crystal structure of this complex.

Acknowledgment

Grant No. A4050209 of the Grant Agency of the Academy of Sciences of the Czech Republic is gratefully acknowledged. The authors thank Dr. J. Dybal for help in analysis of LG-CP ^{13}C NMR measurements.

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