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Solid State NMR Studies of Syndiotactic Polystyrene/ Ethylbenzene and Poly(ethylene oxide)/$LiCF_3SO_3$ Molecular Complexes

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SUMMARY: Solvent dynamics and polymer-solvent interactions in syndiotactic (*s*) polystyrene (PS)/ethylbenzene (PhEt) clathrates, as well as polymer-salt interactions in the poly(ethylene oxide) (PEO)/$LiCF_3SO_3$ complex, were characterized by solid state ^1H and ^{13}C NMR. ^1H static and ^1H MAS NMR spectra have shown that PhEt molecules in *s*-PS clathrates retain relatively large, but spatially anisotropic mobility. ^{13}C CP/MAS (cross polarization/magic angle spinning) spectra and CP dynamics measured for *s*-PS-d_8/PhEt system indicate that at least a part of PhEt molecules are intercalated between phenyl rings of *s*-PS. ^{13}C CP/MAS NMR spectra show that PEO carbons in complex with $LiCF_3SO_3$ are more shielded in comparison to neat crystalline PEO. The results (distances) obtained from CP dynamics are in agreement with the published crystal structure of the PEO/$LiCF_3SO_3$ complex. ^{13}C spin-lattice relaxation time measurements have shown that the mobility of PEO in the complex is lower than that in neat crystalline PEO.

Introduction

The complex polymorphic behaviour of syndiotactic (*s*) polystyrene (PS) is well established now[1)]. *s*-PS can crystallize in four modifications. The so-called δ-form of crystalline *s*-PS consists of clathrate molecular complexes of the polymer with solvent molecules, including ethylbenzene (PhEt)[2-5)]. The four crystalline modifications of *s*-PS were also studied by solid state high-resolution ^{13}C NMR spectroscopy[6,7)]. On the basis of the fact that the solvent resonance is observed in ^{13}C CP/MAS (cross polarization/magic angle spinning) NMR spectra, it was suggested that the solvent included in the δ-form of *s*-PS is relatively rigid[7)].

The existence of solid electrolytes based on poly(ethylene oxide) (PEO)/metal salt complexes is also well known[8)]. PEO/$LiCF_3SO_3$ complex (stoichiometry three PEO monomeric units per one $LiCF_3SO_3$) is one of the most investigated systems. Crystal structure of this complex as determined by X-ray diffraction was reported[9)]. Although solid state NMR spectroscopy (in particular ^7Li and ^{23}Na NMR) has been used to study polymer electrolytes based on PEO[8)], to our knowledge no ^{13}C NMR studies exist for the PEO/$LiCF_3SO_3$ complex.

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The main aim of the present work was to characterize the solvent dynamics and polymer-solvent interactions in *s*-PS/PhEt clathrates, as well as polymer-salt interactions in the PEO/$LiCF_3SO_3$ complex, using solid state ^1H and ^{13}C NMR methods.

Experimental part

Samples of *s*-PS/PhEt and *s*-PS-d_8 (fully deuterated *s*-PS)/PhEt clathrates were kindly provided by Prof. S. J. Spells and Dr. S. Moyses (Sheffield Hallam University, UK). Crystallization from dilute PhEt solution (0.1 wt.-%) leads to a polymer/solvent complex where, after drying, the content of the solvent amounts about 14 wt.-%[4,5)].

A stoichiometric sample of PEO (MW 6000)/$LiCF_3SO_3$ complex (PEO monomer unit/$LiCF_3SO_3$ 3:1) was kindly provided by Dr. J-F. Moulin (Université de Mons-Hainaut). The sample was prepared by evaporation in dry air of a solution of PEO and the salt in methanol, and drying under vacuum at ~100 °C[10)].

Solid state ^1H NMR spectra (static and MAS) at 200 MHz, ^{13}C CP/MAS NMR spectra at 50 MHz and ^{13}C spin-lattice relaxation times T_1 were measured using a Bruker DSX-200 spectrometer. ^{13}C T_1 values were measured with CP by the method of Torchia[11)].

Results and discussion

s-PS/ethylbenzene clathrates

We used ^1H NMR spectra to study PhEt dynamics in *s*-PS clathrates. In Fig. 1A, ^1H NMR spectrum of the static *s*-PS/PhEt sample is shown. In addition to the broad component with the linewidth ~ 40 kHz, the existence of the other, narrower component is clearly visible. That the narrower component corresponds to the solvent is proved in Fig. 1B, where the ^1H NMR spectrum of *s*-PS-d_8/PhEt complex is shown. From this spectrum it follows that the linewidth at half of the maximum height of the PhEt in clathrates is $\Delta\nu_{1/2} = 6$ kHz and super-Lorentzian lineshape with broad wings is revealed; the ratio of linewidths measured at 1/10 and 1/2 of the maximum height is $\Delta\nu_{1/10}/\Delta\nu_{1/2} = 6.2$ (for Lorentzian lineshape this ratio is equal to 3 [12)]). Super-Lorentzian lineshape is characteristic of spatially anisotropic motions (the motion does not cover the whole space angle). The spatial anisotropy of the PhEt motion is confirmed by MAS with spinning frequency $\nu_r \geq 4$ kHz which results in marked narrowing of the line and high-resolution spectrum with two lines corresponding to aromatic and ethyl protons of PhEt is detected (Fig. 1C). Linewidths $\Delta\nu_{1/2}$ in ^1H MAS NMR spectra are 600 Hz and $\Delta\nu_{1/10}/\Delta\nu_{1/2} =$ 3. All these results evidence that PhEt molecules bound in *s*-PS clathrates retain relatively large (correlation time τ_c ~ 100 ns), but spatially anisotropic mobility. The same behaviour was previously found also for semicrystalline *s*-poly(methyl methacrylate) containing bound

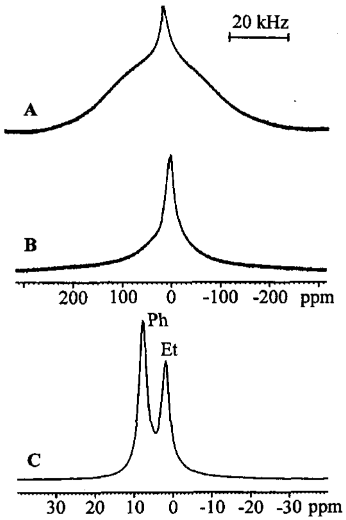

Fig. 1: ^{1}H static (A, B) and MAS (spinning frequency 10 kHz) (C) NMR spectra of *s*-PS/PhEt (A) and *s*-PS-d_8/PhEt (B, C) clathrates (200 MHz, room temperature; ppm scale in spectrum B is referred to the peak)

toluene[13]. Near static dipolar interactions resulting from spatially anisotropic motion make it possible to detect the solvent resonance in ^{13}C CP/MAS NMR spectra of the the δ-form of *s*-PS.

^{13}C CP/MAS NMR spectra of *s*-PS/PhEt and *s*-PS-d_8/PhEt clathrates are shown in Fig. 2. Cross-polarization dynamics for *s*-PS carbons in both systems is shown in Fig. 3. From Fig. 2 it follows that in ^{13}C NMR spectra it is possible to discriminate the lines of *s*-PS and PhEt carbons (with the exception of protonated aromatic 2-6 carbons).

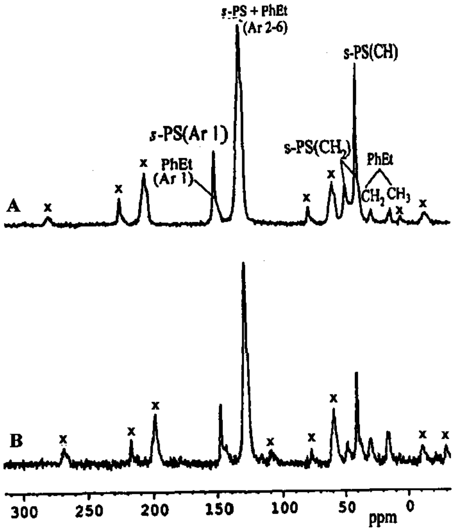

Fig. 2: ^{13}C CP/MAS NMR spectra of *s*-PS/PhEt (A) and *s*-PS-d_8/PhEt (B) clathrates (50 MHz, room temperature; contact times 2 ms and 10 ms for spectra A and B, respectively; symbol x denotes spinning sidebands, Ar 1 denotes quaternary aromatic carbons)

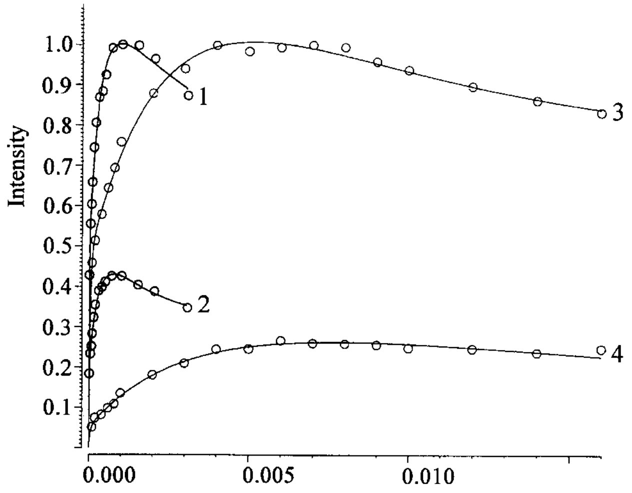

Fig. 3: Cross-polarization dynamics for *s*-PS carbons in *s*-PS/PhEt (curves 1, 2) and *s*-PS-d_8/PhEt (curves 3, 4) clathrates; aliphatic *s*-PS carbons (curves 2, 4), aromatic carbons (curves 1, 3)

The line of CH_2 carbons of *s*-PS is split into a doublet, where its right-hand component appears as a shoulder of the sharp CH peak, confirming TTGG conformational structure[6,7] of *s*-PS chains in the complex with PhEt. The finding that in ^{13}C CP/MAS NMR spectra (where ^{13}C lines originate from dipolar- coupled protons) of *s*-PS-d_8/PhEt, *s*-PS-d_8 lines, in addition to PhEt resonances, were detected, confirms that both components are in contact (the distance between specific proton(s) of PhEt and *s*-PS-d_8 carbons has to be shorter than approximately 0.5 nm). Integrated intensities (taking into account also spinning sidebands) in ^{13}C CP/MAS NMR spectra of *s*-PS-d_8/PhEt clathrates, measured with sufficiently long contact times (≥ 10 ms, cf. Figs. 2B and 3), show that in the close proximity to protons of the PhEt molecule are only ~5 main chain carbons and 2 phenyl groups of *s*-PS-d_8. This result suggests a structural model shown in Fig. 4 and indicates that at least a part of PhEt molecules are intercalated between phenyl rings of *s*-PS. Similar intercalation was suggested recently for thermoreversible gels of *s*-PS in benzene or toluene[14] or for the crystalline δ'-phase of *s*-PS containing benzyl methacrylate[15].

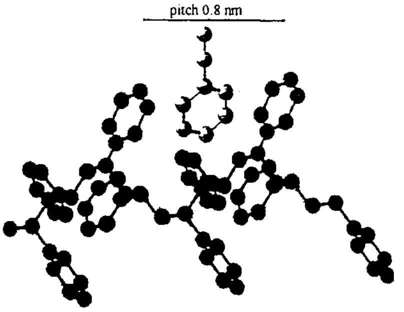

Fig: 4 Model structure of *s*-PS containing intercalated PhEt molecule

Investigation of CP dynamics of s-PS-d_8 carbons (dependences of line intensities on the contact time, cf. Fig. 3) was used to estimate the distances between s-PS-d_8 carbons and nearest PhEt protons. From Fig. 3 it follows that CP rates for aliphatic and aromatic carbons of s-PS-d_8 are virtually the same indicating similar distances to nearest PhEt proton(s) (the fast increase in the intensity of s-PS-d_8/PhEt aromatic carbons at very short contact times is due to the fact that in this case the lines of s-PS-d_8 and PhEt overlap; this arises from PhEt carbons). From the curves in Fig. 3, the cross-polarization relaxation time T_{CH} or the rise time $t_{1/2}$ to half of the total polarization could be determined[16,17]. While for s-PS carbons in s-PS/PhEt clathrates, $t_{1/2}$ = 24 μs and T_{CH} = 20 μs (in agreement with what was described earlier for main- chain carbons of glassy PS [16)]), for s-PS-d_8 carbons in s-PS-d_8/PhEt clathrates $t_{1/2}$ = 1.2 ms and T_{CH} = 2.2 ms. Cross-polarization of s-PS carbons in s-PS-d_8/PhEt is therefore 50-110 times slower than in s-PS/PhEt. Both T_{CH} and $t_{1/2}$ depend on the strength of dipolar interactions between carbons and protons[17,18]

$$T_{CH}^{-1}, t_{1/2}^{-1} \sim \Sigma\, r_i^{-6} \quad , \qquad (1)$$

where r_i are proton-carbon internuclear distances. Taking into account that for s-PS/PhEt, the cross-polarization of s-PS carbons arises from directly bonded protons ($r_{C\text{-}H}$ = 0.109 nm) and assuming that for s-PS-d_8/PhEt only one or two nearest PhEt protons will be effective in term on the right-hand side of relation (1), then from the ratio of T_{CH} or $t_{1/2}$ values obtained for s-PS carbons in s-PS-d_8/PhEt and s-PS/PhEt systems, the effective distance between nearest PhEt proton(s) and s-PS carbons is ≅ 0.22-0.26 nm. Also these values are plausible for the structural model schematically depicted in Fig. 4.

PEO/LiCF$_3$SO$_3$ complex

^{13}CP/MAS NMR spectrum of the PEO/LiCF$_3$SO$_3$ complex is shown in Fig. 5. This spectrum shows that the line of PEO carbons appears at 68.8 ppm, i.e., PEO carbons in the complex with LiCF$_3$SO$_3$ are more shielded in comparison with neat crystalline PEO. The magnitude of the observed "upfield" shift of PEO resonance (3.2 ppm) is larger than the values measured recently for PEO/hydroxybenzene complexes[19)], indicating stronger interactions. The fact that the LiCF$_3$SO$_3$ resonance is also detected in ^{13}C CP/MAS NMR spectrum confirms that the distance between LiCF$_3$SO$_3$ carbon and nearest PEO protons is smaller than ~0.5 nm.

Dynamics of cross-polarization for LiCF$_3$SO$_3$ carbons in complex with PEO is shown in Fig. 6. From the curve in Fig. 6 it follows that cross-polarization relaxation time for LiCF$_3$SO$_3$ carbons, T_{CH} = 5 ms. For PEO carbons, T_{CH} = 20 μs, i.e. the ratio T_{CH}(LiCF$_3$SO$_3$)/T_{CH}(PEO) = 250. While cross-polarization of each PEO carbon is mainly due to the dipolar interactions

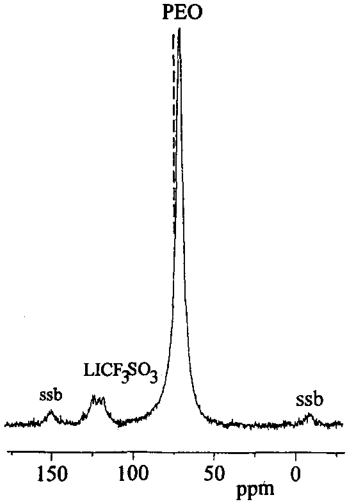

Fig. 5: ^{13}C CP/MAS NMR spectrum of the PEO/$LiCF_3SO_3$ complex (50 MHz, room temperature, contact time 8 ms; the dotted line marks the position of the resonance in neat crystalline PEO, ssb means spinning sideband)

with two directly bonded protons, cross-polarization of the $LiCF_3SO_3$ carbon in the complex with PEO arises from dipolar interactions with nearest PEO protons. Atom modelling of the crystal structure of the PEO/$LiCF_3SO_3$ complex as given in ref.$^{9)}$ has shown that there are nine PEO protons within 0.31-0.38 nm distance from the $LiCF_3SO_3$ carbon; distances of further PEO protons are larger than 0.45 nm. From the $T_{CH}(LiCF_3SO_3)/T_{CH}(PEO)$ ratio, the effective distance between the $LiCF_3SO_3$ carbon and nearest PEO protons amounting to 0.35 nm was obtained, in agreement with the published crystal structure of the PEO/$LiCF_3SO_3$ complex.

For qualitative investigation of the PEO dynamics in the PEO/$LiCF_3SO_3$ molecular complex, we have used measurements of the spin-lattice relaxation time T_1 of PEO carbons. We have

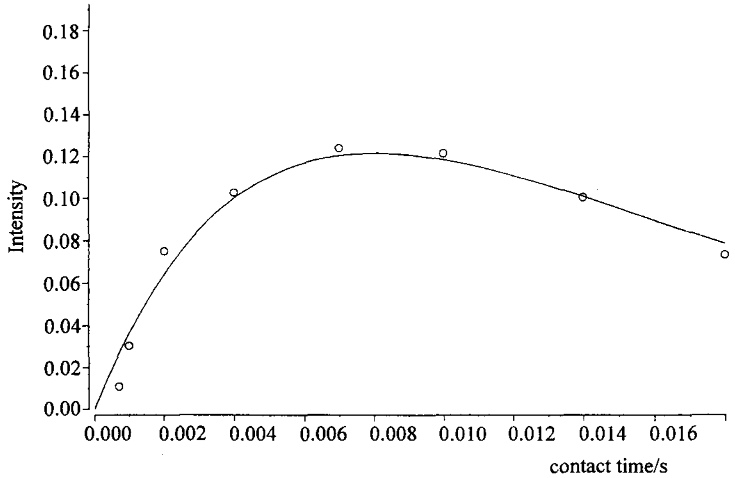

Fig. 6: Cross-polarization dynamics for $LiCF_3SO_3$ carbons in the PEO/$LiCF_3SO_3$ complex

found that while for neat crystalline PEO at 300 K, $T_1 = 10$ s, for PEO carbons in the complex with $LiCF_3SO_3$ at the same temperature, $T_1 = 15.6$ s. This result indicates that the mobility of PEO chains in the complex is lower than in neat crystalline PEO. On the other hand, T_1 observed for the PEO/$LiCF_3SO_3$ complex is shorter than T_1 values in PEO complexes with resorcinol or 2-methylresorcinol ($T_1 = 29$ s), or with *p*-nitrophenol ($T_1 = 236$ s)$^{19)}$. We assume that the higher mobility of PEO chains in the PEO/$LiCF_3SO_3$ complex (molar stoichiometry 3:1) in comparison with PEO/hydroxybenzene complexes (molar stoichiometry 2:1 or 3:2) is associated with lower density of interactions.

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