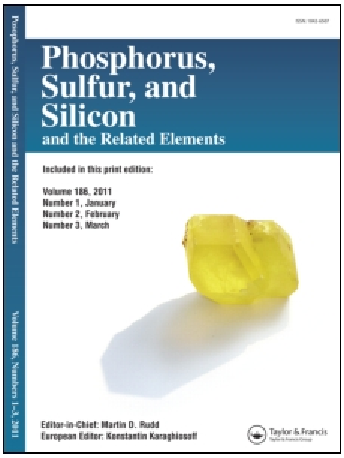

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NMR STUDY OF THE POLYSILOXANEIMIDES DOPED WITH $LiCF_3SO_3$

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Complexes were prepared by cosolution of the lithium trifluoromethanesulfonate ($LiCF_3SO_3$) and the polysiloxaneimides (PSI). PSI copolymers were synthesized by polycondensation reaction of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride with oxydianiline and, α,ω-aminopropyl siloxane of varying molecular weights. The ^{29}Si and ^{13}C-CPMAS NMR spectra and the spin-spin relaxation of complexes have been studied to probe the role of the salt. ^{29}Si NMR spectra of PSI-Li complexes showed two kinds of silicon, which may be assigned to siloxane sequences and siloxane units directly attached to PI. Lithium salt reduces the mobility of the siloxane sequences in PSI-Li complexes. This effect is explained by the interaction between the Li^+ and the oxygen atoms in the polymer backbone.

Keywords: nuclear magnetic resonance; spin-spin relaxation time; polysiloxaneimide electrolytes; lithium doping

INTRODUCTION

Solvent free polymer electrolytes are attractive for high energy-density storage batteries.[1] These materials consist of polyether-based hosts and alkali metal salts guests. However, they are limited to low temperature ($T < 150°C$) application. Polyimide (PI) synthesized from aromatic monomers and doped with lithium salts are candidates of ionic conductors for high-temperature fuel cell and sensor technology.[2,3] The flexible siloxane incorporated into polyimide was reported first by Kuckertz[4], and that was further investigated by many research groups.[5,6] This class of materials has several advantages, such as low dielectric constant, superior adhesion, low moisture absorption, and ease of processing.

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Xu et al. investigated the ion transport of the complexes of PSI with lithium salts, and found that the best conductivity was obtained with $LiCF_3SO_3$.[7,8]

Nuclear magnetic resonance (NMR) is a powerful technique for investigating microphase-separated block copolymers.[9–11] ^1H free induction decays reflects the local environment and mobility of the monomer units. They can be used to probe the existence of different phases in a heterogeneous material. In previous paper, we have investigated the dynamic properties of PSI using spin-spin relaxation measurements.[12] In all these experiments the multiphase nature of PSI is evident. This paper is a further dynamic study on the complexes of PSI copolymers doped with lithium trifluoromethanesulfonate $LiCF_3SO_3$. It is hoped that spin-spin relaxation time T_2 will provide an insight into the effect of lithium ions on the nature of molecular motion.

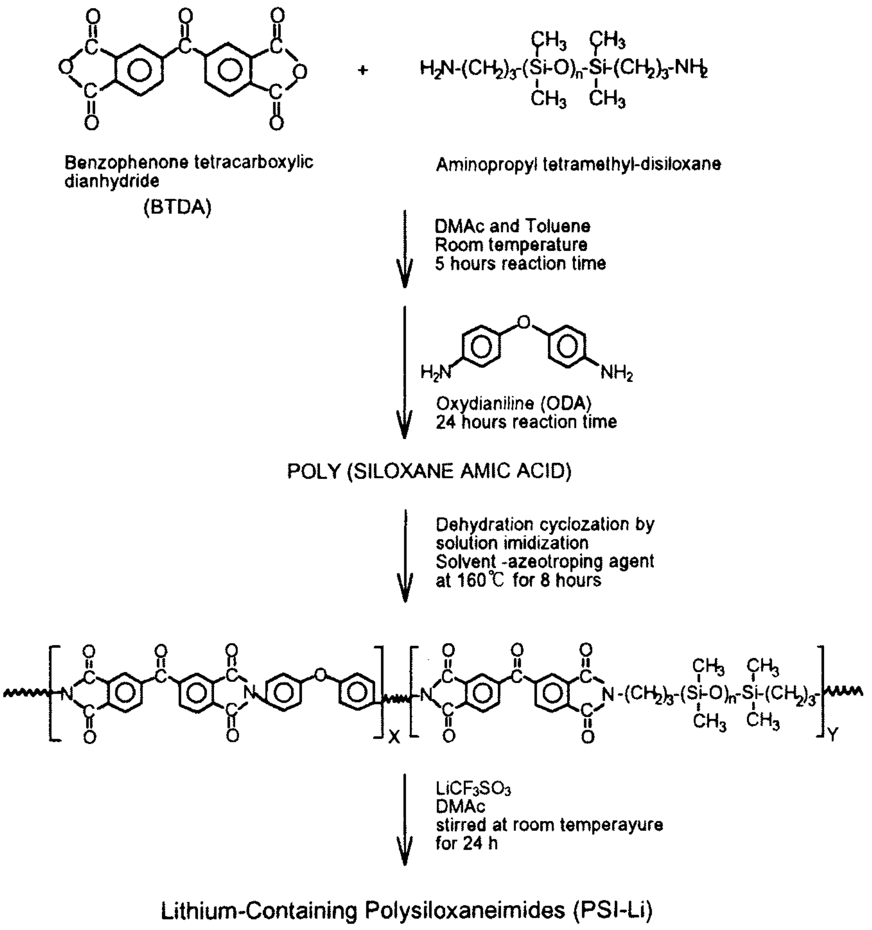
EXPERIMENTAL

Polymerization

The polyimide and polysiloxaneimides were the materials employed in our earlier work.[12] A stoichiometric amount of the siloxane oligomer was first slowly added to a stirring solution of the 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), effectively capping the siloxane oligomer through reaction of its amine end-groups. The aromatic oxydianiline (ODA) is then gradually added as a solution to the free dianhydride and anhydride-capped siloxane. The clear solution was stirred at room temperature for 24 h and then at 160°C for 8 h under nitrogen. Collected water was removed from the distillation trap with toluene. After cooling the reaction mixture was poured into excess methanol. The precipitated polymer was collected by filtration, washed successively with methanol, and dried under vacuum at 80°C for 8 h. Complexes were prepared by cosolution of the 10 wt% $LiCF_3SO_3$ (TCI, Japan) and the PSI in dry N,N′-dimethylacetamide.[2] Yellow ocher solid was obtained, as shown in Scheme 1. PSI copolymers are designed so that, for example, PSI-1300(10) denotes a copolymer containing 10 wt% of siloxane which number-average molecular weight is 1300 g/mol. Furthermore, PSI-1300(10)-Li denotes a complex of PSI-1300(10) with $LiCF_3SO_3$.

Characterization

Lithium-containing copolymers (PSI-Li) and homopolymer (PI-Li) were all soluble in dipolar, aprotic solvents such as N-methylpyrrolidinone (NMP) and dimethylacetamide (DMAc). PSI-Li complexes were confirmed by infrared (IR)



SCHEME 1

spectra (Bomem DA 3.002) of samples prepared as KBr pellets technique. The characteristic imide and siloxane peaks were observed as followings. IR (KBr): 1777–1780 cm^{-1} (imide C=O symmetric stretching), 1720–1723 cm^{-1} (imide C=O asymmetric stretching), 1382–1384 cm^{-1} (C-N stretching), 717–720 cm^{-1} (imide ring deformation), 1013–1015 cm^{-1} (Si-O-Si stretching), and 797–799 cm^{-1} (Si-C stretching). The ^{29}Si and ^{13}C-nuclear magnetic resonance (NMR) spectra of the PSI complexes were determined (Bruker MSL-200). Proton spin-spin relaxation time T_2 were measured at room temperature via solid state ^{13}C-NMR (Bruker MSL-200) using the pulse sequence described by Tékély[10,11]. The lithium content was analyzed with an inductively-coupled plasma atomic emission spectrometer (Allied Analysis System, model ICAP 9000).

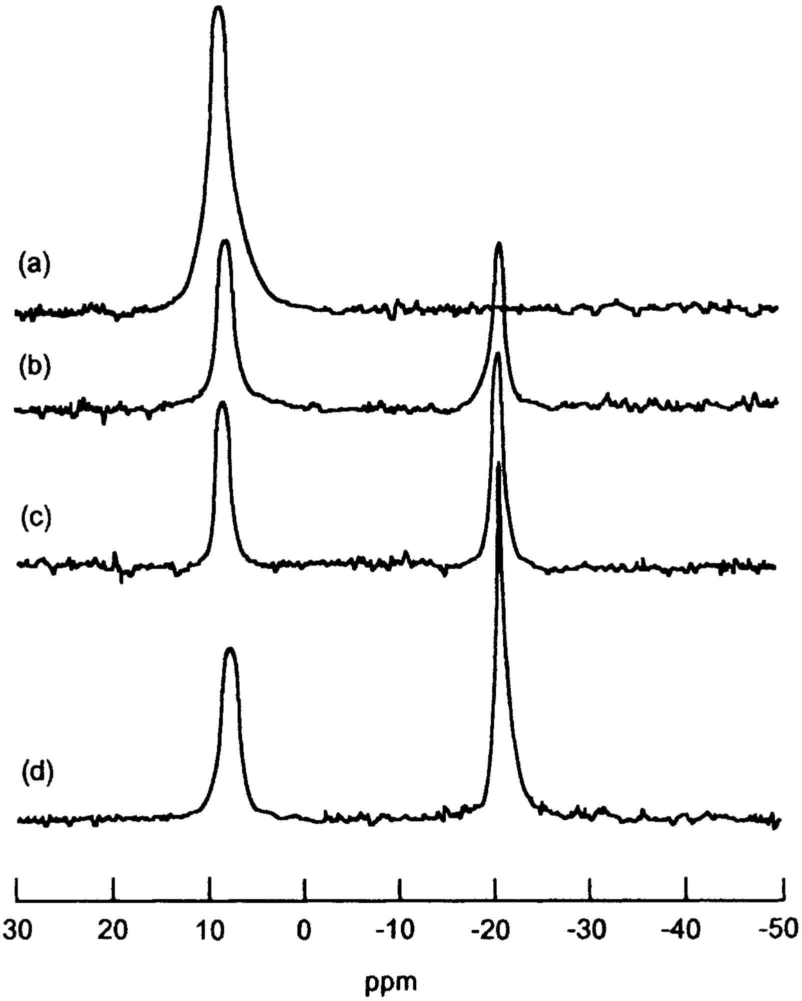


FIGURE 1 ^{29}Si-CPMAS NMR spectra for complexes of (a) PSI-276(20), (b) PSI-1300(10), (c) PSI-1300(20), (d) PSI-1300(30) and (e) PSI-4400(20) doped with $LiCF_3SO_3$.

RESULTS AND DISCUSSION

NMR Spectral Analysis

The siloxane segments in PSI-276(20)-Li complex have one kind electronic environment, which is reflected in one broader peak (7.7 ppm) in ^{29}Si-NMR spectrum (Figure 1(a)). However, the ^{29}Si-NMR spectra of PSI-1300-Li complexes show two peaks (figures 1(b), (c), and (d)), which indicate two kinds of silicon

TABLE I Chemical shifts δ, peak width at half height $\nu_{1/2}$ and percentage peak areas for solid polysiloxaneimides.

Polymer			*^{29}Si NMR*		
	Li/wt %	*δ/ppm*	*$\nu_{1/2}$/Hz*	*δ/ppm*	*$\nu_{1/2}$/Hz*
PSI-276(20)-Li	0.38	7.7(100)	154	—	—
PSI-1300(10)-Li	0.38	7.4(53)	130	−22.2(47)	70
PSI-1300(20)-Li	0.40	6.9(54)	117	−22.2(46)	57
PSI-1300(30)-Li	0.42	6.8(44)	123	−22.5(56)	39
PSI-4400(20)-Li	0.39	—	—	−22.3(100)	37
Polymer			^{13}C NMR		
	Li/wt %	δ/ppm	$\nu_{1/2}$/Hz	δ/ppm	$\nu_{1/2}$/Hz
PI/Li	0.39	165.6	163	—	—
PSI-276(20)-Li	0.38	166.5	192	1.0	202
PSI-1300(10)-Li	0.38	165.6	182	1.3	141
PSI-1300(20)-Li	0.40	165.7	190	1.3	132
PSI-1300(30)-Li	0.42	166.3	224	1.2	71
PSI-4400(20)-Li	0.39	165.8	193	1.0	83

[a] Numbers in parentheses indicate the percentage peak areas from NMR integration.

with markedly different electronic environments. The peaks at around 7.0 and −22.0 ppm can be attributed to the silicon directly connected to PI and in the siloxane sequence, respectively.[12,13] Moreover, the peak width at half height $\nu_{1/2}$ for the former (154 ~ 117 Hz) is broader than that for the latter (70 ~ 37 Hz). The narrow ^{29}Si-NMR peak width for silicon in the siloxane sequence suggests more motional narrowing, and that decreases with increasing siloxane content (Table I). On the other hand, the percentages of the integrated intensities of the ^{29}Si spectra for peaks may represent the percentages of the two kinds of silicon, because the cross polarization rate for both peaks are almost the same.[13,14].

The ^{13}C-NMR spectra of PSI-Li complexes are nearly identical. The peak for siloxane segment' carbons $\text{-OSi(}CH_3)_2\text{-}$ is observed at around 1.0 ppm. Moreover, the value of $\nu_{1/2}$ for peak of siloxane segments' carbons decreases with increasing siloxane content and siloxane length (Table I). The results reveal that the motion of the siloxane segments' carbons increases with increasing siloxane content and siloxane length. However, the values of the chemical shifts δ and $\nu_{1/2}$ for PSI-Li complexes no significant differences were observed as compared that of PSI copolymeres.

NMR Relaxation Times

NMR experiments on PSI-Li complexes were performed at room temperature. At this temperature, the rigid PI segments are in the glassy state, whereas the flexible siloxane segments are well above their glass transition and melting tem-

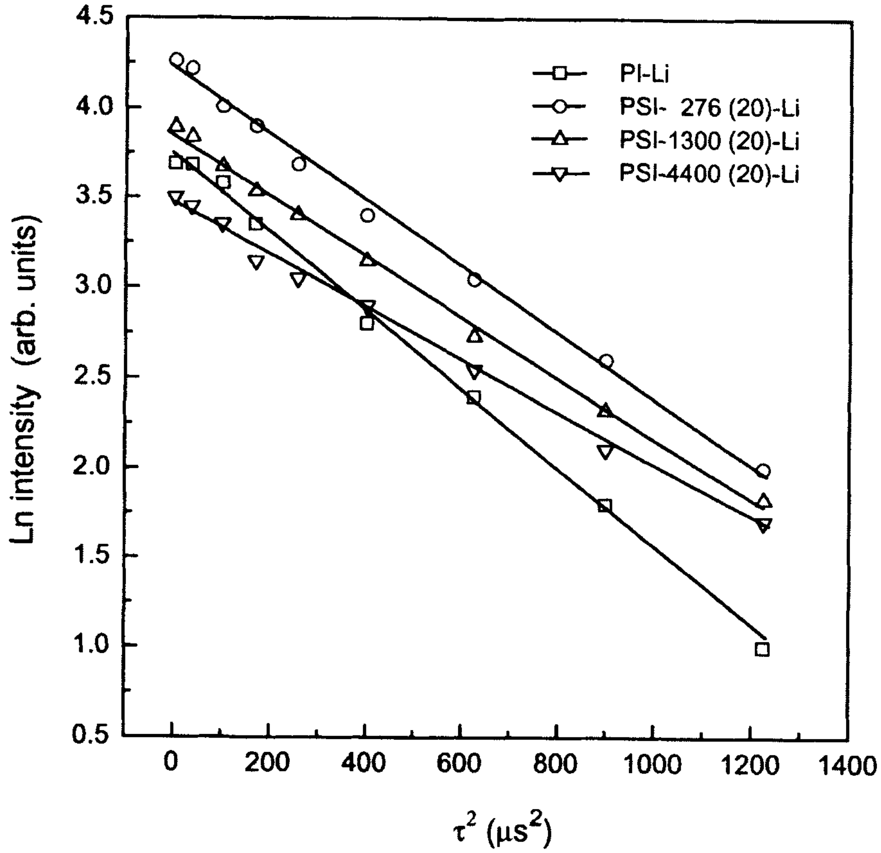


FIGURE 2 Logarithmic intensity (arb. units) of the ^{13}C-CPMAS NMR spectra of PI in PSI complexes versus square of proton relaxation period τ^2.

peratures. Therefore, the two segments exhibit very different chain mobility, which should result in very different nuclear magnetic relaxation properties.

Figure 2 shows the correlation between the logarithmic intensities I_0 of the 166 ppm peak (imide $C=O$) in the ^{13}C-NMR spectra of complexes and the square transverse proton relaxation period (τ^2). It is found that the carbons in PI segments exhibit a Gaussian fast decay, expressed as I_0 (fast) = $\exp[-(\tau/T_2)^2/2]$,[9] with similar spin-spin relaxation time T_2 values (~ 18 μs) in PSI-Li complexes (Table II). They are very close to the T_2 value of the PI-Li complex (15μs). The results indicate that the spin-spin relaxation of the rigid-chain PI protons is not effected by the presence of the flexible siloxane segments in the complexes.

The siloxane segments carbons have a Lorentzian slow decay I_0 (slow) = $\exp[-\tau/T_2]$,[9] as shown in Figure 3. Relaxation times T_2 were calculated from

TABLE II Chemical shifts δ, proton spin-spin relaxation times T_2 and fractions of different domains in different segmented copolymers.

Polymer	*PI phase*		*DMS phase*				
	δ ppm	*T_2/μs*	*δ ppm*	*T_2/μs*	*fraction in %*	*T_2/μs*	*fraction in %*
PI	165.7	15		—	—	—	—
PSI-276(20)	166.4	17	1.1	18	100	—	—
PSI-1300(20)	165.9	17	1.3	25	5	48	95
PSI-1300(30)	166.1	20	1.2	—	—	48	100
PSI-4400(20)	165.7	19	1.0	23	8	46	92

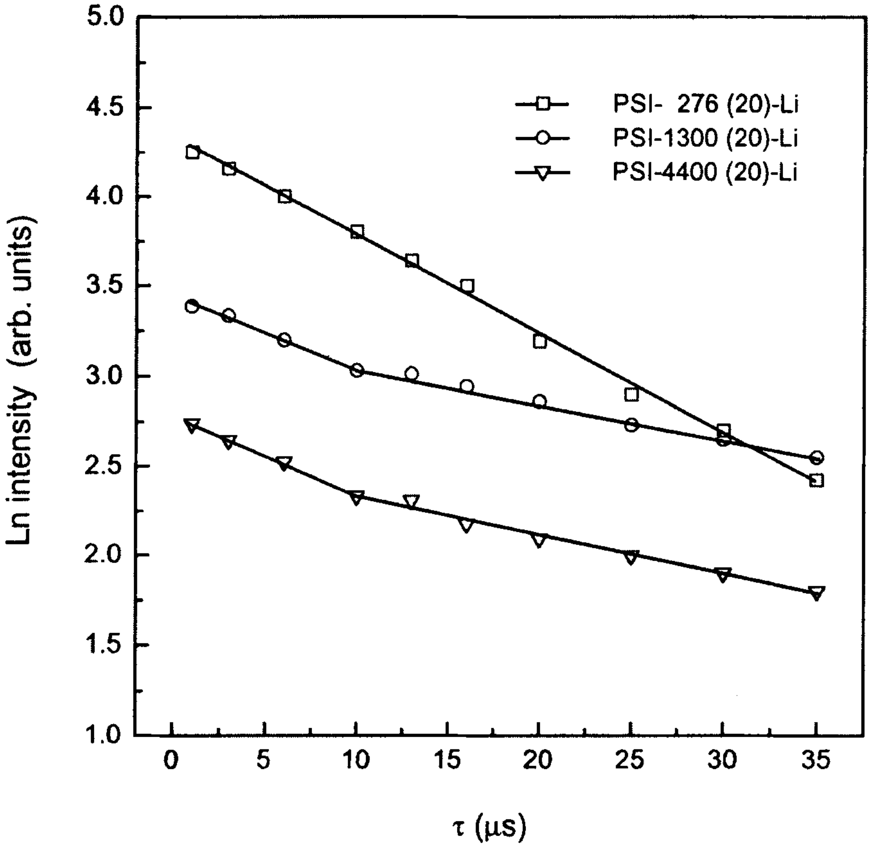


FIGURE 3 Logarithmic intensity (arb. units) of the ^{13}C-CPMAS NMR spectra of siloxane in PSI coplexes versus proton relaxation period τ.

the slopes of Figure 3. Two different slopes in Figure 3(b) and (c) yield the parameters T_2 (fast) and T_2 (slow), indicating that the siloxane protons can be found in two environments. The fast and slow decaying component can be attributed to siloxane units in the interface and in the sequence, respectively. For each type of carbon, the intercepts in Figure 3, are proportional to the percentage of proton atoms[10,11] to be found in each component (Table II). These data demonstrate that the rate of relaxation for siloxane units is about three times higher in interphase (17 ~ 20 μs) than in sequence (~47 μs). It is also shown that T_2 of the siloxane sequence in PSI-Li complexes is lower than that in PSI copolymers (67 ~ 102 μs). This results imply that the motion of the siloxane chains was restricted by the interaction between the lithium salts and the oxygen atoms in siloxane segments in PSI copolymers.

In the PSI-276(20)-Li complex exist one kind of silicon that connects directly to PI segments. Thus, the siloxane segments in PSI-276(20)-Li complex has only single T_2 (18 μs) as expected, and that is very close to PI segments (17 μs). The result indicates that motion of the disiloxane chains is seriously restricted by bonding to the rigid PI segments.[15]

Acknowledgements

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