

Li ion transport in an intercalated polymer electrolyte

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Lithium ions solvated by polyethylene-oxide (PEO) have been confined by intercalation within the galleries of an insulating, inorganic layered solid CdPS₃. The dc conductivity of this confined polymer electrolyte Cd_{0.75}PS₃Li_{0.5}(PEO) displays a distinct change in the mechanism of conduction with temperature, exhibiting a crossover from an Arrhenius temperature dependence at low temperatures to a non-Arrhenius, Vogel–Tamman–Fulcher behavior at higher temperatures. We use ²H, ⁷Li, and ¹³C nuclear magnetic resonance (NMR) in combination with infrared spectroscopy to probe Li ion mobility as well as segmental motion of the intercalated PEO. Within the galleries of Cd_{0.75}PS₃Li_{0.5}(PEO) both rigid and mobile fractions of the intercalated polymer are present with the equilibrium fraction of the mobile species increasing with temperature. The ⁷Li (*I* = 3/2) NMR of the confined polymer electrolyte exhibits an unusual behavior—the appearance of quadrupolar satellites at high temperatures where the conductivity values are appreciable. The results signify the solvation of Li ions by mobile segments of the intercalated PEO. Further proof of this association is seen in the ¹³C NMR as well as infrared spectra, both of which show evidence of the complexation of Li ions by ether linkages of the interlamellar PEO at high temperature and the absence of such an association at lower temperature when polymer motion is absent.

I. INTRODUCTION

Polymers intercalated into low-dimensional host lattices form an attractive class of compounds,^{1,2} since intercalation can combine properties of both the guest polymer and the inorganic host in a single material. These compounds also serve as model systems for understanding the effect of confinement on properties of the guest in relation to those in the bulk.^{3,4} Here we focus on a polymer electrolyte, Li-polyethylene-oxide (Li-PEO), confined by intercalation within the galleries of an inorganic layered host CdPS₃.⁵ The Li-PEO CdPS₃-based intercalated polymer electrolyte Cd_{0.75}PS₃Li_{0.5}(PEO) has been characterized previously⁵ and a detailed study of the conductivity and dielectric properties reported.^{6,7} Intercalated polymer electrolytes (IPEs) formed by insertion of polyethylene oxide or polypropylene oxide in alkali-ion-exchanged layered solids are of particular significance since the corresponding alkali metal salt dissolved in these polymers, the bulk solid polymer electrolytes (SPEs), are well-known ionic conductors.⁸ The solid polymer electrolytes, because of their potential application in electrochemical devices, have been extensively investigated in the last two decades.^{9,10}

Ion conduction in the SPEs is fundamentally different from the conventional ion-hopping conduction observed in solid electrolytes as well as in aqueous or nonaqueous electrolytes. Ionic conductivity in the SPEs is significant only in the elastomeric phase, above the glass transition temperature

of the polymer.¹¹ Alkali ion transport is strongly associated with local polymer segmental motion, as exemplified by the Vogel–Tamman–Fulcher (VTF) form of the temperature-dependent conductivity:¹²

$$\sigma = \sigma_0 T^{-1/2} \exp(-B/T - T_0). \quad (1)$$

In the above equation T_0 is usually interpreted as an equilibrium glass transition temperature below which all segmental motion is frozen and B the pseudoactivation energy. Further evidence for the role of polymer segmental motion comes from ⁷Li and ¹H nuclear magnetic resonance (NMR) spin lattice relaxation rates, which show a similar temperature dependence, suggesting that the fluctuating fields responsible for the relaxation of the Li ion and the polymer are the same.^{13,14} Experimental evidence suggests that the mobility of ions in the SPEs is provided by segmental motion of the polymer and that ion transport is largely determined by local dynamics of the solvating polymer.¹⁵ Knowledge of the structural properties of the ion-conducting amorphous phase is, however, limited and consequently the mechanism of ion conduction, at the molecular level, is still not fully understood.

In PEO- and PPO-based SPEs the alkali ions are solvated by the ether oxygens of the polymer.^{16–18} Structural studies of crystalline PEO complexed with alkali metal salts indicate a crown-ether-like coordination for the alkali ion. These studies, however, are of limited value for predicting properties of the amorphous phase, where ion conduction occurs, since several different structural arrangements which may involve cation–anion pair formation are possible. Although anions are not, generally, solvated, extensive

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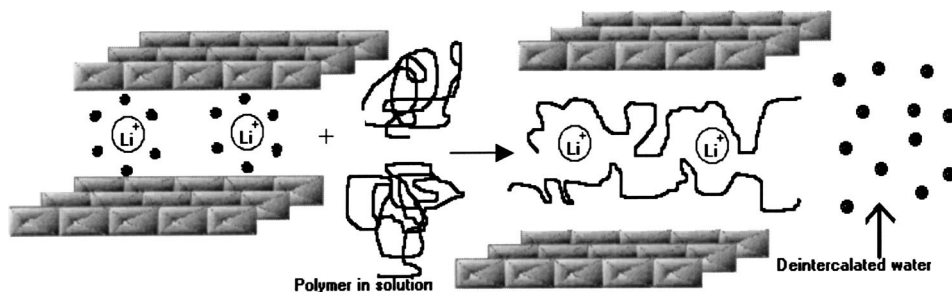
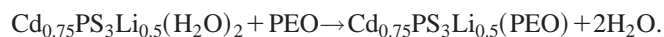


FIG. 1. Drawing illustrating the formation of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$. Intercalation of uncharged PEO molecules occurs by displacement of the water of hydration of the interlamellar-hydrated Li ions in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{H}_2\text{O})_2$.

polymer-mediated cation–anion pair formation is known to occur because of the relatively low dielectric constant of most polymeric solvents.¹⁹ Spectroscopic studies^{20,21} have shown that the solvation reaction is complex and that, in addition to fully dissociated ions, ion pairs, triplets, and clusters of varying abundance are present. It is the presence of the several different types of ionic species which contribute, at least in part, to the complexity of the ion transport mechanism. A further complication in the case of PEO-based SPEs is the coexistence of amorphous and crystalline regions.²² In the corresponding intercalated polymer electrolyte formed by insertion of PEO into a Li-ion-exchanged layered host (Fig. 1) the massive negatively charged inorganic layer not only provides a confining environment, but also plays the role of the anion. In the metal thiophosphates it has been shown that the negatively charged layers may be treated as insulating sheets of uniform charge density.²³ The anion as well as anion–Li ion pair contribution to the conductivity may, therefore, be ignored. These are, therefore, ideal systems to probe the association between Li ion motion and local segmental motion of the polymer.

The intercalated polymer electrolyte $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ is formed by the complete displacement of water molecules from the hydration shell of interlamellar hydrated Li ions (Fig. 1) in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{H}_2\text{O})_2$ (Ref. 5):



Intercalation occurs with a lattice expansion of 8.5 Å, and the ratio of the alkali metal to the ether oxygen of the intercalated PEO is 1:3.3. A detailed characterization of the frequency-dependent electrical response in this family of intercalated polymer electrolytes, $\text{Cd}_{0.75}\text{PS}_3\text{A}_{0.5}(\text{PEO})$ ($A = \text{Li, Na, K, Cs}$) has been reported for a range of PEO molecular weights.^{6,7} At ambient temperatures $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ exhibits ionic conductivity, comparable to the corresponding SPE, with the conductivity values independent of the molecular weight of the intercalated PEO. The layered host lattice is electrically inert, and hence the conductivity may be attributed entirely to the polymer electrolyte confined within the galleries.

The dc conductivity of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ shows a change in conduction mechanism with temperature⁷ (Fig. 2). Below 225 K the dc conductivity values are small and the temperature dependence Arrhenius ($E_a = 2.7$ kcal/mol). Above 225 K the conductivity rises rapidly with temperature and in this regime the temperature dependence is non-Arrhenius following the VTF relation with $B = 5.9$ kcal/mol

and $T_0 = 90.7$ K. Although no T_g is discernible by differential scanning calorimetry (DSC) measurements, the VTF temperature dependence of the conductivity was considered as evidence for the involvement of segmental motion of the intercalated PEO in ion transport. Support for a possible coupling of ion and polymer motion is the fact that the frequency-dependent electrical response in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ showed a single feature—a well-defined conductivity relaxation in the electrical modulus representation—whereas the corresponding dielectric spectra showed no such feature.⁷ In contrast, in intercalated polymer electrolytes in which the conductivity followed an Arrhenius temperature dependence an additional feature—a dielectric loss due to PEO segmental motion—is seen in the ac electrical response, indicating decoupling of ion motion from polymer segmental relaxation.⁷

Here we report results of a multinuclear NMR spectroscopic study of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ as a function of temperature. Multinuclear NMR has been widely used to probe

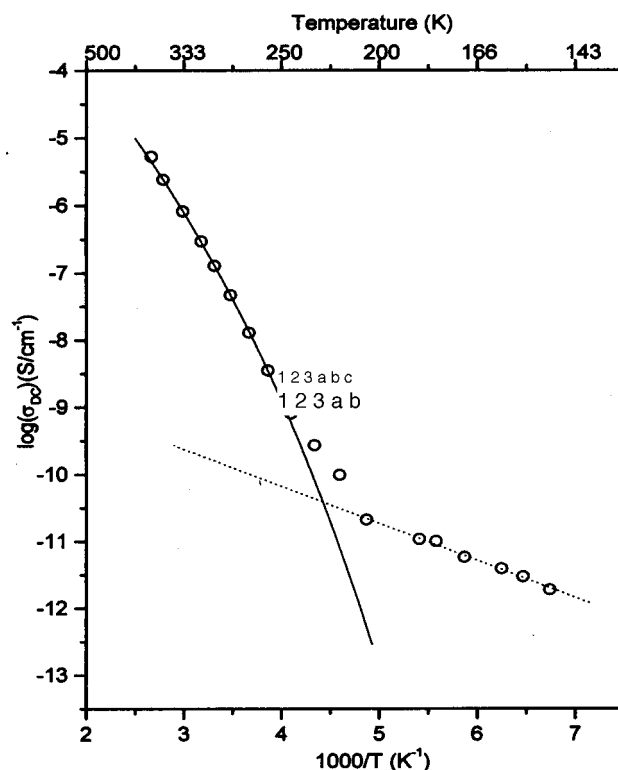


FIG. 2. dc conductivity of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$. The solid line is the fit to the VTF equation (1) and the dotted line the Arrhenius fit (adapted from Ref. 7).

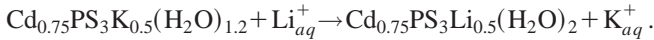
motion of alkali ion in SPEs (Refs. 14, 24, and 25) and also the dynamics in composite polymer electrolytes based on the intercalation of PEO in mica-type silicates.^{26–28} These studies have established that in the SPEs there exist two dynamical regimes: a regime above a temperature T_c ($T_c > T_g$, T_g being the glass transition temperature) where ionic motion and polymer segmental motion are coupled and a regime below T_c where they are decoupled. In the present study ^2H NMR spectroscopy has been used to study local segmental mobility of the interlamellar PEO while ^7Li NMR to probe motion and association of the Li ions. In addition, ^{13}C NMR and infrared spectroscopy have been used to investigate the nature and extent of complexation of the Li ion by PEO in the intercalated polymer electrolyte $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$. The present results are able to provide direct spectroscopic evidence for the association of Li ions with mobile segments of the confined PEO. The results are discussed in the context of the origin of the non-Arrhenius VTF temperature dependence of the Li ion conductivity reported in this material.

II. EXPERIMENT

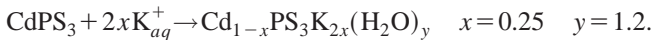
A. Preparation

Cadmium thiophosphate was prepared from the elements following the procedure reported in Ref. 29. Cadmium metal powder, phosphorous, and sulphur, in stoichiometric amounts, were sealed in quartz ampoules at 10^{-5} Torr and heated at 650°C for a period of 2 weeks. The formation of CdPS_3 was confirmed by x-ray diffraction (XRD); the pattern could be indexed in the $C2/m$ space group with lattice parameters $a = 6.313 \text{ \AA}$, $b = 10.787 \text{ \AA}$, $c = 6.906 \text{ \AA}$, and $\beta = 108.35^\circ$, similar to that reported in the literature.³⁰

The intercalated polymer electrolyte $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ is formed by the displacement of water molecules in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{H}_2\text{O})_2$ by PEO.⁵ A facile route for the preparation of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{H}_2\text{O})_2$ is by exchanging the K ion in $\text{Cd}_{0.75}\text{PS}_3\text{K}_{0.5}(\text{H}_2\text{O})_{1.2}$ for Li ions:³¹

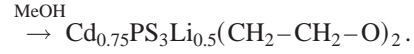
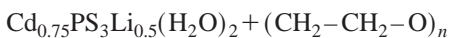


Ion exchange of the K ion by Li ion causes the lattice spacing to increase from 9.4 to 12.2 Å and an increase in the extent of hydration of the interlamellar alkali ion. The potassium-ion-exchanged intercalation compounds were obtained by stirring CdPS_3 powder in aqueous solution of KCl along with a complexing agent EDTA. The pH of the solution was maintained at 10 using a 1 mol $\text{K}_2\text{CO}_3/\text{KHCO}_3$ buffer:



Complete ion-exchange intercalation was ascertained by the absence of the host 00 l reflections and the appearance of new 00 l reflections with lattice spacing, 9.4 Å .⁴

The intercalation of PEO in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{H}_2\text{O})_2$ was carried out by refluxing the lithium-ion-exchanged intercalation compound $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{H}_2\text{O})_2$ with a methanolic solution of PEO [molecular weight (M_w) = 6×10^5] following the procedure reported in Ref. 5:



The intercalation reaction was carried out using Schlenk techniques. $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{H}_2\text{O})_2$ was refluxed with a methanolic solution of PEO ($M_w = 6 \times 10^5$) in a two-necked round-bottomed flask fitted with a rubber septum. The progress of the reaction was monitored by the appearance of a new 00 l reflection with $d = 15.1 \text{ \AA}$ in the powder XRD. Completion of the reaction was ascertained by the absence of the $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{H}_2\text{O})_2$ reflections in the XRD and also by the absence of interlamellar H_2O using infrared spectroscopy.⁵ The powder was filtered and washed with dry methanol to remove PEO adsorbed on the surface of the crystallites. The intercalation of the deuterated PEO followed an identical procedure.

B. Measurements

Static ^2H , ^7Li , and ^{13}C NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ were recorded on a Bruker DSX-300 solid-state Fourier-transformed NMR spectrometer at Larmor frequencies of 46.07, 116.4, and 75.47 MHz, respectively. Temperature variation studies were done using the Bruker variable-temperature accessory (B-VT 2000). The ^2H NMR spectra were recorded with typically a 5-s delay between scans. As the spectra in the temperature range 280–330 K have contributions from mobile and rigid polymer fractions, the spectra were also recorded with longer delays. However, no changes in the spectral pattern and the relative intensities were observed. The significance of these results is discussed in detail in the Results section. The ^2H and ^7Li NMR spectra were recorded as free-induction decays (FIDs) following $\pi/2$ pulses and also as echoes following the solid echo pulse sequence; the line shapes for both methods were essentially the same. ^{13}C spectra of static samples of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ were recorded by the cross-polarization technique with a contact time of 1 ms and a repetition time of 5 s.

Infrared spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ were recorded in the transmission mode in the spectral range 400–4000 cm^{-1} on a Bruker IFS55 spectrometer. The samples were pelletized and mounted on a hollow copper block and cooled using a CTI-Cryogenics closed-cycle cryostat. Sample temperature could be varied from 300 to 40 K. The cryostat was evacuated at 10^{-2} Torr to prevent condensation on the pellet.

III. RESULTS AND DISCUSSION

A. ^2H NMR and the mobility of intercalated PEO

Deuterium NMR has been used to probe the motion of the intercalated PEO in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO}-^2\text{H})$. The ^2H NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO}-^2\text{H})$ at different temperatures is shown in Fig. 3(a). At the lowest temperature (250 K) the spectrum corresponds to a static quadrupolar powder pattern characteristic for a spin $I = 1$ nuclei. The separation between the inner singularities is 116 kHz. The outer steps of the doublet are, however, not visible. With increasing temperature the evolution of a central component

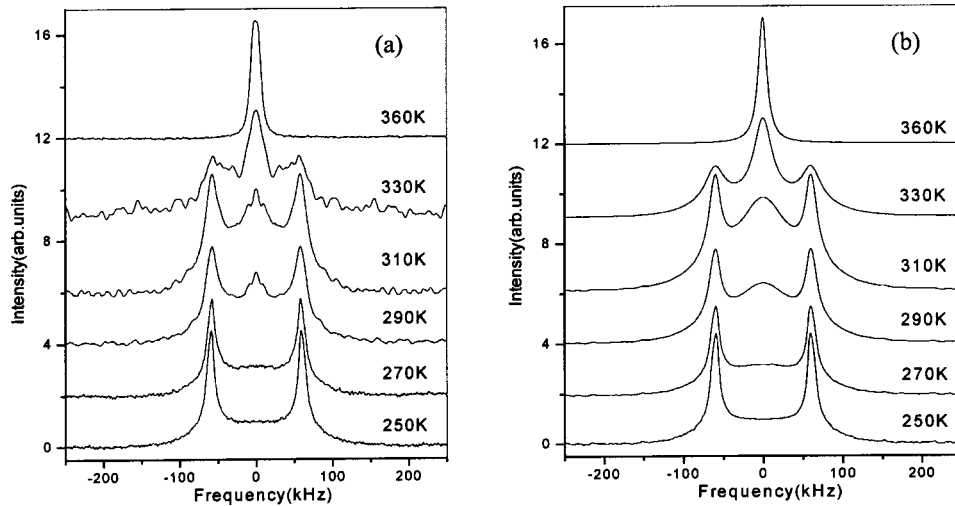


FIG. 3. (a) ^2H NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO}-\text{D})$ powder at different temperatures. (b) Fits to the experimental spectra.

may clearly be seen in Fig. 3(a). This builds up in intensity with a concomitant decrease in the intensity of the quadrupolar doublet. There is, however, no change either in the position or separation of the doublet with temperature. Above 340 K, only the central component is seen as a sharp line with a width [full width at half maximum (FWHM)] of 6.5 kHz.

^2H NMR has been widely used for studying molecular order and dynamics in polymeric systems.³² ^2H NMR line shapes can provide information on the nature of motion and the associated time scales. In addition, motional heterogeneities if present can be detected and the associated distribution of correlation times directly determined. The ^2H NMR of the intercalated PEO in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO}-^2\text{H})$ is typical of many polymeric systems which show distinct spectral features for regions of grossly differing mobilities.³² The static powder pattern seen at low temperatures in the ^2H NMR spectrum of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO}-^2\text{H})$ corresponds to the rigid (immobile) segments of the intercalated PEO: the observed value of splitting (116 kHz) is typical of rigid polymeric systems.³² The evolution of a central component with increasing temperature is due to the mobile polymer segments. It may be seen that the only change in the spectrum with increasing temperature is a reduction in intensity of the doublet with a concomitant increase in intensity at the center of the powder pattern; *no* change in the doublet separation is observed with temperature.

The intensities of the ^2H NMR spectral features reflect the equilibrium population of the rigid and mobile segments of the intercalated PEO. The spectra at any temperature would therefore be a superposition of a quadrupolar doublet due to the rigid fraction and a central component due to the more mobile segments of the intercalated PEO, with the weighted fractions directly proportional to their respective populations. The spectral line shapes have therefore been analyzed accordingly. This method is similar to the one used by Rössler *et al.*³³ to describe the temperature dependence of the ^2H NMR of deuterated benzene and hexamethylbenzene in organic glasses. The line shape at intermediate temperatures was considered as a weighted superposition of the spectra seen at the lowest and highest temperatures, correspond-

ing to the rigid and mobile species, respectively.

The ^2H NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ was analyzed by considering the spectra at the lowest temperature (250 K) as representative of the rigid segments of the intercalated PEO and a Lorentzian, with variable linewidth at the center, as representative of the mobile fraction. The experimental spectra were fitted by floating the intensities of the two components and also the linewidth of the central Lorentzian. The fits to the experimental spectra [Fig. 3(a)] are shown in Fig. 3(b). A test of the above assumption that the intensities reflect the equilibrium population of the rigid and the mobile fractions of the polymer is to examine the temperature dependence of the logarithmic ratio of the intensities of the two components, $\ln(I_{\text{mobile}}/I_{\text{rigid}})$; here, I_{mobile} and I_{rigid} are the intensities of the mobile and rigid fractions in the ^2H NMR [Fig. 3(a)]. This ratio would be directly proportional, if the above argument was valid, to the logarithmic ratio of the concentration of the mobile and rigid components, $\ln([\text{mobile}]/[\text{rigid}])$. This ratio is the equilibrium constant K and should follow the van't Hoff relation [Eq. (2)] if the assumption of equilibrium is correct:

$$\frac{d \ln K}{d(1/T)} = - \frac{\Delta H}{R}. \quad (2)$$

In Fig. 4 the logarithmic ratio $\ln(I_{\text{mobile}}/I_{\text{rigid}})$ has been plotted as a function of inverse temperature. The linearity of the plot clearly justifies the assumption of equilibrium, and the enthalpy as calculated from the linear slope is 4 kcal/mol.

B. ^7Li NMR and motion of Li ions

Lithium ion motion in the intercalated polymer electrolyte was probed using ^7Li NMR spectroscopy. The ^7Li NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ powder at various temperatures are shown in Fig. 5. At the lowest temperature the spectrum consists of a broad line whose width decreases with increasing temperature. Although the spectra were recorded over a spectral width of 250 kHz, the $|\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$ satellite transitions of the $I=3/2$ nucleus were not observed at temperatures below 330 K. At temperatures above 330 K, however, well-defined satellites may clearly be seen from

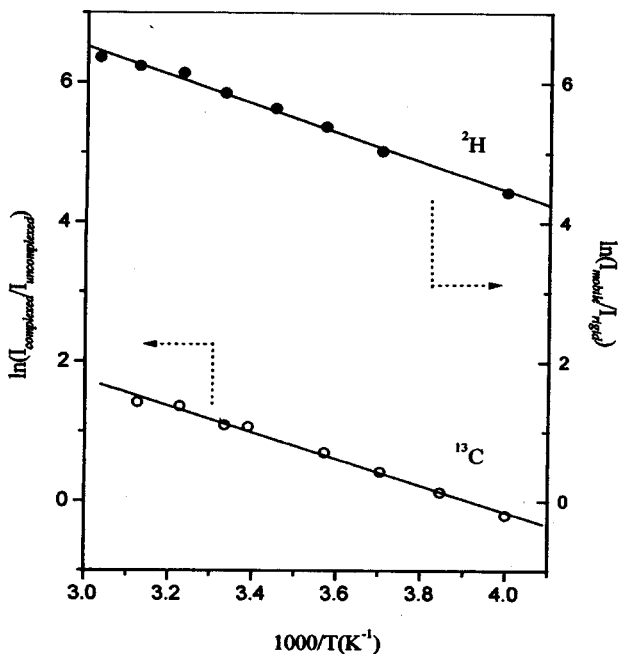


FIG. 4. Logarithmic ratio $\ln(I_{\text{mobile}}/I_{\text{rigid}})$, obtained from the fits to the ^2H NMR, as a function of inverse temperature (shown as solid circles). The temperature variation of the ratio $\ln(I_{\text{complexed}}/I_{\text{uncomplexed}})$ obtained from ^{13}C NMR is also shown (open circles). Solid lines are fits to the van't Hoff equation (2).

Fig. 5. The spectra in the temperature range 330–370 K resemble a static quadrupolar powder pattern expected for a $I = 3/2$ nucleus corresponding to an axial tensor³⁴ and could be fitted to a theoretical powder pattern.³⁵ In the temperature range 330–370 K the quadrupolar coupling constant e^2qQ/h shows a linear increase with temperature.

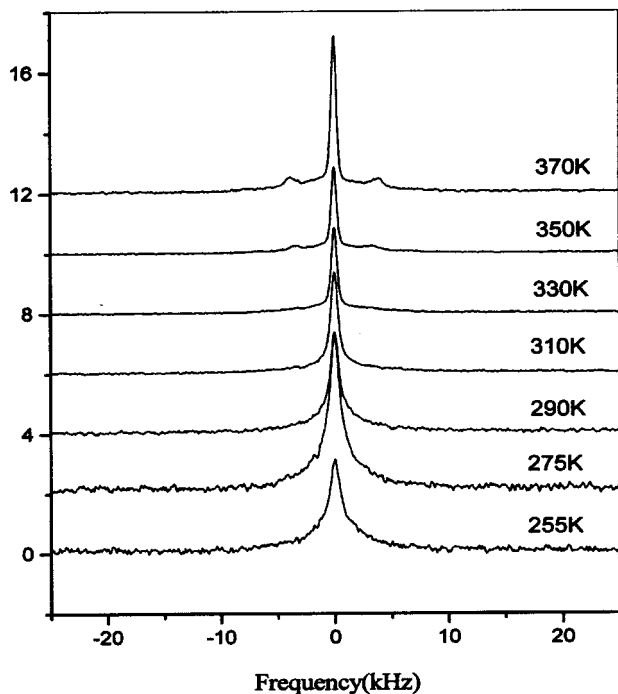


FIG. 5. ^7Li NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ powder at various temperatures.

The narrowing of the ^7Li spectra with increasing temperature from 200 to 330 K indicates an overall increase in mobility of Li ions and is in agreement with the conductivity data of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ (Fig. 2), which shows an enhancement of the conductivity values with temperature. The observation of a powder pattern with well-defined singularities corresponding to the satellite transitions $|\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$ at high temperatures $T > 330$ K is rather unusual. Neither the ^7Li linewidth nor the conductivity data (Fig. 2) show any evidence of change at this temperature. The narrow linewidth of the satellites and central component at $T > 330$ K also suggests that all interlamellar Li ions are in almost identical environments at these temperatures. These observations appear to contradict the conductivity data, which show a high value of the dc conductivity at these temperatures. One would, therefore, expect the increased mobility of Li ions at higher temperatures to lead to more efficient averaging of dipolar and quadrupolar interactions. At these temperatures the ^2H NMR indicates that the intercalated polymer, too, is mobile. The conductivity data at high temperatures (250–370 K) (Fig. 2) clearly rule out any explanation based on localization of Li ions within or close to the CdPS_3 layer. Localization of Li ions is also ruled out by the ac electrical response exhibited by $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$, which shows a well-defined conductivity relaxation in the electrical modulus while the corresponding dielectric spectra showed the absence of any loss feature due to the intercalated PEO. This was interpreted as evidence for the coupling of ionic motion with polymer motion. Such a coupling would not be possible if Li ions were localized in the layer. Thus a mechanism of Li ion motion consistent with both conductivity and NMR results needs to be found.

In analyzing the ^7Li NMR spectra for $T > 330$ K (Fig. 5) it may be emphasized that ionic ^7Li has no field gradient associated with its own electrons as the $1s$ orbitals do not participate in bonding and are spherically symmetric. The magnitude of the quadrupolar interactions is therefore a probe of the distribution of charges in the immediate neighborhood of the ion. The ^7Li NMR spectrum would therefore reflect the time average of the interaction of the nuclear quadrupole moment with a charge distribution in the neighborhood of the ion. In $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$, since magnetic interactions of Li ions with the layer may be ruled out, the field gradient at the ^7Li nuclei would be derived primarily from the ether oxygens of the intercalated PEO, which are expected to solvate the Li ion. The observation of quadrupolar satellites for $T > 330$ K is therefore a clear indication of the association or complexation of the Li ion by the intercalated PEO. The spectra at $T > 330$ K, in fact, bear a striking resemblance to that of the ^7Li NMR spectra reported for Li–crown–ether complexes.³² The ^2H NMR results had, however, indicated the presence of mobile segments of the intercalated PEO at these temperatures. The appearance of quadrupolar satellites in the ^7Li NMR at high temperatures in conjunction with the ^2H NMR results, therefore, implies that the complexation of Li ions are by mobile segments of the intercalated PEO. The lifetime of this associated or quasi-bound state would have to be longer than the inverse of the

observed quadrupolar splitting ($\sim 10^{-4}$ s); a shorter lifetime would destroy the structure.

In comparing these results with the conductivity data it may be emphasized that the ^7Li NMR spectroscopy probes the environment and motion of Li ions in the polymer's frame of reference, either through heteronuclear dipolar or quadrupolar interactions. The conductivity measurements in contrast sense Li ion motion from the laboratory frame. The observed powder pattern in the ^7Li NMR, therefore, does not imply that Li ions are static in the laboratory frame, but static on time scales greater than the quadrupolar splitting, in the polymer's frame of reference: i.e., the Li ion stays bound to the mobile polymer for times of the order of 10^{-4} s. The association of Li ions with mobile segments of the intercalated PEO can therefore explain the observation of quadrupolar satellites at high temperatures as well as enhanced Li ion mobility indicated by the conductivity data (Fig. 2) at these temperatures.⁷

The observation of quadrupolar splitting at $T > 330$ K and the fact that it shows a linear increase with temperature is similar to the behavior observed in the ^7Li NMR of Li-crown-ether complexes.³⁶ In 12-crown-4-lithium chloride, too, no quadrupolar splitting is observed at low temperatures, but on raising the temperature quadrupolar satellites corresponding to the $|\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$ transitions are seen with the quadrupole coupling constant reaching a value of ~ 67 kHz at 360 K.³⁶ In fact, a number of Li compounds have been reported to show an increased ^7Li quadrupolar splitting with temperature and this appears to be characteristic feature of light quadrupolar nuclei.³⁷ This temperature dependence has been explained as a consequence of the fact that the quadrupolar coupling constant is determined by the time-averaged electric field gradient (efg) sampled by the ^7Li nuclei. These gradients vary in the region of space around the Li ion; the magnitude of the time average depends on the shape and extent of the region in which the nucleus moves. Thus anisotropic motion and oscillation of the Li nucleus would give rise to an efg whose magnitude would depend on the anisotropy of the root mean square of the amplitude. An increase in the latter quantity with temperature would lead to an increase in the quadrupolar coupling.³⁷ Indeed, an Einstein oscillator model for such a motion predicts a linear increase in the quadrupolar coupling with temperature^{35,37} [a more detailed analysis of the origin and temperature dependence of the quadrupolar coupling in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ is presented in the following paper].³⁸

The linewidth (FWHM) of the central ($1/2 \leftrightarrow -1/2$) transition of the experimental ^7Li spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ has been plotted as a function of temperature in Fig. 6. Two regions may be clearly seen in Fig. 6, indicating a change in the mechanism of line narrowing at ~ 260 K. It may be recalled that the conductivity data (Fig. 2) of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$, too, shows a change in the mechanism of conduction with temperature.⁷ The variation of the ^7Li NMR linewidths in the two regions were analyzed by relating the linewidth $\Delta\omega$ to a correlation time τ_d by the phenomenological relation³⁴

$$\Delta\omega^2 = \Delta\omega_{\text{HT}}^2 + (2/\pi)\Delta\omega_{\text{RL}}^2 \arctan(\alpha\Delta\omega\tau_d), \quad (3)$$

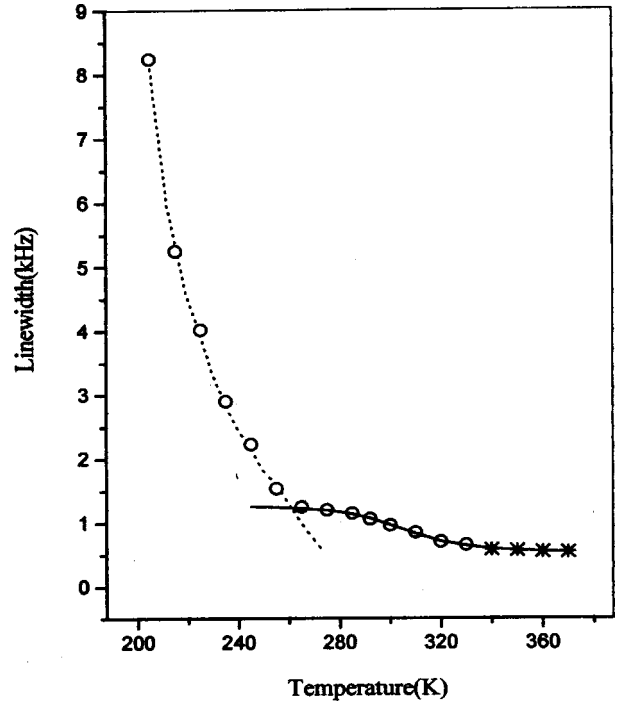


FIG. 6. Linewidth of ^7Li NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ as a function of temperature. At temperatures above 330 K the linewidth is that of the central $|1/2\rangle \leftrightarrow |-1/2\rangle$ component (marked by stars). The Arrhenius fit to the low-temperature data is shown as a dotted line, while the VTF fit as the solid line.

where the numerical factor α is of order unity. $\Delta\omega_{\text{HT}}$ is the high-temperature limiting linewidth and $\Delta\omega_{\text{RL}}$ the rigid lattice linewidth. Equation (3) was fitted to the experimental data of Fig. 6 by floating the values of $\Delta\omega_{\text{HT}}$ and $\Delta\omega_{\text{RL}}$. In the temperature range 200–265 K, where the linewidth drops sharply, the best fit was obtained assuming τ_d had an Arrhenius temperature dependence:

$$\tau_d = \tau_0 e^{E_a/kT}. \quad (4)$$

The dotted line in Fig. 6 shows the fit for data below 265 K: $\tau_0 = 2.3 \times 10^{-6}$ s and $E_a = 3.6$ kcal/mol. For temperatures above 265 K the best fits were obtained assuming a VTF-like temperature dependence of the correlation time τ_d :

$$\tau_d = \tau_0 T^{-1/2} e^{B/(T-T_0)}. \quad (5)$$

In the above expression B is a pseudoactivation energy and T_0 the equilibrium glass transition temperature. The fit, solid line in Fig. 6, is for $\tau_0 = 3.4 \times 10^{-4}$ s, $B = 2.4$ kcal/mol, and $T_0 = 81.1$ K.

It is interesting to note that the value of T_0 in the VTF expression, which in polymeric systems may be interpreted as the temperature at which all segmental motions are frozen, obtained from a fit of the NMR data, 81 K, is close to the value obtained from the conductivity data, 90.7 K.⁷ The value of the kinetic parameters E_a and B as well as the temperature at which the crossover in mechanism occurs is, of course, different for the NMR and dc conductivity since the time scales associated with these measurements are different.

In the intercalated polymer electrolytes where both cation and polymer motions are present the question as to the dynamics of which species is being probed by the ^7Li NMR

linewidth has to be answered with care, since either of these motions could average out Li–polymer interactions leading to a narrowing of the linewidth. At low temperatures it is clearly that of the Li ion since the ^2H NMR indicates the absence of polymer motion at these temperatures. In this temperature regime it is the classical Arrhenius hopping of Li ions which averages out the Li–PEO interactions (since the linewidths in Fig. 6 are of the central transition these interactions would be primarily ^1H – ^7Li dipolar interactions). At temperatures above 265 K both Li ion motion and polymer segmental motion are present. Rigid as well as mobile segments of the intercalated PEO are present at these temperatures. In the intercalated polymer electrolytes $\text{Cd}_{0.75}\text{PS}_3\text{A}_{0.5}(\text{PEO})$ ($A = \text{K}, \text{Cs}$) where conductivity and polymer segmental relaxations are decoupled and the high-temperature dc ionic conductivity remains Arrhenius, it is known that polymer segmental motion is faster than the classical ion hopping rates and has a VTF temperature dependence.^{6,7} In such a situation the alkali ion NMR would reflect the dynamics of the faster species—i.e., the polymer. Such a model for the temperature dependence of the ^7Li NMR in $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ is, however, inappropriate because the narrowing of the ^7Li linewidth for $T > 265$ K is more gradual as compared to that for temperatures below 265 K. This implies that the motions of the two species are correlated. If the motions of the Li ion and mobile segments of the interlamellar PEO were uncorrelated, then a steeper narrowing of the linewidth would be expected at higher temperatures, contrary to what is observed. The observation of Li quadrupolar splitting at high temperature provides further evidence of the association of Li ions with mobile polymer segments. These observations provide direct spectroscopic evidence of the association of Li ions with mobile segments of the intercalated PEO. The Li ion mobility would show a similar temperature dependence as the mobile segments of the intercalated PEO with which it is associated. In the CdPS_3 -based alkali ion intercalated polymer electrolytes it is known from dielectric relaxation studies^{6,7} that polymer segmental relaxation rates follow a VTF temperature dependence and hence the mobilities of the Li ions, too, show a similar temperature dependence.

In the following section we look for further evidence of this association by examining the ^{13}C NMR as well as IR spectra as a function of temperature.

C. ^{13}C NMR

The temperature variation of ^{13}C NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ powder is shown in Fig. 7. At low temperatures the ^{13}C NMR spectra show two features at 3.1 and 6.3 kHz, respectively. With increasing temperature the feature at 6.3 kHz grows in intensity at the expense of the feature at 3.1 kHz. These features may be assigned to ^{13}C nuclei with differing chemical shifts. The feature appearing at 6.3 kHz may be assigned to PEO segments complexing the Li ion while that at 3.1 kHz to uncomplexed PEO. This assignment is based on the fact that complexation of the positive Li ion would lead to a deshielding of the methylene carbons and, hence, a downfield shift with respect to methylene car-

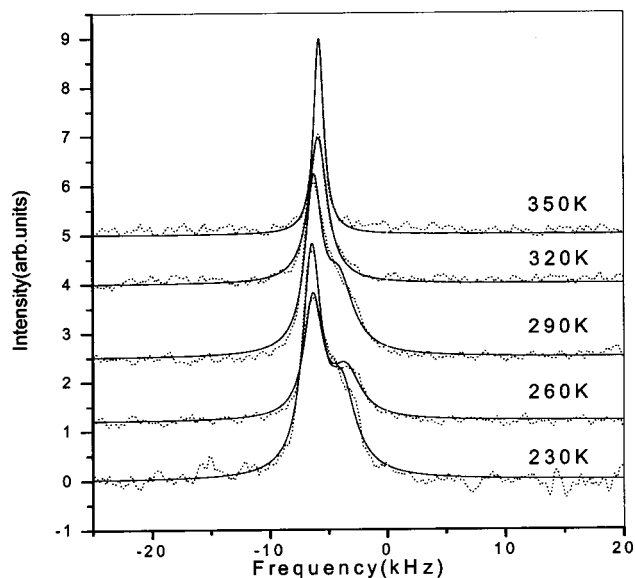


FIG. 7. ^{13}C NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ as a function of temperature along with the fit.

bons of the uncomplexed PEO. The variation in the intensities of the features at 3.1 and 6.3 kHz with temperature would therefore indicate the change in the equilibrium population of the complexed and uncomplexed PEO segments. The spectra have been analyzed accordingly. The spectra at any temperature would be a linear combination of the spectra of the complexed PEO and the uncomplexed PEO with the weighting fractions proportional to the respective populations. This method is similar to that used in the analysis of the ^2H spectra.

The experimental spectrum at all temperatures could be fitted to two Lorentzians (Fig. 7). If the assumption that the complexed fraction, the peak at 6.3 kHz, and uncomplexed fraction, the peak at 3.1 kHz, are in equilibrium is true, then the temperature dependence of the logarithmic ratio of the integrated intensities of the two components should follow the van 't Hoff relation [Eq. (2)]. In Fig. 4 the logarithmic ratio $\ln(I_{\text{complexed}}/I_{\text{uncomplexed}})$, obtained from the fits to the ^{13}C NMR, has been plotted as a function of inverse temperature. The linearity of plot (Fig. 4) clearly justifies the assumption of equilibrium, and the enthalpy as calculated from the linear slope is 3.8 kcal/mol. The temperature variation of the logarithmic ratio of the mobile to rigid fraction, $\ln(I_{\text{mobile}}/I_{\text{rigid}})$, obtained from the ^2H NMR, is also shown in Fig. 4. The interesting feature is that the slopes of the two are nearly identical; the enthalpies calculated from the linear slopes of both the ^{13}C (4 kcal/mol) and ^2H NMR (3.8 kcal/mol) data are close. Figure 4 indicates that the thermal parameters describing the equilibrium between complexed PEO and uncomplexed PEO are same as those between mobile and rigid fractions of PEO and further corroborates the previous conclusion that Li ions are associated and complexed only by the mobile polymer segments.

D. IR spectroscopy

Vibrational spectroscopy is a powerful tool for probing association and complexation of Li ions by polyethers.³⁹ If

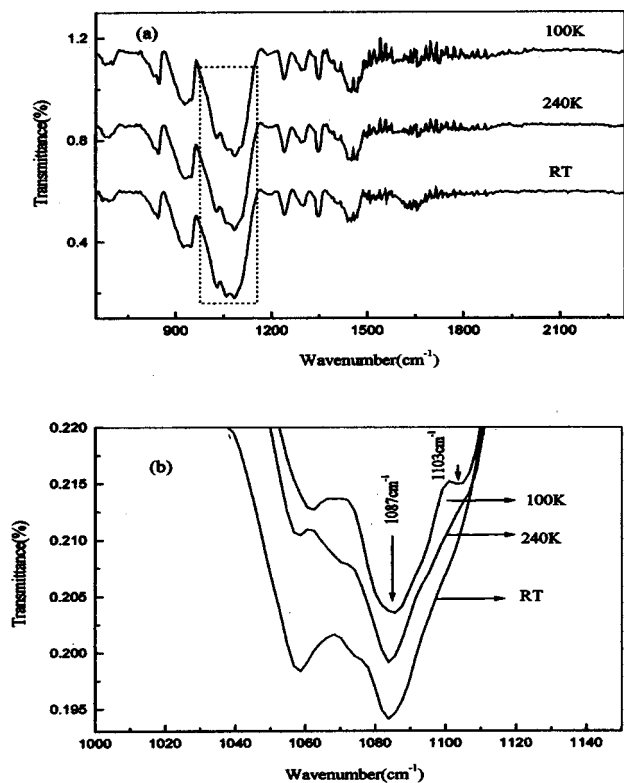


FIG. 8. (a) Mid-IR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ powder as a function of temperature. (b) Magnified view of the 1100 cm^{-1} region [the boxed region in (a)].

Li ions are coordinated to the ether oxygens, then changes in the vibrational modes involving the ether oxygens—the C–O–C stretching and bending modes—may be anticipated. In SPEs such changes have indeed been observed. In pure PEO the C–O–C stretching mode appears as a strong band at 1105 cm^{-1} whereas in the SPEs this band appears at lower wave numbers, the value of which depends on the alkali ion.³⁹ For the PEO–NaSCN SPE this band appears at 1087 cm^{-1} . In a previous study⁵ of the room-temperature infrared spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ ($A = \text{Li, Na, K, Cs}$) the positions of the C–O–C stretching bands for the Na and Li compounds were found to have shifted to lower wave numbers and interpreted as evidence for the association of Li ions with the ether oxygens of the intercalated PEO.

The mid-IR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ at representative temperatures is shown in Fig. 8(a). The 1100-cm^{-1} region where changes are expected is shown in greater detail in Fig. 8(b). At room temperature the IR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ show a strong band at 1087 cm^{-1} : this is assigned to the C–O–C stretching modes of ether linkages coordinated to Li ions. On lowering the temperature a shoulder appears at $\sim 1103\text{ cm}^{-1}$, which is clearly resolved by 100 K. The position of this band is identical to that of pure PEO and suggests dissociation of the Li-ion–PEO complex on lowering the temperature.

It is known from ^2H NMR that at high temperatures the polymer is mobile but at low temperature rigid. The IR spectrum therefore indicates that coordination of the Li ions is only by the ether linkages of mobile PEO segments but once polymer motion is frozen the Li ions are no longer coordi-

nated with the ether oxygens. This result is in agreement with the observation of the previous section where a similar conclusion had been drawn from a comparison of the temperature dependence of the ratios of the *complexed* and *uncomplexed* fraction in the ^{13}C NMR with the ratios of the mobile and rigid fraction in the ^2H NMR.

IV. CONCLUSION

The motions of Li ions and interlamellar PEO in the intercalated polymer electrolyte $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ have been investigated using a combination of multinuclear NMR and IR spectroscopy. The main observations of the present study are summarized below.

(i) ^2H NMR results indicate the presence of both rigid and mobile fractions of the intercalated PEO with the equilibrium concentration of the mobile fraction increasing with temperature.

(ii) ^7Li NMR spectra in the temperature range 230–330 K show a single line whose width decreases with increasing temperature. Above 330 K well-defined singularities corresponding to the satellite transitions $|\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$ are observed.

(iii) The temperature variation of the linewidth of the central transition in the ^7Li NMR shows clear evidence of a change in the mechanism of motional narrowing at 260 K. Below 260 K the correlation time associated with this motion has an Arrhenius temperature dependence, but above 260 K has a VTF temperature dependence. The variation of the ^7Li linewidth with temperature is similar to the temperature dependence observed for the dc conductivity. The VTF T_0 value, which may be interpreted as the temperature below which segmental motion freezes, obtained from fitting the ^7Li linewidth data (81.1 K), is close to the value obtained from the conductivity data (90.7 K).

(iv) The ^7Li NMR spectra exhibit a quadrupolar powder pattern above 330 K with the quadrupole coupling constant increasing linearly with temperature. This behavior is similar to that observed in Li–crown–ether complexes where too quadrupolar splitting is observed only above a certain temperature, increasing with a further rise in temperature. Above 330 K a significant fraction of the intercalated PEO is mobile and therefore the observation of a quadrupolar splitting in ^7Li NMR spectra at these temperatures indicates that the association of Li ions is with ether oxygen of the mobile PEO segments.

(v) The ^{13}C NMR spectra show two features at low temperatures, corresponding to complexed and uncomplexed PEO segments. The intensity of the complexed fraction increases with temperature. The thermal parameters describing the equilibrium between complexed and uncomplexed PEO, obtained from the ^{13}C NMR spectra, is similar to that between mobile and rigid fractions of interlamellar PEO, obtained from ^2H NMR measurements, implying that complexation of Li ions is by mobile segments of the intercalated PEO.

(vi) At room temperature the frequency of the C–O–C stretching mode (1087 cm^{-1}) in the IR spectrum indicates the coordination of Li ions by the ether linkages of the interlamellar PEO. At low temperatures the appearance of a spec-

tral feature (1103 cm^{-1}) identical to that of pure PEO indicates the presence of ether linkages which are no longer coordinated to Li ions.

From these observations it is possible to establish that in the intercalated polymer electrolyte $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$, Li ions are complexed by mobile segments of the intercalated PEO which are present at higher temperatures. The complexation of Li ions by the ether linkages of the intercalated PEO would be enthalpically favorable at all temperatures. At low temperatures, however, when the intercalated PEO segments are frozen, polymer configurations which are favorable for Li ion complexation may not be available. Moreover, at low temperatures, when the polymer is rigid association of Li ions with rigid PEO segments would be entropically unfavorable. The barrier for hopping for the small Li ion is small so that the enthalpy gain by complexation would not compensate for the loss of entropy. In such situations the Li ion exhibits the conventional classical hopping giving rise to the Arrhenius temperature-dependent conductivity observed in the intercalated polymer electrolytes at low temperatures.⁷ In other words, the motion of the Li ion is dissociated from that of the rigid polymer and moves independently.

At higher temperatures, however, when the intercalated polymer too is mobile, polymer configurations which can complex the Li ion would be available. Association of the Li ions with the mobile PEO would be both entropically and enthalpically favorable, especially since the polymer reorientation rates are faster than the classical hopping rates. The present NMR and IR studies provide direct spectroscopic evidence for this association. The quadrupolar splitting of $\sim 10\text{ kHz}$ in the ^7Li NMR of $\text{Cd}_{0.75}\text{PS}_3\text{Li}_{0.5}(\text{PEO})$ indicates that the lifetime of the associated or quasibound state for the Li ion must be greater than 10^{-4} s . The displacement of the Li ion during this period would be described by the VTF temperature dependence since the polymer segments with which it is “bound” show this dependence.⁷

Li ion transport requires that the ion be able to move from one quasibound site to another. This would require breaking of the polyether oxygen–Li linkages with subsequent attachment to a different set of polyether oxygens. The ^7Li NMR, however, does not show any signature of this transitory process, which suggests that the lifetime of these states—i.e., between two quasibound events—must be very small ($\tau \ll 1/\omega_{\text{Larmor}}$, $\omega_{\text{Larmor}} = 116.4\text{ MHz}$). Indeed, molecular dynamics simulations of PEO-based solid polymer electrolytes have observed that dynamical changes in the crown–ether-like coordination shell of the alkali ion occurs in 100–1000 ps regime.⁴⁰ The picture that emerges is that of quasibound motion of the Li ion with an occasional short-lived process involving detachment of the Li ion from one set of ether oxygens and attachment to a different set. A set of breakings and attachment could eventually lead to displacement of the Li ion over macroscopic distances. Significant displacement of the Li ion probably occurs in the long-lived quasibound state of the ion with mobile PEO segments. The mobility of the ion therefore shows a similar temperature dependence (VTF) as the polymer segments with which

it is associated. The present results provide direct spectroscopic evidence of the quasibound state involving association of Li ions with mobile segments of the interlamellar PEO.

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