to the ordered $NbTe_2$. Such a bend is not observed. Therefore, at least for the case of $TaTe_2$ and $NbTe_2$, cation disorder is not a significant structural factor.

It is informative to compare our results with the earlier work of Wilson et al.[2g] on the $13^{1/2}a_0$ distortion present in TaS_2 and $TaSe_2$. In their work they studied the $Ta_xM_{1-x}S_2$ (M = Ti, Nb), $Ta_xM_{1-x}Se_2$ (M = Ti, V), and TaS_ySe_{2-y} systems. Their work shows that for metal doping the distortion is lost for x_c values ranging from 0.95 to 0.90. A much weaker effect is observed for the TaS_ySe_{2-y} systems. They concluded that this was due to a weaker effect for anion as opposed to cation disorder. However, it should be noted that the TaS_ySe_{2-y} system is the only one in which both antipodes (i.e., TaS_2 and $TaSe_2$) are in the $13^{1/2}a_0$ distortion type. In our work, again there are two binary systems that have the $TaTe_2$ distortion ($TaTe_2$ and $NbTe_2$), but for our system the two differ in their cations. It therefore appears that the principal factor governing the stability of the various distortion modes is not cation or anion disorder, not size factors, and not solely d-electron counts (for TaS_2 and $TaTe_2$ are isoelectronic) but instead merely whether the two antipodes belong to the same distortion type.[11]

Finally it should be recalled that the $TaTe_2$ distortion is formed by a commensurate charge density wave.[12] Our work therefore studies the effect of dopants on commensurate charge density wave formation (which is quite different from the effect expected for incommensurate charge density waves[13]). Of special interest are our results for the $Ta_xNb_{1-x}Te_2$ solution. Our results indicate that disorder on the metallic sites need not eliminate the commensurate charge density wave (irrespective of the impurity concentration). This is in contrast to the theoretical results of Baeriswyl,[14] which indicate for one-dimensional commensurate charge density waves that the distortion will be suppressed at high impurity concentration. It is of interest that Baeriswyl's predictions are exactly borne out in the *one*-dimensional commensurate charge density wave (Peierl's distortion) found in $Ta_{1-x}Nb_xO_2$.[15] Perhaps the higher dimensionality of the $TaTe_2$ distortion (two dimensional) plays a role in the differing effects. For other high-dimensional distortions, impurities are also known to cause weaker effects. For example, the three-dimensional distortion found in elemental Se and Te is found for the full range of Se_xTe_{1-x} solutions.[16]

Recent work of Tremel[17] using the extended Hückel method has shown that the forces during the distortion are electronic in nature. Our current work has studied the effect that disorder has on the $TaTe_2$ distortion. We have found that it is the electronic effects brought about by disorder that are of primary importance and not the steric effects brought about by disorder.

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[11] However, when the antipodes are different, our results indicate cation substitution (with change in electron count) have a stronger effect than anion substitution (without change in electron count). For example, $TaTe_ySe_{2-y}$ is known to be in the $TaTe_2$ structure type for all $y > 1$ (this result is presented in: Antonova, E. A.; Kiseleva, K. V.; Medvedev, S. A. *Sov. Phys. JETP* 1971, *32*, 31).

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Physical and Electrical Characterization of Poly[bis((methoxyethoxy)ethoxy)phosphazene]–Metal Polyiodide Complexes

M. M. Lerner, L. J. Lyons, J. S. Tonge, and D. F. Shriver*

Department of Chemistry and Materials Research Center, Northwestern University,
2145 Sheridan Road, Evanston, Illinois 60208-3113

Received June 27, 1989

Complexes of poly[bis((methoxyethoxy)ethoxy)phosphazene] (MEEP = $[NP(OC_2H_4OC_2H_4OCH_3)_2]_p$) with alkali-metal polyiodide salts were prepared by the reaction of solid $MEEP_xMI$ with I_2 vapor. The compositional range $MEEP_xMI_n$ (x = 16–2, n = 1–9, M = Li, Na) was systematically characterized by Raman spectroscopy, differential scanning calorimetry, and electrical measurements. In addition, a number of complexes with higher iodine content (up to 80 wt %), with n = 11–23, as well as salt-free MEEP–I_2 complexes were examined. Triiodide and polyiodide species are observed in all complexes except for n = 1; molecular I_2 is not present in any of the complexes prepared. At lower iodine contents (n = 1–9) conductivity increases with salt concentration until x = 4 and also increases steadily with higher iodine content. At high polyiodide concentrations conductivities are as high as 5×10^{-3} S cm^{-1} at 30 °C. In conventional polymer–salt complex electrolytes, cation and anion diffusion is enabled by polymer segmental motion. Polyiodide complexes, however, appear to be relatively insensitive to polymer dynamics, and the conduction process is thought to involve iodide transfer between polyanions.

Introduction

The study of ion-conducting polymers has been active during the past decade.[1,2] These materials can retain the advantages of polymers (such as processability) and possess useful electrical properties for solid-state devices. Applications for these materials depend upon factors such as

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electrochemical stability and mechanical properties but include use as solvent-free electrolytes or electrode materials in batteries,[3] sensors,[4] and electrochromic displays.[5] In many cases, however, solid-state devices that are practical (and competitive with conventional devices) will require components with high ionic conductivities (10^{-3} S cm^{-1} or greater) at ambient temperature.

Early work in this field has focused upon the salt complexes of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO). PEO is semicrystalline at ambient temperature and forms crystalline phases when complexed with metal salts at moderate temperatures. NMR studies[6,7] demonstrate that ionic conduction occurs in the amorphous regions of these complexes and, taken together with temperature dependence measurements, implicate polymer segmental motion in the conduction mechanism.[8] High ionic conductivity in PEO–salt complexes therefore requires temperatures above the melting point of the polymer and its salt complexes. For this reason, σ_{ionic} for many PEO–$LiClO_4$ complexes is near 10^{-3} S cm^{-1} above 85 °C but falls to less than 10^{-8} S cm^{-1} at ambient temperature.[9,10]

In contrast, noncrystalline atactic PPO forms single-phase, amorphous complexes at relatively low temperatures. The ionic conductivities obtained in low molecular weight PPO-based electrolytes approach 10^{-4} S cm^{-1} at ambient temperature[11] but decrease some 2 orders of magnitude as the mechanical properties of the complexes are improved by cross-linking.[12] Poly[bis((methoxyethoxy)ethoxy)phosphazene], MEEP, has received considerable attention recently due to its low glass transition temperature and amorphous nature. Both salt complexes[13] and single-ion conductors[14] based on MEEP exhibit high ionic conductivities over a broad temperature range. Complexes of MEEP with alkali-metal salts such as $LiClO_4$ can attain ionic conductivities as high as 10^{-4} S cm^{-1} at ambient temperature.[13]

Previous work in this laboratory[15] has demonstrated that the ion-conducting polymer–salt complex $(PEO)_xNaI$ undergoes a dramatic increase in conductivity upon addition of I_2. (Compare PEO_4NaI, $\sigma(25\,°C) = 10^{-6}$–10^{-7} S cm^{-1},[16] and PEO_4NaI_3, $\sigma(25\,°C) = 2 \times 10^{-5}$ S cm^{-1}.) Spectroscopic analyses demonstrated that the added I_2 is incorporated into polyiodide species in these complexes and impedance and dc electrical measurements indicate that both ionic and electronic conduction processes are present in the polyiodide complexes. Studies of the crystalline polyiodide salts NR_4I_n have also shown enhanced electrical conductivity with increasing polyiodide nuclearity.[17,18] The goal of the present research was to prepare and characterize amorphous complexes of MEEP with metal polyiodides and explore the effect of composition on their electrical response.

Experimental Section

Electrical measurements were performed in an air-tight cell with a sample of approximately 1-mm thickness pressed between two disk electrodes each $^1/_2$ in. in diameter. Blocking electrodes of Pt or stainless steel were employed with low iodine content complexes but were subject to chemical corrosion when high iodine content materials were examined. Tantalum metal electrodes were also employed and found to be unreactive toward all complexes. Experiments repeated with different electrode materials revealed no significant changes in bulk electrical response.

Ac impedance measurements were acquired over a frequency range of 0.01 Hz to 5 MHz using a Hewlett-Packard 4192 LF impedance analyzer for high frequencies and the Solartron Instruments (Elmsford, NY) 150 frequency response analyzer for low-frequency measurements, both under computer control. Cyclic voltammetry was performed on a cell of similar dimensions between +20 and −20 mV at 1 mV/s on a Bioanalytical Systems (West Lafayette, IN) 100A electrochemical analyzer. Cells for all electrical measurements were placed in an oven/cooler, and data were acquired at controlled temperatures from −10 to 70 °C.

Resonance Raman spectra were collected between 80 and 250 cm^{-1} on a SPEX 1401 monochromator using a 180° backscattering geometry and an Ar^+ (514 nm) or Kr^+ (647 nm) excitation line. The solid samples were loaded in an inert atmosphere into 5-mm Pyrex tubes and spun to prevent local heating.

Differential scanning calorimetry (DSC) measurements to determine glass transition temperatures were performed as previously described.[19] Samples were loaded under an inert atmosphere into hermetically sealed aluminum pans.

$P_3N_3Cl_6$ (Aldrich chemicals, reagent grade, sublimed prior to use) was thermally polymerized at 250 °C to form linear poly(dichlorophosphazene). MEEP was prepared by the overnight reaction of $(NPCl_2)_p$ with sodium (methoxyethoxy)ethoxide in refluxing THF. The water-soluble polymer was subsequently subject to dialysis (wet cellulose, MW cutoff 3000) to eliminate salts and low molecular weight products, dried, and placed under vacuum ($<10^{-4}$ Torr) for several days.

Complexes with compositions $MEEP_xMI$ (M = Li, Na; x = 16–2) were prepared by the dissolution of stoichiometric quantities of MEEP and the iodide salt in THF. The solvent was removed by evacuation at slightly elevated temperatures, and the product dried under vacuum for several days. A stoichiometric quantity of I_2 (Aldrich, reagent grade, resublimed prior to use) was allowed to diffuse into the polymer–iodide salt complex at 60 °C in a sealed glass cell under an inert atmosphere to form the brownish-black polyiodide complexes, $MEEP_xMI_n$. The reactants were heated for several days, until neither solid nor gaseous I_2 was observed and the complexes were homogeneous in appearance. An alternate synthetic procedure, involving the codissolution of MEEP, metal salt, and I_2 in an organic solvent proved unsatisfactory due to loss of I_2 upon removal of solvent. Polymer–salt complexes $MEEP_xMI_n$ were prepared with n = 1, 3, 5 for M = Li and n = 1–23 for M = Na. In addition to MEEP–metal polyiodide salt complexes, three complexes of MEEP with I_2 alone, $MEEP_yI$, y = 1.3, 0.67, and 0.40, were prepared and characterized. These stoichiometries were selected as they are formed with MEEP:I_2 in the same ratio as $MEEP_xNaI{:}I_2$ in $MEEP_8NaI_7$ and $MEEP_4NaI_7$, and $MEEP_4NaI_{11}$, respectively [$y = x/(n-1)$ for these related sets]. All polymers and complexes were handled under an inert atmosphere following preparation to prevent the inclusion of moisture from the air.

Results and Discussion

MEEP–salt complexes such as $MEEP_xNaSO_3CF_3$, $MEEP_xLiI$, and $MEEP_xNaI$ exhibit high ionic conductivities at ambient temperature. In these complexes, ion

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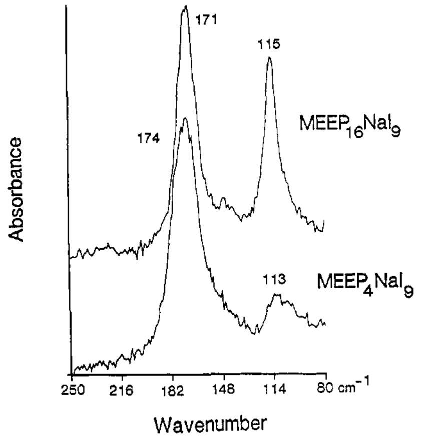

Figure 1. Raman spectra for $MEEP_{16}NaI_9$ and $MEEP_4NaI_9$.

conduction is dependent upon polymer segmental motion.[8] The complexation of polyiodide salts is found to result in an enhancement of conductivity relative to the simple iodide complexes. As will be described below, conductivity in these polyiodide-containing complexes does not show a strong correlation to polymer dynamics as seen in the simple salt complexes. An understanding of the conduction process becomes more difficult in these chemically complicated systems. For this reason, physical characterization and a systematic study of compositional effects are especially important and have been undertaken.

Physical Characterization. Raman spectra for the range of $MEEP_xMI_n$ complexes (Figure 1) contain one or two peaks between 80 and 250 cm^{-1}. These occur at approximately 111–115 and 168–175 cm^{-1}. The 111–115-cm^{-1} peak intensity decreases with an increase in either salt content or iodine content and is quite weak or absent in complexes with $x = 4$ or 2 and higher iodine content ($n > 5$). This low-frequency peak can be assigned to the ν_1 (symmetric stretching) mode of I_3^-.[20] The higher frequency peak at 168–175 cm^{-1} shows the reverse trend and grows in intensity with increasing salt and iodine contents. This peak is typical of those observed in higher polyiodides ($n > 3$ in I_n^-)[21] but is not readily assigned to a particular polyiodide moiety. The increased formation of polyiodides at higher salt concentrations as well as higher iodine content is in agreement with previous results for PEO_xNaI_n complexes[19] and suggests that polyanions can arise from interactions between closely spaced I_3^- units. A sharp peak at 215 cm^{-1} occurs occasionally in spectra of the most iodine-rich complexes ($n > 9$). A comparison of the peak position relative to I_2 in various environments (I_2(s) = 181, 191 cm^{-1}; I_2(g) = 213 cm^{-1};[22] I_2(benzene solution) = 206 cm^{-1};[23] I_2 + diglyme = 204, 168, 110 cm^{-1})[24] as well as the variable intensity of this peak during repeated scans indicates that this corresponds to gaseous I_2 generated during the Raman experiment rather than any species within the polymer complex.

Raman spectra for the three complexes of MEEP with I_2 alone, $MEEP_{1.3}I$, $MEEP_{0.67}I$, and $MEEP_{0.40}I$, are indistinguishable from those obtained for polymer–salt complexes of the higher polyiodides, with a strong polyiodide peak observed at 175 cm^{-1} and a weak triiodide peak at 115 cm^{-1}. No peaks corresponding to the presence of undissociated I_2 are observed. It is clear that I_2 is converted to polyiodide moieties without the addition of an iodide salt to the polymer. As described below, the polyiodide formation appears to occur by redox disproportionation of I_2 in the polar polymer.

Table I. Glass Transition Temperature (kelvin) in $MEEP_xLiI_n$ and $MEEP_xNaI_n$ as a Function of Salt Concentration, $1/x$, and Iodine Content, n[a]

	x				
n	16	8	6	4	2
		$MEEP_xLiI_n$			
1	204	206		209	225
3	198	202		212	235
5	202	206		219	238
		$MEEP_xNaI_n$			
1	204	202		204	247
3	204	202		205	272
7	201	215		234	253
9	203	224		224	250
11				237	249
15			226	245	
19			227	251	
23					243

[a] T_g for the pure polymer MEEP was found to be 193–195 K under similar conditions.

The interaction of I_2 with a many donor molecules, for example pyridine and thiourea,[23] has been examined spectroscopically, and a number of stable complexes such as $py_2I^+I_7^-$ have been isolated and structurally characterized.[25] The reaction of iodine with these bases involves the equilibrium

$$yL + [(n + 1)/2]I_2 = L_yI^+ + I_n^-$$

with $y = 2$ for most isolated complexes. The degree of L–I interaction and the position of this equilibrium depends on the basicity of the donor L and the polarity of the solvent employed. The interaction of iodine with ethers is weaker than with the stronger bases described above[26,27] (we are not aware of the isolation of any complexes involving etheric oxygen with iodine). Resonance Raman studies of iodine in ether and polyethers solutions show that triiodide and polyiodide species are present.[24] The presence of I_n^- upon reaction of MEEP with I_2 alone can similarly involve the dissociation of iodine into an LyI^+ complex (where L = etheric oxygens on MEEP) and I_n^-.

Another origin of polyiodide moieties could be the direct attack on the phosphazene backbone by iodine. Electrochemical measurements on MEEP[28] indicate that the polymer is not significantly oxidized below +2.7 V vs Ag; a net oxidation of the phosphazene backbone would therefore require a more powerful oxidizer than I_2. Additionally, significant degeneration of the polyphosphazene backbone by iodine attack is argued against by both the high glass transition temperatures found in these complexes ($MEEP_{1.3}I$ = 211 K, $MEEP_{0.67}I$ = 215, $MEEP_{0.40}I$ = 226) and the recovery of high molecular weight MEEP after dialysis of the product. The complexation of iodine by nitrogen in the backbone is another possibility, but steric interactions may allow only one N atom close access to iodine.

The polyiodide complexes do not lose I_2 upon standing for several days in an inert atmosphere. Additionally, the effect of brief (30 min) evacuation was examined (see Table

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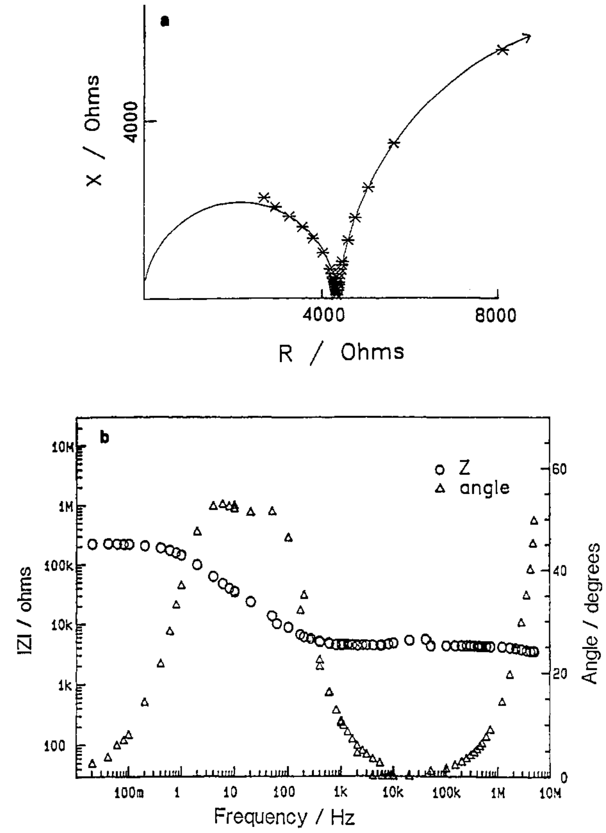

Figure 2. (a) Cole–Cole and (b) Bode plots of ac impedance results for MEEP$_2$NaI$_7$ and two blocking electrodes at 40 °C.

III). Some (the amount was not quantified) I$_2$ is observed in a liquid N$_2$ trap after evacuation, but conductivities remained high.

DSC data show only one event between −90 and 60 °C, a sigmoidal change in heat capacity corresponding to the glass transition of the polymer–salt complex. Glass transition temperatures obtained for MEEP–salt complexes are listed in Table I. For complexes with lower iodine contents and salt contents the glass transition is relatively sharp and T_g is similar to that found in the pure polymer (−78 °C). A higher salt concentration (x = 2), is found to increase T_g by 40 °C or more. This increase in T_g may involve the association of cationic species with the polymer side chains and/or involve ion bridges between polymer segments. The addition of iodine to these complexes results in a gradual increase in T_g along with a considerable broadening and weakening of the transition. Local variations in these trends (for example, T_g = 272 °C in MEEP$_2$NaI$_3$) probably reflect the difficulty in recording these weak transitions and not actual physical effects.

Electrical Response. Ac impedance measurements on all complexes examined show two arcs in the Cole–Cole plot and two plateaus in the Bode plot (Figure 2). The minima in the Cole–Cole plots are typically separated by 2 or more orders of magnitude in both frequency and impedance. The high-frequency arc occurs in a frequency and impedance range similar to that observed in other MEEP–salt complexes[13,29] and is ascribed to a parallel R–C response associated with the ionic conduction through the polymer electrolyte.[30] Bulk conductivity values are derived from the observed intercept of this arc with the real axis.

Table II. Effect of Electrolyte Thickness on Bulk Resistance in MEEP$_x$NaI$_n$ Complexes

		R_1/R_2[b]	
complex	t_1/t_2[a]	high-ν process (30 °C)	low-ν process (50 °C)
MEEP$_8$NaI$_7$	3.5	3.8	0.5
MEEP$_2$NaI$_7$	3.6	2.9	0.09
MEEP$_2$NaI$_9$	3.6	2.7	<0.001

[a] t_1/t_2 refers to the thickness ratio of two cylindrical pellets with equal cross-sectional areas. [b] R_1/R_2 refers to the ratio of bulk resistances measured for each of the two conduction processes.

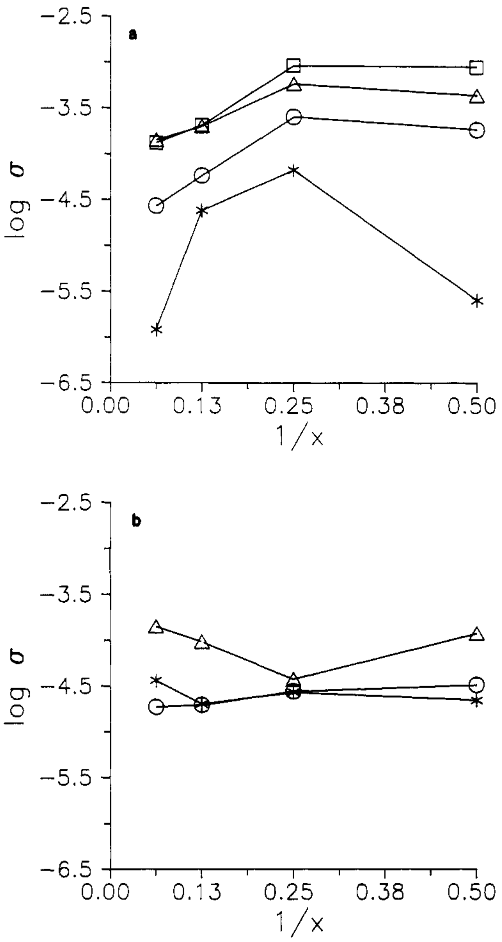

Figure 3. Conductivity in (a) MEEP$_x$NaI$_n$ and (b) MEEP$_x$LiI$_n$ complexes at 30 °C as a function of salt concentration, $1/x$, and iodine content, n.

The conduction process observed at lower frequencies can be measured by dc experiments. Slow cyclic voltammetry (scan potential = −20 to +20 mV, rate = 1–20 mV/s) on the MEEP–polyiodide salt complexes produces a linear (ohmic) response with a resistance matching that derived from impedance measurements. Polarization in these cells was investigated by long-term dc measurement. Current flow was monitored for periods of several minutes to hours upon application of a constant potential (5–20 mV) across the cell; however, a steady-state current was not obtained reproducibly in the polarized cells.

Sample dimensions were varied to differentiate bulk or interfacial conduction processes in the complex impedance data (Table II). The high-frequency process shows proportionality between resistance and sample thickness as expected for a bulk response. By contrast, the low-frequency response is extremely variable and shows no such correspondence, indicating interfacial processes. This

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Table III. Effect of 30-min Evacuation on Conductivity

complex	log σ (30 °C) before evac	log σ (30 °C) after evac
$MEEP_4NaI_7$	−3.2	−3.6
$MEEP_4NaI_9$	−3.0	−3.6
$MEEP_2NaI_7$	−3.3	−3.3
$MEEP_2NaI_9$	−3.0	−3.0

Table IV. Comparison of Conductivities in $MEEP_xNaI_n$ and $MEEP_yI$ Complexes [$y = x/(n - 1)$]

complex	log σ (30 °C)	complex	log σ (30 °C)
$MEEP_8NaI_7$	−3.8	$MEEP_{0.67}I$	−3.5
$MEEP_{1.3}I$	−3.5	$MEEP_4NaI_{11}$	−2.6
$MEEP_4NaI_7$	−3.2	$MEEP_{0.40}I$	−3.0

low-frequency response will not be considered further; instead we concentrate on the bulk process observed at high frequency.

Compositional Effects on Conductivity. Figure 3 shows the variation of ionic conductivity at 30 °C over the range of salt concentrations $x = 16$–2 and iodine content $n = 1$–9 in (a) $MEEP_xNaI_n$ and (b) $MEEP_xLiI_n$. The simple iodide complexes $MEEP_xNaI$ attain a conductivity maximum at $x = 4$ (a cation/ether oxygen ratio of 16, Figure 3a). Several polymer–salt complexes are known to exhibit a conductivity maximum as the salt concentration is increased.[1] The initial conductivity rise has been attributed to the increase in the number of charge carriers as salt is added, and the subsequent decrease in conductivity to the rapid rise in T_g and consequent loss of polymer side chain mobility. Another possible origin of the conductivity decrease is ion aggregation at high salt concentrations.[31,32] In $MEEP_xNaI_n$ complexes with $n = 3$–9, conductivity maxima do not occur over the salt concentration range studied despite much higher T_g's in complexes with $x = 2$. These findings indicate that the conduction mechanism in these polyiodide complexes is less reliant upon polymer segmental motion than is the case for simple polymer–salt complexes. The addition of iodine also results in a steady increase in the conductivity up to 70–80 wt % iodine (Figure 4). Complexes with high iodine content show remarkably high conductivities at 30 °C, for example, $\sigma(MEEP_4NaI_{15}) = 4 \times 10^{-3}$ S cm^{-1}.

$MEEP_xLiI_n$ complexes exhibit less variation in conductivity over the composition range examined than the analogous Na^+-containing complexes (Figure 3b). At the higher salt and iodine concentrations studied, the Na^+ complexes have significantly higher conductivities. These results parallel findings for $PEO_{10}MX$ ($X = CF_3SO_3^-, BF_4^-$) complexes,[33] where conductivities are higher with M = Na than M = Li.

A comparison of conductivity in salt-containing and salt-free complexes is given in Table IV. The conductivities are similar for related sets ($MEEP_yI$, $MEEP_xNaI_n$; $y = x/(n - 1)$), indicating that the presence of sodium cations do not greatly affect the conductivity at these polymer–iodine compositions.

Conduction Mechanism. Free volume and dynamic percolation models relate ionic conduction in many polymer–salt complexes to the high mobility of ions derived from local (or segmental) motion of the polymer chains.[2,8] The temperature difference $T - T_g$ is a measure of the degree of polymer segmental motion. As described previously, a conductivity maximum is often seen with increasing salt content in a polymer–salt complex and is related to the rise in T_g as salt content increases. This maximum does not occur for the polyiodide complexes examined despite an increase in T_g with increasing salt content. Indeed, a comparison of Table I and Figure 3 reveals that the high conductivities are associated with

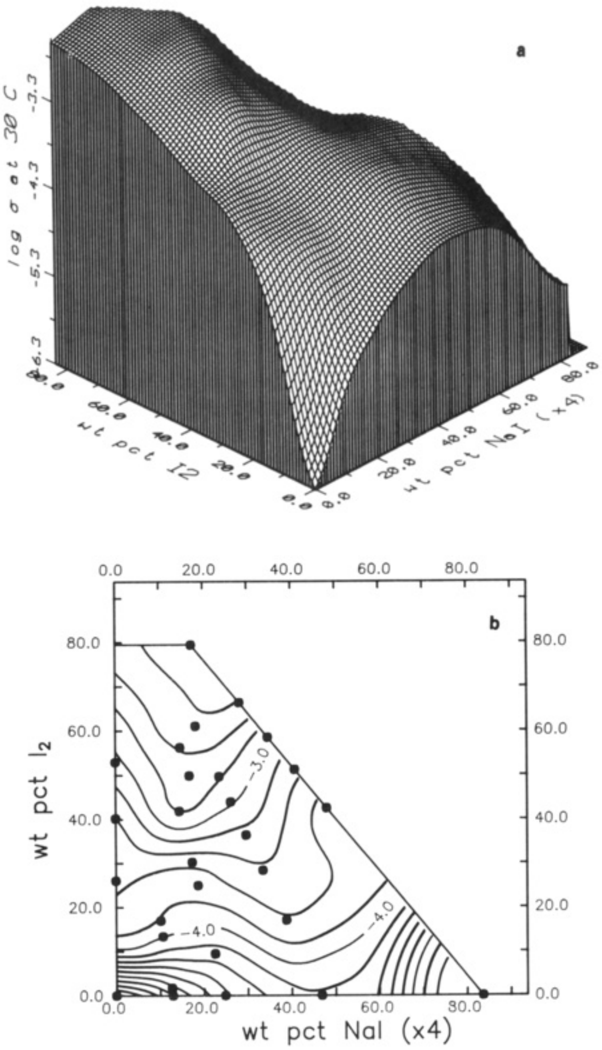

Figure 4. (a) 3-D plot of conductivity in $MEEP_xNaI_n$ complexes at 30 °C as functions of weight percent NaI (x axis) and weight percent iodine (y axis). The surface has been smoothed by both matrix and cubic spline methods to eliminate irregularities and thus indicates general trends more accurately than individual data values. (b) Topographical view of the same data indicating data points and surface boundaries employed in part (a).

Table V. Apparent Activation Energies (electronvolts) for Ionic Conduction in $MEEP_xLiI_n$ and $MEEP_xNaI_n$ Complexes

	x				
n	16	8	6	4	2
			$MEEP_xLiI_n$		
1	0.30	0.30		0.34	0.52
3	0.38	0.39		0.44	0.56
5	0.39	0.41		0.46	0.53
			$MEEP_xNaI_n$		
1	0.22	0.29		0.35	0.46
3	0.40	0.40		0.45	0.67
7	0.31	0.34		0.40	0.60
9	0.31	0.41		0.40	0.52
11				0.43	0.44
15			0.30	0.33	
19			0.48		
23					0.48

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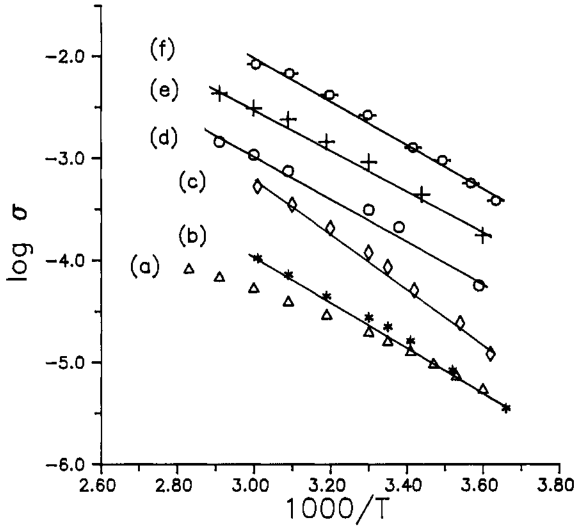


Figure 5. log σ vs 1000/*T* for (a) MEEP$_8$LiI, (b) MEEP$_4$LiI$_3$, (c) MEEP$_2$LiI$_5$, (d) MEEP$_{0.67}$I, (e) MEEP$_4$NaI$_9$, and (f) MEEP$_4$NaI$_{11}$.

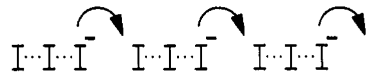
complexes with high glass transition temperatures.

Arrhenius plots for a range of MEEP–polyiodide complexes are shown in Figure 5. Activation energies derived from these plots are listed in Table V. For many complexes the Vogel–Tamman–Fulcher (VTF) equation

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

where T_0 is related to T_g, can be employed to predict the curved-line response observed in an Arrhenius plot of conductivity data.[34] The curvature of the response in these complexes is most evident in the case of the simple iodide complexes MEEP$_x$MI. Higher polyiodides show very shallow curvature and can be as well described as an Arrhenius-type straight-line response.

The nature of the charge carriers in these complexes has not been directly determined; however, alkali-metal cations are not required to produce high conductivities. Whether a cationic species produced by disproportionation of iodine is involved in conduction remains unknown. The high concentrations of iodine (1–10 M) in these complexes, along with the known stability of polyiodides, make these complexes likely candidates for an ion-hopping mechanism involving iodide transfer between polyiodides:



This process might show greater dependence on iodine concentration than on the glass transition temperature of the complex and would be expected to exhibit the Arrhenius behavior observed. Gileadi et al.[35] have examined equivalent conductivity and transference numbers of R$_4$NBr in Br$_2$-containing solutions and implicated an ion-hopping mechanism involving a polybromide species when [Br$_2$] exceeds 1 M. A similar mechanism has also been suggested to account for conduction in iodine.[36,37]

Acknowledgment. This research was supported by DOE Grant DE-FG02-85ER45220, and the facilities were provided by the Northwestern Materials Research Center sponsored by National Science Foundation Grant No. DMR 881571. M.M.L. acknowledges support by an NSF Postdoctoral Fellowship.

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Chemisorbed Phospholipid Monolayers on Gold: Well-Defined and Stable Phospholipid Surfaces for Cell Adhesion Studies[1]

Louis C. Coyle,[2a] Yuri N. Danilov,[2b] R. L. Juliano,*[,2b] and Steven L. Regen*[,2a]

Department of Chemistry and Zettlemoyer Center for Surface Studies, Lehigh University, Bethlehem, Pennsylvania 18015, and the Department of Pharmacology, University of North Carolina School of Medicine, Chapel Hill, North Carolina 27514

Received August 3, 1989

The cell adhesion properties of chemisorbed phospholipid monolayers (CPMs) on gold, prepared from thiol- and disulfide-bearing phosphatidylcholines, have been defined. In the presence of a nonadhesive protein, albumin, adhesion of Chinese hamster ovary (CHO) cells to each CPM surface investigated was minimal; in the presence of fibronectin and vitronectin, substantial adhesion was observed. The ability of CPMs to support adhesion of CHO cells was essentially independent of the molecular structure of the phosphatidylcholine that was employed. Inhibition studies, carried out with GRGDS and with a monoclonal antibody that binds to the fibronectin receptor, provide strong evidence that fibronectin-mediated cell adhesion to CPMs involves a natural ligand–receptor recognition in which the RGD moiety plays a central role. Chemisorbed phospholipid monolayers are proposed as novel surfaces from which to append adhesion-promoting ligands and to investigate, *quantitatively*, their interaction with cell surfaces.

Understanding the structural and functional basis of the adhesive interactions that occur between cell surfaces and the extracellular matrix represents one of the most difficult problems facing chemists and biologists. While extensive investigations have been carried out with fibronectin (Fn) and other cell attachment proteins, the precise interactions that occur between a cell surface and the extracellular matrix remain to be elucidated. The discovery that the Arg-Gly-Asp (RGD) sequence represents a key unit within the fibronectin molecule and other adhesive proteins

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[1] This investigation was supported by the National Science Foundation (Grants CHE-8703780 and CHE-8700833).

[2] (a) Lehigh University. (b) University of North Carolina.

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