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Characterization and Conductivities of Polyphosphazene–Iodine Complexes

Michael M. Lerner, Andrew L. Tipton, and Duward F. Shriver*

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

Alexa A. Dembek and Harry R. Allcock*

Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802

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Complexes of phosphazenes with I_2 have been prepared with molecular and polymeric phosphazene/I_2 ratios ranging from 8 to 0.2. For brevity the phosphazenes are identified as follows: $[NPCl_2]_n$; $[NP(OPr)_2]_n$ ($=[NP(OCH_2CH_2CH_3)_2]_n$); $[NP(OCH_2CF_3)_2]_n$ ($=[NP(OTFE)_2]_n$); $[NP(OC_2H_4OC_2H_4OCH_3)_2]_n$ (=MEEP). Resonance Raman spectra indicate that polyiodides are formed for all but the $[NPCl_2]_n$–iodine system. Impedance measurements demonstrate high bulk conductivities near ambient temperature for the MEEP and $[NP(OPr)_2]_n$-based systems. For all systems, the conductivity increases with increasing iodine loading.

Introduction

The preparation of ionically conducting solids is of broad fundamental interest. These materials have applications in solid-state electrochemical devices.[1,2] Polymer-based complexes possess several advantages over semicrystalline solids, and these advantages include ease of chemical modification and processability. Recent work has shown that high bulk conductivities at ambient temperature can be obtained for etheric polymer complexes that contain polyiodides.[3,4]

Iodine forms charge-transfer complexes with a wide variety of polymers, or it may disproportionate to form polyiodides.[5] Also, conjugated polymers such as polyacetylene become electronically conducting following reaction with many oxidizing agents, including I_2.[6] However, a number of monomers and nonconjugated polymers also form stable, highly conductive complexes with iodine. Examples include poly(vinylpyridine)[7] and poly(alkyl sulfides).[8] The mode of conduction in iodine-doped poly(isoprene) has also been examined by several groups.[9-11]

The poly(organophosphazene) $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (MEEP) was first synthesized and studied in our laboratories as a solid solvent for Li or Ag triflate salts. The solid solutions generated ionic conductivities that were several orders of magnitude higher than those of poly(ethylene oxide).[12-16]

Subsequent investigation of the conductivities of $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_nMI_x$ ($MEEP_nMI_x$; M = Na, Li) complexes has led to the discovery of a number of stable MEEP–iodine complexes, $MEEP_xI$, which are free of alkali-metal salt.[3] At iodine loadings of $NP/I < 4$, the $MEEP_nI$ complexes exhibit conductivities near 10^{-3} S cm^{-1} at ambient temperature. Polyiodides are clearly present in these complexes; the formation of I_x^- from I_2 must therefore be balanced by a compensating oxidation reaction. The nature of this oxidation half-reaction is uncertain, but it seems probable that iodonium cations are formed by I^+ coordination to the oligoether side chains of MEEP.

The primary aim of the present research was to survey the interaction of I_2 with a series of polyphosphazenes and thereby explore the chemical generality of I_2 disproportionation in molecular and polymeric phosphazene systems.

Experimental Section

The polyphosphazene polymers $[NP(OPr)_2]_n$, $[NP(OTFE)_2]_n$, and MEEP were prepared by established methods[17-19] and were purified by successive reprecipitations or dialysis, as appropriate. Residual water was removed by long-term evacuation. Weighed quantities of I_2 (Aldrich chemicals, reagent grade, resublimed prior to use) were allowed to diffuse as the vapor into weighed samples of the solid polyphosphazenes in airtight glass cells at 60 °C. The reactions were allowed to proceed for several days until neither solid nor gaseous I_2 remained and the complexes were homogeneous in appearance.

Resonance Raman spectra were collected at ambient temperature between 80 and 250 cm^{-1} on a SPEX 1401 monochro-

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Table I. Reaction Products Obtained by the Interaction of Polyphosphazenes with Iodine

compound	color	morphology
$[NP(OTFE)_2]_n$	white	soft solid
$[NP(OTFE)_2]_{16}I$	brown	fibrous
$[NP(OTFE)_2]_4I$	brown	fibrous
$[NP(OTFE)_2]_2I$	brown	fibrous
$[NP(OPr)_2]_n$	light brown	elastomeric
$[NP(OPr)_2]_{16}I$	brown-black	tacky liquid
$[NP(OPr)_2]_4I$	brown-black	tacky liquid
$[NP(OPr)_2]_2I$	brown-black	tacky liquid
$[NPCl_2]_n$[a]	white-colorless	elastomeric
$[NPCl_2]_{16}I$	purple	elastomeric
$[NPCl_2]_5I$[b]	purple	elastomeric
MEEP	light brown	tacky viscous liquid
$MEEP_{1.3}I$	brown-black	tacky liquid
$MEEP_{0.7}I$	brown-black	tacky liquid
$MEEP_{0.4}I$	brown-black	tacky liquid

[a] Sometimes has a yellow or brown tinge. [b] Solid I_2 remained even after several days of reaction when a loading of iodine at I: PN::1:5 or higher was attempted. The actual iodine loading is therefore less than indicated by the formula.

mator using a 180° backscattering geometry and a Kr^+ (647 nm) excitation line. The solid samples were loaded under an inert atmosphere into 5-mm Pyrex tubes which were spun during data collection to minimize local heating. Differential scanning calorimetry (DSC) measurements were performed as described previously.[20] Samples were loaded under an inert atmosphere into hermetically sealed aluminum pans. The results were consistent throughout several quenching and heating cycles indicating that loss of iodine from the sample was not a problem. NMR spectra (^{31}P and ^{13}C) were recorded on a JEOL FX spectrometer (FT, 270 MHz) or a Varian spectrometer (FT, 400 MHz). Spectra were recorded in $CDCl_3$ or acetone-d_6 and referenced to the solvent. Chemical shifts (δ/ppm) are referenced to external 85% H_3PO_4 for ^{31}P NMR; upfield chemical shifts are negative.

Ac impedance data were acquired from 10 to 70 °C over the frequency range 10 mHz to 5 MHz using a Hewlett-Packard 4192 LF impedance analyzer for high-frequency and a Solartron Instruments 150 FRA for low-frequency measurements, both under computer control. The sample disks (ca. 1 mm) were pressed between tantalum (blocking) electrodes each $^1/_2$-in. in diameter within an air-tight cell.

Results

The products obtained by the interaction of polyphosphazenes with iodine are described in Table I. In almost all cases, no residual solid or gaseous I_2 remained and the resulting complex was homogenous in appearance. However, as indicated in Table I, high concentrations of iodine in $[NPCl_2]_n$ resulted in systems in which unreacted solid I_2 remained after several days. The products obtained for all stoichiometries prepared with $MEEP_xI$ and $[NP(OPr)_2]_xI$ were brown-black. The mobility of the polymers decreased with increasing iodine content. The $[NP(OTFE)_2]_xI$ complexes were brown and fibrous with morphologies similar to that of the pristine polymer. The addition of iodine to $[NPCl_2]_n$ resulted in the formation of deep purple, rubbery complexes. The $[NPCl_2]_xI$ complexes evolved I_2 rapidly when evacuated. When exposed to an inert atmosphere, they lost coloration slowly until only a faint purple or pink hue remained. All other complexes were stable under an inert atmosphere.

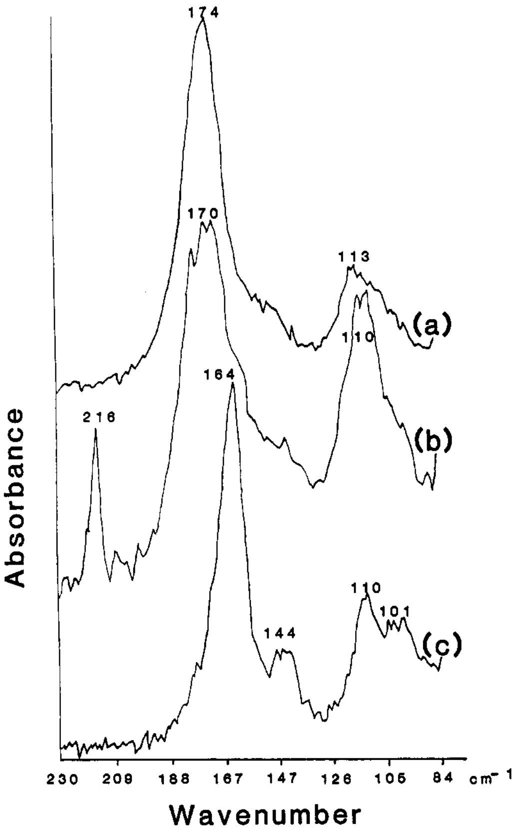

Figure 1. Raman spectra for (a) $MEEP_{1.3}I$, (b) $[NP(OTFE)_2]_2I$, and (c) $[NP(OPr)_2]_{16}I$. Peak positions are indicated.

Table II. Resonance Raman Data for Polyphosphazene–Iodine Complexes

compound	peak position,[a] cm^{-1}	rel intensity
$MEEP_{1.3}I$	113	34
	174	100
$MEEP_{0.7}I$	109	34
	172	100
$MEEP_{0.4}I$	113	41
	178	100
$[NP(OPr)_2]_{16}I$	110	66
	164	100
$[NP(OPr)_2]_4I$[b]	110	41
	168	100
$[NP(OPr)_2]_2I$	100	62
	167	100
$[NP(OTFE)_2]_2I$[b]	112	73
	169	100

[a] There is a shoulder or small peak at ca. 145 cm^{-1} in every spectrum. [b] There is a small peak at 217 cm^{-1} due to I_2 vapor.

Table III. Glass Transition Temperatures and Melting Points for Polyphosphazene–Iodine Complexes

compound	T_g, K	compound	T_m, K
MEEP	193	$NP(OTFE)_2$	311
$MEEP_{1.3}I$	211	$[NP(OTFE)_2]_{16}I$	305
$MEEP_{0.7}I$	215	$[NP(OTFE)_2]_4I$	317
$MEEP_{0.4}I$	226	$[NP(OTFE)_2]_2I$	319
$[NP(OPr)_2]_n$	170		
$[NP(OPr)_2]_{16}I$	169		
$[NP(OPr)_2]_4I$	181		
$[NP(OPr)_2]_2I$	189		
$[PNCl_2]_n$	204		
$[PNCl_2]_2I$	206		

Resonance Raman spectra of $[NP(OPr)_2]_xI$ and $MEEP_xI$ show characteristic features of polyiodide anions (Figure 1, Table II). Peaks in the 109–113-cm^{-1} range are assigned to the symmetric stretching mode of an I_3^- species, while peaks near 170 cm^{-1} are assigned to higher polyiodides. The shoulder or small peak at ca. 145 cm^{-1} in every spectrum is assigned to the asymmetric stretching mode of an I_3^- species. All of these bands were absent in the spectrum of $[NPCl_2]_x$ iodine mixtures because I_2 volatilized from the polymer and recrystallized in the sample tube. Some iodine loss was also observed for the I_2 doped sam-

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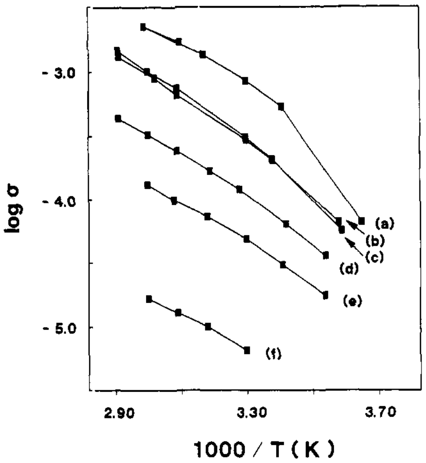

Figure 2. log σ vs 1000/T for (a) MEEP$_{0.4}$I, (b) MEEP$_{0.7}$I, (c) MEEP$_{1.3}$I, (d) $[NP(OPr)_2]_2I$, (e) $[NP(OPr)_2]_4I$, and (f) $[NP(OPr)_2]_{16}I$.

ples of $[NP(OTFE)_2]_4$ and $[NP(OTFE)_2]_2$ samples. For these complexes, however, the polyiodide bands near 110 and 170 cm^{-1} were recorded along with a sharp band at 216 cm^{-1} ascribed to I_2 vapor.[21]

DSC traces (Table III) obtained for both $[NP(OPr)_2]_xI$ and MEEP$_x$I complexes reveal an increase in glass transition temperature (T_g) and a broadening of the transition as the iodine content increased. A strong endotherm was detected for $[NP(OTFE)_2]_n$ at 310 K, which corresponds to the melting of a crystalline phase, and this endotherm shifted to higher temperature with increasing iodine content. All the $[NP(OTFE)_2]_xI$ complexes were, therefore, crystalline at ambient temperature. The DSC results for "$[NPCl_2]_5I$" do not differ significantly from those for $[NPCl_2]_n$.

Ac impedance data obtained for polyphosphazene–iodine complexes typically display two semicircles in a Cole–Cole plot, indicating two processes with widely separated R–C response. Similar results were obtained previously in studies of both MEEP–polyiodide[3] and PPO–polyiodide[4] complexes. The application of both ac and dc methods and observations on samples of different thickness indicated that the high-frequency arc corresponds to a bulk conduction process, while the arc at low frequencies corresponds to an interfacial process. Thus the bulk conductivity of the polyphosphazene–iodine complexes was obtained from the resistance associated with the high-frequency process and the known cell geometric factor. Arrhenius-type plots are presented (Figure 2) as well as bulk conductivities at 30 °C for all the complexes prepared (Figure 3).

^{31}P NMR spectra for $[NPCl_2]_n$, $[NPCl_2]_5I$, $[NP(OPr)_2]_n$, $[NP(OPr)_2]I_2$, $[NP(OTFE)_2]_n$, $[NP(OTFE)_2]_2I$, MEEP, and MEEP$_2$I show no significant chemical shift differences between the parent polymers before and after the addition of iodine, and this indicates no covalent bond formation or cleavage of the polyphosphazenes. Similarly, the ^{13}C spectra for $[NP(OPr)_2]_n$, $[NP(OPr)_2]_nI$, $[NP(OTFE)_2]_n$, $[NP(OTFE)_2]_2I$, MEEP, and MEEP$_2$I show no significant chemical shift differences before and after the addition of iodine.

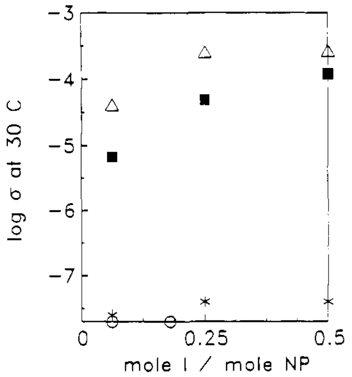

Figure 3. Conductivity in polyphosphazene-iodine complexes as a function of iodine concentration: △, R = $OCH_2CH_2OCH_2CH_2OCH_3$; ■, R = $OCH_2OCH_2CH_3$; ✱, R = OCH_2CF_3; ○, R = Cl.

Discussion

The brown-black color and characteristic Raman bands demonstrate clearly the presence of polyiodide anions, I_n^-, in the MEEP$_x$I, $[NP(OTFE)_2]_xI$, and $[NP(OPr)_2]_xI$ complexes. No Raman bands corresponding to molecular I_2 appeared for MEEP$_x$I and $[NP(OPr)_2]_xI$, and these samples do not readily evolve iodine. This suggests that iodine is not incorporated in the molecular form I_2. $[NP(OTFE)_2]_xI$ complexes did sometimes show I_2 (vapor) bands in the Raman, along with a loss of coloration, which suggest only weak complex formation. The purple color in the $[NPCl_2]_xI$ complexes suggested that molecular I_2 is present in the polymer. Although the instability of the complex precluded direct detection of I_2 by Raman spectroscopy, further indirect evidence for simple I_2 incorporation includes (1) the facile evolution of I_2, (2) the relatively low degree of iodine incorporation, and (3) the unchanged morphology and thermal properties of the polymer following incorporation of the iodine.

Since polyiodide formation involves the reduction of I_2, a compensating oxidative half-reaction must also occur. No oxidation products in the complexes could be detected by NMR methods, and this suggests that in each case the polyphosphazenes remain intact. Apparently, the polymer backbone and side chains are not chemically altered by iodine uptake. DSC traces of the complexes, which show increasing T_g with increasing iodine loading and no new thermal features, also indicate that the polymers do not undergo structural degradation. Oxidation involving the formation of a delocalized positive charge along the polymer backbone (such as is found in conjugated backbone polymers)[6] seems unlikely in the case of polyphosphazenes, which do not possess the extensive electron delocalization characteristic of conjugated carbon chains.[22] The electrochemical stability of MEEP[23] indicates that the polymer should not be oxidized by I_2. This leads us to conclude that the compensating half-reaction is the oxidation of I_2.

The stabilization of iodonium via the complexation equilibrium

$$yL + \tfrac{1}{2}(n + 1)I_2 \rightarrow L_yI^+ + I_n^- \qquad (1)$$

has been suggested[3] previously as a redox disproportionation process that may lead to the formation of polyiodides in MEEP$_x$I complexes. Direct evidence for the existence of an iodonium complex is presently lacking. Poly(propylene oxide) (PPO) will stabilize polyiodide, yet small-molecule ethers such as diethyl ether and diglyme do not bring about redox disproportionation of iodine.[4] Thus, it is unclear whether the oligoether side groups in MEEP can act as stabilizing ligands for the iodonium cation. The

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compounds [NP(OTFE)$_2$] and [NP(OPr)$_2$] contain only a single oxygen atom in each side chain which is sterically restricted and reduced in basicity by bonding to phosphorus.

The conductivities of MEEP$_x$I and [NP(OPr)$_2$]$_x$I were examined well above the T_g and show a temperature dependence that is close to Arrhenius-type exp(1/T) response (Figure 2). The bulk conductivity data do not show a VTF-type correlation[24] with T_g, as both T_g and conductivities increase with increasing iodine content. For these reasons, effects other than local polymer dynamics (for example, carrier number or type) may dominate the conduction process. It is also interesting to note that despite an increase in T_g, the MEEP$_x$I and [NP(OPr)$_2$]$_x$I complexes become markedly less viscous with increased iodine loading; similar observations were made for MEEP$_x$MI$_n$ complexes.[3]

Bulk conductivities as a function of iodine content are given in Figure 3. MEEP$_x$I and [NP(OPr)$_2$]$_x$I show similar behavior, which involves a marked increase in conductivity even at low iodine loadings (x = 16) and a more gradual increase with higher iodine loading. The [NPCl$_2$]$_x$I complexes show no enhancement in conductivity compared with the pristine polymer (approximately 10^{-8} S cm^{-1}). [NP(OTFE)$_2$]$_x$I complexes show only a very slight increase in conductivity over that of the parent polymer. [NPCl$_2$]$_x$I complexes do not contain polyiodides, and [NP(OTFE)$_2$]$_x$I complexes are crystalline at ambient temperature. Therefore, neither exhibits high conductivity. Further illustrations of this behavior can be found in both PPO$_x$MI$_n$ and MEEP$_x$MI$_n$ complexes, in which the amorphous complexes which contain I$_n^-$ are highly conducting.

The mode of conduction within polymer–polyiodide complexes has been addressed previously.[3,4] Impedance measurements for all the polymer–polyiodide complexes studied in these laboratories consistently show that both interfacial and bulk conduction processes are present. In summary, the present research on the interaction of I$_2$ with a diverse set of polymers indicates that the conduction process involves the polyiodides rather than the polymer backbone, and that polyether side chains are conducive to polyiodide formation.

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Sulfonation of (Aryloxy)- and (Arylamino)phosphazenes: Small-Molecule Compounds, Polymers, and Surfaces

Harry R. Allcock* and Richard J. Fitzpatrick

Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802

Lawrence Salvati

Physical Electronics Laboratory, Perkin-Elmer, Inc., Edison, New Jersey 08820

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Sulfonation reactions have been developed that convert aryloxy or arylamino groups linked to phosphazenes to the arylsulfonic acid derivatives. The reactions were developed at three levels—first, with small-molecule phosphazene cyclic trimers; second, with phosphazene high polymers in the solution state; third, at the surfaces of solid polyphosphazenes. The reagents employed included concentrated H$_2$SO$_4$, fuming H$_2$SO$_4$, and ClSO$_3$H. Molecular level products were studied by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy, while the surface-reacted materials were examined by XPS, SEM, ATR-IR, contact angle, and optical microscopy. This chemistry is of broad utility for the preparation of hydrophilic and hydrogel surfaces on polymers and for the development of biocompatible or antibacterial materials.

For the past 50 years polymer chemists have been involved in the design and synthesis of polymers that yield specific bulk properties such as elasticity, strength, or rigidity. However, in recent years it has become evident that the *surface* properties of solid polymers are equally important.[1-4] This is especially true when the polymers are to be used in biomedical devices, surface coatings, or composite materials. Adhesion is another property that depends critically on surface structure.

Occasionally the molecular structure of a polymer will yield an appropriate combination of bulk and surface properties, but more often the control of macromolecular

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