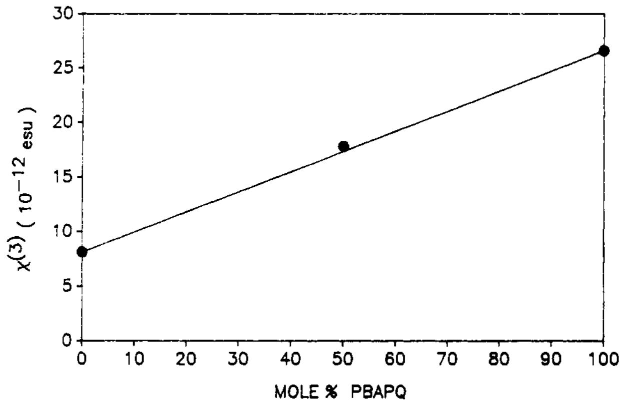

Figure 4. Resonant $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ versus the mole percent of PBAPQ in random copolymer PSPQ/PBAPQ.

values for the three materials at 2.38 µm, as shown in Table I, are all the same (2.2×10^{-12} esu) within experimental errors. Thus, the structural differences between PSPQ, PBAPQ, and the random copolymer have no effect on the off-resonance $\chi^{(3)}$ of these polyquinolines.

The observed resonance peaks at about 1.2 µm in the $\chi^{(3)}$ spectra of the three materials and the lack of any absorption features in the 0.5-2.4-µm region in their optical absorption spectra (Figure 1) show that the peaks are due to a three-photon resonance. The magnitude of the three-photon resonance-enhanced $\chi^{(3)}$ of PSPQ, PBAPQ, and PSPQ/PBAPQ was 8.1×10^{-12}, 2.7×10^{-11}, and 1.8×10^{-11} esu, respectively (Table I). Thus, the off-resonance optical nonlinearities of PSPQ, PBAPQ, and PSPQ/PBAPQ are enhanced at resonance by a factor of 4, 12, and 8, respectively. The systematic decrease in resonant $\chi^{(3)}$ value (PBAPQ > PSPQ(Z)/PBAPQ > PSPQ(Z)) correlates with the decrease in the degree of π-electron delocalization expected from the absorption spectra: PBAPQ (λ_{max} = 399 nm) > PSPQ(Z)/PBAPQ (λ_{max} = 390 nm) > PSPQ(Z) (λ_{max} = 372 nm). Since the E or trans isomer of PSPQ has a higher π-electron delocalization (λ_{max} = 408 nm) than PBAPQ, it is clear that the observed smaller resonant $\chi^{(3)}$ of vinylene-linked polyquinoline (PSPQ) compared to the acetylene-linked polyquinoline (PBAPQ) is due to photoinduced E-Z (trans-cis) isomerization of PSPQ and the associated decrease in π-electron delocalization.

In Figure 4, the resonant $\chi^{(3)}$ is represented as a function of copolymer composition. The $\chi^{(3)}$ of copolymer PSPQ/PBAPQ (50:50) lies on a straight line joining the $\chi^{(3)}$ values of the two constituent homopolymers, suggesting the absence of enhancement in the third-order nonlinearities with the introduction of disorder in the copolymer backbone. In fact, the $\chi^{(3)}$ value of the copolymer is, within experimental errors, equal to the molar average of the $\chi^{(3)}$ values of the homopolymers over the entire spectrum.

In preliminary measurements of the optical loss (α) of thin films of the conjugated rigid-rod polyquinolines, defined as the absorbance per unit thickness, we have found α values of the order 1-10 cm^{-1} in the wavelength range 0.80-2.0 µm.[11] This suggests that low optical loss thin films can be fabricated from the polyquinolines. Also, this gives a figure of merit $|\chi^{(3)}|/\alpha$ estimate for the current thin films to be about 10^{-11}-10^{-13} esu cm.

In summary, we have prepared optical-quality thin films of conjugated rigid-rod polyquinolines, PSPQ and PBAPQ, and their random 50/50 copolymer PSPQ/PBAPQ and investigated their wavelength dependent third-order optical nonlinearities by third harmonic generation. The $\chi^{(3)}$ spectra of the three materials in the 0.9-2.4-µm wavelength range showed a peak near 1.2 µm that was identified as a three-photon resonance. The magnitude of the three-photon enhanced $\chi^{(3)}$ was respectively 8.1×10^{-12}, 2.7×10^{-11}, and 1.8×10^{-11} esu for thin films of PSPQ, PBAPQ, and PSPQ/PBAPQ. Off-resonance at 2.38 µm, it was found that the $\chi^{(3)}$ of the three materials was the same, 2.2×10^{-12} esu. Over the entire spectrum, the $\chi^{(3)}$ value of the copolymer is, within experimental errors, equal to the molar average of the $\chi^{(3)}$ values of the homopolymers, suggesting the absence of enhancement or reduction in the third-order optical nonlinearities with the introduction of disorder in the copolymer backbone. The relative resonant $\chi^{(3)}$ values of the three materials correlate well with their degree of π-electron delocalization. The smaller resonant $\chi^{(3)}$ of vinylene-linked polyquinoline (PSPQ) relative to the acetylene-linked polymer (PBAPQ) appears to be due to photoinduced E-Z isomerization and the associated decrease in π-electron delocalization. The measured magnitude of the $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of the polyquinolines over a wide wavelength range, using THG, makes possible the theoretical modeling of the optical nonlinearity of the materials based on the essential states mechanism.[4b] From such a modeling, we can then predict the real and imaginary parts of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ and $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$. Such modeling studies on the polyquinolines are currently in progress and will be reported in the future.

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Registry No. PBAPQ (SRU), 135614-64-1; PSPQ (SRU), 94751-99-2; PSPQ (copolymer), 106500-72-5; PBAPQ (copolymer), 135663-13-7; PSPQ/PBAPQ (copolymer), 135695-37-3.

Electrochemical Synthesis of Metal Nitride Ceramic Precursors in Liquid Ammonia Electrolyte Solutions

Claudia B. Ross, Travis Wade, and
Richard M. Crooks*

Department of Chemistry and
UNM/NSF Center for Micro-Engineered Ceramics
University of New Mexico
Albuquerque, New Mexico 87131

Douglas M. Smith

UNM/NSF Center for Micro-Engineered Ceramics
University of New Mexico
Albuquerque, New Mexico 87131

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We report a new electrochemical method for synthesizing a range of metal nitride, M_xN_y, ceramic precursors. The experimental conditions (NH_4Br/liquid NH_3 electrolyte solutions and inert atmosphere manipulation of reactants and products) lead to a significant reduction in the levels of C and O contamination compared to previously reported electrosynthetic schemes.[1] Moreover, the

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* To whom correspondence should be addressed.

ceramic materials described here are characterized by high surface area, nanometer-scale primary particle sizes, and a high degree of crystallinity.

The vast majority of commercially produced ceramics are oxides, but nonoxide ceramics such as metal nitrides often have superior properties for many applications. For example, AlN has important advantages compared to the corresponding oxide, including higher mechanical strength, much higher thermal conductivity, and lower thermal expansion,[2,3] and TiN has superior mechanical properties and is a better conductor than TiO_2.[4] Despite these advantages, metal nitride ceramics have not found widespread commercial applications, because they are usually more challenging and costly to synthesize than oxides. As a result, it is desirable to develop new synthetic procedures that yield low-cost, high-purity metal nitride ceramics.

AlN and TiN powders are presently made by direct nitridation of the appropriate metal, carbothermal reduction of alumina, or by the reaction of the metal halides with N_2 or NH_3,[2-5] and thin films are made by polymer pyrolysis or chemical vapor deposition.[2-6] Thin-film syntheses have advanced significantly in recent years,[6] but synthetic routes to powders that have both desirable materials properties and low levels of contamination are still elusive.

Maya[7] and others[8] have studied the electrochemistry of Al in liquid NH_3 electrolyte solutions. The results indicate that anodic dissolution of Al is accompanied by formation of amide-containing Al salts or other complex mixtures of Al salts. Maya[9] has also described synthetic approaches aimed at the preparation of AlN precursors in liquid NH_3 by homogeneous chemistry such as that shown in eq 1.

$$AlBr_3 + 3KNH_2 \rightarrow Al(NH_2)_3 + 3KBr \qquad (1)$$

$Al(NH_2)_3$ was found to lose NH_3 and form oligomers of the form $[Al(NH_2)NH]_n$ at room temperature, and subsequent calcination of this material resulted in 90% conversion of the oligomer to AlN.

Rüssel and Seibold have reported an electrochemical route for the preparation of metal nitride ceramic precursors that involves the oxidation of a metal anode in an electrolyte solution consisting of a primary amine, acetonitrile, and tetrabutylammonium bromide.[1] The mixture that results from extensive electrolysis consists of a solution that can be dried in a vacuum to produce a polymeric foam ceramic precursor. The Al-containing precursor yields crystalline AlN containing 1.8–9.1% O and 1.6–28.3% C depending upon the atmosphere used during calcination.[1b] The Ti-containing precursor yields TiN/TiC mixtures with O and C impurities ranging from 2 to 6% and 5 to 31%, respectively, depending upon conditions.[1d]

We have improved upon previously reported electrochemical schemes for making metal nitride ceramic precursors by significantly reducing the level of C and O in the calcined powders. This improvement results from the use of C-free NH_4Br/NH_3 electrolyte solutions[10] and inert-atmosphere or vacuum-line techniques for manipulation of all reactants and products.

Table I. Summary of the Elemental Composition and Morphological Characteristics of AlN and TiN Prepared in NH_4Br/NH_3 Electrolyte Solutions and Calcined at 1100 °C[a]

	AlN	TiN
elem anal., wt %		
Al or Ti	66.12 (65.9)	73.47 (77.4)
N	33.92 (34.1)	22.55 (22.6)
O	1.4	not available
C	<0.5	<0.5
Br	<0.5	<0.35
H	<0.5	<0.5
total	101.4 (100)	96.02 (100)
mole ratio, Al/N or Ti/N	1.01 (1.00)	0.95 (1.00)
BET surf. area, m^2/g	87	1.2
He density, g/cm^3	2.97 (3.26)	5.08 (5.22)
primary particle size, nm	24	480
mean crystallite size, nm	12	60

[a] Theoretical values, where appropriate, are listed in parentheses.

The electrolysis is performed in a conventional single-compartment, two-electrode electrochemical cell configured with vacuum-tight tungsten electrical feedthroughs and glass joints for attachment to a glass high-vacuum line. Anhydrous grade NH_3 is purified by condensation onto Na metal at reduced pressure. Prior to each experiment, sufficient reagent grade NH_4Br is added to the cell to make the final NH_3 solution 0.1–0.2 M at −70 °C. Anodes and cathodes have areas of about 25 cm^2 and are cut from 0.25–0.50-mm-thick foils of the appropriate metal. The electrodes are configured parallel to each other and are separated by about 1 cm. The cell is evacuated prior to the electrolysis, and then about 75 mL of NH_3 is distilled into the cell.

The constant-current electrolysis takes place at 100–150 A/m^2, and the voltage typically varies between 8 and 25 V. The electrolysis time is usually 6–10 h but can vary over a wider range with satisfactory results. At the conclusion of the electrolysis residual NH_3 is allowed to evaporate through a mercury manometer, and the cell is removed from the vacuum line and transferred to an inert-atmosphere glovebox for removal of the solid mixture of ceramic precursor and electrolyte. A typical electrolysis yields about 1 g of dried precursor after accounting for the initial mass of the electrolyte. The precursor is converted into about 0.5 g of the metal nitride by calcining at 1100 °C under flowing NH_3 (70 mL/min).

Results of elemental and morphological analyses of AlN and TiN powders are shown in Table I. The elemental analysis of the calcined AlN precursor shows that approximately 100% of the total mass recovered consists of Al and N, and for the TiN synthesis 96% of Ti and N are recovered. Moreover, the M/N mole ratios for AlN and TiN are close to unity, indicating that the ceramic powders are stoichiometric. The absence of Br suggests that NH_4Br contamination present in the precursor selectively separates from M_xN_y during calcination, consistent with its low sublimation temperature of 452 °C.[11]

Morphological data, Table I, indicate the calcined ceramics have an open structure and small particle size. BET measurements show that electrochemically syn-

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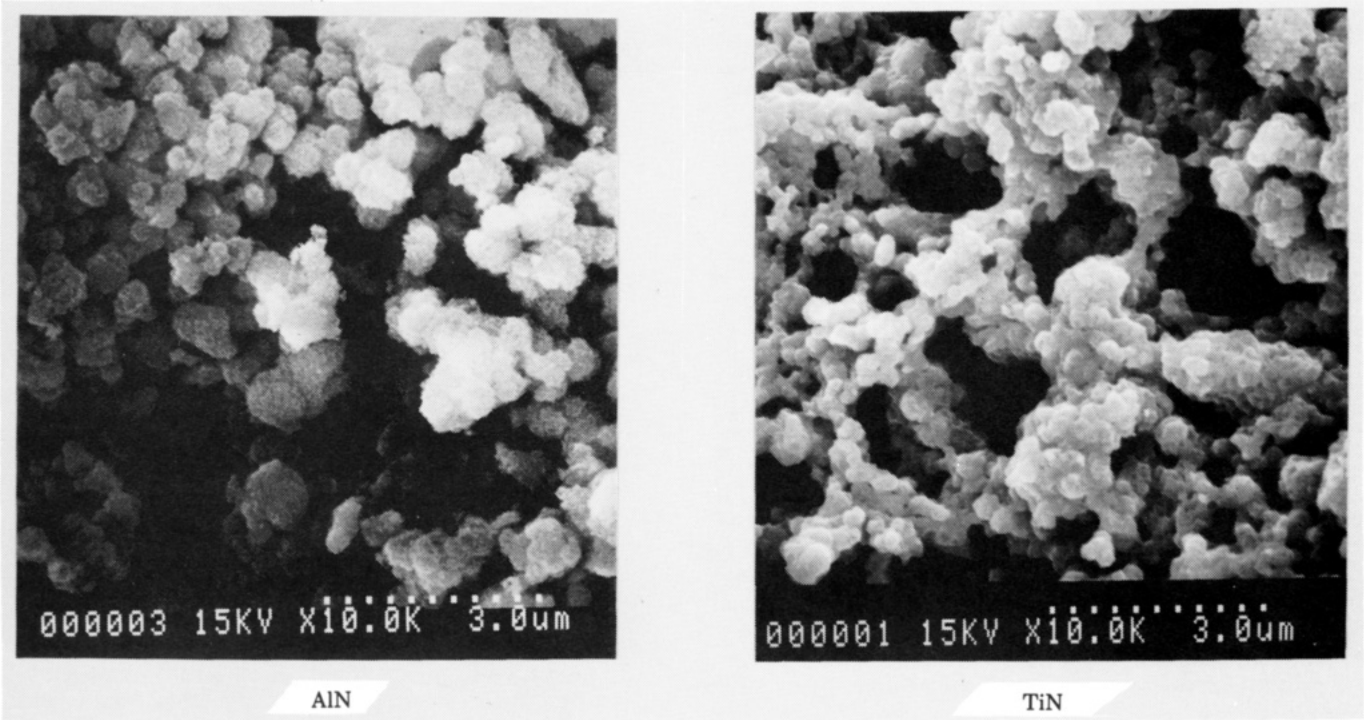

AlN TiN

Figure 1. Electron micrographs of AlN and TiN powders prepared by anodization of the appropriate metal in NH_4Br/NH_3 electrolyte solutions and subsequent calcination of the resulting polymer precursor at 1100 °C under flowing NH_3.

thesized AlN has a high surface area, 87 m^2/g, suggesting that it may have a low sintering temperature and be useful as a catalyst support.[12] True helium density values for the electrochemically synthesized materials (AlN, 2.97; TiN, 5.08 g/cm^3) are comparable to the theoretical densities (AlN, 3.26; TiN, 5.22 g/cm^3).[13] Assuming that the primary particles are smooth spheres, particle sizes of 24 (AlN) and 480 nm (TiN) can be calculated from the surface area and density. Scanning electron micrographs, Figure 1, confirm the open structure of the ceramic powders and indicate that the particles form agglomerates less than 1 μm in diameter.

X-ray diffraction (XRD) analyses were obtained using a Scintag Pad VII X-ray diffractometer (λ 0.154 nm). Figure 2 shows that the only crystalline materials present after calcination are AlN and TiN.[14] TiN prepared by a previously reported electrochemical route was contaminated with a high concentration of crystalline TiC, which is notably absent in the present case.[1d,14] The mean crystallite size, D, can be estimated by the Scherrer equation, eq 2,[15] where B is the XRD peak width at half

$$D = 0.89\lambda/(B\cos\theta) \qquad (2)$$

maximum, θ is the Bragg angle, and λ is the wavelength of radiation. The calculated values for AlN and TiN are 12 and 60 nm, respectively, in good agreement with the surface area and SEM results.

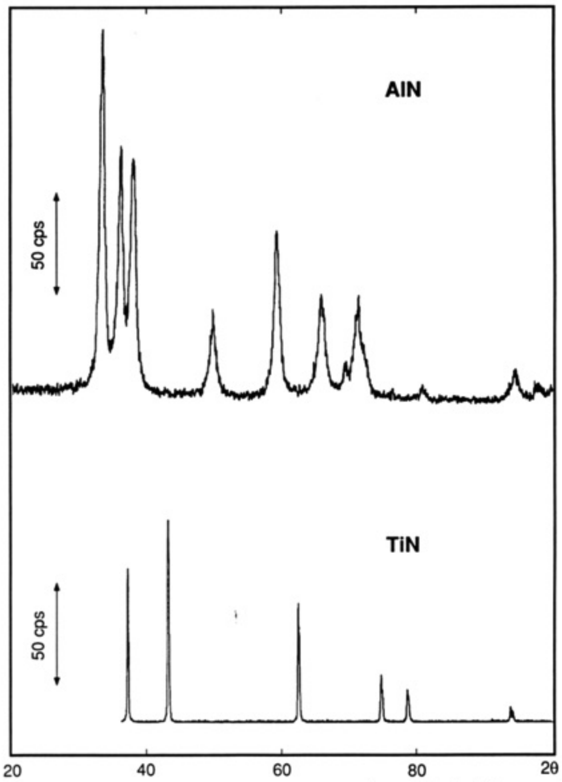

Figure 2. X-ray diffraction patterns of metal nitride powders obtained by calcining electrochemically synthesized precursors of AlN and TiN at 1100 °C under flowing NH_3. Identical patterns are obtained from authentic samples of AlN and TiN obtained from a commercial source.

To summarize, the data presented here clearly show that AlN or TiN precursors result from electrolysis of the appropriate metal in NH_4Br/NH_3 electrolyte solutions. The calcined ceramic powders are characterized by high surface area, purity, and crystallinity. We are not prepared to speculate on the mechanistic electrochemistry responsible for precursor formation or on the structure of the precursor at the present time; however, it seems likely that an intermediate of the form $Al(NH_2)_x$ may play a critical role. Additional work is in progress to elucidate the mechanistic processes responsible for precursor formation and the

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[12] Nitrogen adsorption at 77 K was measured for five relative pressures in the range 0.05–0.30 using an Autosorb-1 adsorption analyzer. Surface areas were calculated by using the BET equation and a molecular cross sectional area of 0.162 nm^2. Before analysis samples were outgassed at approximately 373 K under vacuum for about 3 h.

[13] True helium densities are measured at 25 °C by using a Quantachrome micropycnometer.

[14] *Powder Diffraction File Alphabetical Index, Inorganic Phases*; McClune, W. F., Ed.; JCPDS International Center for Diffraction Data: Swarthmore, PA, 1988. Card numbers: AlN, 25-1133; TiN, 38-1420; TiC, 32-1383.

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experimental conditions that result in high yield and purity. Finally, analyses of ceramic powders formed from the electrolysis of other metals and from mixed-metal systems in NH_3-containing electrolyte solutions are in progress.

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Registry No. AlN, 24304-00-5; TiN, 25583-20-4.

Magnesium Ion Conducting Polymeric Electrolytes

Kaimin Chen and D. F. Shriver*

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

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Most studies of solvent-free polymeric electrolytes have focused on 1:1 type electrolytes (both anion and cation are singly charged),[1] but recently this research has been broadened to dipositive cations.[2-7] Some of the polymer–salt complexes containing dipositive cations show good conductivity at elevated temperatures, but estimated transference numbers of well-defined amorphous samples indicate that these are largely anion conductors.[7,8] The negligible cationic conductivity may be due to the electrostatic trap of the cation by the polymer ether oxygens.[8] Additionally the higher cation charge should greatly increase ion pairing and aggregation in the low dielectric medium.[9] The challenge, therefore, is to obtain dipositive cation conducting polymeric electrolytes with appreciable cation mobility. In the present research, we have synthesized the first magnesium conducting solvent-free polyelectrolyte and studied the influence of complexing agents on the ion transport of the magnesium ion. Previous studies in our laboratory have shown that cryptand and crown ether complexing agents increase the conductivities of sodium poly(phosphazenesulfonates) and amorphous PEO with $NaCH_3SO_3$ salt complexes by reducing ion pairing.[10,11]

Table I. Conductivity and Glass Transition Temperature Data of Magnesium Conducting Polyelectrolytes

polymer[a]	σ,[b] (S/cm)	T_g,[c] K
$[NP(OMEE)_{1.77}(OC_2H_4SO_3Mg_{0.5})_{0.23}]_n$	9.0×10^{-8}	199 (206)[d]
$[NP(OMePEG)_{1.94}(OC_2H_4SO_3Mg_{0.5})_{0.06}]_n$	5.7×10^{-7}	201 (205)
$[NP(OMEE)_{1.77}(OC_2H_4SO_3Mg_{0.5})_{0.23}$-$(2.1.1.)_{0.12}]_n$	5.1×10^{-6}	203 (207)
$[NP(OMEE)_{1.77}(OC_2H_4SO_3Mg_{0.5})_{0.23}$-$(2.1.1.)_{0.23}]_n$	7.4×10^{-6}	201 (209)
$[NP(OMEE)_{1.77}(OC_2H_4SO_3Mg_{0.5})_{0.23}$-$(2.1.1.)_{0.46}]_n$	7.6×10^{-6}	201 (208)
$[NP(OMEE)_{1.77}(OC_2H_4SO_3Mg_{0.5})_{0.23}$-$(12C4)_{0.12}]_n$	5.4×10^{-7}	200 (207)
$[NP(OMePEG)_{1.94}(OC_2H_4SO_3Mg_{0.5})_{0.06}$-$(2.1.1.)_{0.06}]_n$	2.2×10^{-6}	202 (207)

[a] OMEE, $O(C_2H_4O)_2CH_3$; OMePEG, $O(C_2H_4O)_7CH_3$. [b] At 110 °C. [c] At heating of 40 K/min, below which no apparent transitions could be observed. T_g values were taken from the onset points. [d] Number in parentheses is the T_g value taken from the midpoint of the transition curve.

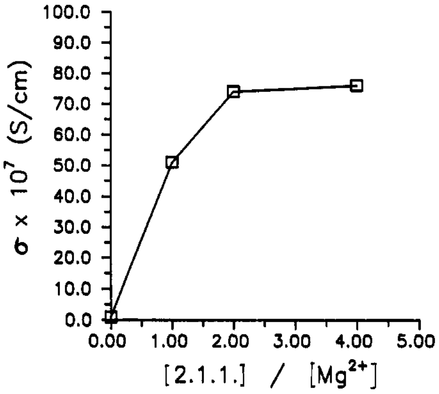

Figure 1. Conductivity variation with the molar ratio of C-2.1.1 to Mg^{2+} ion at 110 °C. $[NP(OMEE)_{1.77}(OC_2H_4SO_3Mg_{0.5})_{0.23}$-$(2.1.1)_x]_n$; X = 0, 0.12, 0.23, 0.46.

Magnesium poly(phosphazenesulfonates) were prepared by ion exchange of sodium poly(phosphazenesulfonates) with magnesium chloride in deionized water and were purified by dialysis against deionized water. The sodium poly(phosphazenesulfonates) were synthesized and characterized as previously described.[12] Complete replacement of the sodium ion (Na^+) by magnesium ion (Mg^{2+}) was confirmed by a magnesium analysis and the lack of detectable amounts of sodium (≤1 ppm).[13] Also, no chlorine was detected (≤25 ppm),[13] indicating the absence of magnesium chloride. The polymers $[NP(OR)_{2-x}(OC_2H_4SO_3Mg_{0.5})_x]_n$ [R = $O(C_2H_4O)_2CH_3$, X = 0.23 (1); R = $O(C_2H_4O)_7CH_3$, X = 0.06 (2)] were obtained. X-ray powder diffraction and differential scanning calorimetry (DSC) measurements indicate that these magnesium conductors are amorphous at room temperature. The ligand-containing polymers were prepared by

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