Tetrazolation of Side Chains and Anhydrous Conductivity in a Hydrophobic Polymer

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ABSTRACT: 1*H*-Tetrazoles possess the lowest pK_a within the azole family of nitrogen-containing heterocycles, making them attractive amphoteric moieties for anhydrous proton conduction. The synthesis of a styrenic, random coil polymer with pendent C-substituted 1*H*-tetrazoles is described in detail. This facile route results in a polymer containing free proton-bearing tetrazoles, limits side reactions, and proceeds using low polarity, halogenated solvents (e.g., 1,2-dichlorobenzene or chlorobenzene), which improve solubility during tetrazole cyclization. The resulting polymer, when probed by NMR spectroscopy and elemental analysis, had no measurable salt content, ensuring accurate proton conductivity measurements. Utilizing interdigitated electrodes (IDEs) in conjunction with electrochemical impedance spectroscopy (EIS), undoped anhydrous proton conductivities were measured to be as high as 10^{-5} S cm⁻¹ at 120 °C. This weakly acidic, 1*H*-tetrazole-bearing polymer is thermally stable to 210 °C, possesses two distinct glass transitions (T_g) at 49 and 74 °C, and exhibits



surprisingly low water uptake, despite its acidic and amphoteric nature. Reduction of T_{g} s, achieved by synthesis of low molecular weight poly(4-vinylphenol) via acid polymerization, shows a minimal dependence of anhydrous proton conductivity on backbone motion.

INTRODUCTION

Amphoteric molecules, acting simultaneously as an acid (proton donor) and base (proton acceptor), similar to water, have been shown to aid in the anhydrous transport of protons.^{1,2} Many recent examples of anhydrous proton conductors rely upon moieties from the azole family of nitrogen-containing heterocycles for charge transport.³⁻⁵ The most acidic member of the azole family, having a pK_a of 4.9, similar to that of acetic acid, is 1H-tetrazole, an aromatic fivemembered ring containing four nitrogens and one carbon atom. For the purposes of proton conduction, it is the least studied azole to date due to the arduous synthesis typically involved. However, 1H-tetrazoles are particularly attractive for proton conducting applications due to their high potential degree of coordination and acidity.^{6,7} A variety of synthetic strategies have been developed to access functionalized azoles with intact N–H protons, which enable structural proton transport.^{8–16} In the absence of a free proton, these materials require additional proton sources (e.g., -SO₃H, H₃PO₄) to generate mobile protons.

While click chemistry of nitriles and azides is an attractive route to tetrazole formation, many methodologies produce Nsubstituted species, resulting in loss of the single azole proton. Additionally, these reactions typically require transition metal catalysts, organic azides, and purification by column chromatography. Removal of spent catalyst using this type of purification method is often impractical postpolymerization due to poor polymer solubility in common solvents, necessitating the development of an alternative synthetic scheme for polymeric materials. Polymer tetrazolation which foregoes transition metal catalysts has, in the past, relied upon strongly dipolar solvents (e.g., DMF or water) and the *in situ* generation of hydrazoic acid, giving rise to safety concerns.^{9,7,11,14,17,18} Herein, an alternative synthesis, purification, and characterization of a styrenic random-coil polymer containing 1*H*-tetrazole side chains **1** (Figure 1) will be discussed along with its proton conductivity within an anhydrous environment.

1H-Tetrazole-bearing polymers are known.^{10,18,15,7,19,14} However, few have been studied in their capacity as materials capable of anhydrous proton transport.^{20–26} The majority of these materials are derived from poly(acrylonitrile), where the tetrazole is directly bound to the backbone and is highly

Received: May 22, 2014



Figure 1. A polystyrenic random-coil polymer with pendent C-substituted 1*H*-tetrazole side chains 1.

dependent on backbone flexibility for increased conductivity or where the reaction of 5-amino-1H-tetrazole, having modified acid-base properties, is reacted with suitable electrophilic precursor polymers. The nature and length of the side chain connecting 1H-tetrazole to the polymer backbone (e.g., shortest in PAN-derived materials) are likely to have a great impact on material properties through both its electronic effects and effects on the local environment of the tethered tetrazole. Because of the complexities involved in synthesis and increasing the spatial distance between the polymer backbone and tetrazole moiety, the postpolymerization synthesis of polymers bearing pendent C-alkyl-1H-tetrazoles has, thus far, not been reported. Inspiration for our synthetic method can be attributed to the work by Aureggi and Sedelmeier and their attention to the safe and thorough quenching of unreacted azide, which is overlooked in most synthetic works.¹⁶ Although their strategy involved small molecules, the reaction of dialkylaluminum azide with nitriles in nonpolar, aprotic organic solvents to achieve the desired 1,3-dipolar cycloaddition has opened the door for further investigation and utilization of this species in the postpolymerization formation of covalently linked 1H-tetrazole side chains.

EXPERIMENTAL SECTION

Reagents. All reagents were purchased from the Aldrich Chemical Co. and used without further purification unless otherwise noted. Azide handling: precautions should always be taken when handling azides to forbid exposure to metals, mitigate possible shock sensitivities, and to avoid the hydrolysis product, hydrozoic acid. Caution should be exercised when using halogenated solvents with azides. Care was exercised to form the non-nucleophilic dialkylaluminum azide prior to introduction of chlorobenzene or 1,2-dichlorobenzene.

Characterization. All solution ¹H, ¹³C, ²³Na, and ²⁷Al NMR spectra were obtained using a Bruker AC-300 spectrometer using DMSO- d_{6} , CDCl₃, or acetone- d_{6} as solvent. All differential scanning calorimetric (DSC) analyses were performed on a TA Instruments DSC Q100 modulated thermal analyzer at a heating rate of 10 °C min⁻¹ and a helium purge of 25 cm³ min⁻¹. Thermal gravimetric analysis (TGA) was performed on a TA Instruments SDT2960 TGA-DTA at a heating rate of 10 °C min⁻¹ and air or nitrogen purge of 100 cm3 min-1. Magic angle spinning solid-state 1H NMR spectra were obtained on an Agilent spectrometer operating at 500 MHz, with sample spinning at 22 kHz. Second moments of proton resonances were calculated by fitting the NMR data to 12 Lorentzian peaks and summing the Lorentzians associated with each band. The reported temperatures of the solid-state NMR data were adjusted upward by 12 °C from the recorded temperature to account for frictional heating of the sample due to spinning. All elemental analysis were conducted by Galbraith Laboratories, Knoxville, TN. A Waters gel permeation chromatography (GPC) system was used to obtain molecular weights of the poly(4-vinylphenol)s only, due to limited solubility of the tetrazolated polymers. The GPC system consisted of Waters Breeze software, a Waters 1515 isocratic HPLC pump, Styragel columns, and a Waters 2414 refractive index detector. Tetrahydrofuran was used as eluent at 35 °C, and the system was calibrated to polystyrene standards.

Synthesis of In-House Poly(4-vinylphenol) 7. To a 500 mL Schlenk flask under nitrogen and fitted with a stir bar was added 4acetoxystyrene 5 (15.90 g, 98.03 mmol) and tetrahydrofuran (0.98 M). After deoxygenation via the freeze-pump-thaw method (3 times), the flask was backfilled with nitrogen, and a 5 M solution of aqueous sodium hydroxide (100 mL, sparged with nitrogen) was syringed into the reaction mixture. The reaction was stirred at room temperature for 1 h or until the reaction was complete as indicated by TLC (SiO₂: R_f = 0.7, 30% ethyl acetate/hexanes). The crude reaction mixture was chilled to 0 °C, at which time 4 N HCl (90 mL) was added slowly until a pH of neutral was reached. The product was extracted into ethyl acetate, washed with distilled water three times, dried over MgSO₄, filtered, and concentrated by rotary evaporation. The resultant oily product was precipitated into cold hexanes, decanted, and dried under vacuum to yield 4-vinylphenol 6 (9.99 g, 85%) as a white powder which was immediately polymerized as described in the literature.²⁷ A Schlenk flask under nitrogen fitted with a stir bar was charged with 4-vinylphenol 6 (5.02 g, 41.8 mmol) and ethanol (4.2 M) while a second Schlenk flask, also under nitrogen, was charged with ethanol (15 mL) and 12 N HCl (17.5 mL). Both flasks were deoxygenated via the freeze-pump-thaw method (3 times) and backfilled with nitrogen, after which the HCl solution was syringed into the reaction mixture containing the 4-vinylphenol 6 and stirred at room temperature for 72 h. Although this reaction was not optimized, it was confirmed by TLC (SiO₂: $R_f = 0.7$ for 4-vinylphenol, 30% ethyl acetate/hexanes) that consumption of the monomer was complete. The resultant polymer was precipitated into distilled water, filtered, and rinsed with distilled water until a pH of neural was reached. The crude materials were then redissolved in acetone, dried over MgSO4, filtered, and concentrated by rotary evaporation. Further drying under vacuum yielded poly(4-vinylphenol) 7 (3.80 g, 78%) as a light tan powder which was used without further purification.

4-Vinylphenol **6**. ¹H NMR (300 MHz, DMSO- d_6): δ 9.53 (s, 1H), 7.28 (d, 2H, ³J = 8.7 Hz), 6.75 (d, 2H, ³J = 8.4 Hz), 6.61 (q, 1H, ³J = 17.7 Hz), 5.57 (d, 1H, ³J = 17.7 Hz), 5.03 (d, 1H, ³J = 11.1 Hz). ¹³C NMR (75 MHz, DMSO- d_6): δ 157.40, 136.45, 128.31, 127.46, 115.38, 110.66.

Poly(4-vinylphenol) **7**. ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.02 (br, 1H), 6.52 (br, 4H), 2.3–0.9 (m, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 155.37, 135.86, 128.59, 115.14, 43.25, 40.77. Commercial poly(4-vinylphenol) (Aldrich Chemical, *M*_w ~ 11 000 Da) displayed a monomodal molecular weight distribution and exhibited *M*_w of 9500 Da and *M*_w/*M*_n = 1.37; the HCl-polymerized poly(4-vinylphenol) was found to have a *M*_w of 4000 Da and *M*_w/*M*_n = 1.33, also in a monomodal distribution.

Synthesis of Polystyrenic Alkoxynitrile 8. To a 500 mL Schlenk flask under nitrogen fitted with a stir bar was added either inhouse or commercially sourced poly(4-vinylphenol) 7 (9.96 g, 82.9 mmol), 6-bromohexanenitrile (21.25 g, 91.9 mmol), and anhydrous DMF (0.4 M). This mixture was deoxygenated via the freeze-pumpthaw method (3 times), backfilled with nitrogen, and heated to 65 °C. Potassium carbonate (58.98 g, 355 mmol) was added to the reaction vessel and allowed to stir for 16 h. After cooling to room temperature, the reaction mixture was neutralized with the addition of 12 N HCl and distilled water. The crude product was extracted into ethyl acetate and washed with 1 N HCl, brine, and excess distilled water until reaching a pH of neutral. The organic layer was dried over MgSO₄, filtered, and concentrated by rotary evaporation. To remove any remaining 6-bromohexanenitrile, the product was stirred over hexanes and decanted. To remove color, carbon black was added to a roundbottom flask containing the product dissolved in ethyl acetate, which was then filtered via gravity filtration. The product was again concentrated by rotary evaporation and further dried under vacuum to yield polymer 8 (15.85 g, 89%) as an off-white solid and used without further purification. ¹H NMR (300 MHz, $CDCl_3$): δ 6.65 (br, 4H), 3.87 (br, 2H), 2.35 (br, 2H), 1.69 (br, 7H), 1.25 (br, 2H) and (300 MHz, DMSO-d₆) δ 6.65 (br, 4H), 3.86 (br, 2H), 2.47 (br, 2H), 1.56 (br, 7H), 1.39 (br, 2H). ¹³C NMR (75 MHz, acetone- d_6): δ 157.71, 138.00, 129.08, 120.49, 114.62, 67.88, 41.29, 41.28, 29.15,

25.88, 25.79, 17.00. Elem. Anal. Calcd: C, 78.10; H, 7.96; N, 6.51; O, 7.43. Found: C, 77.54; H, 8.03; N, 6.16; O, 7.59.

Synthesis of Polystyrenic Alkoxy-1H-Tetrazole 1. Using glovebox techniques, a 1000 mL Schlenk flask fitted with a stir bar was charged with diethylaluminum chloride (25 wt % in toluene, 34.0 mL. 62.5 mmol). The sealed Schlenk flask was taken out of the glovebox, attached to a Schlenk line under nitrogen, and chilled to 0 °C. Sodium azide (4.06 g, 62.43 mmol) was then added to the reaction flask, warmed to room temperature, and stirred for 16 h, which produced a cloudy-white mixture, as previously described.¹⁶ A separate 500 mL Schlenk flask under nitrogen also fitted with a stir bar was charged with polymer 8 at a ratio of 1:3 (ratio of polymer 8 to Et₂AlN₃) (4.46 g, 20.72 mmol) and anhydrous toluene and/or chlorobenzene or 1,2-dichlorobenzene (0.14 M) added (previously deoxygenated) and then backfilled with nitrogen. The diethylaluminum azide mixture was heated to 80 °C, and the solution containing polymer 8 was warmed to 80 °C and then slowly added to the azide mixture via cannula. The reaction flask was sealed and stirred at 80 °C for 18 h. The reaction flask containing the crude reaction mixture was chilled to 0 °C and opened to a Schlenk line under nitrogen while a NaOH/NaNO₂ solution (3.7 M each) was added until a pH of 11 was reached. To this mixture was then added 6 M HCl until a pH of 3 was reached. The product was obtained by filtering via gravity filtration and washed with excess water until a pH of neutral was reached. The crude product was dissolved in a minimal amount of DMSO, precipitated into 1 N HCl, filtered, and dried under vacuum, and polymer 1, isolated as a light tan powder (4.75 g, 89%), was stored in a desiccator. ¹H NMR (300 MHz, DMSO- d_6): δ 16.20 (bs, tetrazole-H, 1H), 6.57 (br, 4H), 3.81 (br, 2H), 2.85 (br, 2H), 1.69 (br, 7H), 1.39 (br, 2H). ¹³C NMR (75 MHz, DMSO- d_6): δ 156.92, 155.86, 137.51, 128.57, 114.26, 67.48, 40.90, 40.85, 28.85, 27.25, 25.50, 23.09. Elem. Anal. Calcd: C, 65.09; H, 7.02; N, 21.69; O, 6.19. Found: C, 64.80; H, 6.99; N, 21.31; O, 6.69.

Measuring Proton Conductivity. Proton conductivity was measured by electrical impedance spectroscopy (EIS) utilizing a Gamry Reference 600 potentiostat with a 100 mV applied RMS (sinusoidal) voltage from 1 MHz to 1 Hz. Temperature control, from 120 to 30 °C, was provided by an ESPEC SH-240 humidity and temperature chamber under a flow of dry nitrogen (0% RH) and verified through the addition of an Omega humidity and temperature data logger OM-CP-RHTEMP101A. The cell consisted of interdigitated electrodes (IDE, Figure 2) which were fabricated in-house,



Figure 2. Schematic for gold-on-chromium interdigitated electrodes, fabricated on 3 in. \times 1 in. glass microscope slides.

composed of a 100 nm Au layer and a 10 nm Cr adhesion layer between the gold and borosilicate glass substrate. The IDE consisted of 50 teeth of 10 μ m in spacing and width and 3 mm in length. A comprehensive review of both the physics of IDEs and the theoretical and experimental calculations of cell constants can be found in the literature.^{28,29} For the IDE cells used to measure the conductivity of polymer **1**, cell constants of $\kappa = 0.115 \pm 0.003$ cm⁻¹ were calculated by

calibration to 0.05, 0.1, 0.5, and 1.0 mM KCl solutions using a typical commercial conductivity probe as a reference. The measured cell constant was close to the value predicted by IDE geometry, 0.106 cm⁻¹, and was valid for film thicknesses greater than 40 μ m. Thick films (~100 μ m, measured by stylus profilometry) of polystyrenic alkoxy-1*H*-tetrazole **1** were drop-cast onto the IDE array from a concentrated DMSO solution and annealed under vacuum at 70 °C prior to measurement. Film resistance was calculated by fitting impedance data to an empirical circuit model.

RESULTS AND DISCUSSION

Traditionally, the conversion of nitrile to 1*H*-tetrazole has been accomplished by reaction either with hydrazoic acid or an equivalent species, such as NH₄N₃, in dimethylformamide (DMF) or sodium azide in water, the latter catalyzed by zinc salts.^{9,7,11,14,17,18} These reagents are less reactive toward alkyl nitriles than aryl and vinyl derivatives, limiting their general utility. Additionally, water is an unsuitable solvent for hydrophobic materials, including the nitrile precursor to polystyrenic alkoxy-1H-tetrazole 1. The direct generation of hydrazoic acid is also a safety concern, given its toxicity and shock sensitivity. Dialkylaluminum azide, however, is a suitable alternative reagent for the conversion of unactivated nitriles to 1H-tetrazoles due to its reactivity toward a wide variety of nitriles and its solubility in nonpolar solvents.¹⁶ These solvents and the dialkyl functionality provide intimate mixing of polymer and azide during cyclization and facilitate azide quenching on completion of the reaction.

Initial attempts at functionalization of a polymer substrate by 1*H*-tetrazole-containing moieties proved unfruitful. Per Scheme 1, compound **3** was chosen as a simple, representative structure

Scheme 1. Synthesis of the Bicyclic Structure 1,5-Pentamethylene Tetrazole 4



to determine the side reaction that inhibits the desired process. Upon attempting the Williamson ether reaction of phenol with bromohexane-1H-tetrazole 2, the unexpected bicyclic structure 1,5-pentamethylene tetrazole 4, also known as the drug pentylenetetrazol, was the only product isolated. Use of a stoiciometric amount of base with formation of phenolate anion prior to the addition of 2 was insufficient to avoid formation of 4. Although diethylaluminum azide is a convenient, nonnucleophilic source of azide, tolerant of a variety of functional groups, the low pK_{2} of the resulting 1*H*-tetrazole causes its selective deprotonation, leading to an intramolecular S_N2 reaction of tetrazolate with the ε -carbon of compound 2. Protection of 1H-tetrazole likewise leads to undesired side products. Thus, to achieve polymers with 1H-tetrazoles containing intact N-H protons, formation of the acidic tetrazole was required to proceed after reaction of the polymeric phenolic group with halo-alkyl nitrile, necessitating a modified tetrazolation methodology.

Polystyrenic alkoxy-1H-tetrazole **I** serves as a first example of both the synthesis and properties of polymers containing alkyl-tethered 1H-tetrazole moieties. To afford a compact, time-



Figure 3. Solution ¹H NMR spectra of parent polystyrene alkoxynitrile 8 and polystyrenic alkoxy-1*H*-tetrazole 1 in deuterated dimethyl sulfoxide (DMSO- d_6).



Figure 4. Solid state ¹H NMR spectrum of polystyrenic alkoxy-1H-tetrazole 1 at 100 °C, showing raw data and 12 component Lorentzian fits.

efficient synthesis of compound 1, a two-step strategy was employed, first forming the ether linkage between poly(4vinylphenol) ($M_w \approx 11\,000$, Sigma-Aldrich) 7, and 6bromohexane nitrile (Scheme 2). Polystyrenic alkoxynitrile 8 resulted when K₂CO₃ was used as base and DMF as solvent. To obtain lower molecular weights, 4-vinylphenol 6 was synthesized from 4-acetoxystyrene 5 and subsequently polymerized in the presence of HCl to yield poly(4-vinylphenol) 7 of variable molecular weight and narrow molecular weight distribution. It should be noted that NMR spectra of commercial and in-house synthesized poly(4-vinylphenol)s 7 are identical.

Diethylaluminum azide was generated *in situ* by the addition of NaN_3 to a solution of diethylaluminum chloride in toluene. The formation and general use of this reagent are documented

in prior work.¹⁶ Tetrazolation commenced on addition of polystyrenic alkoxynitrile **8**, dissolved in chlorobenzene, 1,2dichlorobenzene (DCB), and/or toluene, to the diethylaluminum azide solution, followed by heating and stirring of the reaction mixture overnight. After chilling the solution, diethylaluminum was cleaved from the tetrazole nitrogen by addition of aqueous NaOH and NaNO₂. Subsequent acidification formed the 1*H*-tetrazole and quenched remaining azide by *in situ* formation and immediate reaction of HNO₂ with HN₃ (to N₂, NO, and H₂O). The entire process was conducted under an inert atmosphere. Conversion to polystyrenic alkyoxy-1*H*-tetrazole **1** was confirmed by the growth of a broad 1*H*-tetrazole N–H peak at 16 ppm and shifting of the terminal CH₂ protons from 2.4 to 2.9 ppm in solution ¹H NMR (Figure 3). Although the 1*H*-tetrazole proton is broad in solution NMR and often exhibits reduced intensity due to exchange with residual water, the full integrated intensity of this peak was observed in solid-state ¹H NMR of the polymer, illustrated at 100 °C in Figure 4. Because of changes in tetrazole environment and interactions in the solid state, the N–H proton shifts to ~12 ppm at high temperature.

During the early stages of tetrazolation using toluene as a solvent, polymer 8 precipitated from solution as swollen solid particulate, most likely due to the disparate solubility of the backbone and tetrazole-containing pendent moieties. Nevertheless, conversions in excess of 90% were achieved in the swollen solid, showcasing the facile nature of this reaction. To attain quantitative conversion, DCB was used as cosolvent to maintain solubility of polymer product and facilitate complete removal of residual azide and aluminum salts upon quenching. It was noted that at least 2 equiv of dialkylaluminum azide were required for complete conversion of nitrile to tetrazole. Early experiments with small molecule alkoxy- and alkylnitrile compounds determined that an additional equivalent was required for each alkoxy group present in the structure. It is suspected that the electrophilic aluminum stoichiometrically coordinates to the oxygen in the alkoxy linkage, requiring a second equivalent to completely react with the nitrile. Although using alkoxy substituents requires doubling of the azide, this procedure forgoes potentially explosive and acutely toxic intermediates (e.g., HN_3 , NH_4N_3) and allows safe, in situ quenching of excess azide. This methodology has been demonstrated as a safe and useful reaction pathway to obtain 1H-tetrazoles with labile protons that are covalently tethered by an alkyl substituent to a polymeric backbone.

Cycloaddition of pendant nitriles with diethylaluminum azide permitted the synthesis of polystyrenic alkoxy-1H-tetrazole 1. Although conversions of nitrile to 1H-tetrazole between 90% and 100% were observed depending upon reaction conditions, use of 1,2-dichlorobenzene as cosolvent enabled consistent, quantitative conversion. The various properties of polystyrenic alkxoy-1H-tetrazole 1 reported herein were conducted only on samples of 100% conversion. This class of polymers bearing alkyl-tethered 1H-tetrazoles is of interest for its potential anhydrous proton conducting capability. Proton conduction in tethered systems can only be structural in nature (per the Grotthuss mechanism) due to the lack of long-range translational diffusion in a solid polymer and should thus be strongly coupled to polymer motion.^{30,31} As the synthetic methods to convert nitriles to 1H-tetrazoles generate high levels of salts (e.g., aluminum and sodium salts), care must be taken to rigorously exclude them from the final product. To ensure that measured conductivity could arise only from dissociated azoles, sodium and aluminum salt concentrations were monitored by ²³Na and ²⁷Al NMR in deuterated dimethyl sulfoxide (DMSO d_6). Samples were reprecipitated from DMSO into 1 N HCl and then repeatedly rinsed with distilled water until neutral to reduce salt concentrations below detection limits. Despite the explosive nature of many small molecule tetrazoles, polystyrenic alkoxy-1H-tetrazole 1 was thermally stable under both nitrogen and air to 210 °C. The 14% weight loss observed from 210 to 280 °C by TGA (Figure 5) was controlled under both nitrogen and air and presumably corresponds to off-gassing of N2 and HN₃ by retrocyclization of 1*H*-tetrazole.⁷

For pure, undoped 1*H*-azole materials, autodissociation of azoles to form charged species is expected to be quite low based on acid and base dissociation constants (pK_a and pK_b). For



Figure 5. Thermal gravimetric analysis of polystyrenic alkoxy-1*H*-tetrazole 1 under nitrogen and air. Weight loss of 1% is observed by 210 $^{\circ}$ C and 5% by 250 $^{\circ}$ C.

water, which has a pK_a of 15.7 and pK_b of -1.7, the sum of these values gives rise to the autodissociation constant, pK_d . This results in a proton concentration of only 10^{-7} M, approximately the square root of K_d . In 1*H*-tetrazoles, where $pK_d \approx 22$ based on aqueous measures of $pK_a = 4.9$ and $pK_b =$ 17, autodissociation alone should result in low charge concentrations and conductivities even where charge mobility is high.^{6,32} To measure low conductivities by electrochemical impedance spectroscopy (EIS), blocking interdigitated electrodes (IDEs) were fabricated from gold. Compared to standard parallel plate and plane parallel cell configurations, an interdigitated design requires only small sample volumes (ca. 10 μ L) and can exhibit improved signal-to-noise at low conductivity. The IDE cell constant, κ (cm⁻¹), is determined in the thick film limit by the effective spacing between electrode teeth and the total electrode area. Equation 1 relates conductivity (σ , S cm⁻¹) to κ and solution/film resistance $(R_{\rm soln}, \Omega).$

$$\sigma = \frac{\kappa}{R_{\rm soln}} \tag{1}$$

A comprehensive review of both the physics of IDEs and the theoretical and experimental calculations of cell constants can be found in the literature.^{29,28} For the cells used to measure the conductivity of polymer 1, cell constants of $\kappa = 0.115 \pm 0.003$ cm⁻¹ were calculated by calibration to 0.05, 0.1, 0.5, and 1.0 mM KCl solutions using a typical commercial conductivity probe as a reference. The measured cell constant was close to the value predicted by IDE geometry, 0.106 cm⁻¹, and was valid for thicknesses greater than 40 μ m. Thick films (~100 μ m, measured by stylus profilometry) of polystyrenic alkoxy-1Htetrazole 1 were drop-cast onto the IDE array from concentrated DMSO solution and annealed under vacuum at 70 °C prior to EIS. Electrochemical impedance spectroscopy was conducted on a Gamry Reference 600 potentiostat from 1 MHz to 1 Hz and 120 to 30 °C under flowing nitrogen, using a 100 mV applied RMS (sinusoidal) voltage. A representive Nyquist plot $(-Z'' \text{ vs } Z', \text{ where total impedance } \hat{Z} = Z' + iZ'')$ and the empirical circuit model used to fit the raw data are illustrated in Figure 6. The four-element, empirical circuit model depicted in Figure 6 was originally proposed by Karan et al. for modeling conductivity in thin, hydrated Nafion films with IDE cell geometry.³³ It includes constant phase elements (CPEs) approximating geometric capacitance and electrode polarization (double-layer capacitance) effects, which are known to be good empirical descriptors, over a finite frequency



Figure 6. Left: Nyquist plot of imaginary (-Z'') vs real (Z') impedance of a film of polymer 1, used to calculate resistance by fitting to a circuit model (red line). Full spectrum from 1 MHz to 1 Hz inset. Right: empirical circuit model used to fit impedance data to extract solution resistance and film conductivity.

range, of the nonideal behavior encountered in polymer ionic conductors.

The anhydrous conductivity of polystyrenic alkoxy-1*H*-tetrazole 1 between 30 and 120 °C is illustrated in Figure 7,



Figure 7. Anhydrous conductivity of polystyrenic alkoxy-1*H*-tetrazole **1** between 30 and 120 °C, averaged over three separate films, with standard deviations (log-weighted). Line is VFT fit to conductivity ($T_0 = -33$ °C).

averaged over three batches. The large, non-Arrhenius dependence of conductivity on temperature fits well to a Vogel-Fulcher-Tammann (VFT) empirical relationship, where $T_0 = -33$ °C. At 120 °C, polymer 1 exhibits conductivity on the order of 10^{-5} S cm⁻¹, which is reasonable for an undoped, azole-containing polymer well above its T_g . As frames of reference, deionized water exhibits a conductivity of 6×10^{-8} S cm⁻¹ at 25 °C and phosphoric acid varies between 5×10^{-2} S cm⁻¹ at 25 °C and 4×10^{-1} S cm⁻¹ at 120 °C.³⁴ Differential scanning calorimetry of compound 1 (Figure 8) shows two distinct $T_{g}s$ at 49 and 74 °C, suggesting unexpected, but unambiguous, two-phase behavior. This polymer was extensively purified and verified by NMR and elemental analysis to be free of residual solvents; thus, this behavior cannot be explained by molecular impurities and must arise from the polymer structure. The precise nature of this phase separation is currently unknown. However, as the subject of ongoing investigation, results confirming the existence of two phases by



Figure 8. Differential scanning calorimetry thermogram of polystyrenic 1*H*-tetrazole 1, illustrating two distinct T_{gs} at 49 and 74 °C.

mechanical and microscopic methods can be found elsewhere. 35

Traditionally, VFT dependence of conductivity on temperature suggests coupling of conduction to polymer motion. However, T_0 for polymer 1 was observed to be significantly lower (82 °C) than the T_g of its softer phase (49 °C), raising doubts that conductivity is coupled to polymer segmental relaxation. Temperature-dependent, solid-state NMR spectroscopy, illustrated in Figure 9, was used to examine 1H-tetrazole proton motion, which was found to occur with a similar activation energy, and in a similar temperature range, to side chain motion. The onset of side chain mobility, observed as an increase in the slope of log line width vs inverse temperature, occurs at ~47 °C. Noting that NMR transitions typically occur at higher temperatures than DSC transitions due to differences in the time scales of the processes being probed, side chain motion onsets prior to segmental relaxation of the soft phase. Segmental motion at a similar time scale to side chain motion would additionally be visible as a change in the line width of the aryl protons of 1, which remain relatively broad, and thus immobile, over the range of temperatures investigated. The coupling of proton motion to side chain dynamics, which appear to be independent of backbone dynamics, may explain the VFT behavior of conductivity observed above and below both T_{o} s.

If proton mobility is truly decoupled from segmental motion, changes in polymer T_g should not significantly affect



Figure 9. Average solid-state ¹H NMR line widths of alkyl, aryl, and azole protons in polystyrenic alkoxy-1*H*-tetrazole **1** vs inverse temperature. Inset depicts representative, full polymer spectrum at 92 °C, from which peaks are fit.

conductivity. Aside from modifying the backbone structure, T_{a} can be decreased by either plasticization or reduction of polymer molecular weight. Obtaining a poly(4-vinylphenol) with a lower molecular weight than commercially available was synthetically achievable in only a few additional steps (see Scheme 2). Acid polymerization of 4-vinylphenol with concentrated aqueous HCl was attractive, producing a low molecular weight with a narrow molecular weight distribution and no visible side products. The HCl-polymerized poly(4vinylphenol) was found to have a $M_{\rm w}$ of 4000 Da and $M_{\rm w}/M_{\rm n}$ of 1.33, comparing favorably to the commercial poly(4vinylphenol) (Aldrich Chemical, $M_w \approx 11\,000$ Da) used for prior syntheses, which was determined to have a M_w of 9500 Da with a $M_{\rm w}/M_{\rm n}$ of 1.37. The lower molecular weight polystyrenic alkoxy-1H-tetrazole derived from this polymer exhibits two distinct T_{g} s, shifted to 26 and 44 °C, compared to 49 and 74 °C in the higher molecular weight material. Although conductivity of the low molecular weight polystyrenic alkoxy-1H-tetrazole was found to increase uniformly by a factor of 2 compared to the higher molecular weight polymer, illustrated in Figure 10, this effect is much lower than might be expected for a decrease in T_{σ} of approximately 25 °C. Synthetically, the glass transition can be easily varied in this material. The physics governing both phase separation and proton motion are still not well



Figure 10. Anhydrous proton conductivity of low and high molecular weight polystyrenic alkoxy-1*H*-tetrazole 1, derived from in-house polymerized (low M_w) and commercial (high M_w) poly(4-vinyl-phenol). Color-coded vertical lines illustrate T_g s of the respective materials.

understood and thus the subject of ongoing work. However, a preliminary study of the polymer physics of this material, including mechanical and dielectric relaxation behavior, has recently been published.³⁵

CONCLUSIONS

The Brønsted acidity of 1*H*-tetrazoles ($pK_a = 4.9$ for unsubstituted 1H-tetrazole) causes them to be incompatible with many reactions that might be leveraged to attach a tetrazole-containing small molecule to a polymer backbone. The Williamson ether reaction is one such polymer functionalization technique, where poly(4-vinylphenol) is a convenient, commercially available starting material. However, as illustrated in Scheme 1, under alkaline conditions 1Htetrazole readily deprotonates, forming a nucleophile that competes with phenolate to form 1,5-pentamethylenetetrazole exclusively. Thus, it is synthetically prudent to perform the tetrazole [2 + 3] cycloaddition as the final step in a synthetic procedure. We have demonstrated the facile synthesis of polymeric C-substituted 1*H*-tetrazoles through the $\begin{bmatrix} 2 + 3 \end{bmatrix}$ cycloaddition of diethylaluminum azide, a non-nucleophilic azide donor, and alkyl nitriles. This protocol offers advantages over earlier postpolymerization procedures and employs moderate temperatures, reasonable reaction times, and safe reagents. Because of the facile nature of this cycloaddition reaction, conversion of unactivated nitriles can even be achieved on sparingly soluble or swollen, insoluble polymers. With the correct choice of cosolvent, quantitative conversions of nitrile to 1H-tetrazole are consistently achievable.

The model polystyrenic alkoxy-1H-tetrazole 1, synthesized using the reported procedure, exhibits intrinsic anhydrous proton conductivity of up to 10⁻⁵ S cm⁻¹, despite its relatively high T_{os} of 74 and 49 °C. The duals T_{os} of this material are unlike other polymers containing pendent 1H-azoles reported in the literature, which characteristically exhibit only one glass transition. This behavior is especially unusual given this material's short side chains and homopolymer nature. Additionally, despite the apparently VFT behavior of conductivity, common to most azole-functionalized polymers, side chain motion and conductivity appear to be decoupled from segmental motion, according to solid-state NMR spectroscopic measurements. This is supported by observation of only a factor of 2 increase in anhydrous proton conductivity on decreasing the T_{gs} of both phases by ~25 °C. As this behavior has not been reported in other 1H-azole-containing homopolymers, it is currently under further investigation. As part of this ongoing work, mechanical spectroscopy, dielectric relaxation spectroscopy, and atomic force microscopy are published elsewhere which provide preliminary insight into the physical characteristics of this material.³⁵

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the Office of Naval Research and the Naval Research Laboratory for financial support of this project. Additionally, B.L.C., S.M.D., and M.A.B. acknowledge NRL's

Student Temporary Employment and Pathways Programs while K.M.S. acknowledges ONR's Science & Engineering Apprentice Program.

ABBREVIATIONS

CPE, constant phase element; DCB, 1,2-dichlorobenzene; DSC, differential scanning calorimetry; DMSO, dimethyl sulfoxide; EIS, electrochemical impedance spectroscopy; IDE, interdigitated electrode; NMR, nuclear magnetic resonance (spectroscopy); PS-Tet, polystyrenic alkoxy-1*H*-tetrazole; T_{g} , glass transition; TGA, thermal gravimetric analysis; TLC, thin layer chromatography; VFT, Vogel–Fulcher–Tammann.

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