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Probing Hydrogen Bonding and Proton Mobility in Dicyanoimidazole Monomers and Polymers

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ABSTRACT: Hydrogen bonding and proton mobility are important features in many polymers. In this work, hydrogen bonding is studied in both monomers and polymers of dicyanoimidazoles using infrared and solid-state NMR spectroscopy and polymer viscosity studies. Hydrogen bonding accounts for an unusual complexity in the nitrogen−hydrogen stretching region of the infrared spectra. The influence of hydrogen bonding on properties was observed in several dicyanoimidazole polymers through polymer viscosity studies and estimation of Mark−Houwink parameters. The Mark−Houwink *a* value decreases, representing a less stiff chain, in poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) compared to poly(2-vinyl-4,5-dicyanoimidazole) because hydrogen bonding is eliminated. By dissolving poly(2-vinyl-4,5-dicyanoimidazole) in NH_3(aq), a polymer electrolyte results. Although hydrogen bonding is eliminated, electronic repulsions contribute to an increase in *a* or chain stiffness. Proton mobility in dicyanoimidazole polymers was studied with an innovative solid-state NMR technique using double-quantum (DQ) filtering and fast magic angle spinning (MAS = 30 kHz). Using this approach, several types of hydrogen bonds were identified and proton mobility in poly(2-vinyl-4,5-dicyanoimidazole) was detected.

Introduction

Hydrogen bonding is of pivotal importance in the properties of many polymers. It accounts for much of the crystallinity and strength of nylons and the unusual solubility and reactivity of poly(vinyl alcohol) and has a profound influence on the structure and function of polypeptides and polynucleotides.[1] In imidazoles hydrogen bonding has been established as an important feature of enzymatic systems.[2] However, the effects of imidazole hydrogen bonding in polymers are not well understood even though a number of small molecule crystalline systems have been investigated.[3−6] Proton mobility is desirable as an intrinsic property of fuel cell membrane materials. An extended network of hydrogen bonds can lead to mobilization of protons via structural diffusion (Grotthus mechanism) rather than requiring high degrees of humidification or the addition of a large excess of strong acid to effect bulk diffusion by molecular diffusion ("vehicle" mechanism).[7]

Dicyanoimidazoles are readily synthesized in one step from the tetramer of HCN, diaminomaleonitrile (DAMN).[8] This can be accomplished using ortho esters as electrophiles or by Schiff base reactions followed by oxidation.[8] Dicyanoimidazoles typically have $pK_a = 5.5$, a striking 9 orders of magnitude more acidic than imidazole itself. Acidity trends in imidazole derivatives are illustrated in Figure 1.

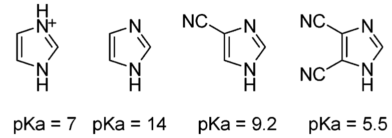

Figure 1. pK_a trends in imidazole derivatives.

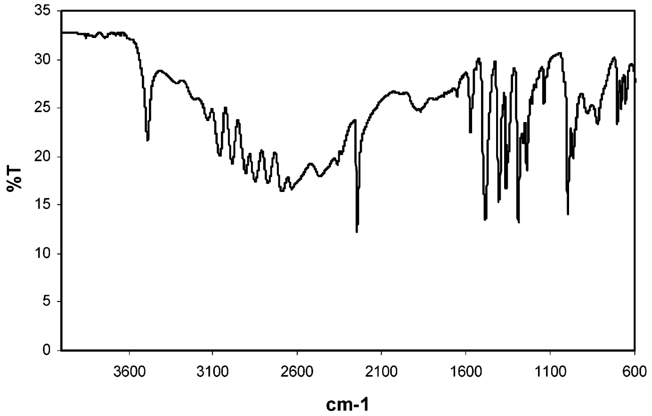

Figure 2. FT-IR spectrum of 2-bromo-4,5-dicyanoimidazole.

Results

Monomer Hydrogen Bonding. We first became aware of the unusual hydrogen-bonding tendencies of cyanoimidazoles after examination of the infrared spectrum of 2-bromo-4,5-dicyanoimidazole.[9] This spectrum shows much greater complexity in the nitrogen−hydrogen stretching region than would be expected for a molecule containing a single nitrogen−hydrogen bond. The mystery intensified since dicyanoimidazole itself does not show this complex infrared pattern, see Figures 2 and 3.

Recently, we reported the synthesis and polymerization of 2-vinyl-4,5-dicyanoimidazole (**1**),[10,11] see Figure

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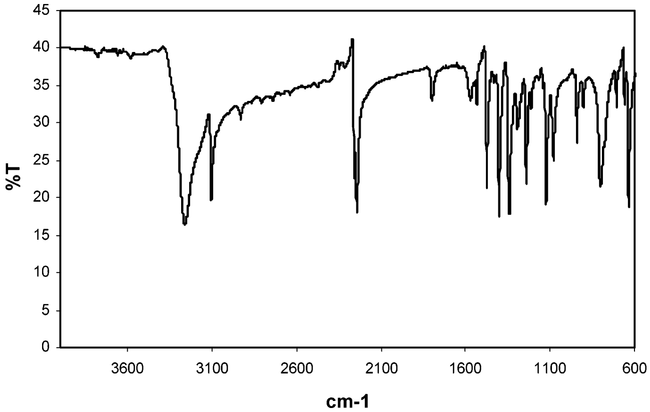


Figure 3. FT-IR spectrum of dicyanoimidazole.

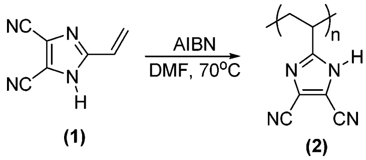


Figure 4. Polymerization of 2-vinyl-4,5-dicyanoimidazole (**1**).

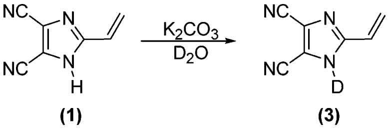


Figure 5. Deuteration of 2-vinyl-4,5-dicyanoimidazole (**1**).

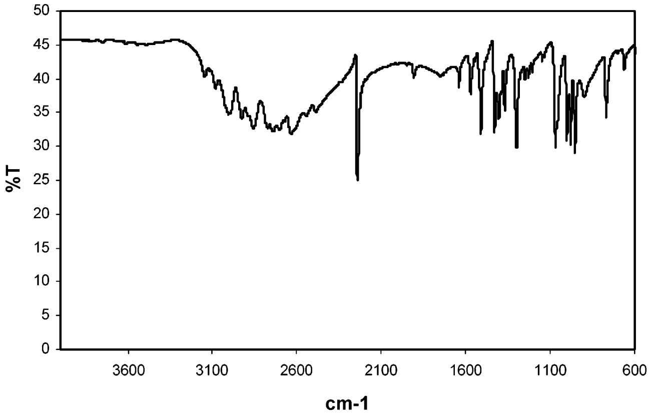


Figure 6. FT-IR spectrum of 2-vinyl-4,5-dicyanoimidazole (**1**).

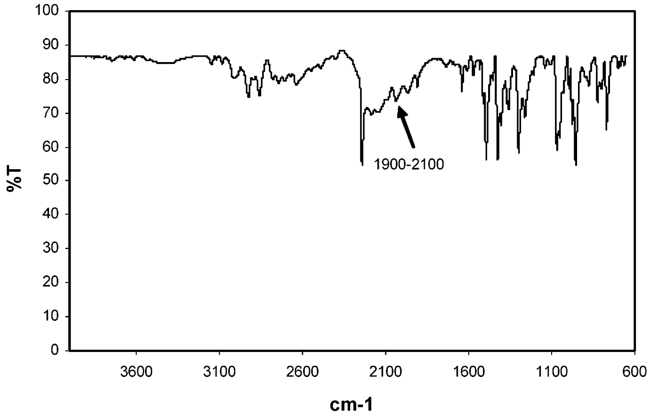


Figure 7. FT-IR spectrum of partially deuterated 2-vinyl-4,5-dicyanoimidazole (**3**).

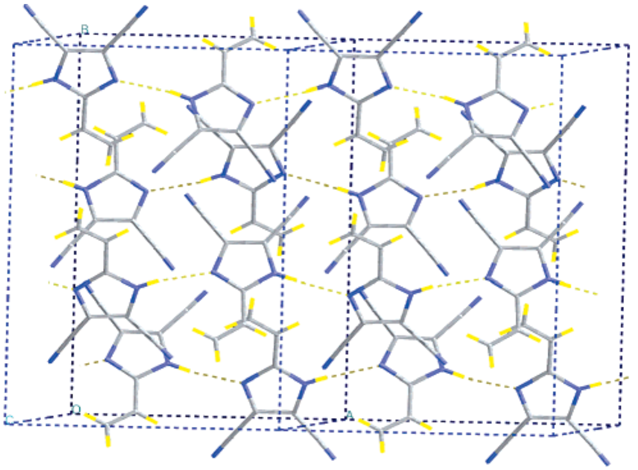


Figure 8. Crystal structure of 2-vinyl-4,5-dicyanoimidazole (**1**); N(1)−H−N(3) = 2.878 Å.

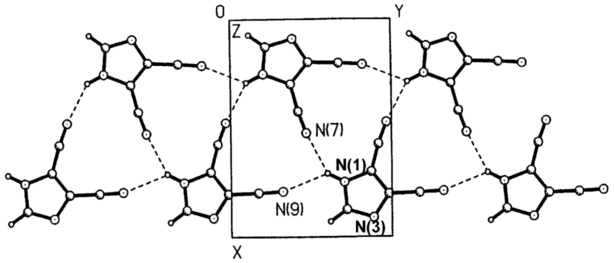


Figure 9. Crystal structure of dicyanoimidazole.[3,6]

4. Both the monomer and polymer show a complex pattern of infrared absorptions similar to those described above for 2-bromo-4,5-dicyanoimidazole. To verify that hydrogen bonding was responsible for the spectral complexity in the monomer, 2-vinyl-4,5-dicyanoimidazole (**1**) was partially deuterated, see Figure 5.

Compared to Figure 6, the spectral complexity in Figure 7 shifted following partial deuteration, and new peaks emerged between 1900 and 2100 cm^{-1}. This establishes that the infrared absorptions between 2600 and 3200 cm^{-1} are due to hydrogen bonding associated with nitrogen−hydrogen bonds.

To further extend our understanding of these observations, we examined the crystal structure of 2-vinyl-4,5-dicyanoimidazole (**1**). The crystal structure of 4,5-dicyanoimidazole has previously been reported.[3,6] Comparing these structures reveals interesting differences, see Figures 8 and 9. The structure of 2-vinyl-4,5-dicyanoimidazole (**1**) contains a clear 1,3-hydrogen-bonded chain which extends throughout the crystal. This 1,3-interaction is absent in dicyanoimidazole. However, dicyanoimidazole is packed in such a way that hydrogen bonding is evident between the 1-position hydrogen and a nitrile nitrogen on a neighboring dicyanoimidazole molecule.[3,6]

Our observation of infrared complexities in imidazole derivatives is not unique. Bellocq and co-workers studied the infrared complexity of a variety of halogenated and deuterated imidazole species over 30 years ago.[4] More recently, this complexity was observed by Barni and co-workers in 4-cyanoimidazolium-5-olate and was attributed to hydrogen bonding.[3] In the case of 2-vinyl-4,5-dicyanomidazole (**1**), we conclude that the 1,3-hydrogen-bonded chain is responsible for the unusual and complex pattern in the infrared spectrum. This hypothesis was strengthened by noting that the crystalline structure of 2-amino-4,5-dicyanoimidazole also has 1,3-hydrogen bonding and shows spectral complexity

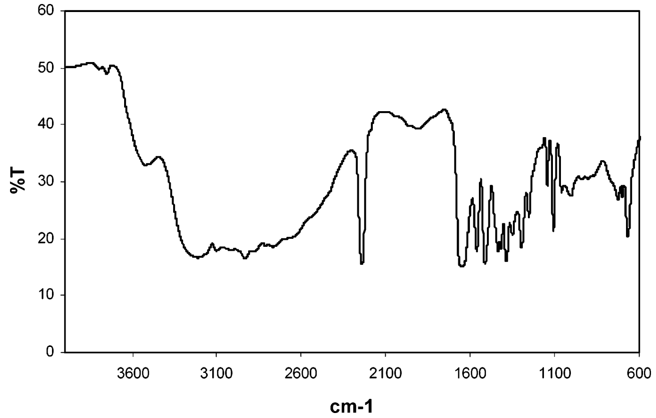


Figure 10. FT-IR spectrum of poly(2-vinyl-4,5-dicyanoimidazole) (**2**; solid polymer in KBr pellet).

similar to the 2-vinyl-4,5-dicyanoimidazole (**1**) monomer.[5] The potential well for hydrogen bonding is quite shallow, compared to normal covalent bonds, and the vibrations of a hydrogen-bonded system are correspondingly quite anharmonic. This anharmonicity can lead to an unusually large degree of Fermi resonance between the fundamental and other combination frequencies, especially when the combination frequencies are of the same symmetry class.[12] This latter factor may explain why in some cases unresolved broadening is observed, whereas in our linear 1,3-H-bonded chains, we observe a number of well-resolved bands. The frequencies of the hydrogen bond stretch, that is the H···Y vibrations in the X−H···Y system, are generally observed by Raman spectroscopy to fall between 100 and 200 cm^{-1} and, as noted above, can strongly interact with the X−H fundamental.[13] There is a complex interplay between the hydrogen-bonding motif adopted in the crystalline state and the competition between steric factors and hydrogen bonding. We noted that imidazoles with substituents at the 2-position favor the 1,3-chain motif. The added bulk at this position may drive the crystal packing toward the 1,3-hydrogen-bonded chain.

Polymer Hydrogen Bonding. Turning to the properties of poly(2-vinyl-4,5-dicyanoimidazole) (**2**), we observe that the polymer has considerable solubility in polar organic solvents such as dimethylformamide (DMF), methanol, and acetonitrile. These solutions can be used to cast films which are somewhat brittle. When the polymer is dried under reduced pressure at temperatures above 100 °C, the material becomes hard and insoluble. Compared to the monomer spectrum, poly(2-vinyl-4,5-dicyanoimidazole) (**2**) shows similar infrared complexity though less resolved as one would expect for a polymer; see Figure 10.

For the soluble polymer, the Mark−Houwink parameters, assessed by GPC in NMP, are consistent with a stiff chain.[10] The viscosities of poly(2-vinyl-4,5-dicyanoimidazole) (**2**) and poly(1-methyl-2-vinyl-4,5-dicyanoimidazole (**5**) were determined to compare the Mark−Houwink parameters of both polymers. The viscosity of poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) (**5**) was measured in dimethylformamide (DMF). The viscosity of poly(2-vinyl-4,5-dicyanoimidazole) (**2**) was measured in DMF and aqueous ammonia, $NH_3(aq)$. In $NH_3(aq)$, poly(2-vinyl-4,5-dicyanoimidazole) is actually a polymeric electrolyte (**6**) due to the acidity of the 1-position hydrogen. The Mark−Houwink parameters were estimated to compare the differences in chain stiffness of poly(2-vinyl-4,5-dicyanoimidazole) (**2**), poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) (**5**), and the polymer electrolyte (**6**).

By independent GPC analysis with light-scattering detection, the Mark−Houwink parameters for poly(2-vinyl-4,5-dicyanoimidazole) (**2**) in NMP with 0.05 M LiBr are $K = 3.3 \times 10^{-5}$ and $a = 0.89$.[10] Poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) (**5**) was demethylated with LiCl and precipitated with HCl to give poly(2-vinyl-4,5-dicyanoimidazole) (**2**) with the same chain length. A portion of **2** was dissolved in $NH_3(aq)$ to give the polymer electrolyte (**6**). Since the molecular weight is relatively unchanged, we can use the change in intrinsic viscosity to estimate a new a value. Since we lack independent K and a values in the GPC solvent, the universal calibration method for GPC was not used.[14,15]

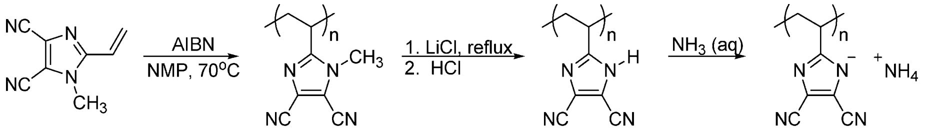
From our viscosity data we determined the intrinsic viscosity of **2**, $[\eta]_{\mathbf{2}}$. With $[\eta]_{\mathbf{2}}$ and known values of K and a, we determined the viscosity average molecular weight of **2**. For comparison purposes, we assumed that the viscosity average molecular weights of **5** and **6** are similar. From our viscosity data we determined the intrinsic viscosity of **5** in DMF and **6** in $NH_3(aq)$. If the K value remains unchanged, an a estimate can be calculated for **5** and **6**; see Table 1. The a estimate for poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) (**5**) is lower than the value for poly(2-vinyl-4,5-dicyanoimidazole) (**2**), indicating that **2** is a more rigid polymer, likely due to hydrogen bonding. Simply comparing the intrinsic viscosity of **5** and **2** illustrates the influence of hydrogen bonding: $[\eta]_{\mathbf{2}} = 2.80$ dL/g and $[\eta]_{\mathbf{5}} = 1.24$ dL/g. Poly(2-vinyl-4,5-dicyanoimidazole) (**2**) was dissolved in $NH_3(aq)$, giving a polymeric salt (**6**). The a value for poly(2-vinyl-4,5-dicyanoimidazole) (**2**) in NMP is lower than the value found for the salt of poly(2-vinyl-4,5-dicyanoimidazole) (**6**) in $NH_3(aq)$. Although hydrogen bonding is eliminated, electronic repulsions are present along the polymer backbone that contribute to the increase in chain stiffness for the poly(2-vinyl-4,5-dicyanoimidazole) electrolyte (**6**).

The combination of small molecule data and observations of polymer viscosity properties suggests that, like the monomer, poly(2-vinyl-4,5-dicyanoimidazole) (**2**) is also involved in extensive 1,3-hydrogen bonding. This could be either intramolecularly, along the chain, or intermolecularly. This is consistent with the brittleness of the films, chain stiffness, unusual solubility features, and infrared spectrum of the polymer.

Solid-State NMR. Along with our examination of hydrogen bonding in the monomers and polymers of dicyanoimidazole, we also investigated proton mobility in poly(2-vinyl-4,5-dicyanoimidazole) (**2**). To do this we use a new solid-state ^{1}H NMR approach developed for the study of proton mobility.[16] Following this approach

Table 1. Estimated Mark−Houwink Parameters

sample	K	a
poly(2-vinyl-4,5-dicyanoimidazole) (**2**) in NMP[11]	3.35×10^{-5}	0.89
poly(2-vinyl-4,5-dicyanoimidazole) (**2**) in DMF	3.35×10^{-5}	0.89
poly(2-vinyl-4,5-dicyanoimidazole) electrolyte (**6**) in NH_3 (aq)	3.35×10^{-5}	0.92
poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) (**5**) in DMF	3.35×10^{-5}	0.83



(4) **(5)** **(2)** **(6)**

Figure 11. Polymerization of 1-methyl-2−4,5-dicyanoimidazole (**4**). Demethylation of poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) (**5**). Dissolution of poly(2-vinyl-4,5-dicyanoimidazole) (**2**) in NH_3 (aq) to give (**6**).

high-resolution 1D ^{1}H MAS NMR spectra are compared with double-quantum-filtered spectra (DQ), allowing us to directly identify which protons are mobile and quantify their mobility. Double quantum-filtered NMR experiments, such as the 1D BaBa (back to back) sequence used here, investigate proton mobility via the motional averaging of the dipolar couplings between protons and the resulting effect on the intensity of the double-quantum coherence.[17] Resonances observed in the DQ spectrum arise from protons which experience homonuclear dipolar couplings on the time scale of the experiment (about 2 μs). Conversely, the absence of a DQ signal for a pair of protons means either they are too far apart (>0.5 nm or 5 Å) to be coupled or there is molecular or proton motion on the experimental time scale.

A series of variable-temperature ^{1}H MAS NMR spectra was acquired under fast MAS conditions to achieve high resolution ($\nu_r = 30$ kHz). These spectra provide a snapshot of the number and comparative strengths of the hydrogen-bonding interactions, which typically arise in the frequency range of 10−20 ppm. If local motion is fast on the NMR time scale, the spin−spin relaxation times (T_2) are reflected in the line widths and are correlated with the proton mobility. The line width decreases, corresponding to a decrease in relaxation time or similarly an increase in molecular motions; in this case, it is attributed in part to proton mobility. Motional exchange processes which are slow on the NMR time scale can be detected by coalescence of the resonances due to sites involved in slow exchange.

To investigate ^{1}H−^{1}H dipole−dipole couplings directly, we make use of the BaBa DQ sequence, which allows us to distinguish between strongly and weakly dipolar coupled nuclei. Strongly coupled systems can be used to generate double-quantum coherences between pairs of protons.[17] In contrast, weakly coupled systems give rise to incoherent processes such as dipolar cross relaxations that are the basis of nuclear Overhauser effect (NOE) experiments but lack DQ signals.[18] Thus, the relative intensity of the direct excitation (single pulse) MAS spectrum as compared to the 1D DQ-filtered spectrum provides an immediate indication of the relative strengths of the dipolar couplings in the system. Combining these observations with our knowledge of the chemical structures, it is straightforward to identify those protons which are influenced by motional processes from those which are rigid on the time scale of our experiments.

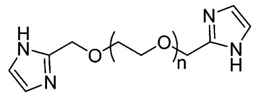


Figure 12. Imidazole−*n*ethylene oxide (Imi-nEO) where *n* = 1, 2, 3, 5.

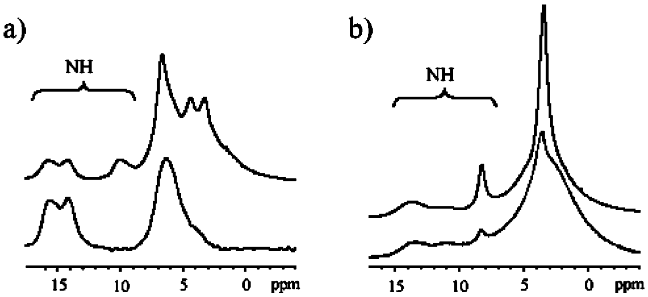


Figure 13. (a) (top) ^{1}H solid-state MAS spectrum of Imi-1EO; (bottom) with DQ filtering. (b) (top) ^{1}H solid-state MAS spectrum of poly(2-vinyl-4,5-dicyanoimidazole) (**2**); (bottom) with DQ filtering.

It is useful to compare proton transport observed in other imidazole-based systems. An investigation of an imidazole-containing polymer tethered by flexible ether units was carried out by Goward et al.,[16] Figure 12. The oligomers served as model compounds for proton-exchange membranes. Their report suggests the possibility of a structural diffusion mechanism in heterocycles as an important alternative to mechanisms that take place in hydrated systems. Our observations on imidazoles further confirm the validity of this hypothesis. Recently, we have been investigating poly(2-vinyl-4,5-dicyanoimidazole) (**2**) as a possible proton-transfer membrane for fuel cell applications. The specialized solid-state NMR method discussed above is particularly well adapted for our project because the solid-state methodology allows investigation of real multicomponent or composite materials that cannot be studied by solution methods. Figure 13 shows a comparison of ^{1}H solid-state NMR spectra acquired under 30 kHz MAS, with and without DQ filtering, for both Imi-1EO[16] and poly(2-vinyl-4,5-dicyanoimidazole) (**2**). In contrast to the solution spectrum where a single N−H resonance is observed at approximately 9 ppm, the ^{1}H solid-state MAS spectrum of Imi-1EO shows three N−H resonances (Figure 13a, top). This observation is expected for solid materials forming multiple types of hydrogen bonds.[19] Comparing the two solid-state NMR spectra, the N−H resonance at 10 ppm clearly disappears when double-quantum filtering is applied (Figure 13a, bottom). The peak disappearance indicates that the imidazole-tethered material has protons that are mobile on the NMR time scale.

By observing the proton line width as a function of temperature, ^{1}H MAS spectra can also be used to characterize proton mobility. In Figure 14 the effect of raising the temperature can be observed for both Imi-5EO and poly(2-vinyl-4,5-dicyanoimidazole) (**2**). As previously noted, the spin−spin relaxation times (T_2) are reflected in the line widths and correlated with the proton mobility. As proton mobility increases, the line width decreases. Figure 14a, clearly shows peak narrowing with increasing temperature for mobile protons in Imi-1EO. This combination of solid-state NMR methods has proved useful for determining proton mobility in model proton-exchange membranes.

The solid-state ^{1}H NMR spectra of poly(2-vinyl-4,5-dicyanoimidazole) (**2**) are shown in Figure 13b. The ^{1}H

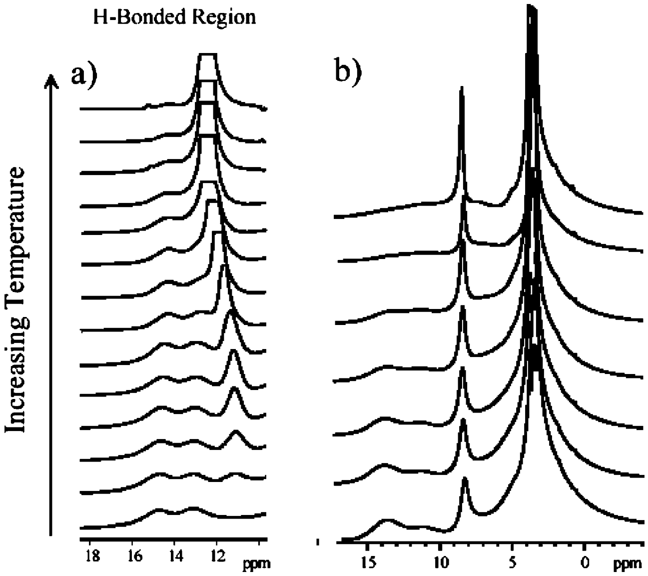


Figure 14. Variable-temperature ^1H solid-state MAS spectrum of (a) Imi-5EO (280−350 K) and (b) poly(2-vinyl-4,5-dicyanoimidazole) (**2**) (280−400 K).

MAS NMR spectra of poly(2-vinyl-4,5-dicyanoimidazole) (**2**) are indicative of complex hydrogen bonding. Three hydrogen-bonded N−H resonances similar to those observed in Imi-*n*EO materials in both line shape and position reflect this complex yet ordered structure. Local order is presumed based on the reasonable resolution found between the high-frequency resonances (11−14 ppm). Locally mobile protons are presumed to be present based on the low-frequency and comparatively narrow N−H resonance at 8.5 ppm. Moreover, this resonance is significantly lower in relative intensity in the DQ-filtered spectrum, consistent with motionally averaged dipolar couplings.

To further probe the nature of these mobile protons, variable-temperature (VT) ^1H MAS spectra were acquired (Figure 14b). The data show significant line narrowing as a function of temperature. This is attributed to a combination of molecular dynamics in the polymer itself and proton exchange or mobility, which would facilitate proton conductivity. Further evidence for this fundamental molecular motion, necessary for conductivity, is found in the VT-DQ data, which show that this low-frequency N−H resonance remains low in intensity throughout this temperature range. Another feature of these spectra, also common to Imi-*n*EO materials, is the gradual disappearance of the high-frequency N−H resonances, consistent with more protons becoming available for conductivity with increasing temperature as crystalline or locally ordered domains are consumed.[16]

Finally, we make special note of the chemical shift trend observed as a function of temperature. We have seen that the high-frequency N−H resonances disappear at high temperature and trend toward lower frequency. This trend can be interpreted as a coalescence process driven by exchange between the rigid and mobile domains. Coincidentally, the low-frequency resonance trends to continually lower frequency in poly(2-vinyl-4,5-dicyanoimidazole) (**2**). We interpret this as evidence for an increasingly dynamic hydrogen-bonding network with exchange between free and hydrogen-bonded imidazole rings occurring more rapidly at increased temperature.

These processes are common to our previous observations on the comparatively small Imi-*n*EO molecules. In both cases we conclude that local molecular motions (evident in the line narrowing of both the aliphatic/aromatic and N−H resonances) together with a dynamic hydrogen-bonding network evident in the coalescence processes and DQ behavior of the N−H resonances are necessary for proton conductivity to be achieved. For poly(2-vinyl-4,5-dicyanoimidazole) (**2**) a proton conductivity mechanism which combines "vehicle" (molecular diffusion) and Grotthus (structural diffusion) is a plausible hypothesis.

Conclusions

The combination of small molecule data and observations of polymer properties suggests that both the monomer and polymer are involved in extensive 1,3-hydrogen bonding. Both the monomer and polymer exhibit unusual complexity in their infrared spectra that can be attributed to this type of hydrogen bonding. In addition, an increase in the intrinsic viscosity and *a* value of poly(2-vinyl-4,5-dicyanoimidazole) (**2**) compared to poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) (**5**) illustrate the influence of hydrogen bonding. Using double-quantum-filtered solid-state NMR, we confirmed the presence of complex hydrogen bonding in poly(2-vinyl-4,5-dicyanoimidazole) (**2**) involving multiple types of hydrogen bonds. We have also seen evidence for proton mobility in the solid state. The NMR results may be used to guide our membrane formulations, and by observing the correlation with membrane conductivity measurements, we can develop a unique means of evaluating fuel cell membranes.

Experimental Section

Methods. Viscosity measurements were made in a constant-temperature bath using a Cannon (100−388H) viscometer. FT-IR spectra were collected with a Perkin-Elmer Spectrum BX FT-IR system (2 cm^{-1} resolution and 16 scans). KBr pellets were prepared. NMR data were collected on a 11.7 T magnet with a Bruker AV 500 spectrometer using a double-resonance MAS probe supporting rotors of 2.5 mm o.d. The resonance frequency of ^1H is 500.13 MHz. The samples were spun at 30 kHz. The $\pi/2$ pulse lengths were set to 2 μs. A recycle delay of 3 s was used. The spectra are referenced to adamantane (1.63 ppm, ^1H). Variable-temperature experiments were performed in the range of 250−370 K, bearing gas temperature, and the sample temperature was correct to include heating effects arising from the high-speed MAS. Five minutes were allowed following each temperature change to allow for equilibration of the sample.

Reagents and solvents were purchased from Aldrich or Fisher Scientific and used as received.

Characterization. *Partial Deuteration of 2-Vinyl-4,5-dicyanoimidazole (**3**).* To a 50 mL round-bottom flask fitted with a magnetic stir bar were added 2-vinyl-4,5-dicyanoimidazole (500 mg) and 30 mL of D_2O. A solution of 10% K_2CO_3 in D_2O was added until the pH reached approximately 9. The solution was allowed to stir for several hours and then acidified with DCl. The deuterated 2-vinyl-4,5-dicyanoimidazole was extracted using ethyl acetate. The combined extracts were dried with $MgSO_4$. The mixture was filtered, and the ethyl acetate filtrate was evaporated to dryness under reduced pressure. Note: Attempts to completely deuterate 2-vinyl-4,5-dicyanoimidazole lead to hydrolysis of the nitrile groups.

FW (calcd) 145.14; mp 176−180 °C; FT-IR (KBr pellet) 2924, 2859, 2636, 2240, 1639, 1493, 1423, 1356, 1297, 1261, 1068, 977, 954, 876, 823, 770.

*Poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) (**5**).* The monomer 1-methyl-2-vinyl-4,5-dicyanoimidazole (**4**) was polymerized in NMP using AIBN as a free-radical initiator. Polymerization details have been reported previously.[10,11]

*Poly(2-vinyl-4,5-dicyanoimidazole) (**2**).* For viscosity studies, **2** resulted from deprotection of poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) (**5**). For NMR studies, **2** resulted from the free-radical polymerization of 2-vinyl-4,5-dicyanoimidazole (**1**). Details of both methods have been previously reported.[10,11]

*Poly(2-vinyl-4,5-dicyanoimidazole) Electrolyte (**6**).* To a 500 mL round-bottom flask fitted with a magnetic stir bar were added poly(2-vinyl-4,5-dicyanoimidazole) (**2**; 3 g) and 100 mL of 1 M NH_4OH. The mixture was allowed to stir with gentle warming (60 °C) until the polymer completely dissolved.

Viscosity. The viscosities of poly(2-vinyl-4,5-dicyanoimidazole) (**2**) and poly(1-methyl-2-vinyl-4,5-dicyanoimidazole) (**5**) were measured with solutions ranging from 0.1 to 0.5 g/100 mL in DMF. The viscosity of the poly(2-vinyl-4,5-dicyanoimidazole) electrolyte (**6**) in NH_3 (aq) was measured with solutions ranging from 0.1 to 0.5 g/100 mL. Viscosity measurements were made in a constant-temperature bath using a Cannon (100−388H) viscometer.

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