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Self-Conducting Benzimidazole Oligomers for Proton Transport

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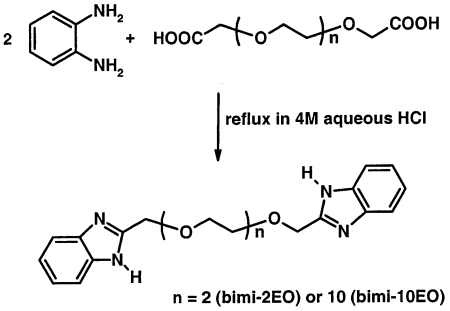
Proton-conducting polymers are key materials in applications such as polymer electrolyte fuel cells (PEMFCs), electrochemical sensors, and electrochromic devices.[1,2] The perfluorosulfonic acid polymer Nafion, marketed by DuPont, is one of the most extensively studied proton-conducting polymers for application in PEMFC because it combines mechanical, chemical, and thermal stability with a high proton conductivity under humidifying conditions.[3] However, the proton conduction in Nafion, and other similar polymers, relies on the high mobility of the water present in the material because the protons migrate in the hydrated state. Thus, the operating temperature of the PEMFC is essentially limited to temperatures below the boiling point of water.

It is possible to greatly simplify and improve the overall performance of the PEMFC system by increasing the operating temperature above 100 °C.[4,5] Consequently, it is attractive to develop new polymeric materials that conduct protons in the absence of water. Several different approaches have emerged during recent years, but the most investigated one is the complexation of strong oxo-acids with basic polymers. For example, successful work has been carried out with phosphoric acid complexed with polybenzimidazole.[6−9] The long-term durability of these electrolytes is, however, still questionable, as reliable data have not yet been published.

Perhaps the most attractive concept is to prepare self-conducting polymers carrying covalently immobilized heterocycles such as imidazole or benzimidazole.[10−12] On one hand, the conductivity of neat imidazole is higher than that of neat benzimidazole at a given temperature.[1] On the other hand, benzimidazole modified compounds are more accessible because they may be prepared through a convenient one-pot synthesis. Recently, Schuster and co-workers prepared and studied self-conducting ethylene oxide (EO) oligomers tethered to imidazole units.[11] Their results showed that immobilization has to be carried out in such a way that a high proton mobility is retained, because the proton transport relies completely on a structure diffusion mechanism where the heterocycles act as both proton acceptors and donors in a hydrogen bonded domain. In the present communication, we report on a model system consisting of EO oligomers tethered to benzimidazole units. The conductivity and the thermal behavior of two oligomers having 2 and 10 EO units in the chain between the benzimidazole units, denoted bimi-2EO and bimi-10EO, respectively, have been investigated.

Scheme 1. Preparation of Bimi-*n*EO



The EO oligomers were conveniently tethered to benzimidazole according to Scheme 1. 1,2-Benzenediamine and poly(ethylene glycol) bis(carboxymethyl) ether, both from Aldrich, were first dissolved in 4 M HCl, and then the solutions were refluxed under N_2 atmosphere for 48 h. During the reaction, the solutions changed color from red to dark blue. The products were precipitated in tetrahydrofuran, dissolved in methanol, and passed through a column with basic Al_2O_3, and finally carefully dried in a vacuum for several days. All further handling of the samples was done in a drybox.

The chemical structure of the purified bimi-*n*EOs was evaluated by ^{1}H NMR spectroscopy using a Bruker 400 MHz spectrometer. Characteristic signals from the benzimidazole protons were observed at $\delta = 7.5$ and $\delta = 7.8$ ppm, and signals arising from the ether protons appeared around $\delta = 3.5$ ppm. Integration of the characteristic signals showed that the reactions reached very high conversions, essentially 100% within the error limit of the method. Bimi-2EO was a powder-like material, whereas bimi-10EO was a highly viscous liquid. Analysis by differential scanning calorimetry showed that bimi-10EO was fully amorphous and displayed a single glass transition temperature (T_g), whereas bimi-2EO was semicrystalline and displayed a melting transition (Figure 1).

The proton conductivity was measured by complex impedance spectroscopy in the frequency range 10^{-1} to 10^7 Hz during cooling. Samples of bimi-2EO, pressed into tablets, and bimi-10EO, employed as a liquid, were sandwiched between two gold-plated stainless steel electrodes. As seen in Figure 2, the Arrhenius conductivity plots for the two oligomers showed convexly shaped curves, an indication that the proton conductivity was promoted by the segmental mobility. Basically, the bulk conductivity (σ) of an electrolyte can be

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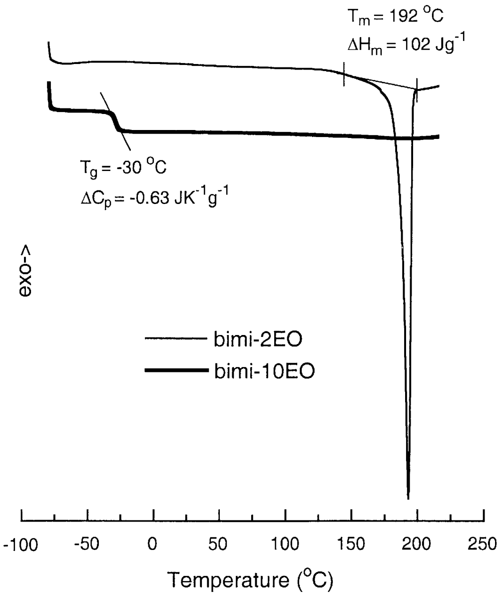

Figure 1. DSC heating traces of bimi-2EO and bimi-10EO, showing the fully amorphous nature of the latter oligomer and the semicrystalline nature of the former oligomer.

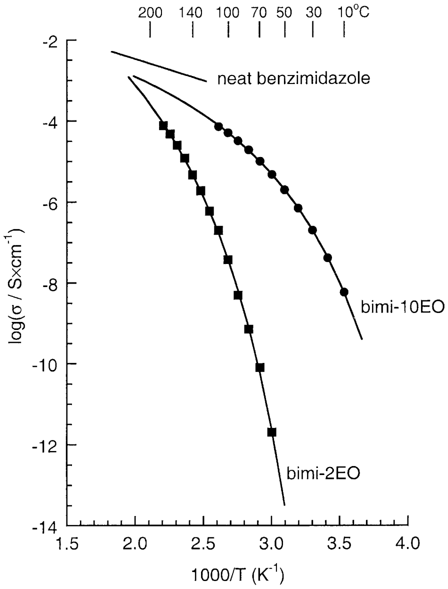

Figure 2. Influence of temperature on the proton conductivity of bimi-2EO and bimi-10EO as evaluated by impedance spectroscopy. The lines are VTF (eq 2) fits to the experimental values (markers). The data for neat benzimidazole were obtained from Kreuer (ref 1).

Table 1. VTF Parameters Obtained by Fitting Experimental Conductivity Data to Equation 2 (Correlation Coefficient > 0.9997)

	VTF parameters		
sample	log σ_0	$E_V \times 10^{-3}$ (Jmol^{-1})	T_V (K)
bimi-2EO	0.88	8.2	254
bimi-10EO	−1.17	4.2	212

obtained by a summation of the contributions of all the different charge-carrying species:

$$\sigma = \sum_i n_i \mu_i q_i \qquad (1)$$

where n denotes the number of charge carriers, μ is the mobility, and q represents the charge of the carriers. It is likely that the completely amorphous bimi-10EO had a lower degree of hydrogen bonding because of its lower concentration of benzimidazole units, as compared to bimi-2EO. It can therefore be assumed that the former oligomer had a higher local mobility at a given temperature. A recent high-resolution solid-state ^{1}H NMR study by Goward et al. indicates that the proton transport in imidazole-terminated oligomers occurs almost exclusively in the disordered amorphous phase.[13] As shown in Figure 2, the conductivity was higher for bimi-10EO in the temperature region studied because of a larger content of conductive amorphous phase, and also because of a higher segmental mobility. However, with increasing temperatures, the conductivity of bimi-2EO rapidly approached that of bimi-10EO because the concentration of benzimidazole units became increasingly important. Because the conductivity was linked to the segmental mobility, the temperature dependence of the conductivity followed the Vogel−Tamman−Fulcher (VTF) equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_V}{R(T - T_V)}\right) \qquad (2)$$

where σ_0 is the ultimate conductivity, E_V is the Vogel "activation" energy, R denotes the gas constant, T is the temperature, and T_V is the Vogel scaling temperature. The VTF parameters obtained by fitting the experimental data to eq 2 are contained in Table 1. It was noted that T_V was 42 K lower for bimi-10EO than for bimi-2EO, indicating a lower T_g of the former oligomer. The experimental data of benzimidazole and the fitted curves of the oligomers in Figure 2 suggested that the oligomers may reach values of conductivity that are just below those of neat benzimidazole at temperatures around 200 °C.

Schuster et al. have reported conductivities of 20−80 μScm^{-1} at 120 °C for EO oligomers tethered to imidazole units.[11] These values may be compared to 0.2 and 70 μScm^{-1} for bimi-2EO and bimi-10EO, respectively, at 110 °C. It is reasonable to believe that the conductivity of bimi-2EO might be greatly improved by suppressing the crystallinity, thus increasing the amorphous content, and also the mobility, in the material. The work by Schuster and co-workers also demonstrated the possibility of raising the conductivity considerably by doping the imidazole oligomers with strong acids.[11]

The results obtained with the present nonoptimized model compounds suggest that it might be possible to prepare self-conducting benzimidazole functional polymers with sufficiently high proton conductivities to make them interesting for application in PEMFCs at temperatures approaching 200 °C. Furthermore, these polymers may be prepared quite conveniently from carboxylic acid functionalized polymers by reactions with 1,2-benzenediamine. In this context, it is important to emphasize that these benzimidazole functional polymers must have a substantially higher stability than the EO oligomers, because of the chemically and thermally aggressive environment in the fuel cell.

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