Macromolecules **2005,** *38,* 3283−3289

Intrinsically Proton-Conducting Benzimidazole Units Tethered to Polysiloxanes

J. Christian Persson and Patric Jannasch*

Department of Polymer Science & Engineering, Lund University, P.O. Box 124,
SE-221 00 Lund, Sweden

Received December 7, 2004; Revised Manuscript Received January 31, 2005

ABSTRACT: Polysiloxanes with pendant benzimidazole units have been prepared by free radical thiol−ene coupling reactions of 2-(2-benzimidazolyl)ethanethiol and vinyl-functional polysiloxanes. The latter polymers were prepared by anionic ring opening copolymerization of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclosiloxane and 1,3,5-hexamethylcyclosiloxane. Copolymers with different degrees of benzimidazole functionality were conveniently obtained by varying the monomer ratios. The coupling reaction was found to be very efficient, and the vinyl groups were completely consumed, as confirmed by NMR and FTIR spectroscopy. The glass transition temperature (T_g) of the benzimidazole functional copolymers increased dramatically with the benzimidazole content at low contents to reach a plateau value just above 50 °C at a content of approximately 33 mol % benzimidazole functional siloxane residues in the copolymer. Conductivity measurements carried out at 60 and 140 °C indicated that the level of polymer segmental mobility, and thus the T_g, was the most decisive parameter for the proton conductivity at low temperatures (60 °C), while the benzimidazole concentration was more important at elevated temperatures (140 °C). A conductivity of 7×10^{-6} S/cm was reached at 140 °C by a polysiloxane carrying 57 mol % benzimidazole-grafted siloxane residues under completely anhydrous conditions.

Introduction

Proton-conducting polymers have a key function in many important technical devices, such as polymer electrolyte fuel cells (PEMFCs), electrochemical sensors, and electrochromic devices.[1,2] Especially PEMFC technology has attracted considerable interest due to its high energy efficiency and environmentally friendly qualities.[3,4] The polymer membranes in PEMFCs must be able to facilitate fast proton conduction and at the same time be thermally and mechanically stable. It is considerably more favorable to operate PEMFCs at high temperatures, e.g., above 100 °C, due to the many advantages reached at the system level.[3−5] The high proton conductivities reached by the membranes of today are mainly facilitated by water or other volatile low molecular weight compounds present in the polymer membrane. Consequently, a loss of these species will immediately result in a parallel loss of conductivity. For example, Nafion, the most widely used polymer membrane, quickly loses conductivity at temperatures above 100 °C due to the evaporation of water. The replacement of water by less volatile compounds is one possible way to improve the membranes to enable operation above 100 °C. For example, strong oxo acids, e.g., phosphoric acid and sulfuric acid, have been complexed with basic polymers such as polybenzimidazole.[6,7] However, since the potential risk of depleting the conducting phase still exists, many problems remain unsolved. There is consequently a need to explore new concepts and new polymeric materials that are capable of fast proton conduction in the absence of any volatile compounds, and that are durable at elevated temperatures.[8]

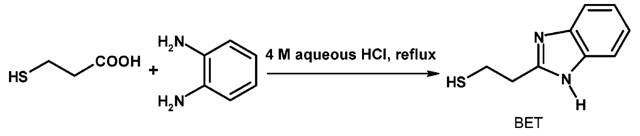
Kreuer has pointed out the possibility to develop fully polymeric proton-conducting membranes based on nitrogen-containing heterocycles.[2] Heterocycles such as imidazole, benzimidazole, and pyrazole have in many respects properties similar to those of water if compared relative to their respective melting points.[9] Especially the amphoteric behavior and the ability to form intermolecular hydrogen bonds are important characteristics which are related to the proton conductivity of both water and imidazoles. However, in contrast to water, the latter compounds may be covalently tethered to a suitable polymer. This allows for the preparation of fully polymeric materials in which the proton-conducting species are prevented from being leached out and lost. A crucial point when molecularly designing these polymers is to allow for a high local mobility of the heterocycles after the immobilization.[10,11] Thus, a sufficiently low glass transition temperature (T_g) seems to be essential to reach highly conductive systems. Immobilization of the heterocycles further implies that no proton transport can take place via a so-called vehicle mechanism, where the protons diffuse as protonated species through the material. Instead, the transport must rely entirely on structure diffusion where the protons are transferred between the charge-carrying heterocycles in a complex manner. This is similar to the "Grotthuss" mechanism of proton transfer, which is well-known for water.[12−14] Recently, Schuster et al. showed, using a series of model compounds with imidazole tethered to the chain ends of oligo(ethylene oxide)s, that it is possible to reach conductivities of 20−80 μS/cm at 120 °C in systems which rely only on structure diffusion.[10,11] In addition, similar oligomers based on benzimidazole tethered to both ends of oligo(ethylene oxide)s have recently been studied in our laboratory and were found to reach conductivities between 0.2 and 70 μS/cm at 110 °C, depending on the length of the oligo(ethylene oxide) spacer.[15] Furthermore, two fully polymeric proton conductors consisting of imidazole tethered to a polystyrene and benzimidazole tethered to a branched siloxane network have

---

* To whom correspondence should be addressed. E-mail: patric.jannasch@polymer.lth.se.

10.1021/ma047482+ CCC: $30.25

Scheme 1. Synthesis of 2-(2-Benzimidazolyl)ethanethiol (BET)



recently been investigated by Hertz et al.[16] Conductivities as high as 700 μS/cm at 200 °C were obtained for the former system.

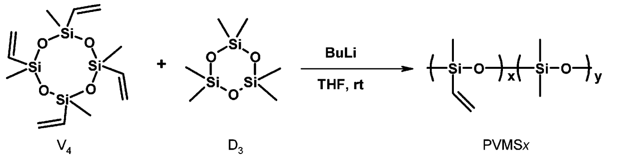
In the present work we have focused on linear polysiloxanes tethered with benzimidazole. Polysiloxanes have a high degree of segmental mobility and consequently low T_g values, and the stability issue of benzimidazole is less critical than that of imidazole. Several different procedures to tether various functional groups to polysiloxanes have been reported in the literature. For example, Hooper et al. have tethered oligo(ethylene oxide) chains onto a polysiloxane backbone by hydrosilylation.[17] In other studies functional groups have been tethered to polymers via thiol−ene free radical coupling reactions.[18−20] We have in the present work combined the excellent segmental mobility of the polysiloxanes with the intrinsic proton-conducting properties of benzimidazole to establish structure−property relationships for these new materials. For this reason, a modulated method of synthesis was chosen to conveniently obtain relevant model polymers with different molecular structures. A series of polymeric proton-conducting compounds were thus synthesized by tethering benzimidazole units onto polysiloxane backbones via short aliphatic thioether spacers. The polysiloxane precursor backbones were prepared by anionic ring opening polymerization, and the coupling reaction was subsequently performed via a thiol−ene free radical reaction. Polymers having different concentrations of benzimidazole were prepared by varying the composition of the precursor copolymers. The present paper focuses on the synthesis and structural characterization of these novel polymers. In addition, the solubility and the thermal properties, as well as proton conductivity data, will be discussed. In a future paper we will report and discuss the conductivity behavior and the effect of doping the benzimidazole-tethered polymers with selected oligomeric and polymeric acids.

Experimental Section

Synthesis of 2-(2-Benzimidazolyl)ethanethiol. 2-(2-Benzimidazolyl)ethanethiol (BET) was readily prepared by reacting a slight excess of 3-mercaptopropionic acid (Aldrich, 99+%) with 1,2-diaminobenzene (Aldrich, 98%) in 4 M aqueous HCl at 100 °C during 40 h of reflux as shown in Scheme 1. In a typical synthesis procedure, 7.83 g (73.8 mmol) of 3-mercaptopropionic acid was reacted with 6.57 g (60.8 mmol) of 1,2-diaminobenzene in 30 mL of a 4 M HCl solution. After the reaction, distilled water was added to the mixture to obtain a total volume of 500 mL. After neutralization using the required volume of a 4 M aqueous NaOH solution, the BET precipitated as a white powder. Finally, the product was carefully rinsed with water to remove excess 3-mercaptopropionic acid and salt.

Preparation of the Copolymers. The precursor copolymers were synthesized by copolymerizations of cyclosiloxanes. The monomers 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclosiloxane (V_4) (≥97%) and 1,3,5-hexamethylcyclosiloxane (D_3) (98%) were purchased from Fluka and Aldrich, respectively, and were used without further purification. Anionic ring opening copolymerizations of V_4 and D_3 using different monomer ratios were carried out in anhydrous THF (Labscan, 99.8%) at room temperature according to Scheme 2. The THF was stored above molecular sieves prior to use. Before initiation using a 2.5 M solution of *n*-butyllithium (Acros), the reaction solution was cooled to −40 °C, carefully degassed, and left under a blanket of argon. All reactions were run for 40 h under an argon atmosphere, and the polymerizations were finally terminated by addition of a small excess of Me_3SiCl (Aldrich, 98%). The polymer products were precipitated twice in MeOH to remove unreacted species, and then dried under vacuum to remove the remaining solvent.

Scheme 2. Preparation of PVMS*x* by Anionic Ring Opening Copolymerizations of the Monomers V_4 and D_3



The copolymer samples were designated PVMS*x*, where *x* denotes the mole percent of vinylsiloxane residues in the polymer, as determined by ^1H NMR spectroscopy. In the study, a commercial PVMS copolymer (United Chemical Technologies, Inc.) containing 5 mol % vinylsiloxane residues was also included. The polymers were characterized by NMR spectroscopy and chromatography, as described below. Table 1 summarizes some general structural data of the PVMS copolymers.

Tethering Benzimidazole Functionalities onto the PVMS Copolymers. A 100 mL two-necked, round-bottomed glass reactor was fitted with a heater and reflux condenser and was further equipped with a magnetic stirrer. The reactants were dissolved in THF and then transferred to the reactor. The temperature was slowly increased to the boiling point of THF (66 °C), and the reactor was carefully degassed with N_2 before the initiation of the reaction. The reactions were performed under reflux in THF using an excess of BET, and 2,2′-azobis(2-methylpropionitrile) (AIBN) (Acros, 98%) as the radical source. The relative amounts of the reactants corresponded to the molar ratio [thiol]:[vinyl]:[AIBN] equal to 10:5:3. A slight overpressure of N_2 gas was kept in the reactor during the reaction to avoid air. All reactions were carried out for 40 h to convert all the vinyl groups into thioether links. In accordance with the designation of the PVMS copolymers, the benzimidazole-functionalized polymers were designated as bimiPVMS*x*, where *x* denotes the molar percentage of benzimidazole-grafted siloxane residues in the polymer. After the reaction, bimiPVMS5 and bimiPVMS16 were precipitated in methanol (PROLABO, >98.5%) while bimiPVMS33 and bimiPVMS57 were precipitated in ethyl acetate (KEBO, >99.5%) because of the higher benzimidazole content of the latter. Finally, the samples were carefully dried under vacuum and stored in an argon-filled glovebox until analysis.

Characterization. ^1H and ^{13}C NMR spectra were recorded with a Bruker 400 MHz spectrometer using chloroform-*d* or dimethyl sulfoxide-d_6 as solvent depending on the benzimidazole content of the samples (bimiPVMS5 and bimiPVMS16, chloroform; bimiPVMS33 and bimiPVMS57, DMSO). The compositions of the copolymers and the results of the coupling reactions were determined by comparing the integrated NMR signals from the vinyl protons and the $SiCH_3$ protons. The PVMS copolymer compositions are shown in Table 1. To determine the origin of the different signals, various correlation experiments were also performed, including $^1H-^1H$ correlation ($^1H-^1H$ COSY) and $^1H-^{13}C$ heteronuclear multiple quantum coherence (HMQC). Infrared spectra were obtained using a Bruker IFS 66 FTIR spectrometer with the samples in the form of pressed tablets of ground mixtures of polymer and KBr salt, or directly applied films of viscous liquids on KBr tablets. The samples were subsequently analyzed in transmission mode at a resolution of 4 cm^{-1}.

Differential scanning calorimetry (DSC) measurements were performed using a TA Q1000 instrument. The samples were carefully dried in a vacuum oven and then quickly transferred to aluminum sample pans which were hermetically sealed. The

Table 1. Copolymerization and PVMS*x* Data

copolymer	monomer feed ratio [V_4]/[D_3]	copolymerization time (h)	copolymer composition[a] (mol % vinylsiloxane residues, *x*)	M_n[b]	M_w/M_n
PVMS5[c]			5	13300	2.2
PVMS16	0.5	40	16	15800	1.4
PVMS33	1.125	40	33	10600	1.4
PVMS57	3	40	57	10800	1.3

[a] Determined by ^{1}H NMR. [b] Determined by size exclusion chromatography (SEC) using polystyrene standards. [c] Commercial sample obtained from United Chemical Technologies, Inc.

samples were analyzed at a scan rate of 10 °C/min from −90 to +250 °C. To investigate the thermal stability of the copolymers, thermogravimetric analysis (TGA) was performed on a TA Q500 analyzer under nitrogen purge from room temperature to 600 °C at a heating rate of 10 °C/min.

The neat PVMS copolymer samples were analyzed by size exclusion chromatography (SEC). Three Shodex columns in series (KF-805, -804, and -802.5) and a refractive index detector were employed in the setup. All chromatograms were recorded at room temperature and at a THF elution rate of 1 mL/min. The calibration was based on polystyrene standards purchased from Polymer Laboratories, Ltd.

The solubility of the different bimiPVMS*x* samples was investigated by placing pieces of dry samples in a range of selected solvents contained in test tubes. The samples were then left for 24 h at 22 °C. If the samples were then found to be completely dissolved after visual inspection, they were considered as soluble; if not they were considered as nonsoluble.

To measure the proton conductivity of the bimiPVMS samples, they were sandwiched between two gold-plated electrodes, either as a liquid or as a pressed tablet. Carefully dried samples were prepared in an argon-filled glovebox to avoid water contamination. The sample dimensions were defined by circular Teflon spacers having thicknesses ranging from 100 to 250 μm, and diameters between 10 and 12 mm. Conductivity data were collected at 60 and 140 °C using a Novocontrol high-resolution dielectric analyzer in the frequency range 10^{-1} to 10^7 Hz at a voltage amplitude of 1.0 V. The dc conductivities were then determined at the frequency that corresponded to the minimum imaginary response in complex conductivity plots.[21]

Results and Discussion

Copolymer Synthesis. Polysiloxanes tethered with benzimidazole units via short aliphatic thioether spacers were prepared and characterized as intrinsic proton conductors. The syntheses were performed in three steps involving first preparation of BET, then copolymerizations of the monomers V_4 and D_3 to form PVMS copolymers, and finally thiol−ene coupling reactions between the PVMS copolymers and the BET.

BET was synthesized by reacting 3-mercaptopropionic acid with 1,2-diaminobenzene under acidic conditions, as shown in Scheme 1. BET was subsequently characterized by ^{1}H NMR spectroscopy, and characteristic shifts from the protons of the benzimidazole unit and the carbon chain were observed (Figure 1). The integrals of the signals corresponded well to the relative number of the various protons in BET. It was also noted that the signal from the thiol proton was absent. Moreover, no signals from residual reactants were detected, which indicated a high purity of the product. Analysis of the reaction mixture by FTIR spectroscopy showed that the strong absorption of the carbonyl group at 1700 cm^{-1} gradually disappeared as the reaction proceeded (not shown). Simultaneously, absorption bands from the imidazole ring appeared at around 1540 cm^{-1} (N−H) and at 1623 cm^{-1} (C=N).

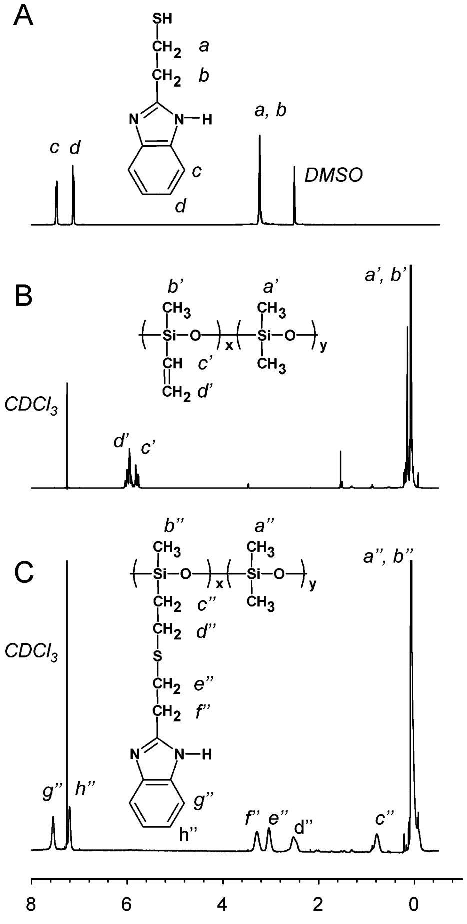
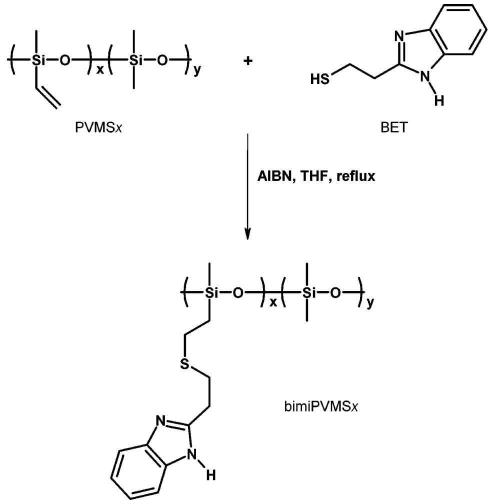


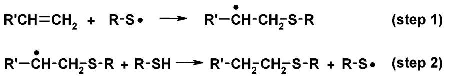
Figure 1. ^{1}H NMR spectra of BET (A), PVMS16 (B), and bimiPVMS16 (C). Please note the absence of the shifts from the vinyl protons in spectrum C, indicating the complete conversion of the vinyl groups in the coupling reaction.

Three PVMS copolymer samples with different compositions were prepared by anionic ring opening copolymerization (Scheme 2). Also, a commercial PVMS sample was included in the investigation (PVMS5). The compositions of the copolymers were determined by comparing the integrated ^{1}H NMR signals from the protons of the vinyl groups between 5.7 and 6.1 ppm with the integrated signal of the $SiCH_3$ protons at approximately 0.1 ppm. It should be pointed out that the vinylsiloxane residues were arranged in groups of four due to the structure of the monomer V_4. We were not able to determine the sequence distribution of the vinylsiloxane residues in the present samples. However, it was observed in our experiments that the ratio of V_4 residues in the copolymers was below the monomer feed ratio of the V_4 monomer charged to the reactor at the start of the copolymerizations. This suggested that the reactivity of V_4 was lower than the reactivity of D_3 under

Scheme 3. Preparation of Benzimidazole-Grafted Polydimethylsiloxane via the Free Radical Thiol–Ene Coupling Reaction



Scheme 4. Proposed Reaction Steps in the Thiol–Ene Coupling Reaction[23,24]



$$R'CH{=}CH_2 + R\text{-}S\bullet \longrightarrow R'\text{-}\overset{\bullet}{C}H\text{-}CH_2\text{-}S\text{-}R \quad \text{(step 1)}$$

$$R'\text{-}\overset{\bullet}{C}H\text{-}CH_2\text{-}S\text{-}R + R\text{-}SH \longrightarrow R'\text{-}CH_2\text{-}CH_2\text{-}S\text{-}R + R\text{-}S\bullet \quad \text{(step 2)}$$

these conditions. This is in agreement with the finding of Herczynska et al., who also observed a lower reactivity of V_4 than that of D_3 during anionic copolymerization in toluene, which caused concentration gradients of vinylsiloxane units along the copolymer chains.[22] As seen in Table 1, the molecular weights of the PVMS copolymers prepared in this study ranged from 10 600 to 15 800, and the polydispersity index (PDI) was in the range from 1.3 to 1.4 when calibrated with polystyrene standards. The lower molecular weight of the vinyl-rich copolymers was probably a direct consequence of the lower reactivity of the monomer V_4 as compared to D_3.

As shown in Scheme 3, the coupling reaction between PVMS and BET was achieved via a free radical thiol–ene coupling reaction. The coupling reaction has been reported to involve the propagation of a thiyl radical through the vinyl groups of the PVMS copolymers.[23,24] A new thiyl radical is then regenerated by chain transfer from the resulting carbon radical to a thiol, as outlined in Scheme 4. The modifications of the PVMS copolymers were monitored by observing the disappearance of the ^{1}H NMR signal arising from the protons of the vinyl groups (Figure 1). Simultaneously, signals from the protons of the thioether chain and the benzimidazole unit emerged as the reaction proceeded. After 40 h of reaction, all vinyl groups had been efficiently converted into thioether links. It was also possible to monitor the reaction by following the disappearance of the absorption from the CH_2 wag vibration of the vinyl group at 960 cm^{-1}, using FTIR (Figure 2). Furthermore, the IR absorption bands from the N–H deformation and C=N in the imidazole rings of the product were observed at 1540 and 1623 cm^{-1}, respectively. In addition, the complete conversion was confirmed by ^{13}C NMR by observing the disappearance of the shifts arising from the vinyl carbons (not shown). All the bimiPVMS*x* samples were slightly yellow after the purification. It was noted that bimiPVMS5 was a highly viscous liquid, bimiPVMS16 was a soft solid, and the other samples were quite brittle solid materials at room temperature.

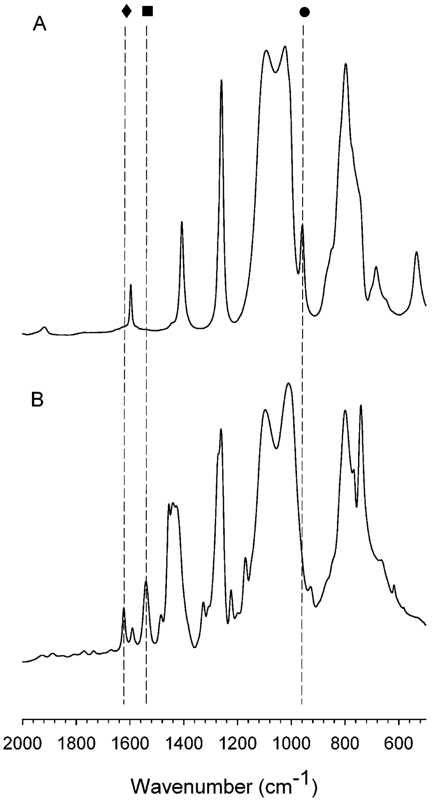


Figure 2. FTIR spectra of PVMS57 (A) and bimiPVMS57 (B). The dashed lines indicate the positions of the absorption peaks arising from $-CH{=}CH_2$ (●), imidazole N–H deformation (■), and imidazole C=N (◆).

Copolymer Solubility. The solubility of the bimiPVMS*x* copolymers was investigated in a wide range of solvents. Expectedly, the solubility was highly dependent on the degree of benzimidazole functionalization (x) of the copolymers. The solubilities of the various samples in a number of selected solvents, arranged according to their hydrogen-bonding capacity and solubility parameter (δ), are shown in Table 2. As anticipated, due to their hydrophobicity, the PVMS copolymers were readily soluble in toluene, but not in hydrogen-bonding solvents such as methanol. The solubility properties then changed quite dramatically as increasing amounts of benzimidazole were incorporated and the polymers became increasingly hydrophilic and hydrogen bonded. Sample bimiPVMS57 was soluble in methanol but not in toluene, which was the reverse situation compared to that found for the PVMS copolymers. Because of its amphoteric and hydrogen-bonding character, the presence of benzimidazole promoted the solubility of the copolymers in polar and hydrogen-bonding solvents. It was noted that the bimiPVMS*x* copolymers were all soluble in the moderately hydrogen-bonding THF and in the strongly hydrogen-bonding 1-butanol, while no copolymers were soluble in acetonitrile or water. Also, it was found that the solubility of the copolymers in methanol was the reverse of that in diethyl ether and chloroform. It was finally observed that all the solutions foamed when shaken, which indicated that the copolymers had an amphiphilic character.

Thermal Properties. All the bimiPVMS*x* copolymers were fully amorphous materials and showed single glass transition temperatures (T_g). As shown in Figure 3, the T_g values of the bimiPVMS*x* copolymers increased dramatically in comparison to those of the PVMS copolymers. The latter copolymers all showed a T_g close

Table 2. Solubility of the bimiPVMS*x* Samples at 22 °C

	solvent[a]								
polymer sample	water, $\delta = 48$ (s)	methanol, $\delta = 30$ (s)	1-butanol, $\delta = 23$ (s)	DMSO, $\delta = 25$ (m)	THF, $\delta = 19$ (m)	diethyl ether, $\delta = 15$ (m)	acetonitrile, $\delta = 24$ (p)	chloroform, $\delta = 19$ (p)	toluene, $\delta = 18$ (p)
PVMS5	−	−	−	−	+	+	−	+	+
bimiPVMS5	−	−	+	−	+	+	−	+	+
bimiPVMS16	−	−	+	+	+	+	−	+	+
bimiPVMS33	−	+	+	+	+	−	−	−	−
bimiPVMS57	−	+	+	+	+	−	−	−	−

[a] The symbols "+" and "−" indicate solubility and nonsolubility, respectively. Solubility parameters (δ, MPa$^{1/2}$) were obtained from the *Polymer Handbook*,[25] and the letters s, m, and p denote strongly, moderately, and poorly hydrogen-bond-forming solvents, respectively.

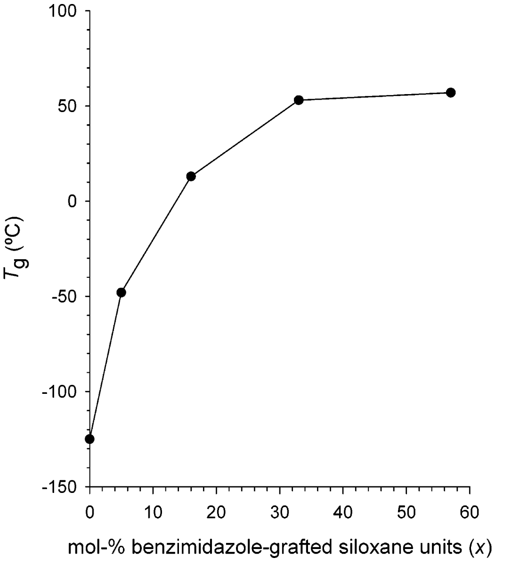


Figure 3. Influence of the benzimidazole content of the bimiPVMS*x* copolymers on the T_g, as evaluated by DSC.

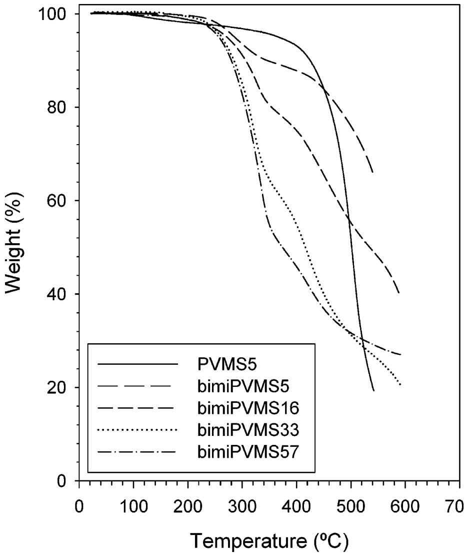


Figure 4. Thermal stability as evaluated by TGA under nitrogen.

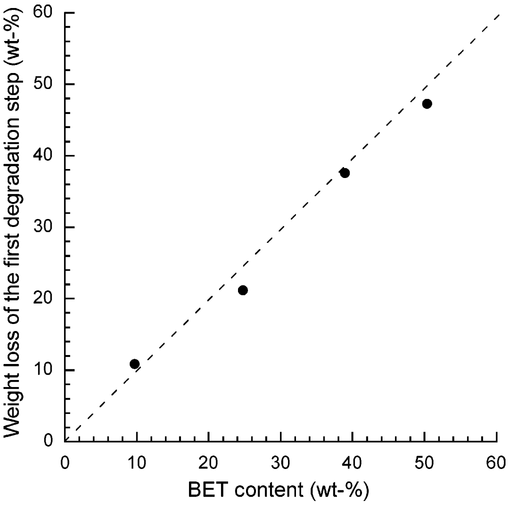


Figure 5. Weight loss of the first degradation step recorded by TGA as a function of the BET content of the bimiPVMS copolymers. The dashed line indicates the diagonal of the plot ($x = y$).

to −125 °C, while bimiPVMS57 had a T_g at 57 °C, as measured by DSC. The major reason for the large increase of the T_g was most likely the result of the very strong hydrogen-bonding character of the benzimidazole units, causing both intra- and intermolecular hydrogen-bonding interactions. The hydrogen bonds between the benzimidazole units thus suppressed the mobility of the polymer chain segments to a large extent. However, after approximately 33 mol % benzimidazole-grafted siloxane residues was reached, the effect of additional benzimidazole on T_g seemed to stabilize, and the T_g values leveled out to reach a plateau at around 53 °C. This implies that it might be possible to incorporate additional benzimidazole units without any further significant increase of T_g, which may favor high conductivities at high temperatures.

The DSC analysis also revealed a weak exothermic peak at approximately 165 °C for both the PVMS and the bimiPVMS copolymers. These exotherms were, after DSC heating−cooling−heating cycles, found to be irreversible and might arise from limited degradation reactions. A similar exothermic peak was found at 250 °C for a neat poly(dimethylsiloxane) sample, indicating the limited thermal stability of polysiloxanes. In this context it is important to note that the conductivity measurements discussed below were carried out below 150 °C.

Figure 4 shows the traces from the thermogravimetrical analysis of the bimiPVMS*x* samples carried out under a nitrogen atmosphere. The first weight loss occurred at temperatures above 200 °C, and was found to increase with the content of benzimidazole-grafted siloxane residues (*x*). Indeed, the magnitude of this weight loss was nicely found to be equivalent to the BET content of the bimiPVMS copolymers, as shown in Figure 5. This indicated the relatively weak nature of the C−S−C bonds. The second weight loss occurred at about 360 °C and most probably involved a drastic degradation of the polysiloxane backbones. In fuel cells, where both oxidative and reducing conditions are present in combination with high temperatures, the material must be durable enough to resist the aggressive environment. Here it should again be emphasized that the materials prepared and studied in the present investi-

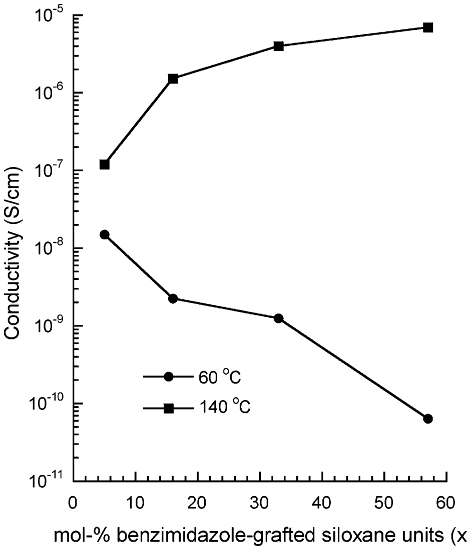


Figure 6. Influence of the benzimidazole content of the bimiPVMSx copolymers on the proton conductivity at 60 and 140 °C.

gation were model polymers to establish structure−property relationships which may serve as guidelines for the molecular design of materials intended for use in fuel cells. Having said this, it might be possible to improve the stability of the C−S−C bonds in the present case by converting the weak thioether links to sulfoxide or sulfone links through carefully controlled oxidations.[26,27] The latter links are known to have a much higher chemical stability than the thioether link.

Proton Conductivity. The proton conductivity was measured by impedance spectroscopy with the bimiPVMS*x* samples sandwiched between two gold-plated electrodes. The bulk conductivity (σ) of a sample can be described as the sum of the contributions of all the charge-carrying species according to

$$\sigma = \sum_i n_i \mu_i q_i \tag{1}$$

where n is the number of charge carriers, μ is their mobility, and q is the electric charge of the carriers. Figure 6 shows the influence of the benzimidazole content (x) on the proton conductivity at 60 and 140 °C. At 60 °C, bimiPVMS5 displayed a superior conductivity because of its higher segmental mobility (lower T_g) and the conductivity gradually decreased when the benzimidazole content was increased. However, at 140 °C the situation was reversed. At this temperature the conductivity of bimiPVMS57 was the highest because of its higher benzimidazole content. The more pronounced temperature dependence of the copolymers with high benzimidazole content indicated higher activation energies for the proton transport in these systems. This shows that the proton carrier density and the segmental mobility are closely interconnected in this kind of system. An increase in the benzimidazole content caused a suppression of the segmental mobility in the polymers, and vice versa, which was consistent with the dramatic increase of the T_g, as seen in the DSC study. It is therefore necessary to reach a suitable balance between the charge carrier density and the segmental mobility if these kinds of materials are to be used in a broad temperature interval.

As mentioned above, the influence of the benzimidazole content on the T_g seemed to stabilize at high contents, and the difference in T_g between bimiPVMS33 and bimiPVMS57 was only 4 °C. A further increase of the benzimidazole content will thus increase the number of proton carriers without suppressing the segmental mobility significantly. If the material is to be used at high temperatures, e.g., 140 °C, it may be considered advantageous for the conductivity to incorporate a maximum amount of proton-carrying species. However, as seen in Figure 6, the increase of the conductivity with the concentration of benzimidazole seems to level off at high concentrations.

Hertz et al. have previously reported conductivities of approximately 30 μS/cm at 140 °C and 0.2 μS/cm at 70 °C for a fully polymeric material based on benzimidazole tethered to an inorganic siloxane network polymer via flexible spacers.[16] This value may be compared with that of the sample with the highest conductivity in our study, bimiPVMS57, reaching conductivities of 7 μS/cm at 140 °C and 0.6 nS/cm at 70 °C. The higher conductivity in the former system might be due to the longer spacer units, which facilitated the local mobility of the benzimidazole units. However, it is difficult to make a detailed analysis because no data, e.g., on the T_g of the benzimidazole-tethered polysiloxane networks, were reported. We have previously reported a conductivity of 70 μS/cm at 110 °C for benzimidazole tethered to oligo(ethylene oxide) chain ends.[15] It should be noted, however, that the T_g of this oligomer was −30 °C, which was considerably lower than for bimiPVMS57. As demonstrated by Schuster et al., there are possibilities to further improve the conductivities of imidazole-based systems by doping the materials through addition of suitable acidic species which introduce excess protons into the hydrogen-bonded networks.[10,11]

Conclusions

Benzimidazole units have been tethered to polysiloxanes via short aliphatic thioether spacers to obtain samples to study structure−property relationships for this kind of intrinsically proton-conducting polymer. The conversion of the vinyl groups of the PVMS copolymers into thioether links proceeded readily via thiol−ene coupling, and was quantitative in all experiments. The functionalizations resulted in a dramatic increase of the T_g, which can be explained by the strong intra- and intermolecular interactions existing between the tethered benzimidazole units. All samples were shown to be stable up to 165 °C under nitrogen purge according to DSC data. Obviously, in comparison to the present samples, the thermal stability needs to be greatly improved to withstand the aggressive chemical and physical conditions in a fuel cell. The proton conductivity was found to be promoted by high benzimidazole contents and low T_g values. These parameters are however conflicting in the present materials. Generally, low benzimidazole contents will result in low T_g values, but also in low proton carrier concentrations. On the other hand, high benzimidazole contents will provide more efficient paths for the proton transport due to the higher carrier concentrations, but will be accompanied by unfavorably high T_g values. A maximum conductivity of 7 μS/cm at 140 °C was reached by the studied copolymers under completely dry conditions. However, doping with suitable polymeric and oligomeric acids is expected to increase the conductivity, and this will be the next step in our investigation of these new materials. Also, the effects of spacer length and the nature of the spacer still remain to be explored.

Acknowledgment. We thank the Swedish Research Council for financial support.

References and Notes

(1) Kreuer, K. D. *Chem. Mater.* **1996**, *8*, 610−641.
(2) Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29−39.
(3) Yang, C.; Costamagna, P.; Srinivasan, S.; Benziger, J.; Bocarsly, A. B. *J. Power Sources* **2001**, *103*, 1−9.
(4) Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345−352.
(5) Jannasch, P. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 96−102.
(6) Wang, J. T.; Savinell, R. F.; Wainright, J.; Litt, M.; Yu, H. *Electrochim. Acta* **1996**, *41*, 193−197.
(7) Bozkurt, A.; Ise, M.; Kreuer, K. D.; Meyer, W. H.; Wegner, G. *Solid State Ionics* **1999**, *125*, 225−233.
(8) Kreuer, K. D.; Paddison, S. J.; Spohr, E.; Schuster, M. *Chem. Rev.* **2004**, *104*, 4637−4678.
(9) Kreuer, K. D.; Fuchs, A.; Ise, M.; Spaeth, M.; Maier, J. *Electrochim. Acta* **1998**, *43*, 1281−1288.
(10) Schuster, M.; Meyer, W. H.; Wegner, G.; Herz, H. G.; Ise, M.; Schuster, M.; Kreuer, K. D.; Maier, J. *Solid State Ionics* **2001**, *145*, 85−92.
(11) Schuster, M. F. H.; Meyer, W. H.; Schuster, M.; Kreuer, K. D. *Chem. Mater.* **2004**, *16*, 329−337.
(12) Agmon, N. *Chem. Phys. Lett.* **1995**, *244*, 456−462.
(13) Tuckerman, M.; Laasonen, K.; Sprik, M.; Parrinello, M. *J. Phys. Chem.* **1995**, *99*, 5749−5752.
(14) Munch, W.; Kreuer, K. D.; Silvestri, W.; Maier, J.; Seifert, G. *Solid State Ionics* **2001**, *145*, 437−443.
(15) Persson, J. C.; Jannasch, P. *Chem. Mater.* **2003**, *15*, 3044−3045.
(16) Herz, H. G.; Kreuer, K. D.; Maier, J.; Scharfenberger, G.; Schuster, M. F. H.; Meyer, W. H. *Electrochim. Acta* **2003**, *48*, 2165−2171.
(17) Hooper, R.; Lyons, L. J.; Moline, D. A.; West, R. *Organometallics* **1999**, *18*, 3249−3251.
(18) Scibiorek, M.; Gladkova, N. K.; Chojnowski, J. *Polym. Bull.* **2000**, *44*, 377−384.
(19) Herczynska, L.; Lestel, L.; Boileau, S.; Chojnowski, J.; Polowinski, S. *Eur. Polym. J.* **1999**, *35*, 1115−1122.
(20) RozgaWijas, K.; Chojnowski, J.; Boileau, S. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 879−888.
(21) Bruce, P. G. In *Polymer Electrolyte Reviews*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science Publishers Ltd.: New York, 1987; pp 237−274.
(22) Herczynska, L.; Chojnowski, J.; Lacombe, L.; Lestel, L.; Polowinski, S.; Boileau, S. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 137−145.
(23) Pojman, J. A.; Varisli, B.; Perryman, A.; Edwards, C.; Hoyle, C. *Macromolecules* **2004**, *37*, 691−693.
(24) Cramer, N. B.; Reddy, S. K.; O'Brien, A. K.; Bowman, C. N. *Macromolecules* **2003**, *36*, 7964−7969.
(25) Brandrup, J., Immergut, E. H., Grulke, E. A., Eds. *Polymer Handbook*, 4th ed.; Wiley-Interscience: New York, 1999.
(26) Allcock, H. R.; Olmeijer, D. L. *Macromolecules* **1998**, *31*, 8036−8046.
(27) Oyama, T.; Naka, K.; Chujo, Y.; *Macromolecules* **1999**, *32*, 5240−5242.

MA047482+