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Polymer 47 (2006) 991–998

polymer

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Polysulfones tethered with benzimidazole

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Received 19 August 2005; received in revised form 16 December 2005; accepted 19 December 2005

Abstract

Benzimidazole units have been grafted onto a polysulfone (PSU) backbone via long alkyl thio–ether chains using a two-step procedure. In the first step, lithiated PSU was reacted with 10-undecenoyl chloride to graft PSU with undecenoyl side chains. The second step involved a free-radical thiol–ene coupling reaction between the C=C bonds of the pendant undecenoyl chains and 2-(2-benzimidazolyl)ethanethiol. In this reaction, all the C=C bonds were converted into thio–ether linkages without any detectable structural degradation, as confirmed by ^{1}H NMR spectroscopy and size-exclusion chromatography. The procedure constitutes a convenient and general pathway to attach functional or mesogenic groups to PSU via long flexible spacers. Thermogravimetry showed that the benzimidazole-functionalized polymers were stable up to 250 °C under nitrogen atmosphere, and that the first degradation step was attributed to the cleavage of the thio–ether bond. While the grafting of the undecenoyl side chains was found to significantly decrease the glass transition temperature (T_g), the subsequent tethering of the benzimidazole only slightly increased the T_g of the grafted PSU backbone. The concentration of benzimidazole was probably too low for the formation of a percolating benzimidazole domain. This explains the quite modest proton conductivity measured under completely dry conditions, e.g. 34 nS/cm at 180 °C for a polymer functionalized with 1.7 benzimidazole units per repeating unit of PSU.

Keywords: Thiol–ene coupling reactions; Grafting of imidazoles; Anhydrous proton conducting electrolyte membranes

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1. Introduction

Benzimidazole and its simple derivatives are planar, bi- and heterocyclic compounds that exhibit high melting points and thermal stability [1]. Like other nitrogen-containing heterocycles, such as imidazole and pyrazole, benzimidazole has an amphoteric nature, and may thus show both basic and acidic characteristics [1,2]. Furthermore, benzimidazoles typically form intermolecular hydrogen bonds, which results in higher melting points than would be expected from comparable non-hydrogen bonding compounds [1]. Fast intermolecular exchange of protons occurs between the benzimidazole molecules via the formation and breaking of hydrogen bonds, very much in the same way as described by the Grotthuss mechanism thoroughly described for water [1–5]. Because of their quite unique properties, benzimidazole derivatives have found a wide range of use, e.g. as fungicidal and antimicrobial agents [6,7], as high-performance polymers such as polybenzimidazoles [8], and as so-called 'proton pump inhibitors' used to decrease the amount of acid produced in the stomach in order to treat gastric acid related diseases, e.g. peptic ulcer [9].

The high inherent stability, amphoteric characteristics, and the ability to form hydrogen bonds have made benzimidazole-containing polymers attractive for use in fuel cell membrane applications. For example, fuel cell membranes based on polybenzimidazoles and phosphoric acid are currently extensively studied and developed [10–13]. In addition, Kreuer et al. have quite recently suggested heterocycles such as pyrazole, imidazole, and benzimidazole as the proton conducting moieties in intrinsically conducting, all-polymeric materials [2]. Since then a number of different oligomeric and polymeric systems with covalently linked heterocycles have been evaluated as proton conductors under essentially water-free conditions [14–18]. For example, we have previously reported on the synthesis and properties of polysiloxanes with pendant benzimidazole units, which reached proton conductivities of 14 μS/cm at 150 °C under completely anhydrous conditions [17]. The research on polymers containing covalently linked heterocycles shows that these groups have to be introduced into the polymer structures in such a way that a high local mobility. The reason is that the proton transport relies completely on a structure diffusion mechanism where the heterocycles act both as proton acceptors and donors in hydrogen bonded domains [14,15]. By tethering the heterocycles via flexible side chains,

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0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.12.077

or spacers, they are separated from the polymer backbone, which allows for a high local mobility.

The conditions in a fuel cell are quite demanding and require membrane materials, which have excellent mechanical, thermal, and chemical stability [19–21]. The polymers tethered with heterocycles studied up until now may be regarded as model systems with a rather limited thermo-chemical stability. It is therefore important to develop methods to tether, e.g. benzimidazole, to aromatic main-chain polymers which possess the necessary stability for use in fuel cells, and to study their structure–property relationships. Polysulfones (PSU's) constitute a class of low-cost, high-performance aromatic main-chain polymers that exhibit excellent chemical, mechanical and thermal properties [22]. These polymers can be readily modified, which make them versatile for use as functional membrane materials [23]. For example, both sulfonated [24–26] and phosphonated [27,28] PSU's have been prepared and investigated as ionomer membrane materials for fuel cells. In the current paper, we present a procedure to tether benzimidazole to a PSU backbone. The procedure involved grafting of long side chains having terminal C=C groups, followed by coupling of benzimidazole to these C=C groups. This general scheme can also be used to tether other functionalities onto PSU via long spacer units. The resulting polymers were characterized with respect to their thermal properties, solubility, and proton conductivity.

2. Experimental section

2.1. Grafting of undecenoyl side chains onto PSU

PSU was grafted with undecenoyl side chains by lithiation, followed by electrophilic reaction with 10-undecenoyl chloride (UD, Aldrich, 98%), according to Scheme 1. An amount of 1.5 g of PSU (Aldrich, $M_n = 26{,}000$ g/mol) was first dissolved in 100 ml anhydrous THF (Labscan, 99.8%, stored above molecular sieves for 1 week) in a 250 ml reactor equipped with thermometer, an Ar gas inlet/outlet and a septum. The solution was carefully degassed several times and then cooled to approximately −40 °C using dry-ice in isopropanol. Next, the solution was carefully titrated with *n*-butyllithium (BuLi, 2.5 M in hexane, Acros) until a yellow color persisted, before adding the appropriate amount of BuLi via a syringe. After 30 min, a 1.5-fold excess of UD was added and the reaction solution was left to react for another 60 min before the product was precipitated twice in MeOH (Prolabo, >99.8%) in order to remove the excess UD. The grafted samples were designated as ud*x*PSU, where *x* denoted the degree of substitution, i.e. the average number of undecenoyl side chains per repeating unit of PSU. The amounts of the reactants charged in the three modifications are given in Table 1.

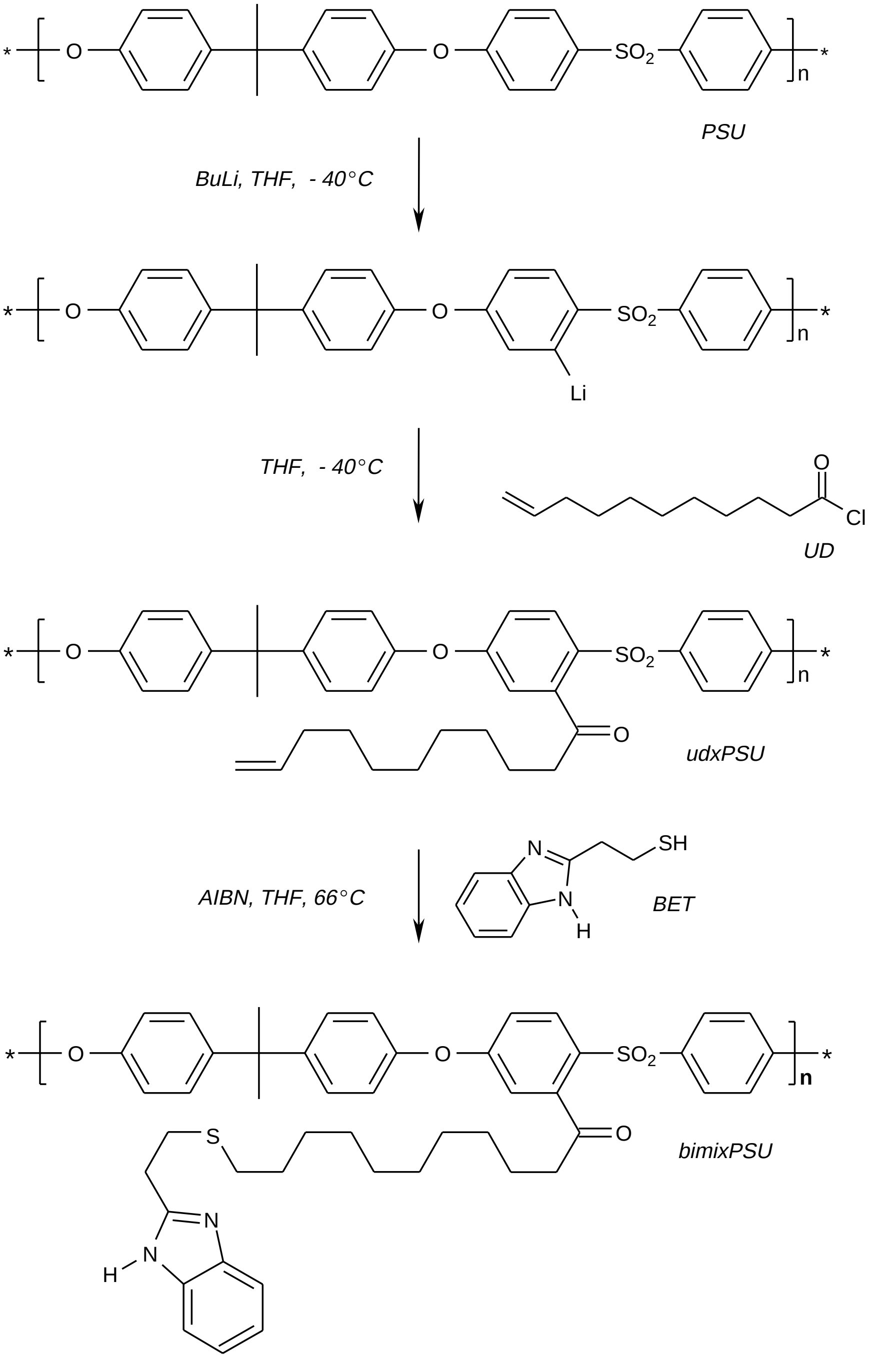
2.2. Tethering of benzimidazole

Benzimidazole units were tethered to the undecenoyl side chains of the ud*x*PSU samples by using a free radical thiol–ene coupling reaction with 2-(2-benzimidazolyl)ethanethiol (BET). BET was readily synthesized in quantitative yields by reacting an excess of 3-mercaptopropionic acid with 1,2-diaminobenzene in an aqueous solution of HCl. This synthesis has been described in more detail elsewhere [17]. The BET and ud*x*PSU reactants were dissolved in 50 ml THF in a two-necked 100 ml round-bottomed reactor. The reactor was fitted with a reflux condenser, a gas inlet/outlet, and a magnetic stirrer. Next, the reaction mixture was heated to the boiling point of THF (66 °C) and then degassed by flowing N_2 gas through the reactor for 1 h. Subsequently, the coupling reaction was initiated by adding 2,2′-azobis(2-methylpropionitrile) (AIBN, Acros, 98%). The reaction was allowed to proceed for 10 days under N_2 atmosphere in order to completely convert all the C=C bonds of the undecenoyl side chains into thio-ether linkages. Also, additional amounts of AIBN were added every 24 h during the first 9 days. The amounts used in the reactions are given in Table 2. After terminating the reaction, the excess BET was removed by precipitation of the product in ethanol. Finally, the samples were carefully dried in vacuum at 40 °C for 2 days prior to analysis. The samples of PSU tethered with benzimidazole were designated as bimi*x*PSU, where *x* denoted the average number of benzimidazole units per repeating unit of PSU.

2.3. Characterization

^{1}H NMR spectra of the tethered PSU's were obtained from a Bruker 400 MHz spectrometer, using either chloroform-*d* or dimethyl sulfoxide-d_6 solutions, depending on the solubility of the samples (see below). The degree of substitution (DS) was calculated by comparing the integrated signals of the PSU methyl protons with the characteristic signals of the protons in the undecenoyl side chains. The progress of the thiol–ene coupling reaction was monitored by observing the gradual disappearance of the signals of the protons of the undecenoyl C=C bond. Infrared spectra were recorded using a Bruker IFS 66 FTIR spectrometer. The samples were prepared either by grinding the polymers together with KBr salt and then pressing tablets, or by casting films from THF solutions directly onto KBr tablets. Spectra were subsequently recorded in transmission mode at a resolution of 4 cm^{-1}. Size-exclusion chromatography (SEC) was used to investigate if any degradation of the PSU backbone occurred during the thiol–ene coupling reaction. THF solutions of PSU samples were analyzed using a setup equipped with three Shodex columns (KF-805, -804, and -802.5) in series and a refractive index detector. The chromatograms were recorded at an elution rate of 1 ml/min at room temperature.

Differential scanning calorimetry (DSC) measurements were performed using a TA Q1000 instrument. Carefully dried samples were quickly transferred to aluminum pans, which were hermetically sealed. The samples were first annealed at 180 °C for 5 min and then cooled to −50 °C before analysis during scans from −50 to 250 °C at a scan rate of 40 °C/min. A TA Q500 thermogravimetric analyzer (TGA) was used to determine the thermal stability of the polymers



Scheme 1. Synthesis pathway for the preparation of PSU tethered with benzimidazole.

Table 1
Preparation and properties of PSU grafted with undecenoyl side chains

Sample	Charged amounts			DS[a]	T_g (°C)
	PSU[b] (g (mmol))	BuLi (mmol)	UD (g (mmol))		
ud0.5PSU	1.5 (3.4)	1.7	0.5 (2.6)	0.5	109
ud1.0PSU	1.5 (3.4)	3.4	1.0 (5.1)	1.0	104
ud1.7PSU	1.5 (3.4)	6.8	2.1 (10.2)	1.7	79

[a] Determined by ^{1}H NMR spectroscopy.

[b] Amount given in g and the corresponding mmol repeating units of PSU.

Table 2
Preparation and properties of PSU tethered with benzimidazole

Sample	Charged amounts			T_g (°C)	σ (180 °C) (nS/cm)
	ud*x*PSU[a] (g (mmol))	AIBN (g/day (mmol/day))	BET (g (mmol))		
bimi0.5PSU	0.7 (0.7)	0.07 (0.43)	0.24 (1.35)	115	3
bimi1.0PSU	0.7 (1.2)	0.11 (0.67)	0.41 (2.30)	116	13
bimi1.7PSU	0.7 (1.6)	0.16 (0.97)	0.58 (3.26)	83	34

[a] Amount given in g and the corresponding mmol undecenoyl side chains.

under nitrogen atmosphere. The temperature was swept from room-temperature to 600 °C at a heating rate of 10 °C/min.

The solubility of the bimi*x*PSU samples in a series of solvents was investigated at 22 °C. Dry polymer samples were transferred to test tubes, which were then filled with the different solvents. After 24 h, the contents of the test tubes were visually inspected. A polymer was considered soluble in a particular solvent if the sample was found to be completely dissolved. In any other case, the polymer was considered to be non-soluble.

The proton conductivity (σ) of the bimi*x*PSU samples was investigated at 180 °C using a Novocontrol high-resolution dielectric analyzer equipped with a Novocool temperature control system. Films of the different samples were cast from THF solutions onto teflon-coated moulds at room-temperature, followed by careful drying under vacuum at 60 °C. The thicknesses of the films ranged from 100 to 150 μm, while the diameter of the samples (20 mm) was defined by the sample cell. Each film was placed between two stainless steel blocking electrodes and the impedance was subsequently measured through the plane of the film at frequencies ranging from 10^{-1} to 10^7 Hz using a voltage amplitude of 1.0 V. The conductivity of each sample was obtained as the real value at the frequency that produced the minimum imaginary response in a complex conductivity plot.

3. Results and discussion

3.1. Polymer synthesis

Three PSU samples having different concentrations of pendant benzimidazole units were synthesized by the two-step procedure shown in Scheme 1. As seen, the synthesis included grafting of undecenoyl side chains onto PSU through the reaction of lithiated PSU with 10-undecenoyl chloride, followed by a thiol–ene coupling reaction between the C=C bond of the undecenoyl side chains and the –SH group of BET. Generally, lithiation is a powerful route to modify PSU's and exhibit many advantages as compared to other methods. If modifications via lithiation are carefully devised, they are usually close to quantitative and do not cause degradation or crosslinking. Furthermore, a wide variety of modifications are possible due to the huge number of electrophiles available [22,26]. Lithiation of PSU is exclusively directed to the ortho position of the sulfone groups in the PSU backbone [22]. This is a consequence of the strong electron-withdrawing characteristics of the sulfone group, and the ability of the sulfone oxygen atoms to complex with the lithiation agent. In the present case, the lithiated sites were quickly quenched by addition of an excess of UD. The values of the DS were calculated by comparing the ^{1}H NMR signals from the methyl protons of the PSU backbone at $\delta = 1.6$ ppm with the signal from the protons of the –CH$_2$– units of the undecenoyl side chains at $\delta = 1.2$–1.4 ppm (Fig. 1). In addition, the chemical shifts from the protons of the C=C bonds were observed at $\delta = 4.9$ and 5.8 ppm. The amounts charged and the values of DS achieved are shown in Table 1. The target value of DS was 0.5, 1.0 and 2.0 for ud0.5PSU, ud1.0PSU, ud1.7PSU, respectively. The deviation between the target DS and the DS obtained in the latter case was most likely due to the presence of small amounts of impurities, which consumed some of the highly reactive BuLi, or steric hindrance at high values of DS. The precision was possibly also affected by difficulties to observe the color change during the titration procedure prior to the grafting reaction. The results of the grafting reactions were also confirmed by FTIR after identifying the absorption bands of the C=C bond at 990 and 1640 cm^{-1} (Fig. 2). Furthermore, the carbonyl band of the ketone link gave rise to two absorption peaks at 1753 and 1711 cm^{-1}, respectively.

Thiol–ene coupling reactions have previously been successfully used to couple various thiol-functional molecules to polymers carrying C=C bonds [17,29,30]. In the present case, the progress of the thiol–ene coupling reaction between the C=C double bond of the undecenoyl side chains and the –SH group of BET was followed by observing the disappearance of the ^{1}H NMR shifts of the protons of the C=C carbons at $\delta = 4.9$ and 5.8 ppm, respectively. In parallel, new shifts appeared in the region $\delta = 2.2$–3.2 ppm, which were attributed to the protons of the –CH$_2$–S–CH$_2$– link. Unfortunately, the signals from the benzimidazole protons appeared in the same region as the shifts of the aromatic protons of PSU and could therefore, not be clearly observed. Comparisons of the integrated signals of the –CH=CH$_2$ protons before coupling and the –CH$_2$–S–CH$_2$– protons after coupling showed that the C=C bonds were quantitatively, within the error margin of the analysis method, converted into thio–ether links without any apparent limitation or side reactions. The ketone links of the undecenoyl side chains can be expected to be involved in a keto-enol equilibrium. However, this equilibrium did not seem to limit the conversion. Thiol–ene reactions are generally known to be efficient [29]. However, compared to our previous study, where BET was coupled to vinyl-functional polysiloxanes, the current

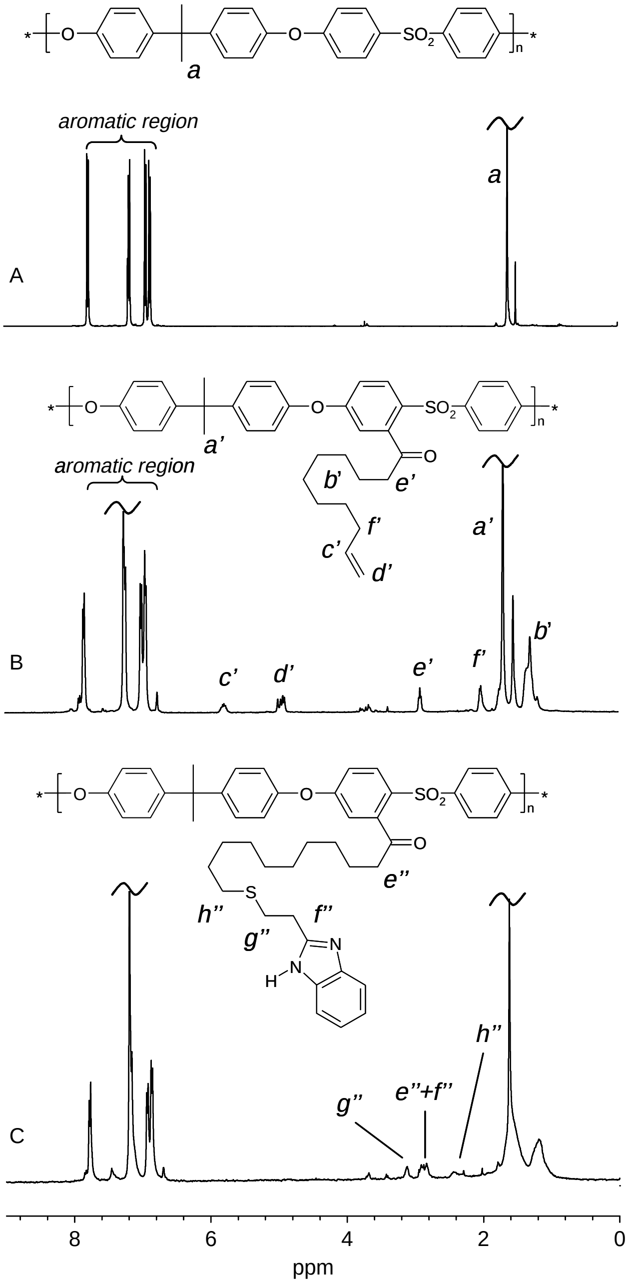


Fig. 1. ^{1}H NMR spectra of neat PSU (A), ud0.5PSU (B) and bimi0.5PSU (C) recorded in $CDCl_3$.

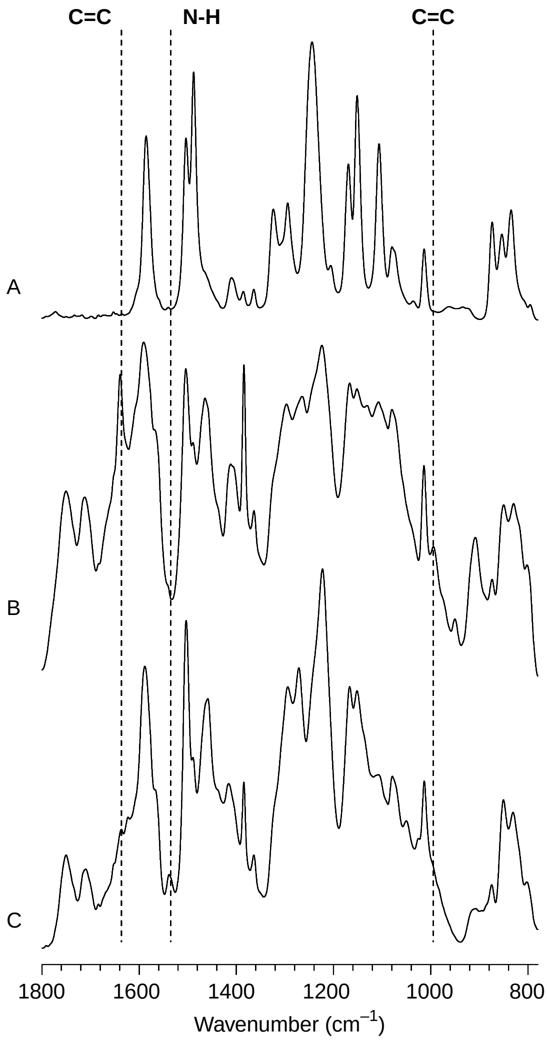


Fig. 2. FTIR spectra of PSU (A), ud1.0PSU (B) and bimi1.0PSU (C), showing the complete conversion of the C=C bond and the appearance of a N–H absorption band during the thiol–ene coupling reaction.

reaction rate was observed to be quite slow [17]. In order to convert all the C=C bonds into thio–ether links, 10 days of reaction was required and additional amounts of AIBN were charged every 24 h. A slight haziness was observed in the reaction vessel after approximately 24 h. Thus, one explanation for the low reaction rates might be that the partly reacted ud*x*PSU polymers aggregated in the reaction mixture, which limited the accessibility of the reactive groups. During the reaction, the PSU backbone was subjected to reactive radicals for 10 days. In order to ensure that no degradation of the PSU backbone occurred under these conditions, neat unmodified PSU was kept under exactly the same conditions, in the presence of AIBN and BET, as during the coupling reactions. The PSU sample was then isolated and analyzed by SEC and ^{1}H NMR spectroscopy, and finally compared with the original neat reference PSU. No differences in the molecular weight distribution or in the ^{1}H NMR spectra were observed between the two samples, which gave the conclusion that no degradation of the PSU took place during the thiol–ene coupling reactions.

The result of the coupling reaction was also successfully monitored by FTIR spectroscopy as seen in Fig. 2. The absorption bands from the C=C bond at 990 and 1640 cm^{-1} disappeared gradually as the coupling reaction proceeded and, in parallel, an absorption band from the N–H deformation of the benzimidazole units appeared at 1623 cm^{-1}. Furthermore, a weak absorption peak from the C=N groups of the benzimidazole units was observed close to 1640 cm^{-1}. The benzimidazole-tethered PSU's were all slightly yellowish, film-forming solid materials. Because all the C=C bonds were converted into thio-ether links, the benzimidazole content may conveniently be varied, potentially up to DS = 2, by changing the graft density of undecenoyl side chains in the first reaction step.

Table 3
Solubility of the bimi*x*PSU samples

Polymer sample	Solvent[a]					
	1-Butanol $\delta=23$ (s)	DMSO $\delta=25$ (m)	DMF $\delta=22$ (m)	THF $\delta=19$ (m)	Chloroform $\delta=19$ (p)	Toluene $\delta=18$ (p)
PSU	−	−	−	+	+	−
bimi0.5PSU	−	−	+	+	+	−
bimi1.0PSU	−	+	+	+	−	−
bimi1.7PSU	−	+	+	+	−	−

[a] The symbols (+) and (−) indicate solubility and non-solubility, respectively. Solubility parameters (δ in [MPa]$^{1/2}$) were obtained from Polymer handbook, and the letters s, m, and p denote strongly, moderately, and poorly hydrogen bond forming solvents, respectively [33].

3.2. Solubility

The solubility of neat PSU and the different bimi*x*PSU samples was evaluated in a range of solvents at 22 °C. As seen in Table 3, the polymer solubility varied considerably with the concentration of covalently tethered benzimidazole. As expected, neat PSU was readily soluble in THF and chloroform, but was non-soluble in polar and hydrogen bonding solvents such as water, alcohols, dimethyl sulfoxide (DMSO) or dimethyl formamide (DMF). The solubility of the bimi*x*PSU samples in moderately hydrogen-bonding solvents such as DMSO and DMF gradually increased as the concentration of benzimidazole increased. This finding was most probably a consequence of the hydrogen bonding capacity and the polarity of the benzimidazole units. However, none of the bimi*x*PSU samples were soluble in strongly hydrogen bonding 1-butanol, methanol or water. Furthermore, the solubility of the samples was observed to be the opposite in chloroform, which is poorly hydrogen bonding. In this solvent, the solubility of the polymers gradually decreased as the benzimidazole concentration increased, again indicating the strong role of hydrogen bonding and polarity. Finally, none of the bimi*x*PSU samples were soluble in toluene. The solubility of the present samples followed closely the trends previously reported for the benzimidazole-functionalized polysiloxanes [17]. Thus, the solubility of the bimi*x*PSU samples was dependent on the balance of the concentrations of hydrogen bonding benzimidazole on one hand, and the non-hydrogen bonding PSU backbone on the other hand. This implied that the bimi*x*PSU samples had an amphiphilic nature with the hydrophilic benzimidazole units separated from the hydrophobic backbone by long thio-ether spacers.

3.3. Thermal properties

Fig. 3 shows the TGA traces of neat PSU and the bimi*x*PSU samples recorded from room temperature up to 600 °C under N_2 atmosphere. The first weight loss occurred at approximately 250 °C and corresponded roughly to the weight of the tethered BET units, as seen in Fig. 4. This was in line with the degradation mechanism of the benzimidazole-functionalized polysiloxanes [17]. The second weight loss started at around 360 °C and was attributed to the degradation of the undecenoyl spacer residues. This was concluded after TGA analyses of the ud*x*PSU samples, which showed a weight loss approximately corresponding to the weight of the grafted undecenoyl side chains at 360 °C (not shown). Finally, the PSU backbone began to decompose at around 500 °C. It was noted that the thermal stability decreased with increasing degree of modification. Generally, the C–S–C bond has a weak nature. It may however, undergo selective oxidations to the more stable sulfone or sulfoxide links [17,31,32].

According to the results of the DSC analysis, all the polymers were completely amorphous. Neat PSU showed a distinct glass transition temperature (T_g) at 190 °C. As seen in Table 1, the T_g decreased quite dramatically after grafting the undecenoyl side chains. This clearly showed that the flexible side chains had plasticizing effect on the PSU backbone. As seen in Table 3, the incorporation of benzimidazole units in the polymers only had a small increasing effect on the T_g, as compared to the T_g of the respective ud*x*PSU samples. This finding suggested that the molecular mobility of the benzimidazole units to a large extent was decoupled from that of the stiff PSU backbone. This was in sharp contrast to the behavior of the benzimidazole-functionalized polysiloxanes, where the incorporation of small concentrations of benzimidazole caused a dramatic increase of the T_g due to hydrogen bonding between the benzimidazole units [17]. The difference between the two systems in this respect was most

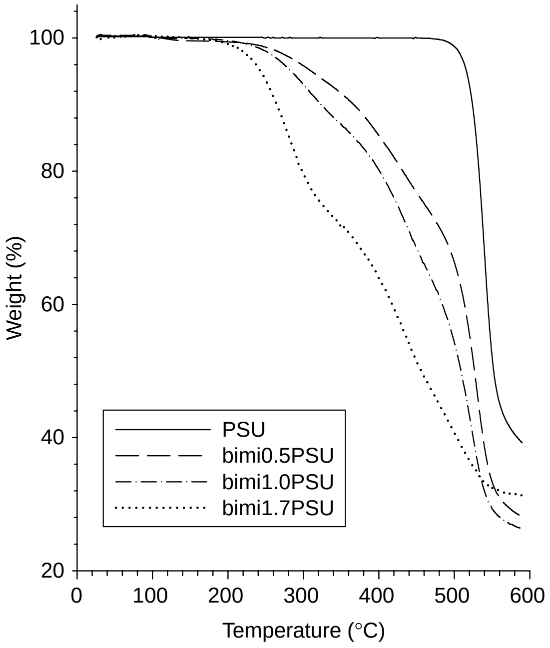


Fig. 3. TGA traces showing the thermal stability under nitrogen atmosphere of neat PSU and the PSU's tethered with benzimidazole.

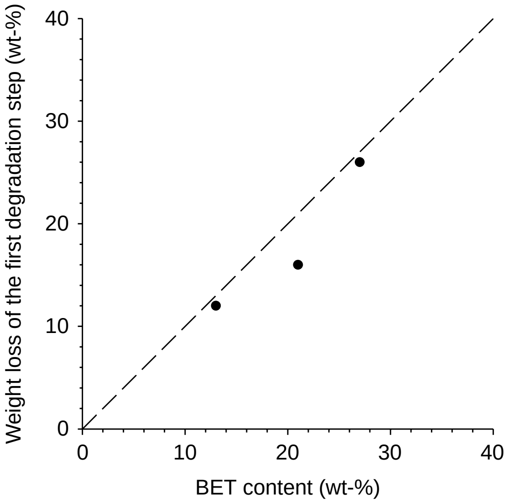


Fig. 4. Weight loss connected with the first degradation step of the bimi*x*PSU samples (as measured by TGA analysis) plotted as a function of the BET content. The dashed line indicates the diagonal ($x=y$).

likely due to the difference in the spacer length. In the PSU's, the spacer unit was much longer (14 atom links) than in the polysiloxanes (5 atom links), which may have enabled the dynamics of the benzimidazole units of the former polymers to be largely decoupled from the dynamics of the PSU backbone. It should be noted that the concentration of benzimidazole was much lower in the present PSU's (approx. 0.8–1.7 mmol benzimidazole/g polymer) than in the polysiloxanes (approx. 1.5–3.1 mmol/g polymer).

3.4. Conductivity

As seen in Table 2, the benzimidazole-tethered PSU's reached only quite modest proton conductivities, e.g. 34 nS/cm at 180 °C for bimi1.7PSU. This value may be compared to 14 μS/cm at 150 °C observed for the benzimidazole-tethered polysiloxanes [17], or 30 μS/cm at 140 °C reported for benzimidazole tethered to a polysiloxane network [18]. The low values of conductivity found in the present case were probably due to the low concentrations of the benzimidazole units. As expected, the conductivity was observed to increase with the concentration of benzimidazole. However, most likely the volume concentration of benzimidazole units was not high enough for the formation of a percolating hydrogen bonded network for efficient proton transfer. Also, as already mentioned, the T_g was much higher in the current bimi*x*PSU samples in comparison with the previously investigated polysiloxanes, indicating a lower segmental mobility of the backbone polymer in the former case.

3.5. Conclusions

Polysulfones with pendant benzimidazole units were successfully synthesized by reactions of lithiated PSU with UD, followed by a thiol–ene coupling reaction with BET. Both reaction steps were found to be close to quantitative, although the latter required long reaction times. The grafting of undecenoyl side chains onto the PSU backbone resulted in a decrease of T_g, as compared to neat PSU. Tethering of the benzimidazole units did not result in any significant increase in T_g, which may indicate that the benzimidazole units were sufficiently separated from the PSU backbone not to be significantly affected by the backbone.

The benzimidazole-tethered materials exhibited only modest proton conductivities, 34 nS/cm at 180 °C, which was a likely consequence of the relatively low benzimidazole concentrations. Because an increase in the benzimidazole concentration did not raise the T_g significantly, it is likely that a higher concentration of benzimidazole may be incorporated in the polymers without suppressing their segmental mobility. An increase in the benzimidazole concentration may be achieved by using a brominated PSU as the precursor polymer backbone. Lithiation at low temperature will then first lead to a bromine-to-lithium exchange ortho-to-ether. Further lithiation, beyond the bromine concentration, will result in hydrogen-to-lithium exchange ortho-to-sulfone as for the non-brominated PSU. In this way values of DS approaching four may be reached for a fully brominated and lithiated polymer. In addition, it might also be possible to shorten the length of the alkenoyl side chains in order to increase the benzimidazole concentration without compromising their mobility.

Acknowledgements

We thank the Swedish Research Council (VR) for financial support.

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