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Modified Polysulfones. VI. Preparation of Polymer Membrane Materials Containing Benzimine and Benzylamine Groups as Precursors for Molecularly Imprinted Sensor Devices*

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ABSTRACT: A modified polysulfone containing benzylamine groups was synthesized as a reactive membrane material. Polysulfone was activated at the *ortho*-sulfone site by direct lithiation with *n*-butyllithium, and the resulting lithiated polysulfone was then reacted with benzonitrile; this yielded a polymer with pendant benzimine groups. The structure was confirmed by NMR and IR spectroscopy and by the transformation of imine to ketone by acid hydrolysis. The polymeric benzimine was also reduced to benzylamine with sodium cyanoborohydride in an acidic medium. The structure and degree of substitution of both benzylamine derivatives were determined by NMR and IR spectroscopy. The modified polysulfone containing benzylamine groups initiated the polymerization of *N*-carboxyanhydride of γ-benzyl-L-glutamate [Glu(OBzl)–NCA]. The side-chain oligopeptide of Glu(OBzl)–NCA attached to polysulfone was converted into molecular recognition sites. © 2003 Wiley Periodicals, Inc.* J Polym Sci Part A: Polym Chem 41: 1316–1329, 2003

Keywords: functionalization of polymers; polysulfones; modification; lithiation; membranes; amine

INTRODUCTION

Amines are functional groups useful for attaching onto polymers for numerous applications, including polymeric membranes, because of their reactivity and coordinating ability. Daly et al.[1] reported the amination of polysulfone (PSf) by nitration with a milder nitrating agent, ammonium nitrate/trifluoroacetic anhydride, which avoided extensive degradation. Naik et al.[2] and Conningham et al.[3] reported nitration reduction for the amination of poly(ether ether sulfone)s and poly(ether sulfone)s. Others reported the preparation of aminated and aromatic PSf copolymers from nitro- and amine-containing monomers, respectively.[4,5] Strongly nucleophilic aminomethyl PSf was prepared by Roos et al.[6] and also by Kahana et al.[7] in their studies of the complexing and transporting properties of macrocyclic crowns. PSf's modified by weaker bases such as pyridyl have also been reported.[8–10]

Our previous studies have focused on the preparation of modified PSf's for membrane applications.[11] Amine-modified PSf was prepared by li-

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thiation azidation followed by reduction[12,13] and tested as a material used in the preparation of membranes for gas mixture separation[11,14] and also as a material for the chelation of trace metals from seawater.[15]

The purpose of this work was the preparation of reactive polymeric membrane materials for affinity and molecular recognition. PSf is an excellent film-forming membrane material; therefore, membranes with pendant benzylamine groups provide binding sites for optically active imprint molecules. Amines are also reactive sites for the attachment of enantioselective molecules with chiral centers that are selective for a single component of an enantiomeric mixture. In this article, the synthesis of a modified PSf with pendant benzylamine groups is reported. PSf was activated by direct lithiation followed by the addition of the electrophilic benzonitrile, which resulted in the formation of a benzimine-modified polymer. PSf-benzimide has the potential to be reacted in many different ways and converted into other functional polymers. In this study, the attached imine groups were further reduced to primary amines after treatment with a cyanoborohydride reducing agent. The process provides an easily controllable degree of substitution (DS), up to 1.5 benzylamine groups per repeat unit, with site specificity to the sulfone ring. Confirmation of the presence of an imine group was conducted by the successful conversion of the imine group into a ketone by hydrolysis. Both benzimine and benzylamine derivatives were fully characterized by NMR and IR spectroscopy and DS values.

EXPERIMENTAL

Materials and Characterization

PSf Udel P-3500 (BP Amoco Polymers, Inc.) was dried for 24 h at 110 °C. Reagent-grade tetrahydrofuran (THF) was freshly distilled over lithium aluminum hydride ($LiAlH_4$). *n*-Butyllithium (10 M in hexanes) and sodium cyanoborohydride ($NaBH_3CN$) were obtained from Aldrich Chemical Co. and used as received. Benzonitrile was dried by vacuum distillation over phosphorus pentoxide (P_2O_5). All reactions were conducted under a constant argon purge. Dry ice/ethanol was used for cooling reaction mixtures. All modified polymers were recovered by precipitation in a nonsolvent in a Waring blender.

NMR analyses were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz for ^{1}H and 100.579 MHz for ^{13}C. Both homonuclear decoupling and correlation spectroscopy (COSY) were used for proton assignments. A 10-mm broadband probe was used for acquiring carbon spectra and carbon–hydrogen heteronuclear chemical-shift correlation (HETCOR) spectra; one-bond ^1JC—H was set to 140 Hz, and three-bond ^3JC—H was set to 7.5 Hz. Quantitative ^{13}C spectra were acquired with a 70° pulse angle, a 3.5-s acquisition time, and a 15-s relaxation delay for 4096 scans. For each analysis, a 5–15 wt % polymer solution was prepared in $CDCl_3$ or dimethyl sulfoxide-d_6 (DMSO-d_6), and tetramethylsilane was used as the internal standard.

IR spectra were obtained with a Midac M Fourier transform infrared spectrometer. The samples were prepared as thin films (50 mg of polymer dissolved in 2 mL of THF) by the evaporation of solutions on a glass plate and the release of the films by water immersion. Films were vacuum-dried before being scanned for IR. A DuPont 951 thermogravimetric analyzer was used for measuring degradation temperatures (T_d's) under a nitrogen atmosphere at a heating rate of 10 °C/min. Elemental analyses were obtained from Galbraith Laboratories.

A TA Instruments model 2950 thermogravimetric analysis (TGA) instrument was used for measuring T_d, and a TA Instruments model 2920 differential scanning calorimeter calibrated with indium at 156.61 °C was used for measuring the glass-transition temperature (T_g). Polymer samples for TGA analysis were preheated to 150 °C at 10 °C/min under a nitrogen atmosphere, held there isothermally for 60 min, equilibrated at 80 °C, and then heated to 800 °C at 10 °C/min for the T_d measurements. Therefore, the degradation data reported here were assumed to be in the absence of moisture. Samples for differential scanning calorimetry analysis were initially heated at a rate of 10 °C/min under a nitrogen atmosphere to well below the polymer T_d point, quenched in liquid nitrogen, and then reheated at the same rate.

Reaction of Benzonitrile with Lithiated Polysulfone (PSf-Li; DS = 0.50)

A mechanically stirred PSf solution (20.00 g, 45.2 mmol in 1 L of THF) cooled to −50 °C was lithiated to DS = 0.50 with *n*-butyllithium (2.71 mL,

27.1 mmol) according to previously reported procedures.[12,16] The slightly viscous, orange solution of PSf-Li was stirred for an additional 15 min, and then precooled benzonitrile (9.30 mL, 90.4 mmol) was poured quickly into the reaction flask under vigorous stirring; this resulted in a viscous and orange heterogeneous mixture. The viscosity decreased while the reaction was gradually warmed to −10 °C over a period of 1.5 h. The modified PSf was recovered by precipitation from 95% ethanol and then washed, filtered, and dried in a vacuum oven at 60 °C for several hours. The yellowish addition product (20.31 g, 92% yield) had a DS of 0.50 imine groups per repeat unit. The polymer should be protected from light and heat.

Reaction of Benzonitrile with PSf-Li (DS = 1.68)

PSf (20.00 g, 45.2 mmol) in THF (1 L) was lithiated to DS = 2.0 with 2.15 equiv of *n*-butyllithium (9.72 mL, 97.2 mmol) over a period of 20 min, and then the clear, dark orange, viscous solution was stirred for an additional 15 min at −50 °C. Precooled benzonitrile (46 mL, 452 mmol) was poured quickly into the reaction flask under vigorous mechanical stirring (which was critical for preventing crosslinking). Within 2 min, a highly viscous gel formed that gradually changed into an orange-red heterogeneous mixture. The viscosity decreased rapidly while the reaction was gradually warmed to −10 °C over a period of 1.5 h. Ethanol (95%; 50 mL) was added to the mixture, and the resulting clear and lemon-yellow solution was concentrated with a rotary evaporator at 40 °C and then precipitated from 95% ethanol and recovered as before. The yellow benzonitrile addition product (24.59 g, 93% yield) had a DS of 1.68 benzimine groups per repeat unit. The polymer should be protected from light and heat.

Reduction of Benzimine to Benzylamine (DS = 0.43)

A clear, yellow solution of PSf-benzimine (DS = 0.50; 20.00 g, 40.5 mmol) in THF (400 mL) was magnetically stirred and cooled to 0 °C. $NaBH_3CN$ (8.3 g, 132.1 mmol) was added to the solution and was completely dissolved within a few minutes. A mixture of concentrated HCl (33 mL) and water (66 mL) was added dropwise over several hours, and gas bubbling was observed (caution: HCN gas could be generated). The solution gradually turned bright yellow and contained a white precipitate. Acid addition was continued slowly overnight, and this resulted in more precipitate. The heterogeneous mixture was poured into 95% ethanol, filtered, and then resuspended in fresh ethanol. The polymer solution was neutralized with a solution of sodium hydroxide until a stable pH of about 7.5 was obtained. The modified PSf was stirred for several hours, filtered, and then stirred with two fresh batches of ethanol/water (3:1) before being dried in a vacuum oven at 80 °C. The resulting white polymer (18.57 g, 94% yield) had 0.43 benzylamine group per repeat unit and was soluble in THF and chloroform.

Reduction of Benzimine to Benzylamine (DS = 1.49)

A solution of PSf-benzimine (DS = 1.68; 20.00 g, 34.1 mmol) in THF (400 mL) was reduced with $NaBH_3CN$ (24.00 g, 381.9 mmol) and a mixture of concentrated HCl (33 mL) and water (66 mL) as before. The heterogeneous mixture was precipitated into 95% ethanol, neutralized as before with sodium hydroxide, and left stirring overnight. The next morning, an agglomerated polymer precipitate was recovered, dissolved in a mixture of THF and *N*-methylpyrrolidinone (NMP), reprecipitated from ethanol, washed with ethanol, and dried. The white powder PSf-benzylamine derivative (17.61 g, 90% yield) had 1.49 benzylamine groups per repeat unit and was insoluble in chloroform, partly soluble in THF, and completely soluble in polar aprotic solvents such as DMSO and NMP.

Acid Hydrolysis of Benzimine to Ketone

The yellow PSf-benzimine powder (DS = 1.68) was refluxed in HCl/water (1:1) for several days until IR and NMR confirmed the complete transformation of the imine functional group into a ketone.

Assessment of Potential Sensor Devices Derived from Benzylamine-Modified PSf

A sensor device was prepared by the spin casting of a DMF solution of PSf-$E_{5.8}$ with 9-ethyladenine (9-EA) as a print molecule onto a pretreated and gold-deposited glass plate. The molecular recognition of the prepared films toward the target molecule adenosine (As) was evaluated by surface plasmon resonance (SPR) spectroscopy.[17] During the measurement, a 0.02 wt % NaN_3 aqueous

buffer was passed over the molecularly imprinted material surface at 5 mm^3 min^{-1}. The flow was periodically replaced with solutions of the same buffer containing As or guanosine (Gs). The experiment was carried out at 27 °C.

RESULTS AND DISCUSSION

Syntheses

Lithiation chemistry allows the attachment of a variety of functional groups onto PSf, often quantitatively.[11,12,16] In this study, two modified polymers with different amounts of pendant benzimine groups (PSf-benzimine) were prepared by the addition of benzonitrile to PSf-Li. Although the reaction of PSf-Li (DS = 0.5) with benzonitrile was quantitative, PSf-Li (DS = 2.0) resulted in a less than fully substituted addition product with a DS of 1.68. The most likely reason is steric hindrance of the electrophile around the sulfone linkage because the electrophilic carbon center of the benzonitrile triple bond is not easily accessible. The addition of benzonitrile onto PSf-Li gave yellow benzimine products that could be isolated. We demonstrated in previous studies that the direct lithiation derivatization process applied to PSf's did not result in any significant change in the molecular weight.[12,13] Structures were confirmed by elemental analysis, NMR and IR spectroscopy, and chemical transformation of imine into benzylamine by reduction and into a ketone by acid hydrolysis. The attempted substitution with acetonitrile did not result in the methyl aminomethyl derivative. This was anticipated because the methyl proton of acetonitrile is acidic and would protonate the lithiated polymer.

A survey of the literature revealed a variety of reducing agents for transforming imines to amines. The limited range of solvents in which the polymer is soluble led us to first consider conventional reducing agents soluble or partially soluble in THF solvent systems. Sodium borohydride ($NaBH_4$) in THF/ethanol, with conditions similar to those we reported before[13] for the reduction of PSf-azide to PSf-amine, was not an effective reducing agent for this conversion, giving a reduction of only about 5%. Similarly, zinc borohydride was prepared[18] and tested for imine reduction but was equally ineffective. $NaBH_3CN$ is known to reduce a wide variety of organic functional groups with remarkable selectivity, and it is highly soluble in several solvents, including water, alcohols, and THF.[19,20] Furthermore, $NaBH_3CN$ is stable in acid to pH 3, and Borch et al.[21] found that the BH_3CN^- reduction of imines is pH-dependent. Because the reduction consumes acid, Borch et al. used indicators while adding acid to maintain the pH. We avoided the use of indicators that could be trapped in the polymer and could be difficult to wash out during the recovery process. The PSf-benzimines were effectively converted into the respective benzylamines in the presence of $NaBH_3CN$ by the dropwise addition of acid over a long period of time. The DS of the benzylamine polymers (DS = 0.43 or 1.49) were slightly lower than those of the starting PSf-benzimine. This suggests either that the reduction step was not complete or that the differences in DS between the imine and benzylamine were due to the limits of accuracy in their methods of determination. Another possibility is a side reaction of the imine group, such as a interchain or intrachain reaction with other active lithiated sites. To minimize any possible side reactions, we added a large excess of benzonitrile rapidly into the reactive lithiated polymer under vigorous stirring. The synthetic scheme for preparing the PSf-imine and PSf-benzylamine derivatives is represented in Figure 1.

We performed TGA to assess the heat stability of the modified polymers. Both high-DS benzimine and benzylamine derivatives had similar degradation curves, in which the 1% weight loss was observed at 279 °C for PSf-benzimine and 297 °C for PSf-benzylamine. In comparison, PSf had a higher T_d; the 1% weight loss for PSf was at 496 °C.

Structural Characterization by NMR Spectroscopy

All signals were primarily assigned unequivocally by homonuclear decoupling experiments. Hydrogen COSY was applied when necessary for overlapping signals. Table 1 lists the chemical shifts, multiplicity, and couplings of proton absorptions for PSf and the modified polymers.

The ^1H NMR spectrum of Udel PSf **1** in $CDCl_3$ is composed of four aromatic doublets and one aliphatic singlet.[22,23] On the two bisphenol rings, *ortho*-ether protons H_{2-6} are coupled to *ortho*-isopropylidene protons H_{3-5}, and on the two phenyl sulfone rings, *ortho*-ether protons H_{8-12} are coupled to *ortho*-sulfone protons H_{9-11}. The latter protons are shifted downfield because of the deshielding effect of the sulfone group. All the

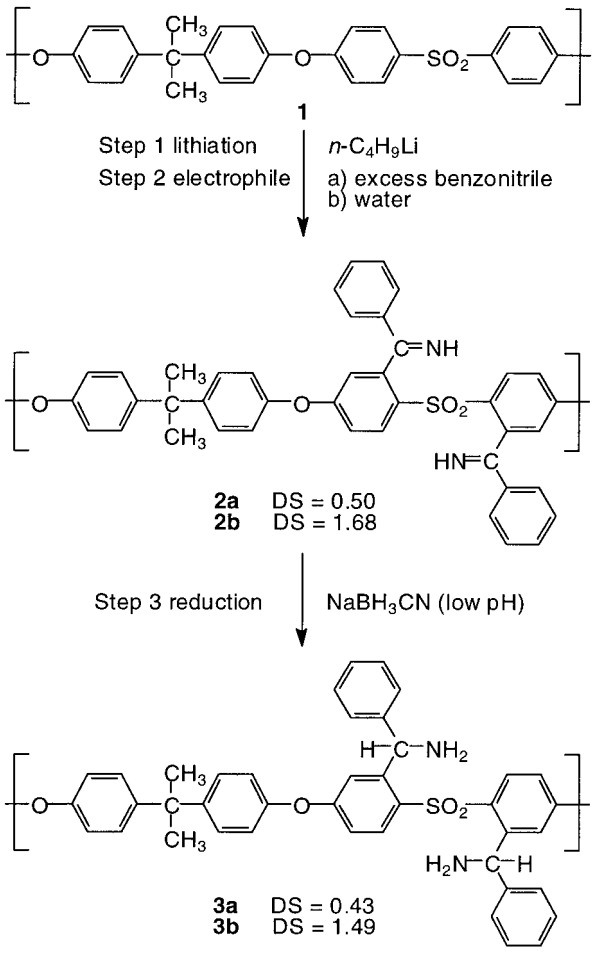

Figure 1. Reaction scheme for the preparation of PSf-benzimine **2** and PSf-benzylamine **3** derivatives.

aromatic protons have three-bond coupling (^3J = 8.8 Hz).

NMR of PSf-Benzimines

In the ^{1}H NMR spectrum, a characteristic imine broad signal from 8 to 11 ppm can be observed that is due to ^{1}H–^{14}N coupling and the proton exchange rate with the nitrogen atom. The downfield chemical shift of N—*H* is a result of the deshielding effect of the C═N double bond. The NMR spectrum of PSf-benzimine **2a** with a DS of 0.50 (Fig. 2) is composed mainly of unsubstituted (U) and monosubstituted (M) repeat units, with a trace amount of disubstituted (D) repeat units. Proton signals of the two spin systems, H_8–H_9–H_{12} and H_8'–H_9', were readily assigned with homonuclear decoupling. The more intense aromatic signals correspond to unsubstituted PSf repeat units. The H_9 signal of the benzimine substituted benzene ring is shifted downfield by 0.37 ppm because of a deshielding effect of the electron-withdrawing imine group, whereas the two H_9' seem to be subject to a shielding effect through the space of the C═N bond and are shifted upfield by 0.25 ppm. These *ortho*-sulfonyl protons, H_9 and H_9', are strongly three-bond-coupled with H_8 at 7.07 ppm and H_8' at 6.76–6.82 ppm, respectively. Meta coupling through four bonds occurs between H_8 and H_{12} at 6.78 ppm (J = 2.0 Hz). On the bisphenol segment, $H_{3,5}$ and $H_{2,6}$ remain largely unchanged. Benzyl protons H_{15-17} are all within 0.2 ppm of one another, the furthest downfield being H_{15}, which is affected by the electronic effect of the imine group. The H_{17} ^{1}H triplet is coupled with H_{16}. A trace amount of disubstituted repeat units was observed for H_9 at 7.89 ppm and for H_{15} at 7.50 ppm.

The PSf-benzimine **2b** with a higher DS of 1.68 (Fig. 2) consists mainly of M and D repeat units, with the more intense NMR signals arising from the latter. The spectrum is simplified because of the symmetrical aspect of the D repeat units. Bisphenol protons $H_{3,5}$ and $H_{2,6}$ are two coupled doublets. The *ortho*-sulfonyl spin system H_8–H_9–H_{12} can clearly be identified as H_8 ortho-coupled to H_9 and also meta-coupled to H_{12}. H_8 appears as a broadened doublet but is revealed as a doublet of doublets (J = 2.4 Hz) after resolution enhancement by the application of a sine bell function (1.00) on the free induction decay (FID). The remaining signals arise from M repeat units but do not have the same chemical shift as their counterpart in the lower substitution polymer. This can be explained by the fact that the M repeat units in the lower DS polymer are adjacent to U repeat units, whereas in the higher DS, they are adjacent to D repeat units.

The aromatic region of a quantitative ^{13}C NMR spectrum of PSf-benzimine **2b** (DS = 1.68) is shown in Figure 3, and the chemical shifts are listed in Table 2. The experimental number of carbons signals matches the expected 15 different signals for disubstituted repeat units. The effect of the C═N double bond on C_{13} gives an expected downfield shift at 173.40 ppm that is broadened as a result of the electrical quadrupole moment of ^{14}N. All protonated carbons were readily assigned with HETCOR (^1JC—H). Long-range HETCOR (^3JC—H) was used to assign several other signals, such as $^3JC_1$—$H_{3,5}$ and $^3JC_4$—$H_{2,6}$, on the bisphenol ring. On the sulfone phenyl ring, both C_7 and C_{11} can be coupled with H_9, but C_7 is the one furthest downfield; this leads to $^3JC_7$—H_9

Table 1. ^{1}H NMR Data for PSf **1,** Low-DS PSf-Benzimine **2a,** High-DS PSf-Benzimine **2b,** Low-DS Amine **3a,** High-DS PSf-Benzylamine **3b,** and Phenyl Ketone Derivatives

			Benzimine **2b**				
H	Udel **1**	PSf-Benzimine **2a**	M Repeat units	D Repeat units	Benzylamine **3a**	Benzylamine **3b**	Phenyl ketone
2	6.93, d, *J* 8.8	6.82–6.88, m	6.93, d, *J* 8.8	6.87, d, *J* 8.0	6.90–6.96, m		6.94, d, *J* 8.0
3	7.24, d, *J* 8.8	7.18–7.26, m	7.20–7.24, m	7.20, d, *J* 8.8	7.20–7.28, m		7.21, d, *J* 8.8
5	7.24, d, *J* 8.8	7.18–7.26, m	7.20–7.24, m	7.20, d, *J* 8.8	7.20–7.28, m		7.21, d, *J* 8.8
6	6.93, d, *J* 8.8	6.82–6.88, m	6.93, d, *J* 8.8	6.87, d, *J* 8.0	6.90–6.96 m		6.94, d, *J* 8.0
8	7.00, d, *J* 8.8	7.07, dd, *J* 8.8, 2.4	7.07, dd, *J* 8.8, 2.4	6.78, dd, *J* 8.8, 2.4	6.81–6.87, m		7.05, dd, *J* 8.8, 2.0
8′	—	6.76–6.82, m	7.00, d, *J* 8.8	—	7.01, d, *J* 8.8		
9	7.84, d, *J* 8.8	8.21, d, *J* 8.8	7.60, d, *J* 8.8	7.89, dd, *J* 8.8	8.12, d, *J* 8.8	7.80–8.20	7.97, d, *J* 8.8
9′	—	7.60, d, *J* 8.8	7.84, d, *J* 8.8	—	7.81, d, *J* 8.8		
11	7.84, d, *J* 8.8	—	—	—	—	—	
12	7.00, d, *J* 8.8	6.76–6.82, m		6.70, d, *J* 2.4	7.14–7.20, m		6.81, d, *J* 2.0
13	—	—	—	—	5.93, s	5.75–6.03	
15	—	7.44, d, 8.0	7.44, d, *J* 7.6	7.51, d, *J* 7.6	6.81–6.87, m		7.78, d, *J* 7.2
16	—	7.24–7.30, m		7.30, t, *J* 7.6	7.14–7.20, m		7.41, t, *J* 7.2
17	—	7.37, t, *J* 6.4		7.39, t, *J* 7.6	6.96–7.04, m		7.54, t, *J* 7.2
C—CH_3	—	1.65–1.70, m		1.67, s	1.64–1.72, m		1.66, s
C═N–*H*	—	8.7–10.7 broad		8.5–10.5, broad	1.78, broad		

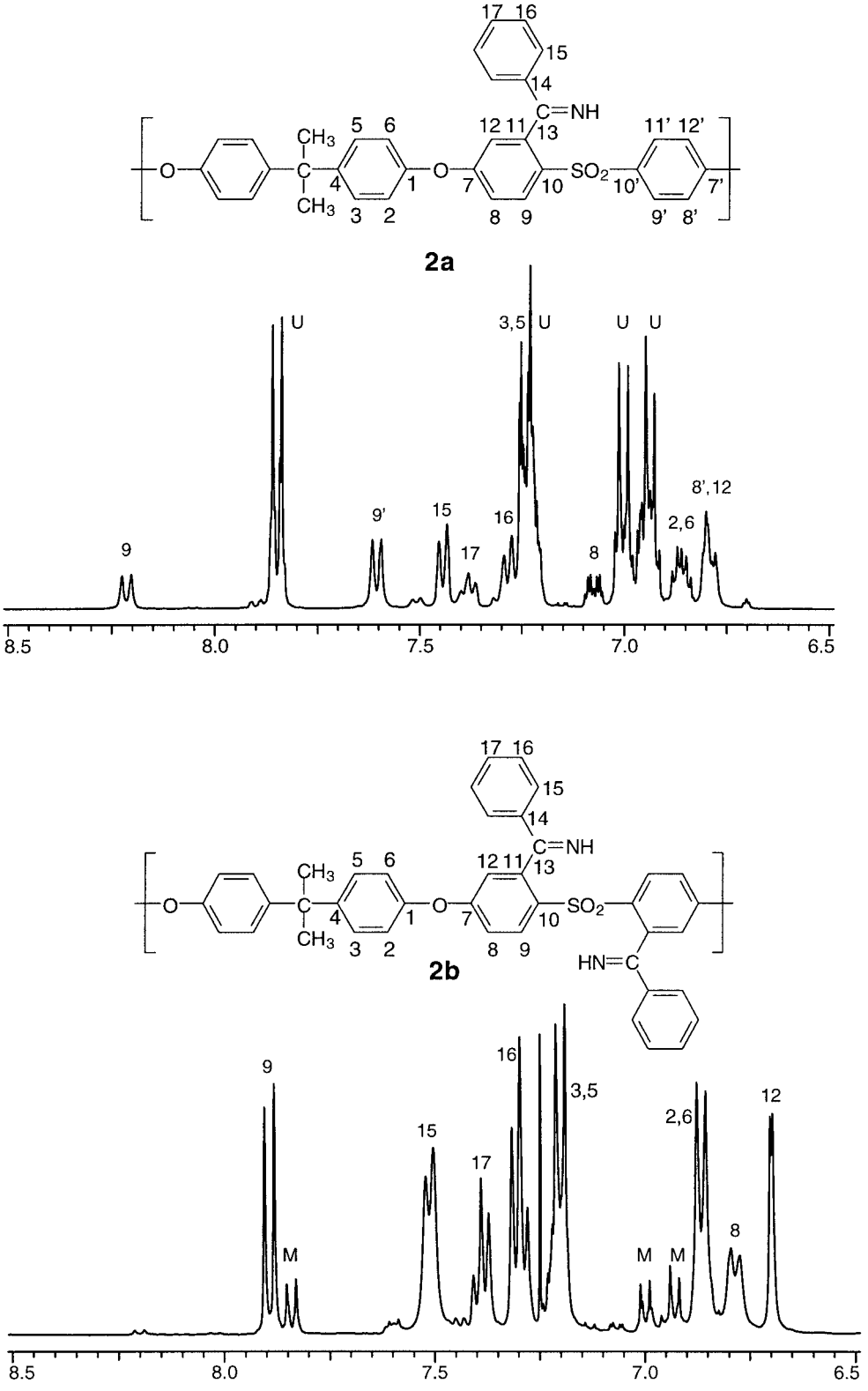

Figure 2. ^{1}H NMR spectra of low-DS PSf-benzimine **2a** and high-DS PSf-benzimine **2b**.

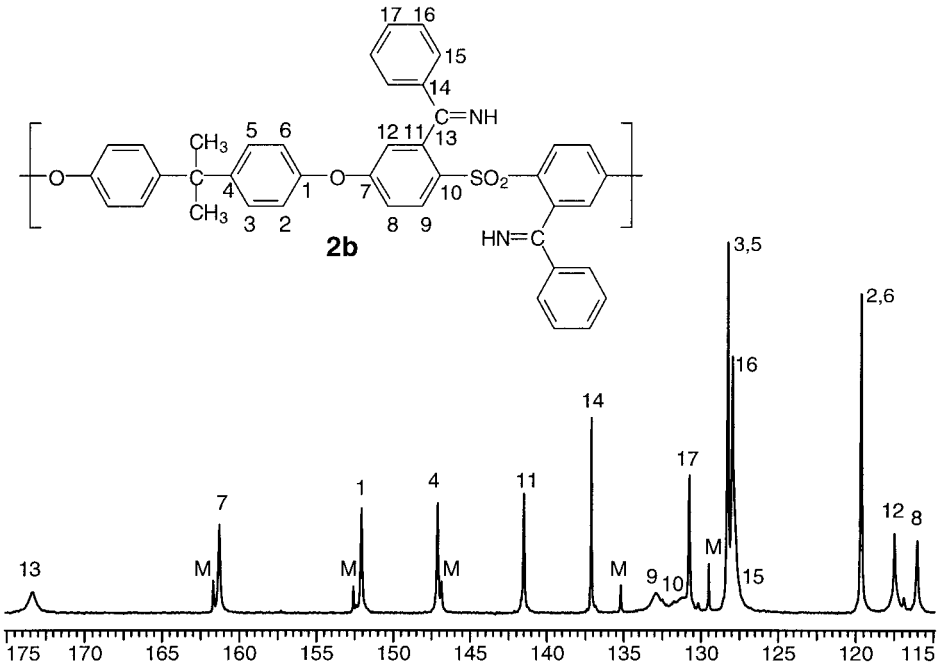

Figure 3. ^{13}C NMR spectrum of high-DS PSf-benzimine **2b**.

and $^3JC_{11}$—H_9. On the benzyl ring, C_{14} was assigned by $^3JC_{14}$—H_{16}. The remaining broad C_{10} integrates to one carbon. Interestingly, both C_9 and C_{10} are broad, probably because they are under the electronic and mesomeric influence of the nearby imine group.

Table 2. ^{13}C NMR Data for High-DS PSf-Benzimine **2b**

Carbon	PSf **1**	PSf-Benzimine **2b**
1	152.82	152.05
2	119.80	119.64
3	128.43	128.26
4	147.15	147.08
5	128.43	128.26
6	119.80	119.64
7	161.95	161.27
8	117.67	116.01
9	129.68	132.82
10	135.40	131.20
11	129.68	141.49
12	117.67	117.48
13		173.40
14		137.09
15		127.78
16		127.96
17		130.74
CH_3	30.94	30.89
CH_3—*C*—CH_3	42.40	42.37

NMR of the Hydrolysis Product PSf-Ketone

The ^{1}H NMR spectrum of the phenyl ketone derived from the hydrolysis of benzimine **2b** (Fig. 4) is very similar to that of **2b** because of a similar geometry and electronic environment. The main difference in the chemical shifts occurs for protons in ortho (H_{12}) and para (H_8) positions to the ketone functionality. In addition, the broad N—H signal is absent, and H_{15} is shifted downfield by 0.26 ppm because of the stronger carbonyl deshielding effect over the C═N bond. The ^{13}C NMR spectrum showed the disappearance of the imine signal and a new carbonyl signal at 194.38 ppm, 21 ppm further downfield.

NMR of PSf-Benzamines

The assignment of chemical shifts for benzylamine derivatives in the ^{1}H NMR spectra (Fig. 5) was more difficult because of more extensive signal overlap. For both lower and higher DS values (**3a** and **3b**, respectively), the H_{13} proton resulting from the reduction of imine groups can readily be identified. H_{13} is on an asymmetric carbon and appears as several signals in the range of 5.5–6.1 ppm because of a complex mixture of isomers and repeat units in

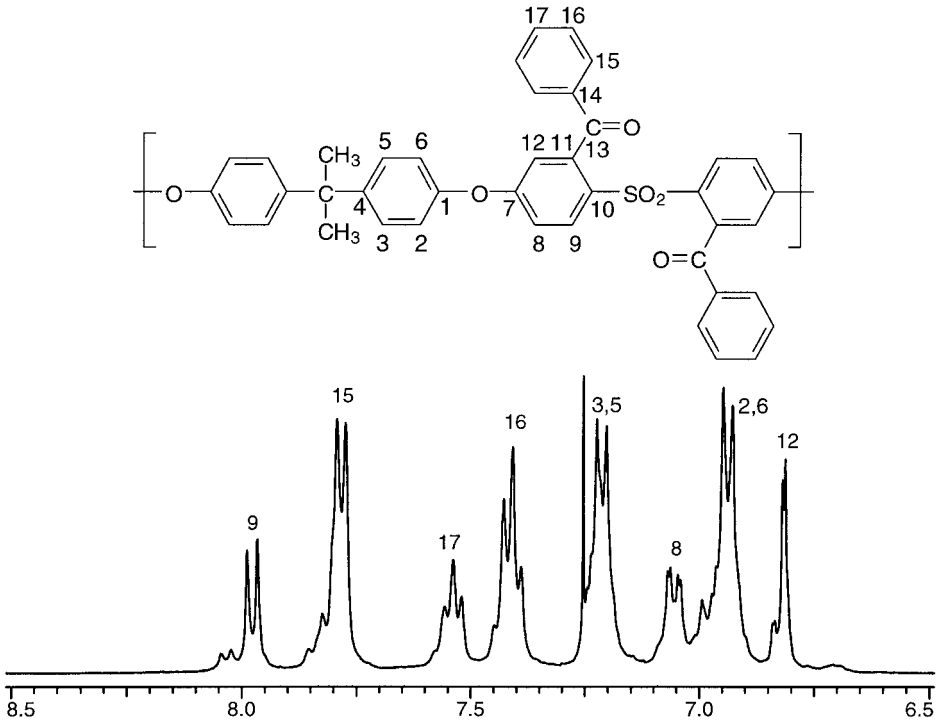

Figure 4. ^{1}H NMR spectrum of the phenyl ketone derivative.

3b. The NH_2 signal of **3a** in $CDCl_3$ appears at 1.8 ppm, whereas **3b** in DMSO-d_6 appears at 3.2 ppm. Only the simpler aromatic region of the lower DS polymer **3a** was analyzed for peak assignment. Four major doublets arise from U repeat units. The downfield *ortho*-sulfonyl protons of the benzamine ring segment are readily assigned: H_9 and H_9' are ortho-coupled with H_8 and H_8', respectively, but the H_{12} proton of the same spin system is likely masked beneath the multiplet at 7.14–7.20 ppm. The benzyl protons were assigned unambiguously with COSY. The amine nitrogen has an electron-donating effect, opposite to that of the imine. Its effect can be seen on the chemical shifts of the benzyl protons because H_{15} is shifted considerably upfield to 6.85 ppm. By comparison, the electron-withdrawing imine and ketone groups shifted H_{15} downfield to 7.52 and 7.78 ppm, respectively.

IR Spectroscopy

The IR spectra shown in Figure 6 are from higher substitution polymers. Both imine and amine N—H bands appear as weak absorptions between 3200 and 3400 cm^{-1}.[24] The main imine C═N stretching absorption cannot be identified because it occurs in the same region as the aromatic ring C═C stretching. However, a shoulder at 1606 cm^{-1} may be due to imine C═N stretching. Another imine absorption occurs as an intense peak at 1351 cm^{-1}, seen only in the PSf-benzimine IR spectrum [Fig. 6(A)]; it is characteristic of the aromatic C—N stretching vibration. The imine carbon is conjugated with the aromatic ring system on either side, allowing electron delocalization. In fact, the yellowish color of the PSf-benzimine is a good indication of conjugation. This aromatic C—N band disappeared when the conjugation was absent, as in the reduced amine [Fig. 6(B)]. IR was used to monitor the conversion of the imine into a ketone. It is well known that imines undergo acidic hydrolysis to be converted to ketone. PSf-benzimine was partially hydrolyzed under mild conditions by a treatment with 10% aqueous HCl at room temperature for 12 h. A small carbonyl band at 1674 cm^{-1} appeared on the spectrum. More vigorous hydrolysis conditions of refluxing 50% HCl for 6 days resulted in full conversion to the ketone. The 1351-cm^{-1} band disappeared, whereas a new carbonyl peak at 1674 cm^{-1} appeared [Fig. 6(C)].

Thermal Analysis

The thermal stabilities of benzimine and benzylamine derivatives were determined by TGA for

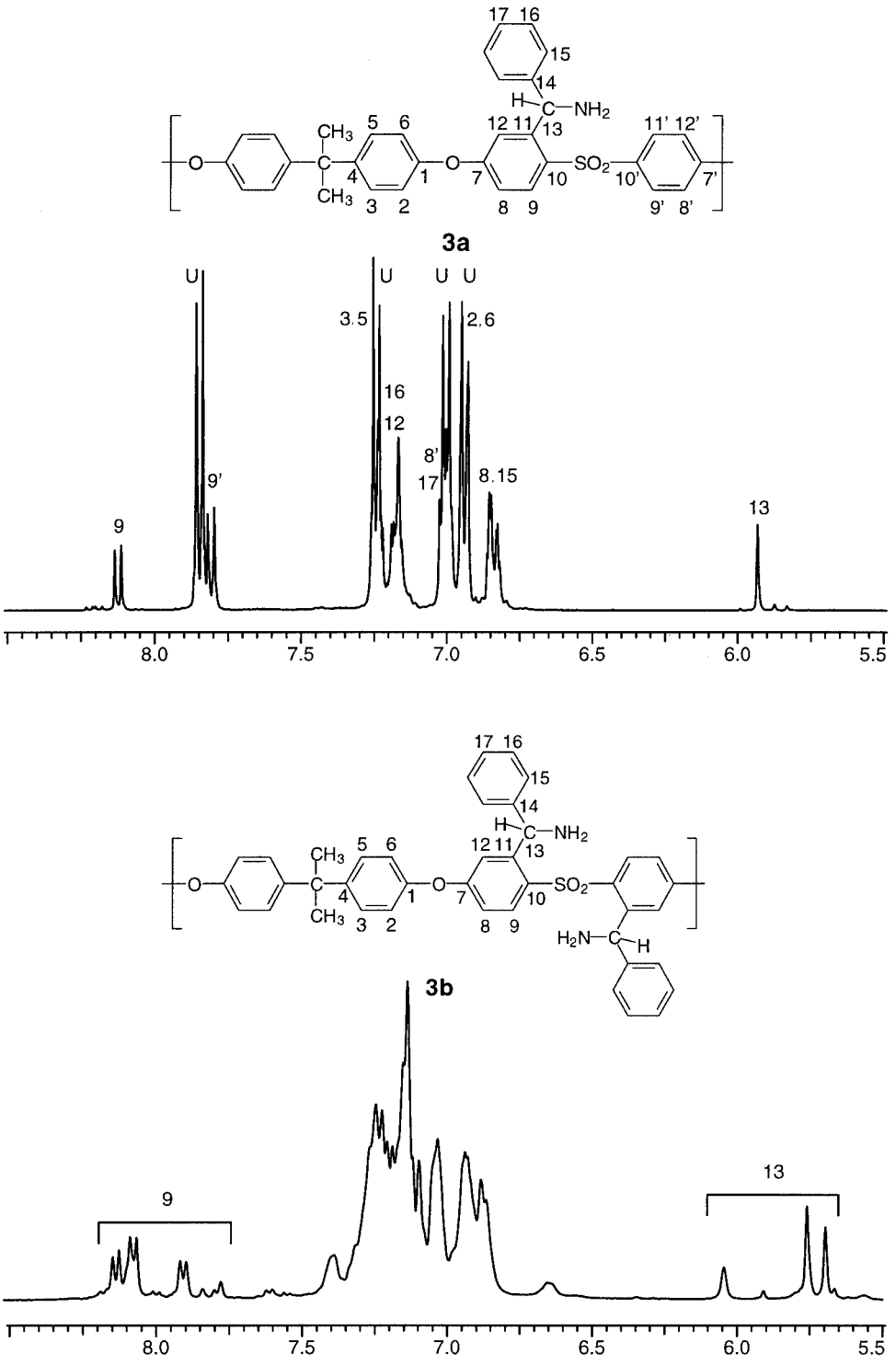

Figure 5. ^{1}H NMR spectra of low-DS PSf-benzylamine **3a** and high-DS PSf-benzylamine **3b**.

the high-DS polymer only. Figure 7 shows the degradation curves, and Table 3 lists significant curve values. The 1% weight-loss temperatures show that the modified polymers are less thermostable than PSf by approximately 100 °C. The amine derivative has slightly higher onset and 1%

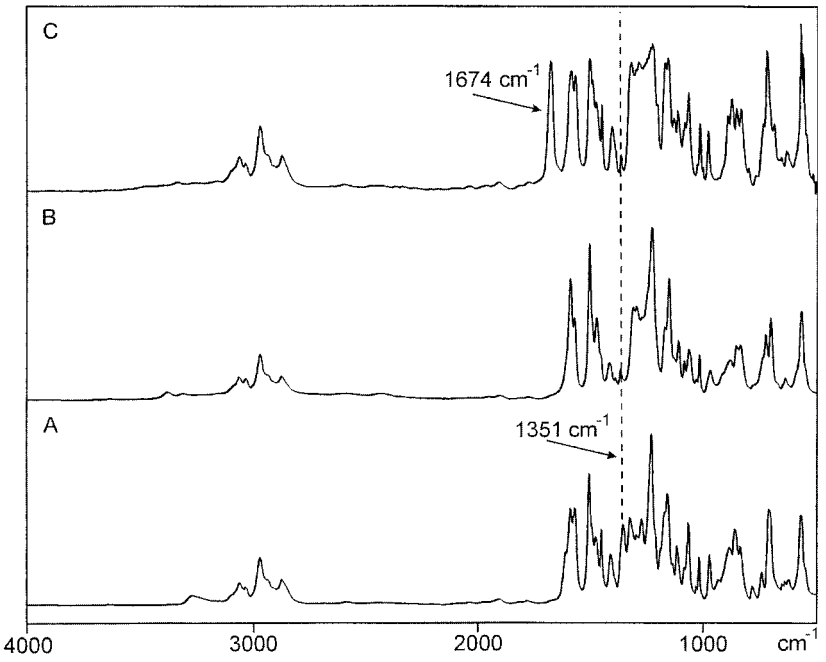

Figure 6. IR spectra of (A) high-DS PSf-benzimine **2b**, (B) high-DS PSf-benzylamine **3b**, and (C) phenyl ketone.

weight-loss temperature values than the imine derivative. The TGA curves show two onset temperature values for each polymer; indicating some degradation activity possibly associated with the loss of the substituents. The weight-loss percentages correspond to only a partial loss of benzimine or benzylamine groups, suggesting complex degradation, possibly through some rearrangement of the substituents.

The T_g's of PSf and the substituted polymers with high DS values are also listed in Table 3. As observed before,[13] hydrogen-bonding interactions between the amine functional groups increase rigidity; therefore, T_g is 9 °C higher for PSf-benzylamine than for PSf. However, T_g of the PSf-benzimine derivative is significantly lower by nearly 20 °C, even though it might be expected to participate in hydrogen bonding. A possible explanation for the reduced T_g is that the benzimine is conjugated with the polymer backbone and the benzyl side group. Delocalization through conjugation could reduce the electron density on nitrogen, thereby reducing hydrogen-bonding interactions.

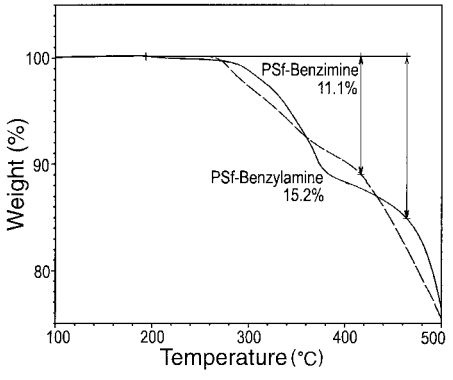

Figure 7. Thermal data for polymer derivatives.

Determination of DS

PSf-benzimines and PSf-benzylamines were prepared, each having a lower DS and a higher DS. In terms of molecularly imprinted membranes and sensor devices, DS is an important parameter because the ratio of imprint molecule to the functional group is determined during the fabrication process. The accurate determination of DS was difficult because of the complexity of the polymers, which consisted of three different repeat units: U, M, and D. Several methods, summarized in Table 4, were used to determine the number of benzimine and benzylamine groups substituted onto the polymer.

Table 3. Thermal Analysis Data for the Polymers

	T_g (°C)	T_d 1% Weight Loss (°C)	First Extrapolated Onset (°C)	Second Extrapolated Onset (°C)	Weight Loss between Onsets
PSf	188.1	495.7	518.0	—	—
PSf-benzimine	169.7	278.8	268.1	422.7	11.1
PSf-benzylamine	197.3	297.4	286.1	484.2	15.2

Elemental Analysis

The nitrogen content of PSf–CH(NH_2)Ph was 1.19 and 3.30% for the lower and higher DS values, respectively. Figure 8 shows the calculated percentage of nitrogen as a function of DS. By extrapolation, DS values of 0.41 and 1.38 benzylamine groups per repeat unit for the two polymers were obtained. We believe this method is less accurate than NMR, especially with the higher substitution polymers. Benzylamine groups are highly hydrophilic groups that may strongly associate with residual water or alcohol that is difficult to remove; this effectively reduces the apparent nitrogen percentage.

^{1}H NMR of the Benzimine Derivatives

The benzyl ring protons have chemical shifts identifiably different from the rings of the polymer backbone. A comparison of their signal area with that of the 6H upfield isopropylidene was used for DS determination. For the lower DS benzimine polymer, three distinct protons in the ortho and para positions (H_{15} and H_{17}, 7.33–7.54 ppm) integrate for 1.53H, leading to a DS of 0.50. The higher DS polymer has an 8.44H signal for all five benzyl proton signals (H_{15-17}, 7.26–7.56 ppm), which are distinct from those of the backbone protons, giving a corresponding DS of 1.68.

Table 4. DS Determination from NMR and Elemental Analysis Methods

Method	Benzimine Low DS	Benzimine High DS	Benzylamine Low DS	Benzylamine High DS
Benzyl: aliphatic (^{1}H NMR)	0.50	1.68		
C*H: aliphatic (^{1}H NMR)			0.42	1.48
C*H: aromatic (^{1}H NMR)			0.45	1.41
C*H: CH_3s (^{13}C NMR)			0.43	1.50
Elemental analysis			0.41	1.38

^{1}H NMR of the Benzylamine Derivatives

For the higher DS polymer, the signals from 5.2 to 6.2 ppm arise from the hydrogen on the asymmetric carbon H—C*—NH_2. Several factors explain why they appear as more than one singlet, such as different repeat units (monosubstituted and disubstituted), different sequences of different repeat units, and isomers. Comparing the integration of this signal grouping with the 6H isopropylidene singlet at 1.6 ppm leads to a DS of 1.48. For the lower DS polymer, both amine and isopropylidene signals appear in the same chemical-shift region. Considering the fixed ratio of 1 CH proton for 2 NH_2 protons, one can subtract the calculated area of the amine peak from the overlapped upfield protons and get only the area responsible for the methyls. After this is done, the calculated DS

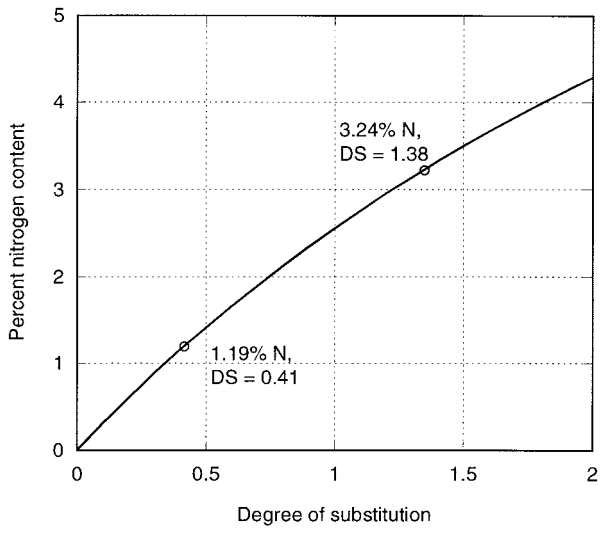

Figure 8. DS determination from the nitrogen content (%) by elemental analysis.

value is 0.42. Finally, one other method using only low field signals can be used to estimate the DS. This method involves a comparison of the integration of the hydrogen on the asymmetric carbon (H_{13}) with the entire aromatic proton area:[25]

$$A_{13}/A_a = \mathrm{DS}/[(16 - \mathrm{DS}) + 5\mathrm{DS}] \rightarrow$$

$$\mathrm{DS} = -16A_{13}/(-A_a - A_{13} + 5A_{13})$$

where A_{13} is the area of H_{13} (5.2–6.2 ppm) and A_a is the area of all aromatics (8.2–6.2 ppm). With this method, the DS values of the amine derivatives were 0.45 and 1.41. The accuracy of this method is very much dependant on the quality of the integration over a wide chemical-shift range. Although it is useful for getting a DS estimate, we believe it is less accurate than the other methods.

^{13}C NMR of the Benzylamine Derivatives

The aliphatic carbon signals of the PSf-benzylamine derivatives were compared for DS determination. Three distinct signals are expected in the aliphatics, two of these from the isopropylidene group of the polymer backbone: one peak for the quaternary carbon and one peak for the two tertiary carbons. The remaining aliphatic carbon signal is the primary asymmetric carbon. The signals were initially assigned with a simple distortionless enhancement by polarization transfer (DEPT) experiment. A pulse sequence was selected with parameters for quantitative ^{13}C experiments, and then the integrations of the CH's were compared with those of the CH_3's. With this method, the measured DS values of the amine derivatives were 0.43 and 1.50.

Potential of Benzylamine-Modified PSf for Molecular Recognition Precursors

The amino groups in the modified PSf's initiated the polymerization of *N*-carboxyanhydride of γ-benzyl-L-glutamate [Glu(OBzl)–NCA]. The resulting oligopeptides of Glu(OBzl)–NCA, the degree of polymerization of which was 5.8, were converted into molecular recognition sites toward As by the application of an alternative molecular imprinting method.[26] In the preliminary experiments, 9-EA was adopted as a print molecule for the conversion of the oligopeptide of Glu(OBzl)–NCA into molecular recognition sites toward As, and their molecular recognition ability was evaluated with SPR spectroscopy.[17] In this study, for the molecular imprinting condition, the ratio of the amount of 9-EA to that of the oligopeptide was fixed at unity. The sensor device prepared in the presence of 9-EA as a print molecule recognized As in preference to Gs. The theoretical selectivity for molecular recognition toward As against Gs, being the ratio of the amount of As adsorbed to that of Gs, was calculated to be 4.6 at a substrate concentration of 5.0×10^{-5} mol dm^{-3}. Further investigations of these potential sensor devices are in progress, and the results will be reported soon.[17]

CONCLUSIONS

Two modified PSf's with 0.43 and 1.50 pendant benzyl amine groups per repeat unit were prepared by a synthesis method involving two steps. The electrophile benzonitrile was first reacted with PSf-Li, and the resulting addition benzimine product was reduced to a benzylamine product upon treatment with $NaBH_3CN$. The anticipated DS of 2.0 could not be achieved, most likely because of steric hindrance. The DS was determined with quantitative measurements from both ^{1}H and ^{13}C NMR. The benzimine and benzylamine polymer derivatives were confirmed by NMR and IR spectroscopy and also by chemical modification of the imine group into a ketone as a result of acid hydrolysis. The benzylamine-modified polymers were further reacted to introduce oligopeptide side chains, which were converted into molecular recognition sites favoring As over Gs.

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