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Modified Polysulfones. III. Synthesis and Characterization of Polysulfone Aldehydes for Reactive Membrane Materials

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ABSTRACT: Polysulfones (PSfs) containing pendant aldehyde groups have potential uses as reactive polymer supports or affinity membranes to bind enzymes and ligands. The polymeric aldehydes may also be utilized to prepare crosslinked membranes and to covalently bond inorganic species to the matrix. A series of polymers containing pendant aldehydes with degrees of substitution (DS) ranging from 0.1 to 2.0 groups per repeat unit was prepared by lithiation at the orthosulfone site and then treatment of the intermediate with dimethylformamide (DMF), a formyl equivalent electrophile. A polymer with aldehyde groups (DS 2) at the orthoether site was also prepared by lithiation of brominated PSf followed by DMF. The new polymer structures were characterized in detail by NMR spectroscopy, and their thermal properties were investigated by DSC and thermogravimetric analysis. © 2001 John Wiley & Sons, Inc.* J Polym Sci A: Polym Chem 39: 675–682, 2001

Keywords: polysulfone modification; lithiation; polymeric aldehyde; reactive membrane; affinity

INTRODUCTION

Functional polymers are of interest for reagents, catalysts, chromatography media, membranes, and many other purposes.¹ Polymers containing aldehyde groups have been a subject of interest as membrane materials used in biochemistry and in optical chemistry.² Because aldehyde is strongly reactive toward a variety of nucleophiles, aldehyde polymers have been reported as materials for affinity membranes for adsorption and separation. As a result of the reactivity of the aldehyde group, polymeric aldehydes are less common than other functional polymers. At least four approaches for the preparation of polymeric aldehydes have

been used: polymerization of a functional monomer, end-capping a polymer, oxidative bond-cleavage, and polymer postmodification.

Wolpert³ synthesized an aldehyde copolymer (PAN-PAL) from acrolein and acrylonitrile monomers because acrolein homopolymers give insoluble polymers as a result of spontaneous condensation of aldehyde groups into tetrahydropyran rings. Soluble polymers were obtained where the aldehyde content was limited to < 20 mol % to impede condensation from occurring. Enzymes were bonded covalently with the reactive affinity PAN-PAL (> 10 : 1) membrane surface. Vishwanath et al.⁴ immobilized alkaline phosphatase onto an aldehyde-modified commercial Ultra-bind® poly(ether sulfone) (PES) membrane either directly or using spacer arms. Recently, PES with pendant aldehyde groups was prepared by polymerizing functional bisphenol monomers, and, subsequently, photosensitive azobenzene units were attached to the resulting PES aldehyde.^{5,6}

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Using another approach, Quirk and Kuang⁷ end-capped functionalized polymeric organolithium compounds with aldehyde groups using 4-morpholinecarbaldehyde as an electrophile. The rapid reaction of aldehyde with nucleophiles, especially amines to form the Schiff base, is well known. The aldehyde further reacted with primary amines such as hydroxylamine to form oxime derivatives, and the resulting Schiff base was reduced with NaCNBH₃ for particular medical applications.⁸

Polyaldehydes are also accessible through oxidative bond-cleavage reactions. A polysaccharide containing aldehyde groups was prepared by sodium-periodate ring-cleavage of sodium poly(guluronate), produced from sodium alginate.⁹ Crosslinked hydrogels with enhanced mechanical and chemical stabilities were prepared from the resulting poly(aldehyde guluronate). The hydrogels are potentially well suited for soft-tissue and drug-delivery applications. Cataldo et al.¹⁰ reported polymeric aldehydes prepared by ozonolysis of polymers containing pendant double bonds such as vinyl, methylvinyl, and dimethylvinyl. Apart from aldehyde groups, ozonolysis also resulted in ketonic and carboxylic groups.

Coutterez and Gandini¹¹ prepared both oligofurylene and oligothiénylene vinylenes bearing a terminal aldehyde functionality as new-generation polymeric materials for optoelectronic devices. The electrochemical reactivity and photochemical properties are derived through exploitation of the reactive aldehyde groups. Polyimides containing aldehyde groups have been used to prepare nonlinear optical materials by the reaction of pendant aldehyde groups with methanesulfonylacetonitrile. A polyimide aldehyde was prepared by Kim et al.¹² by polymerization of an aldehyde-containing azobenzene monomer with a 6F-diimide monomer.

A postmodification method was reported whereby polysulfone (PSf) was first chloromethylated and then partially oxidized to give aldehyde groups along with several other side-product groups.¹³

The focus of our studies has been on the preparation of modified PSfs by lithiation,^{14,15} primarily as materials for specialty membranes. PSf is commonly used as a membrane material that has a chemically stable backbone on which a variety of functional groups can be attached using established modification chemistries. Our group and others previously reported the preparation of modified PSfs containing a variety of functional

groups by lithiation.^{15–21} These materials have been applied to membrane-separation processes including ultrafiltration, nanofiltration, reverse osmosis, gas separation, pervaporation, affinity separation, and electromembrane.²¹

In the present article, we report on a novel chemical modification for the conversion of PSf into soluble PSf aldehydes (PSf-CHO) using lithiation chemistry and a masked formyl electrophile. We utilized the reactive polymeric aldehydes prepared in the present work for the preparation of covalently bound polymer-zeolite membranes for selective gas separations. The membrane casting and reactive-binding technique as well as the membrane-permeation data are reported elsewhere. PSf-CHO also has potential use in the preparation of crosslinked membranes and for ligand-binding or affinity membranes.

EXPERIMENTAL

Materials

PSf Udel P-3500 (BP-Amoco) was dried at 110 °C for at least 24 h. Reagent-grade tetrahydrofuran (THF) was freshly distilled over lithium aluminum hydride (LiAlH₄). *n*-Butyllithium (10 M in hexane) was obtained from Aldrich Chemical Co. and used as received. Dimethylformamide (DMF) was dried by vacuum distillation over barium oxide. Reactions were conducted under a constant argon purge and with mechanical stirring. A mixture of dry ice and ethanol was used for cooling the reaction mixtures. All modified polymers were recovered by precipitation in ethanol using a Waring blender, washed thoroughly, then dried in a vacuum oven.

Characterization Methods

Nuclear magnetic-resonance spectra were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz for ¹H and 100.579 MHz for ¹³C. For each analysis, ~ 10 wt % polymer solution was prepared in CDCl₃, and tetramethylsilane was used as the internal standard.

Infrared spectra were obtained using a Midac "M" Fourier transform infrared spectrometer equipped with a deuterated tri-glycine sulfate (DTGS) detector. Polymer samples were measured as thin films by dissolving 50 mg of polymer

in 2 mL of THF, pouring the solution onto a glass plate, and allowing it to evaporate. Films were released by immersion into water and then vacuum-dried.

A DuPont 951-thermogravimetric analyzer was used for measuring the degradation temperatures by thermogravimetric analysis (TGA), whereas DSC was used for measuring the glass-transition temperature (T_g). Polymer samples for TGA were ramped to 60 °C at 1 °C/min, held isothermally for 120 min, and then heated to 600 °C at 10 °C/min for the degradation temperature measurement. Samples for DSC were heated initially to 230 °C at 10 °C/min, quenched with liquid nitrogen, held isothermally for 10 min, and reheated to 250 °C at 10 °C/min for the T_g measurement.

Preparation of Polysulfone(Orthosulfone) Aldehydes (DS 0.1 ~ 2.0) from Lithiated Polymers

A solution of PSf (3.80 g, 8.6 mmol) in THF (100 mL) was mechanically stirred under argon atmosphere and cooled to approximately -60 °C. *n*-Butyllithium was injected dropwise at a rate of ~ 30 mLh⁻¹ using a syringe pump. The polymer was lithiated with a quantity of *n*-butyllithium adjusted by the required degrees of substitution (DS) ranging from 0.1 to 2.0 using previously established procedures.¹⁸ Because PSf-CHO was not produced quantitatively in the next step by reaction of the lithiated polymer with DMF, an additional 0.2 mol equivalent of butyllithium was added to give the required DS of aldehyde. Lithiated PSf was stirred for 20 min, and then a cooled (-60 °C) mixture of DMF (3.3 mL, 43 mmol) and freshly distilled THF (3.3 mL) was syringed rapidly into the reaction flask under vigorous stirring. The clear solution of lithiated polymer rapidly changed to an opaque pink mixture. After approximately 5 min, the viscosity decreased rapidly, and the mixture was stirred for an additional 40 min at -50 °C. During the last 15 min, the mixture had a milky appearance. The reaction was terminated by adding dilute acid (20 mL of 3% HCl), which resulted in a clear yellowish solution. PSf-CHO was recovered as a white solid by precipitation from ethanol 95%, then washed and filtered several times before being vacuum-dried at 70 °C overnight. The PSf-CHOs were prepared in a DS range of 0.1–2.0 aldehyde groups per repeat unit at the orthosulfone site and recovered in 90–95% yield. The polymers were protected

from light and high temperature to prevent unwanted side reactions of the aldehyde groups.

Preparation of Polysulfone(Orthoether) Aldehydes (DS ~ 2) from Lithiated Polymers

PSf orthoether aldehydes were prepared with ~ 2 DS by following an established lithiation procedure of dibrominated PSf at -78 °C¹⁸ and then quenching with DMF at ~ -60 °C, following a procedure similar to the preceding one.

Determination of DS

DS was readily determined using ¹H NMR by comparison of the integration of the distinct downfield aldehyde signal with that of the two isopropylidene methyl groups. For example, DS of disubstituted PSf orthosulfone aldehyde can be calculated either by the distinct new aromatic signal at 7.50 ppm for H12 or by the aldehyde proton.

RESULTS AND DISCUSSION

Synthesis

A series of aldehyde-functionalized polysulfones with DS ranging from 0.1 to 2.0 was prepared by direct lithiation followed by reaction with DMF, a masked formyl electrophile. The scheme for preparing PSf-CHO (DS ~ 1 and ~ 2) at the orthosulfone site is illustrated in Figure 1. DS of PSf orthosulfone aldehydes that are derived by quenching PSfs of various degrees of lithiation are listed in Table I. DS of PSf-CHO could be readily controlled by the molar ratio of *n*-butyllithium to PSf by using the required molar equivalent plus 0.2.

Many of our initial attempts to prepare soluble PSf-CHO derivatives from PSf-Li were only successful when the degree of lithiation was 0.5 or less. Above this value, insoluble or crosslinked polymer derivatives were obtained. Above a DS value of 0.5, the presence of unsubstituted, mono-substituted, and disubstituted sites exist on the polymer chain according to a distribution determined previously.²⁰ This result led us to suspect that inter and intramolecular reactions about the sulfone linkage were occurring between a lithiated site and a DMF reacted site. A number of reaction variables such as reaction temperature, the amount and method of added DMF, and the

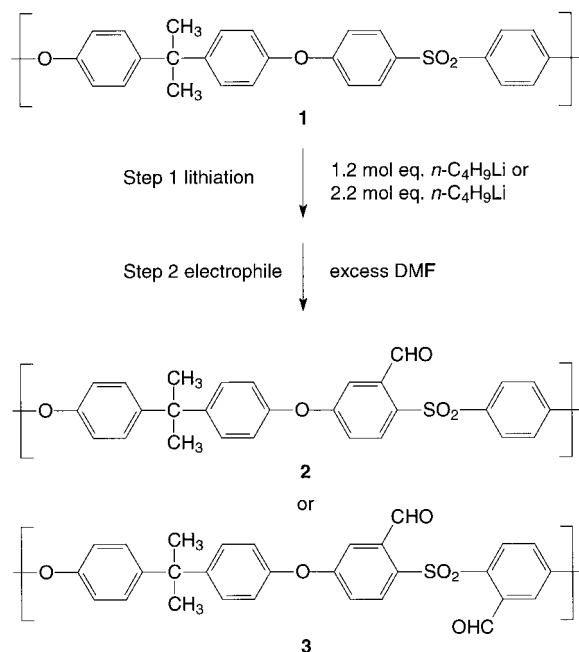


Figure 1. Reaction scheme for polysulfone aldehyde modified at the orthosulfone site.

speed of stirring were investigated to obtain higher DS for PSf-CHO.

In one experimental reaction, iodomethane was added to quench the reaction soon after reaction with DMF. During the workup procedure a strong smell of trimethylamine was detected, suggesting that the lithiated intermediate converted rapidly into the aldehyde form. Because the orthosulfone PSf-CHO is very reactive, being influenced by the electron-withdrawing effect of the sulfone, it is probable that interchain crosslinking competes with DMF addition on unreacted lithiated sites. The probable pathway for the formation of PSf-CHO as well as the formation of crosslinks under unfavorable reaction conditions are shown in Figure 2.

Initially, reactions were performed in the temperature range of approximately -40 to -50 °C,

Table I. The DS of Polysulfone(Orthosulfone)-Aldehydes Derived from Lithiated Intermediates

DS of PSf-Li	DS of PSf-CHO Orthosulfone
0.35	0.16
0.50	0.29
1.20	0.97
2.20	1.93

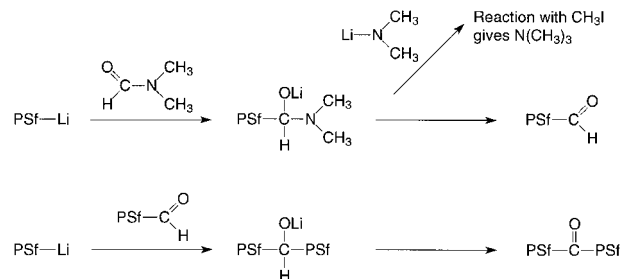


Figure 2. Possible mechanism of polysulfone-aldehyde formation and formation of crosslinked sites.

which led to insoluble polymers at higher DS values. A range of polymer concentrations was also tested indicating that inconsistent results were obtained when $> 7\%$ solutions were used. The mode of addition of DMF was also found to be an important variable. Addition of DMF to lithiated PSf initially results in a highly viscous mixture. To minimize side reactions, it is necessary for all the polymer-lithiated sites to be quenched rapidly with DMF to reduce the chances of reactions with already DMF-reacted sites. Addition of DMF diluted with THF and cooled to the optimal temperature increased the mixing efficiency of DMF with the lithiated polymer.

Because of the reactive nature of aldehyde groups, carefully controlled reaction conditions are important for preparing fully soluble PSf-CHO polymers free of crosslinking or side reactions. Soluble PSf-CHO polymers in the full DS range of 0.1–2.0 were successfully prepared using the appropriate conditions. A 4% solution of PSf

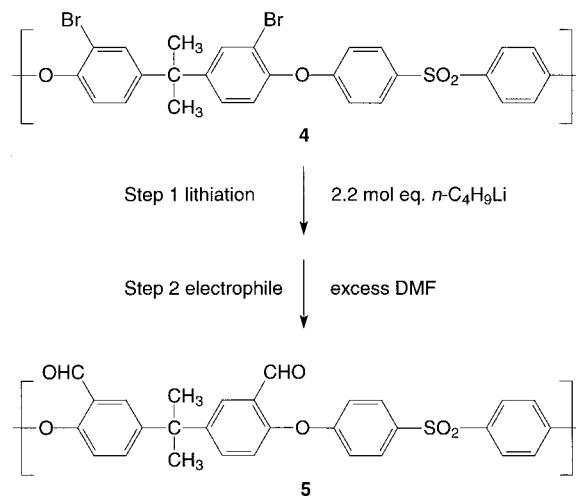


Figure 3. Reaction scheme for polysulfone aldehyde modified at the orthoether site.

Table II. Solubilities of Polysulfone Aldehydes

Polymer	THF	CHCl ₃	DMAc	DMSO
PSf-CHO 2 DS~ 1	S ^a	S	S	P ^b
PSf-CHO 3 DS~ 2	S	S	S	S
PSf-CHO 5 DS~ 2.0	S	S	S	S

^a S = Soluble.^b P = Partly soluble.

was reacted directly with *n*-butyllithium at approximately -60 °C, resulting in a THF-soluble homogeneous intermediate. These intermediates were lithiated with high regioselectivity and reacted readily with sequentially added DMF at approximately -60 °C. The low reaction temperature was necessary to obtain soluble polymers, presumably by suppression of the crosslinking reaction. If lower temperatures had been used, the reaction would have been less effective because DMF would have frozen thereby becoming less reactive. A THF solution of DMF cooled to -60 °C was used to prevent a temperature increase.

Dibrominated PSf was lithiated at -78 °C using previously established methods.¹⁸ The intermediate was treated with DMF at -60 °C according to the previously described procedure. PSf-CHO with DS = 1.98 at the orthoether site was obtained as outlined in Figure 3.

Solubility Test

Solubility tests confirmed that all the aldehyde-substituted PSfs were not crosslinked when pre-

pared under controlled conditions. Solubility was observed during the day of sample preparation, then 14 d later to determine if the solutions were stable. The samples were protected by an inert atmosphere and light to eliminate the possibility of an environmental reaction. The results of the solubility tests are summarized in Table II.

Structural Characterization

¹H NMR

The chemical shifts (ppm), multiplicity (s: singlet, d: doublet, and m: multiplet), and couplings (Hz) of proton signals for the starting materials and the aldehyde-functionalization polymers are listed in Table III. Unsubstituted, mono, and disubstituted repeat units are abbreviated as U, M, and D, respectively, in the spectra.

The proton spectra A and B are of orthosulfone PSf-CHOs in Figure 4. Spectrum A is polymer **2** and is approximately monosubstituted (DS 0.97), whereas B is polymer **3** and is approximately disubstituted (DS 1.93). The disubstituted polymer has a simple unambiguous spectrum B showing the H8 doublet of doublets at 7.22 ppm three-bond coupled (8.8 Hz) to H9 at 8.05 and also long-range (four-bond, 2.8 Hz) coupled to H12 at 7.50 ppm. As expected, the H13 aldehyde proton is deshielded by the anisotropic effect of the carbonyl and appears far downfield at 10.62 ppm. Downfield shifts of protons in the phenylsulfone ring occur because of the deshielding effect of aldehyde, whereas protons on the unsubstituted ring remain virtually unchanged. Any remaining

Table III. ¹H NMR Data for Polysulfone and Polysulfone Aldehydes

Proton Number	PSf 1	PSf-CHO 2 DS~ 1	PSf-CHO 3 DS~ 2	PSf-CHO 5 DS~ 2
H2	6.93 (d, <i>J</i> 8.8)	6.89–7.05 (m)	6.96 (d, <i>J</i> 8.8)	6.89 (d, <i>J</i> 8.8)
H3	7.24 (d, <i>J</i> 8.8)	7.18–7.31 (m)	7.28 (d, <i>J</i> 8.8)	7.39 (dd, <i>J</i> 8.8, 2.8)
H5	7.24 (d, <i>J</i> 8.8)	7.18–7.31 (m)	7.28 (d, <i>J</i> 8.8)	7.83 (d, <i>J</i> 8.8)
H6	6.93 (d, <i>J</i> 8.8)	6.89–7.05 (m)	6.96 (d, <i>J</i> 8.8)	—
H8	7.00 (d, <i>J</i> 8.8)	7.18–7.31 (m)	7.22 (dd, <i>J</i> 8.8, 2.8)	7.07 (d, <i>J</i> 8.8)
H9	7.84 (d, <i>J</i> 8.8)	8.09 (d, <i>J</i> 8.8)	8.05 (d, <i>J</i> 8.8)	7.89 (d, <i>J</i> 8.8)
H9'	—	7.78 (d, <i>J</i> 8.8)	—	—
H11	7.84 (d, <i>J</i> 8.8)	—	—	7.89 (d, <i>J</i> 8.8)
H12	7.00 (d, <i>J</i> 8.8)	7.50 (dd, <i>J</i> 8.8, 2.8)	7.50 (d, <i>J</i> 2.8)	7.07 (d, <i>J</i> 8.8)
H13	—	10.77 (s)	10.62 (s)	10.26 (s)
CH ₃	1.69 (s)	1.69 (s)	1.71 (s)	1.71 (s)

Chemical shifts and multiplicity, coupling constants.

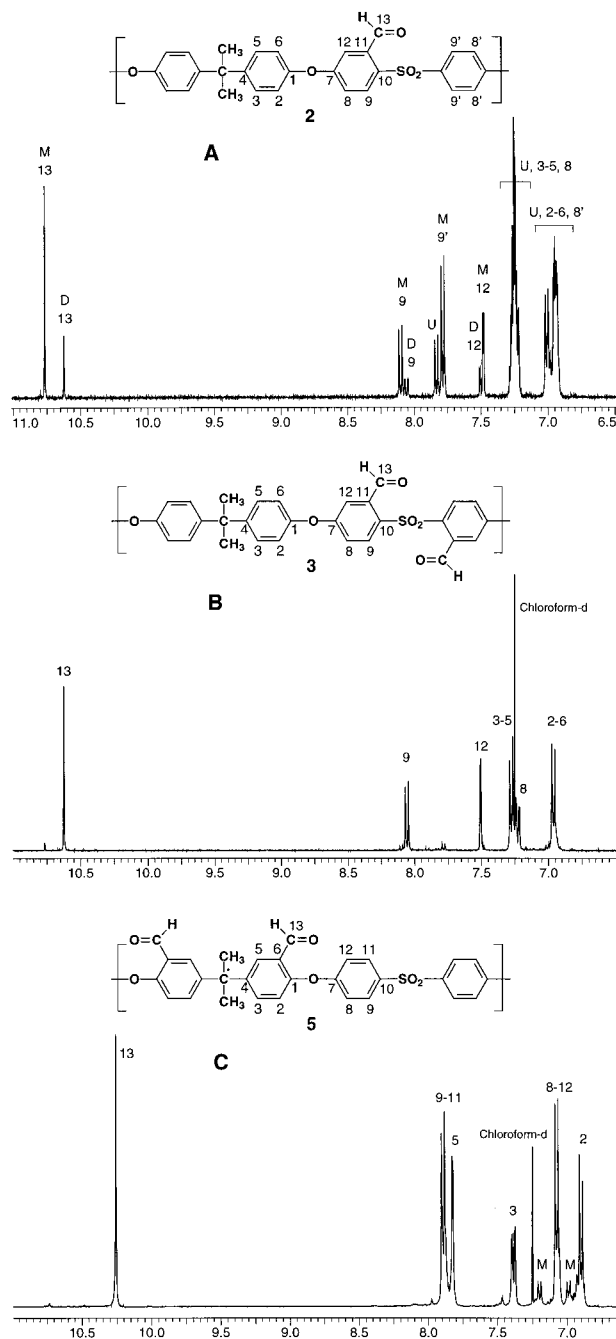


Figure 4. ^1H NMR spectra of aldehyde-functionalized polysulfones.

minor signals represent monosubstituted repeat units as a result of incomplete disubstitution.

The more complex spectrum of the monosubstituted (DS 0.97) aldehyde derivative [Fig. 4(a)] is due to the presence of three different repeat units bearing one, two, or no aldehyde groups. Two distinct aldehyde singlets separated by 0.15 ppm

represent the mono and disubstituted repeat units. From the integration values of the aldehyde signals, the ratio of mono to disubstituted sites is estimated at 5.6. The remaining absorptions were readily assigned by simple a comparison with the spectrum of the disubstituted polymer, attributing the remaining signals to mono-substituted and unsubstituted repeat units.

Spectrum C of the disubstituted orthoether PSf-CHO **5** [Fig. 4(c)] resembles that of the orthosulfone polymer in the sense that it has the same spin systems. The H3 doublet of doublets at 7.39 ppm is coupled with H2 at 6.89 ppm and with H5 at 7.83 ppm. The characteristic aldehyde absorption appears downfield at 10.26 ppm, and the aromatic protons of the substituted ring are shifted downfield because of the deshielding effect of the aldehyde group. Residual signals are attributed to monosubstituted repeat units.

We observe that the chemical shift of the orthosulfone-aldehyde proton of the sulfone-disubstituted polymer was 0.37 ppm further downfield than that of the orthoether derivative. This suggests that the orthosulfone aldehyde is more polarized because of the electron-withdrawing effect of the sulfone group as well as more reactive.

^{13}C NMR

The ^{13}C NMR chemical shift values for disubstituted PSf-CHOs are listed in Table 4. The carbon spectra of PSf-CHOs **3** and **5** are represented in

Table IV. ^{13}C NMR Chemical Shifts of Disubstituted Polysulfone Aldehydes (ppm)

Carbon Number	PSf 1	PSf-CHO 3 DS~ 2	PSf-CHO 5 DS~ 2
C1	152.82	151.97	155.67
C2	119.80	120.05	120.35
C3	128.43	128.70	134.65
C4	147.15	147.81	146.81
C5	128.43	128.70	126.56
C6	119.80	120.05	127.16
C7	161.95	162.81	161.09
C8	117.67	121.05	118.36
C9	129.68	131.47	130.02
C10	135.40	135.67	136.45
C11	129.68	135.99	130.02
C12	117.67	117.70	118.36
C13	—	188.22	188.37
$\text{CH}_3\text{—C—CH}_3$	42.40	42.52	42.64
CH_3	30.94	30.86	30.52

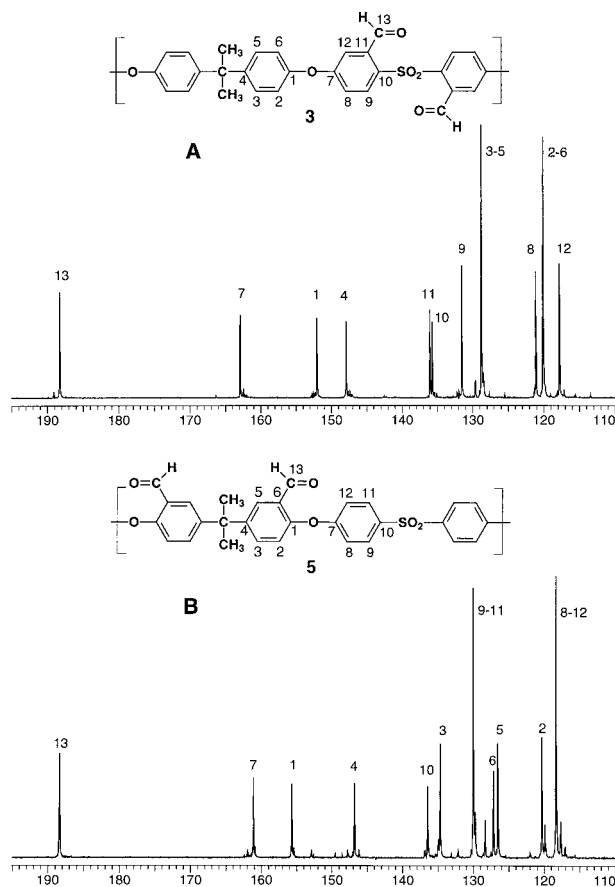


Figure 5. ^{13}C NMR spectra of polysulfone aldehydes.

Figure 5. The signals were assigned unambiguously by a combination of one- and three-bond long-range ($^3J_{\text{C-H}}$ set to 7.5 Hz) carbon–hydrogen heteronuclear correlations. Each aldehyde carbon had a characteristic downfield shift of ~ 188 ppm.

Infrared

Films of the aldehyde derivatives show strong sharp absorptions at 1690 cm^{-1} for orthosulfone aldehydes and at 1691 cm^{-1} for orthoether aldehydes, arising from $\text{C}=\text{O}$ asymmetric stretching vibrations. The absorption band also became more intense with increasing DS values.

Thermal Stability

The thermal stabilities of disubstituted PSf-CHOs were measured using TGA, and the weight-loss curves are shown in Figure 6. The orthosulfone aldehyde **3** curve exhibits a two-step degradation, whereas the orthoether aldehyde **5** curve shows only a single-step degradation. The extrap-

olated onsets of weight loss for **3** and **5** derivatives occurred at 302.1 and 392.8 $^{\circ}\text{C}$, and the actual onsets of degradation occurred at 235.0 and 292.9 $^{\circ}\text{C}$, respectively. The initial-step degradation for polymer **3** is believed to be the loss of aldehyde because the weight loss is close to the theoretical weight loss of 11.3% from PSf with $\text{DS} = 1.93$. Orthoether derivative **5** has a higher thermal stability than orthosulfone **3**. The reason for the lower stability of **3** is probably that the aldehyde groups are more polarized and easier to remove because of the strong electron-withdrawing effect of the sulfone linkage.

Weight losses below 220 $^{\circ}\text{C}$ occurred for both of the aldehyde derivatives. This is most likely a result of desorption of water, which is strongly bound to the polymers containing the strongly polar aldehyde group.

Glass-Transition Temperature

The glass-transition temperatures (T_g) for disubstituted polymers were determined from DSC measurements. Compared to the T_g value of 188.1 $^{\circ}\text{C}$ for PSf, both aldehyde polymers had reduced T_g values. The T_g value of polymer **5** is 178.0 $^{\circ}\text{C}$, whereas that of polymer **3** is 165.3 $^{\circ}\text{C}$, which suggests that the aldehyde had the effect of reducing chain-stiffening on the polymer backbone.

CONCLUSION

Polymeric aldehydes were prepared by modification of PSf by a two-step procedure of lithiation

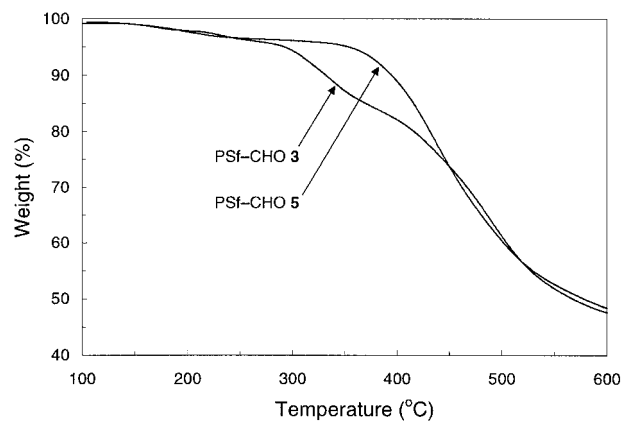


Figure 6. TGA curves of orthosulfone-**3**- and orthoether-**5**-aldehyde derivatives.

followed by treatment with DMF, a formyl equivalent. Orthosulfone PSf-CHOs in the full range of DS 0.1 ~ 2.0 were obtained by adding the desired quantity of *n*-butyllithium from the lithiation step before reaction with DMF. Similarly, disubstituted orthoether PSf-CHO was prepared by a lithium–bromine exchange of dibrominated PSf. The appropriate reaction conditions for preparing derivatives free of crosslinking and side reactions were determined. Using the reaction conditions developed in the present article, all the PSf-CHOs were completely soluble in chloroform and other solvents.

The structures of the aldehyde-functionalized PSfs were well characterized by detailed NMR spectroscopic measurements. Measurements of the thermal stabilities by TGA showed that the orthoether aldehyde has a higher thermal stability than orthosulfone, which exhibits a two-step degradation. The onsets of degradation for both derivatives are at 235.0 and 292.9 °C, respectively. The T_{g} values of both orthosulfone and orthoether PSf-CHOs were less than the unmodified polymer (165.3 and 178.0 °C, respectively).

We have utilized the PSf-CHO polymers prepared in the present work for the preparation of mixed-matrix membranes comprising polymer and zeolites for selective gas separations. Membrane casting as well as a technique that utilizes the reactive aldehyde group on which to bind the inorganic matrix are reported elsewhere. PSf-CHO also has potential use in the preparation of crosslinked membranes as well as obvious utility for ligand-binding or affinity membranes.

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