

Functionalized Polysulfone Membranes by Heterogeneous Lithiation*

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SYNOPSIS

Polysulfone membranes were modified heterogeneously by lithiation, using *n*-butyllithium and low concentrations of tetrahydrofuran (THF). The effects of various conditions of reactant concentration, temperature, and time were determined quantitatively. The degree of substitution was measured by XPS and FTIR, using the carbonyl absorption band of lithium-activated membranes that had been converted to ones containing acyl fluoride substituents. The optimum conditions for membrane functionalization were 0.2M *n*-butyllithium in hexane at room temperature. The reaction rate increased substantially in the presence of 2% THF. The surface-lithiated membranes can be derivatized, potentially with a wide variety of functional groups. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Commercial membranes are usually fabricated from commercial polymers, for example, cellulose derivatives, aromatic polysulfones, or polyacrylonitrile. Each polymer has a balance of desirable properties for membranes such as fouling resistance, hydrophilicity, temperature and solvent resistance, pH stability, and mechanical strength.

No single material is ideally suited to all situations because of the wide range of applications and operating conditions under which membranes are used. Polysulfones are extensively used for ultrafiltration membranes and as supports for thin-film composites because of their good combination of mechanical and chemical properties. The addition of functional groups to the polymer can enhance some properties of the material in certain ways. For example, the addition of carboxyl groups increases hydrophilicity and alters the solubility characteristics, allowing greater water permeability and better separation.^{1,2} Blood compatibility may also be improved by functionalization. In addition, functional groups are an intrinsic requirement for affinity, ion exchange, and other specialty membranes.

Polysulfone membranes with functional groups may be prepared by casting functionalized polymer or by chemical modification of a preformed membrane. In the former case, the membrane material is distinct and may have solubility characteristics unlike the parent polymer, resulting in a functionalized membrane that has a quite different microstructure and pore size. In the latter case, functional groups can be added to an existing polysulfone membrane, without altering the defined microstructure and pore size.

Homogeneous modification of polysulfones has been achieved by a number of methods. Sulfonation techniques^{3–6} have resulted in hydrophilic and negatively charged membranes.^{7–11} Polysulfones have been halomethylated^{12–15} to provide useful intermediates that have been subsequently derivatized or quaternized to cationic membranes.^{14–17} Several types of functional group polymers have been derived from lithiated^{1,18–22} and brominated^{17,21} polysulfones. Other functionalization techniques have led to nitro,^{17,23} amino,²³ and aminomethyl^{17,24} derivatives.

Heterogeneous modification entails the functionalization of a membrane surface only, thus changing the surface forces at the membrane–solution interface. The chemical nature of this interface influences fouling and other characteristics of the membrane. Surface modification is potentially

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more economical and provides a means of functional group attachment to reduce fouling as well as for affinity and immobilized enzyme membranes. Cross-linking reactions can be tolerated since the reaction is on a preformed membrane, but conditions should be mild enough to prevent chain scission or deleterious effects on the pores. Higuchi et al. surface-modified polysulfone membranes by Friedel-Crafts chemistry using propane sultone^{25,26} and propylene oxide²⁷ and showed their advantage in protein separations.²⁸ The group of Staude et al. made a comparison between polysulfone membranes functionalized both heterogeneously²⁹ and homogeneously³⁰ by several chemical methods including lithiation.

In this paper, we have extended our previous work on the homogeneous modification of polysulfone^{1,18,19} to report on the heterogeneous functionalization of polysulfone membranes by lithiation. A variety of conditions and their effect on the degree of substitution (DS) at the surface of the membrane have been examined. Once activated by lithiation, the membrane surface is amenable to *in situ* derivatization with a number of different electrophilic species. Thus, in contrast to many other modification procedures, this procedure has the potential to provide membranes containing a variety of functional group classes.^{19,31}

EXPERIMENTAL

Membrane Preparation

Udel® polysulfone P-3500 was obtained from Amoco Performance Products. Casting dopes were 22% w/w solutions of polysulfones in *N*-methyl-2-pyrrolidinone (NMP). The solutions were cast mainly onto glass plates, or some onto a polyester backing material, with a doctor knife (blade clearance 254 μm). The cast solutions were gelled rapidly into ice-cold deionized water. Residual NMP was leached from the membranes by soaking them in water replaced each day over a 5 day period. Drying was accomplished by solvent-exchange using the following procedure: 50% aqueous isopropanol (24 h), isopropanol (24 h), then storage in hexane. Chemical treatment was equally effective on either hexane wetted or vacuum-dried membranes.

Chemical Treatment

Commercially obtained reagent-grade solvents were used without further purification. Technical-grade

NMP, butyllithium, and potassium *t*-butoxide were obtained from Aldrich Chemical Co. Reaction mixtures containing THF were freshly prepared because butyllithium is known to cleave THF at 35°C.³² Membranes were immersed in the reactive bath under N₂ for time periods of 1, 5, 15, 30, and 60 min. Depending on the extent of lithiation, the membranes changed color from white to yellowish brown. The majority of the lithiated membranes were quenched with CO₂ by immersing them in a hexane bath containing freshly prepared crushed dry-ice for 4 h under a N₂ atmosphere. The reacted membranes were washed for 1 h in 3N HCl and then for 15 h in distilled water to convert the lithium carboxylate functionality to carboxylic acid and to remove all Li⁺ salt residues. After vacuum drying, these membranes were exposed to sulfur tetrafluoride (SF₄) gas for approximately 15 h at ambient temperature in polyethylene containers. The resulting acyl fluoride derivatives were analyzed for DS by internal reflection spectrum, Fourier transform infrared (IRS-FTIR) spectroscopy.

Analytical Techniques

The membranes were too thick and opaque to be examined by conventional transmission infrared (IR). Both surfaces of each acyl fluoride-derivatized membrane were examined by IRS-FTIR using a Nicolet 7199 with a LN₂-cooled MCT detector. Surface spectra were recorded by mounting the required membrane surface ($\sim 5 \text{ cm}^2$) against a germanium crystal and recording the IRS of the membrane surface as described previously.³³ These conditions generate wavelength-dependent surface spectra, corresponding to $\sim 0.5 \mu\text{m}$ surface layer at 1600 cm^{-1} .

Surfaces of selected unmodified and modified membranes were further examined by X-ray photoelectron spectroscopy (XPS), using a Perkin-Elmer Physical Electronic's Model 5500 (aluminum K α monochromated illumination). Surface atomic composition and functional group information were obtained on each membrane surface, before and after carboxylation. Samples ($\sim 1 \text{ cm}^2$) were mounted on the XPS stage and evacuated at $< 1 \times 10^{-9}$ Torr, and surface spectra corresponding to about 75 Å surface layer were collected, employing charge neutralization with an electron floodgun. Photoelectron core-level energies corresponding to atoms present and chemical shifts caused by neighboring groups were compared to published assignments.³⁴

RESULTS

Spectroscopic Analysis

IRS-FTIR

The relatively weak 1740 cm^{-1} carboxylic acid IRS absorptions produced by surface carboxylation were enhanced by reaction with sulfur tetrafluoride gas. Carboxylic acids are quantitatively converted to acid fluoride [$-\text{C}(=\text{O})\text{F}$] groups with sharp, intense IRS absorptions at $1800\text{--}1850\text{ cm}^{-1}$, well separated from the normal carbonyl region ($1700\text{--}1780\text{ cm}^{-1}$).³⁵ Absolute DS for carboxylate substitution on each polysulfone repeat unit were estimated from the 1834 to 1582 cm^{-1} absorbance ratio (acid fluoride and phenyl ring absorptions, respectively). This ratioing to an invariant backbone absorption corrects for fluctuations in sample size and any contact problems on the Ge crystal. This absorbance ratio was calibrated in terms of DS from a comparison with the absorbance ratios measured on SF_4 -treated, homogeneously modified carboxylated polysulfones¹ that had known DS (0.1–1.0 range) and had been cast into membranes so that the IRS could be recorded in exactly the same way as for heterogeneously carboxylated membranes. The DS values were measured by ^1H -nuclear magnetic resonance (NMR) spectroscopy of methyl ester derivatives.¹ A linear relationship relates the DS values of cast films and the 1834 to 1582 cm^{-1} absorbance ratio. This calibration line is shown in Figure 1.

Figure 2 shows representative IRS-FTIR spectra of the surface of a membrane cast from an homogeneously modified carboxyl polysulfone (C) com-

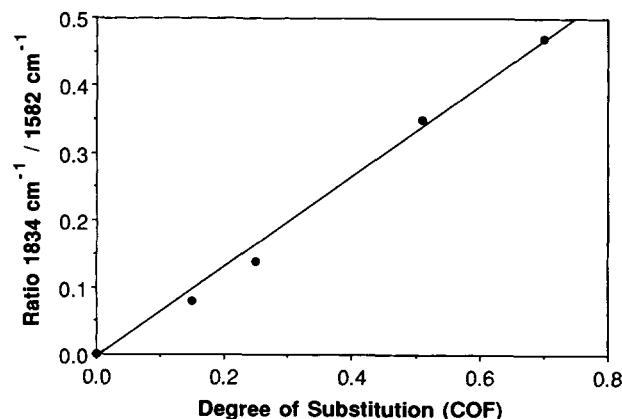


Figure 1 IRS-FTIR calibration line for the 1834 to 1582 cm^{-1} absorbance ratio vs. the degree of substitution of carboxyl groups (determined from ^1H -NMR measurements of homogeneously modified polymer).

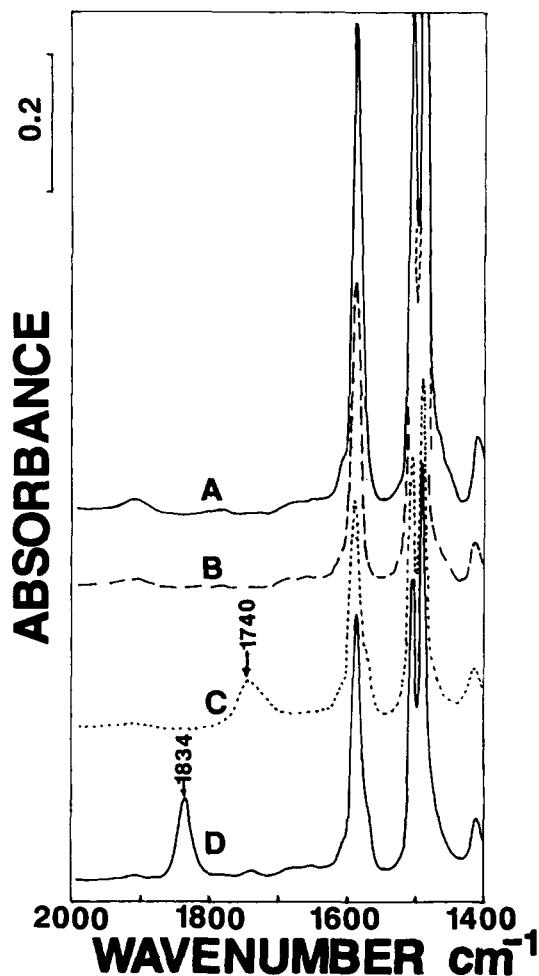


Figure 2 Comparative IRS-FTIR spectra of unmodified, $-\text{COOH}$ and $-\text{COF}$ derivatized polysulfone membranes cast from homogeneously modified polysulfone. All spectra recorded on Ge reflection element with 45° incidence. (A) Top (active skin layer) surface of polysulfone membrane, as cast, identical to surface after SF_4 treatment. (B) As for (A), but back surface. (C) Top surface of membrane, as cast from homogeneously carboxylated polysulfone. Back surface shows the same spectral features. (D) Top surface of membrane cast from homogeneously carboxylated polysulfone, then SF_4 treated. Back surface shows the same spectral features.

pared with an unmodified polysulfone membrane (A and B). The spectra of both the top and bottom surface of the membrane for the carboxyl polysulfone show the same carbonyl signal (C). The enhancement brought about by SF_4 treatment (D) is shown by a shift in frequency as well as an increase in the signal intensity and decrease in bandwidth.

Representative absorption spectra for the surface-modified membranes are shown in Figure 3. The top

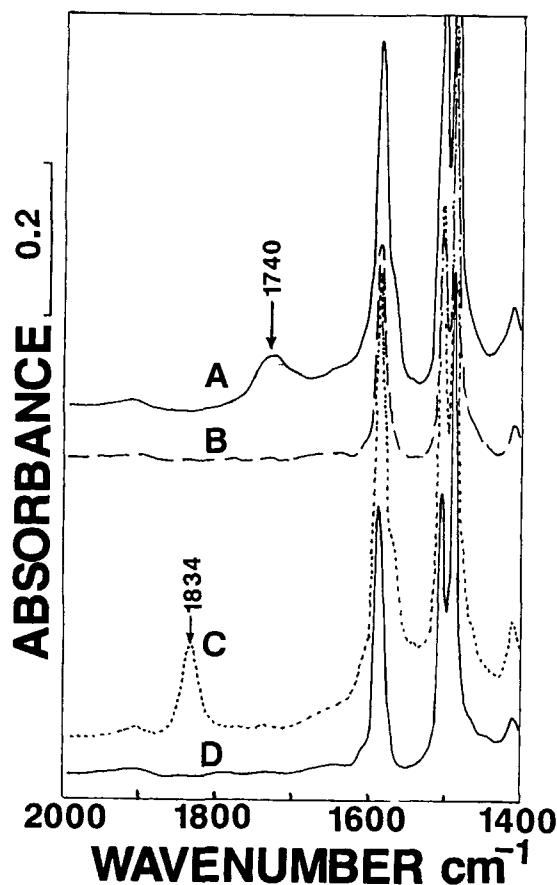


Figure 3 Comparative IRS-FTIR spectra of unmodified, $-COOH$ and $-COF$ derivatized surface-modified polysulfone membrane. Spectra recorded as in Figure 2. (A) Top (active skin layer) surface of membrane after surface carboxylation. (B) Bottom surface of the membrane shown in (A). (C) Top surface of membrane after surface carboxylation followed by SF_4 treatment. (D) Bottom surface of the membrane shown in (C).

surface of the membrane (A) has an identical spectrum to that of the carboxylated polymer prepared homogeneously [Fig. 2(C)]. No measurable carboxyl absorption was observed on the bottom surface (B). The spectra of the SF_4 -treated surfaces (C and D) augmented this observation.

XPS

Figure 4 shows a representative XPS spectrum of a surface lithiated/carboxylated membrane. XPS spectra of carboxylated membranes show the presence of the $-C(=O)-O-$ functionality (C1s peak at ~ 4.5 eV higher energy than the carbon-carbon peak at 284.6 eV) from the phenyl rings and isopropylidene group. The peak at 6.5 eV above the C-C binding energy is the aromatic ring “shake-

up” peak and is known to be sensitive to substituent effects.³⁶ The shoulder (at ~ 286.1 eV when deconvoluted) is assigned to carbons in the C-O-C linkages in the polysulfone.

Membranes prepared from homogeneously modified polysulfone showed the same DS based on $[-C(=O)-O-]/\sum [-C-]$ for both top and bottom surfaces. For surface-treated membranes, even the bottom (nonactive) surface was shown to be carboxylated to the same degree by XPS study. In contrast, IR-IRS showed that only the top (active) surface was substituted. Both methods gave fair agreement for the DS of the active surface (within $\pm 15\%$).

Metalating Agent

The chemical modification of polysulfone by lithiation¹⁸ and subsequent carboxylation¹ under homogeneous conditions has been described previously. *n*-Butyllithium was found to be the most convenient and effective metalating agent, although other alkyl and aryl lithium compounds were also effective. In this procedure, reaction at reduced temperature is essential to prevent the formation of insoluble, possibly cross-linked products. When this chemistry is applied heterogeneously to a membrane surface, some degree of cross-linking can be tolerated, and may even be beneficial, provided the membrane surface contains reactive aryllithium

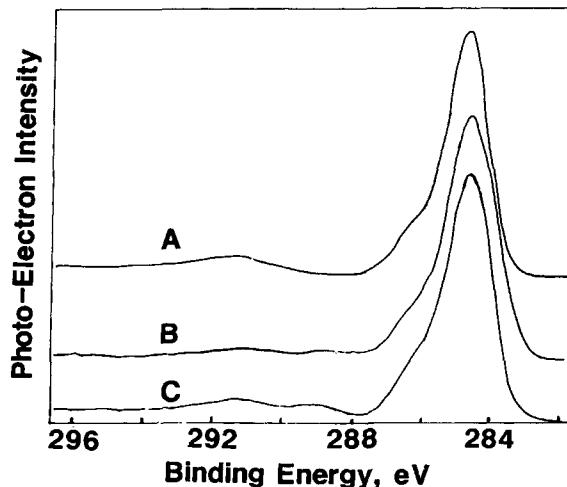


Figure 4 (A) XPS spectrum depicting the C1s region of an untreated membrane; (B) a surface-carboxylated membrane; (C) a membrane cast from homogeneously carboxylated Udel. Photoelectron intensity in arbitrary units, all spectra being normalized to equivalent intensity of the maximum at 284.6 eV.

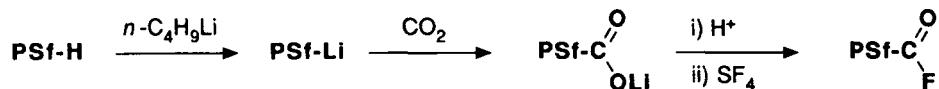


Figure 5 Reaction scheme for heterogeneous modification to prepare membrane samples for IRS-FTIR spectroscopy.

sites. To indirectly determine the DS of these sites, the lithiated polymer was carboxylated, then converted to an acyl fluoride as outlined in Figure 5.

Initially, several metalating agents and media were compared to determine their relative effectiveness. The metalating agent concentration was approximately 0.2 M in each case and the temperature was 25°C, except for the cyclohexene system, which was 0°C. The order of reactivity was 0.20 M *n*-C₄H₉Li-hexane/2% THF > 0.20 M *n*-C₄H₉Li-hexane > 0.23 M *n*-C₄H₉Li/TMEDA-cyclohexene > 0.20 M *n*-C₄H₉Li/*t*-C₄H₉OK-hexane > 0.20 M *t*-C₄H₉Li-hexane. The comparative reactivities of each metalating system are shown in Figure 6. A 15 min treatment with *n*-butyllithium in hexane without THF gave a DS of 0.33, whereas with THF, 0.47 was obtained. This contrasts with a low value of less than 0.05 obtained using 0.226 M *n*-butyllithium/tetramethylethylenediamine (TMEDA) in cyclohexene, the conditions reported by Breitbach et al.²⁹ However, it must be pointed out that the DS value increased substantially after 60 min and that the reaction is conducted at 0°C. In our experiments with homogeneous lithiation, we have not observed any reactivity enhancement using TMEDA. The strongly basic systems with potassium *t*-butoxide and with *t*-butyllithium gave surprisingly poor results.

The system 0.20 M *n*-C₄H₉Li-hexane/2% THF was adopted as the standard condition by which to compare the effect of reaction time, temperature, and butyllithium and THF concentration.

The Effect of Temperature and Time

Membranes were treated with 0.20 M *n*-C₄H₉Li-hexane/2% THF at -78, 0, and 25°C for certain periods of time to determine the effect of temperature on the DS of lithiation. The results are shown by the plots given in Figure 7. Figure 7(A) shows the effect of temperature on the reactivity of the system. Contour plot 7(B) illustrates the interactions between temperature and time. Temperature has a greater effect than reaction time on DS. At reduced temperatures, only a low level of reactivity was observed. A DS of less than 0.1 was obtained

even after 60 min exposure to *n*-C₄H₉Li. For 0.20 M, *n*-C₄H₉Li-hexane/2% THF, a DS of 0.50 could be achieved at room temperature after 40 min. The reaction proceeds rapidly during the first 5 min.

The Effect of Butyllithium and THF Concentration

Membranes were immersed in hexane containing *n*-C₄H₉Li at 0.05, 0.2, and 0.5 M concentration and containing 0, 0.05, 0.5, 2, and 4% of THF coreactant. All reactions were carried out at 25°C. The interactions of butyllithium and THF on the system reactivity are represented by the three contour plots in Figure 8.

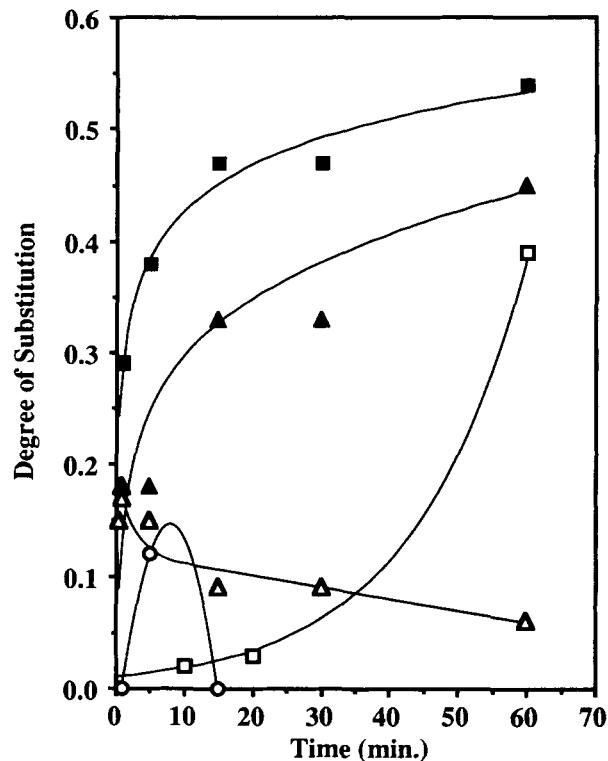


Figure 6 Comparison of chemical treatments for membrane lithiation: (■) 0.20 M *n*-C₄H₉Li-hexane-2% THF at 25°C; (▲) 0.20 M *n*-C₄H₉Li-hexane at 25°C; 0.23 M *n*-C₄H₉Li/TMEDA-cyclohexene at 0°C; (△) 0.20 M *n*-C₄H₉Li/*t*-C₄H₉OK-hexane at 25°C; (○) 0.20 M *t*-C₄H₉Li-hexane at 25°C.

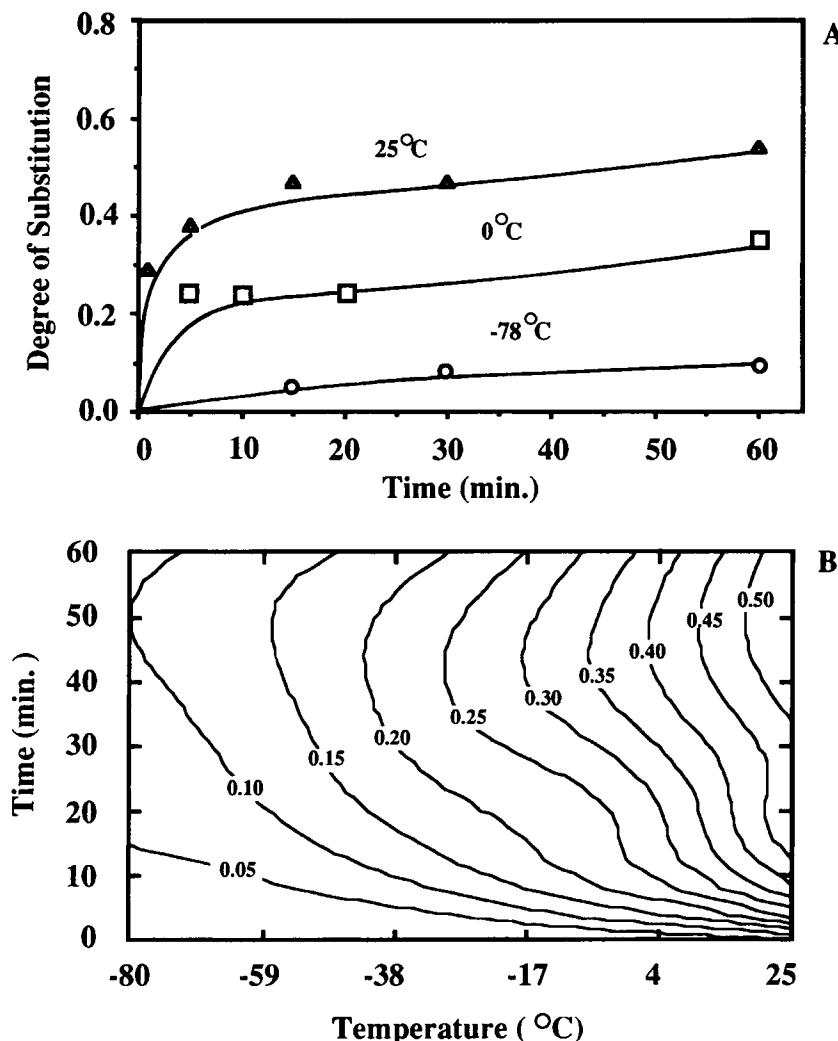


Figure 7 Plots showing the reactivity of membranes treated with 0.20 M $n\text{-C}_4\text{H}_9\text{Li}$ and 2% THF at -78°C , 0°C , and 25°C : (A) DS vs. time and (B) contour plot.

The first contour plot [Fig. 8(A)] illustrates the effect butyllithium concentration and reaction time on the DS values obtainable. In the absence of THF, higher DS values (0.5) can be achieved only by extended reaction periods with butyllithium of 0.3 M or greater. A low concentration of THF coreactant reduces the requirement for extended reaction time and butyllithium concentration [Fig. 8(B)]. A further increase to 2% THF concentration of the reaction medium has a significant effect in reducing the time and concentration factors for higher DS values. This can be visualized by the comparison of the shift of the $\text{DS} = 0.5$ contour line in plots A, B, and C. The contours of plot C show that reactivity increases sharply after a short reaction time, then begins to decrease after the membrane has been ex-

posed for an extended period of time. This anomalous behavior could be caused by the degradation of THF and depletion of butyllithium.³² The role of THF is to increase the basicity of butyllithium by reducing the aggregate size. In nonpolar hydrocarbon solvents such as hexane, n -butyllithium exists as hexameric aggregates. The reactivity or basicity is lower than in less aggregated dimeric states that exist in the presence of strong electron donors such as THF.³¹ The lower aggregate size possibly enhances the ability of the reagent to gain access and coordinate to the sulfone group in the polymer chain.

The reactant concentrations of butyllithium and THF required to derivatize membranes to certain DS values after 1, 15, and 60 min are given by the three contour plots of Figure 9. After a 1 min re-

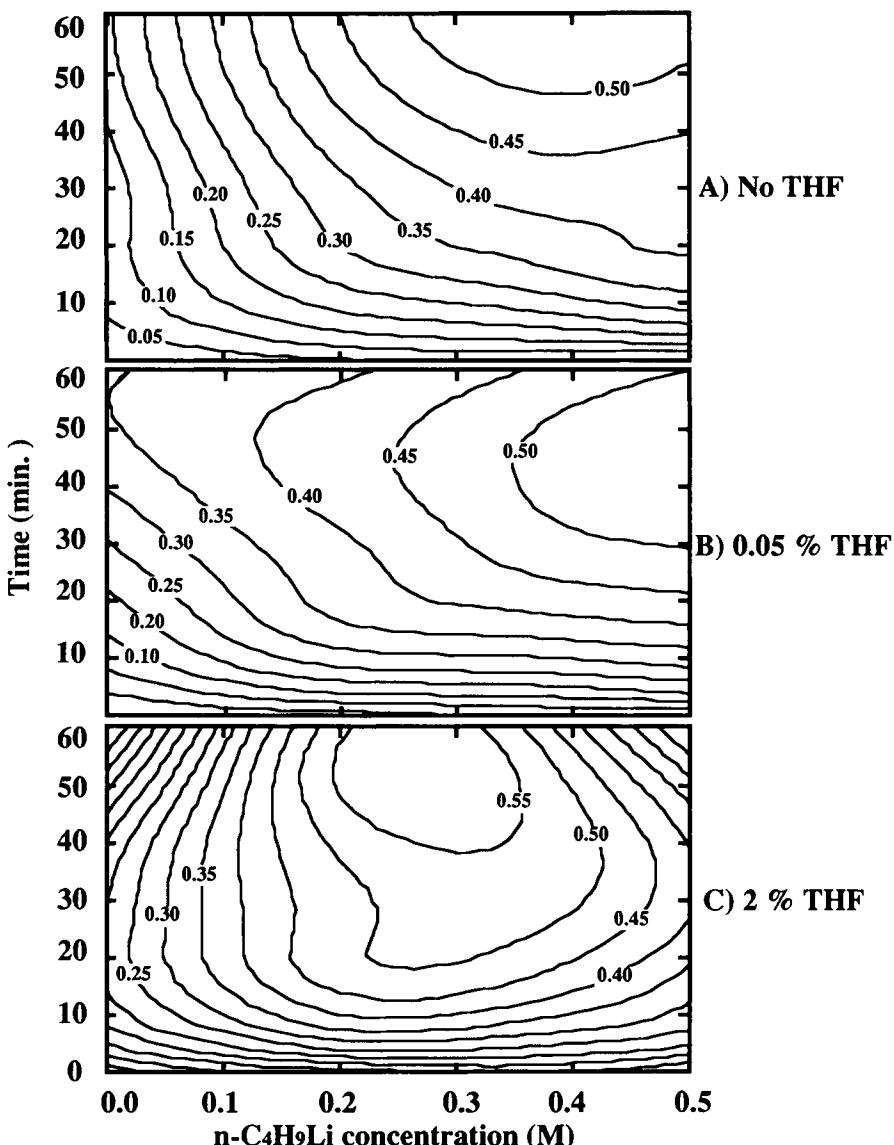


Figure 8 Contour plots of DS showing the effects of time and $n\text{-C}_4\text{H}_9\text{Li}$ concentration in the presence of (A) no THF, (B) 0.05% THF, and (C) 2% THF. Selected from experimental data measured at 1, 5, 15, 30, and 60 min intervals for 0.05, 0.2, and 0.5 M $n\text{-C}_4\text{H}_9\text{Li}$ in hexane and containing 0, 0.05, 0.5, 2, and 4% of THF coreactant.

action time, a DS of about 0.30 could be obtained using 0.2 M $n\text{-C}_4\text{H}_9\text{Li}$ with 2 or 4% THF. A DS of nearly 0.5 was obtained after 15 min with 0.2 M $n\text{-C}_4\text{H}_9\text{Li}$ and 2% THF. This was among the highest values obtained throughout the experiments, signifying that an extended reaction time is unnecessary. THF concentrations of 2% or less combined with high $n\text{-C}_4\text{H}_9\text{Li}$ concentration do not result in high DS values. Membranes immersed for 60 min actually underwent a decrease in DS in many cases, probably for the reasons already mentioned. Values

higher than 0.55, the maximum obtained experimentally, are predicted by the contour plot extrapolation. However, a required THF concentration above 4% is predicted, which could be detrimental to the porous structure of the membrane because of the solubility of polysulfone in this solvent.

DISCUSSION

The DS values obtained by heterogeneous lithiation (0.55 maximum) were considerably lower than the

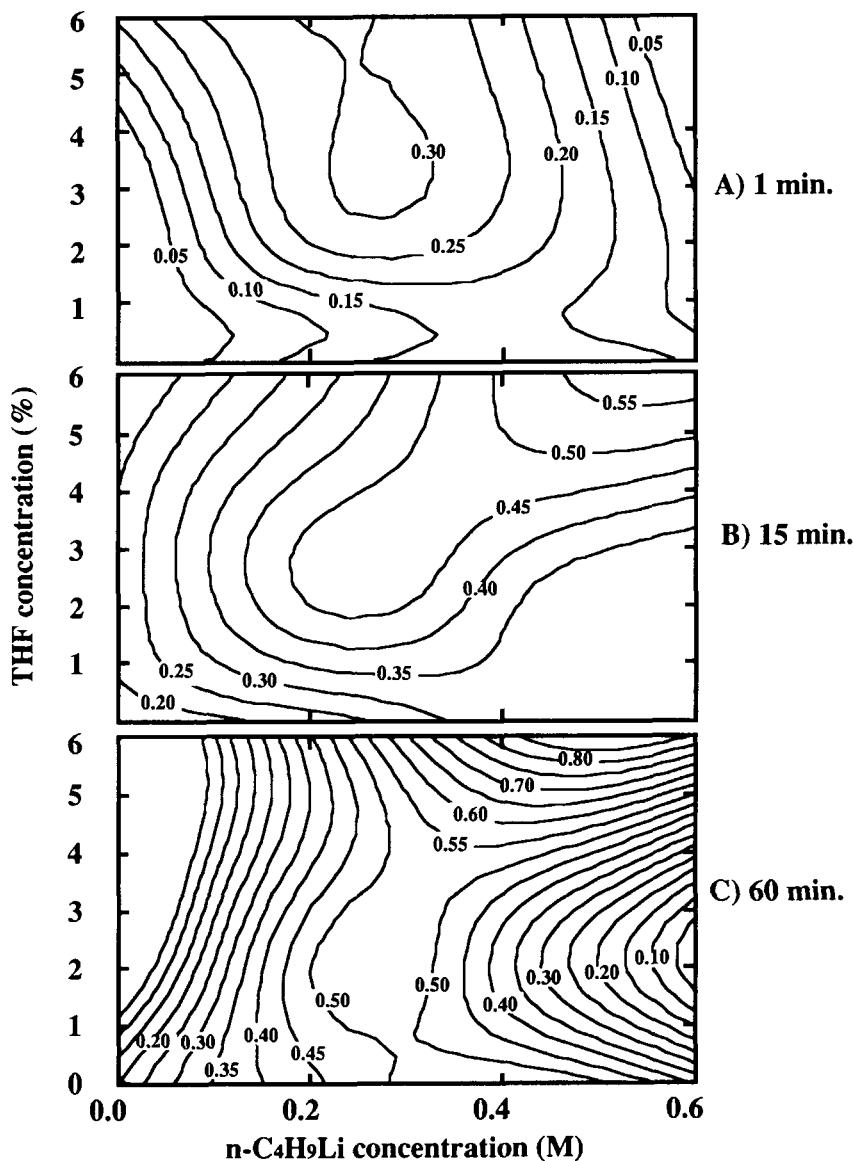


Figure 9 Contour plots of DS showing the effects of THF and *n*-C₄H₉Li concentration after (A) 1 min, (B) 15 min, and (C) 60 min. Selected from experimental data measured at 1, 5, 15, 30, and 60 min intervals for 0.05, 0.2, and 0.5 M *n*-C₄H₉Li in hexane and containing 0, 0.05, 0.5, 2, and 4% of THF coreactant.

two substituents per repeat unit obtained by homogeneous reaction.¹⁸ Presumably, this results from the restricted penetration of the reactant into the porous structure to gain access to the potentially reactive sites. One consideration is the effect of the membrane pretreatment on site availability. In these experiments, membranes were pretreated with 2-propanol. It is possible that other pretreatments that swell the membrane (e.g., methanol or ethanol) could improve site availability. Another factor is the lower reactivity of the metalating agent when only

small amounts of THF are present. However, the limitation of low THF concentration is necessary to avoid damaging the microstructure of the membrane.

The failure of IRS-FTIR to detect $-\text{C}(=\text{O})\text{F}$ in the back surface of the carboxylated/SF₄-treated membrane that did show carboxylation by XPS implies that lithiation is occurring on the back (coarse-textured) membrane surface. The XPS technique views a surface layer of about 75 Å thickness only, whereas IRS-FTIR views a surface layer of \sim 5000

\AA thickness for a Ge reflection element at 45° incidence. This suggests that on the back surface the reaction is confined to a very thin layer, probably < 1000 \AA , and that the anomaly in detecting surface modification probably arises from differences in the polymer porosity and density of each surface. Dense polysulfone membranes cast from THF solutions could not be carboxylated on either surface by this procedure as measured by IRS.

Although lower substituent levels were obtained under heterogeneous conditions than under homogeneous reaction, the lithiation reaction provides a key reactive intermediate to surface-functionalized polysulfone membranes. A great variety of functional groups other than carboxyl are potentially accessible by contacting lithiated membranes with suitable electrophilic reactants.^{19,30} Preliminary experiments show that commercially available polysulfones other than Udel are amenable to this heterogeneous lithiation process. The effect of surface modification on the membrane pore structure, as shown by water and solute permeability studies, as well as the preparation of some derivatized membranes will be published at a later date.

CONCLUSIONS

The parameters that control the reaction rates of the heterogeneous lithiation process required to functionalize polysulfone membranes were studied quantitatively. These are: the type of metalating agent and concentration, coreactant THF concentration, reaction time, and temperature. Temperature had the greatest effect on reactivity: After 15 min there is approximately a 10-fold difference in DS at 25°C than at -78°C. For low concentrations of *n*-C₄H₉Li (0.05 M), a low DS (0.12) was obtained after 15 min, rising to 0.23 after 1 h. When 2% THF was present, the DS increased to 0.28 after 15 and 30 min, but declined to 0.08 after 1 h. The optimum concentration of *n*-C₄H₉Li was 0.2 M, the mid-range of the concentration series. The rate of functionalization increased rapidly, reaching a value of 0.33 within 15 min and rising to 0.45 after 1 h. In the presence of 2% THF coreactant, the values increased to 0.47 and 0.54, respectively. There was only a marginal increase in DS when 0.5 M *n*-C₄H₉Li and 4% THF was used.

Under the conditions tested, a DS of about 0.5 can be obtained for surface lithiation. The reaction conditions appear to be mild enough to prevent mechanical and surface deterioration of the membrane.

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