

Microstructure of Polyurethane Ionomers Derivatized With Dodecylamine and Polyethylene Oxide in the Hard Segment

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SYNOPSIS

Segmented polyether-polyurethanes containing sulfonate groups in the hard segment were modified by the grafting of polyethylene oxide and C₁₂ hydrocarbon chains. The grafts were attached via the sulfonate groups. The physical properties of the materials, including stress-strain behavior, thermal behavior, and water uptake were studied. Grafting was found to alter material behavior significantly. Both the alkyl and polyethylene oxide grafts appear to alter the packing of the hard segments in microdomains because the grafted materials, in contrast to their sulfonated precursor, do not exhibit a melting transition. However, the polyethylene oxide chains appear to interact with the hard segments, probably through hydrogen bonding. For the C₁₂ grafted materials, differential scanning calorimetry showed that a third microphase, consisting largely of C₁₂ chains, may be formed by annealing. Stress-strain and water uptake data support these interpretations. The grafted materials were found to absorb more water than the sulfonated precursor. Most of the water taken up by the C₁₂ material appears to be bulk water whereas for the PEO material the absorbed water behaves as if it is bound. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The structure and morphology of linear segmented polyurethanes (SPU) in the solid state are governed by microphase separation of the hard and soft segment domains. This phase separation varies with the molecular weights of the prepolymer, the soft segment, and the hard segment; with the chemical properties of the hard and soft segments; and with conditions during formation of the solid.¹ Phase separation has an influence on many solid-state properties such as elastic character, tensile strength, elongation, and thermal transitions.¹

The tendency to undergo microphase separation is to a large extent governed by interactions tending to promote cohesion between hard segments. Hydrogen bonding, with the NH group acting as the donor and the urethane carbonyl as the acceptor, is generally considered to contribute significantly to

hard domain cohesion. It should be noted that hydrogen bonding may also occur between the hard and soft segments, with the NH group as donor and the ester carbonyl (in polyesterurethanes) or the ether oxygen (in polyetherurethanes) as acceptor.

With the incorporation of ionic functional groups into polyurethanes^{2,3} ionic interactions can become significant in determining the solid-state structure. Recent theories of polyurethane ionomer structure² stem from work on simpler ionomers such as sulfonated polystyrenes and sulfonated fluorocarbon polymers.⁴⁻¹¹ Eisenberg and King⁴ postulated the existence of two types of ionic aggregates, termed multiplets and clusters. A multiplet is defined as a group of tightly bound ion pairs, with dimensions on the order of 0.6 nm. A cluster is defined as a domain containing several multiplets as well as a significant amount of chain backbone. Cluster diameters are reported¹¹ to be on the order of 2-10 nm and are thus comparable in size to the hard segment domains of "classical" polyurethanes.¹

Grafting of different side chains to polyurethane hard segments has also been reported.^{12,13} Both alkyl chains¹² and polyethylene oxide chains terminated

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with sulfonate groups¹³ have been studied. The incorporation of alkyl side chains resulted in changes in both the thermal and mechanical properties, and it was suggested that the presence of these side chains causes a rearrangement of the structure of the hard segment such that the cohesion of the hard segment domains is decreased. Incorporation of the alkyl chains¹² was achieved by alkyl halide grafting reactions on a preformed polymer, so that differences between the alkylated and nonalkylated polyurethanes were attributable to the presence of the side chains in the hard segments. Polyethylene oxide (PEO)/polypropylene oxide (PPO) side chains were incorporated using a diol chain extender (Tegomer) containing terminal sulfonate or methoxy groups¹³ as well as PEO/PPO sequences. In this case it is more difficult to attribute effects uniquely to PEO/PPO side chains.

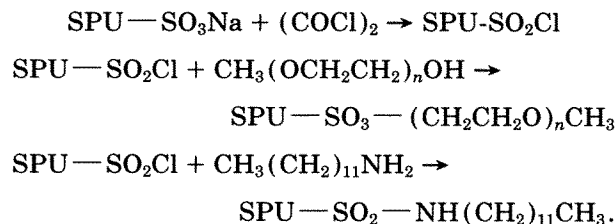
We have been interested in the use of segmented polyurethanes in biomedical applications. Because of their elastomeric character these materials have found considerable favor in the construction of implantable devices where flexibility is required.¹ Examples are vascular grafts, intraaortic balloons, and other heart assist devices. Unfortunately the biocompatibility of polyurethanes is inadequate. In particular, contact with blood provokes coagulation and thrombosis causing, for example, strokes in artificial heart recipients. Various attempts have been made to modify the hard segments of polyurethanes to improve their biocompatibility. In previous work we have devised methods to introduce sulfonate groups¹⁴ and amino acids¹⁵ into the hard segment. In the present communication we report on the incorporation of pendant C₁₂ hydrocarbon and polyethylene oxide chains via the reaction of suitable reagents with sulfonate groups. The effects of these modifications on polymer physical properties are presented.

EXPERIMENTAL

Synthesis of Derivatized Segmented Polyurethanes

Sulfonated SPU were synthesized using a standard two step solution polymerization procedure.¹⁴ Prepolymers were made by reacting 4,4'-diphenylmethane diisocyanate (MDI) with PPO of molecular weight 1025. These were chain extended using a sulfonated diamine, 4,4'-diamino-2,2'-biphenyl disulfonic acid disodium salt (BDDS). The details of this polymerization are given in Santerre et al.¹⁴

The derivatization reactions used in the present work are as follows:



Sulfonated SPU was dissolved in distilled dimethylformamide (DMF) at a concentration of 5 g/100 mL. Oxalyl chloride (in a stoichiometric amount relative to sulfonate groups) was added to the polymer solution and the system stirred under nitrogen for 4 h at -5°C to convert sulfonate to sulfonyl chloride groups.¹⁵

Dodecylamine (DDA) or PEO monomethyl ether was dissolved in DMF (1% w/v) in a second reactor and stirred under dry nitrogen at room temperature.¹⁵ After 4 h the contents of the first reactor were transferred to the second reactor by aspiration. The reaction between the terminal amine of DDA or the terminal hydroxyl of PEO methyl ether and the sulfonyl chloride groups of the polyurethane was allowed to proceed under nitrogen for 15 h at 20°C. The resulting polymer was precipitated in distilled water, washed several times in either methanol or distilled water, and dried at 60°C in an air convection oven for 48 h.

The polymers are named by chain extender, sulfur content, and type of side chain. All of the materials used in the present study were derived from polymer BDDS-1.4 containing 1.4 wt % sulfur. BDDS-1.4-DDA and BDDS-1.4-PEOMe (occasionally shortened to DDA and PEOMe) refer, respectively, to the dodecylamine- and polyethylene oxide methyl ether-containing polymers.

MDI and BDDS were from Eastman Kodak Chemicals and PPO 1025 was from BDH Chemical (Toronto, Ontario). Oxalyl chloride, DDA, and PEOMe (molecular weight 550) were from Aldrich Chemicals (Milwaukee, WI).

Fourier Transform Infrared (FTIR) Spectroscopy

The presence of the C₁₂ and PEO side chains was detected using FTIR spectroscopy. Information regarding hydrogen bonding was also obtained from the infrared spectra. Polymer films were cast on a Teflon sheet using a 0.5 wt % solution of polymer in DMF. Spectra were obtained on a Nicolet model 320 FTIR instrument at a resolution of 2 cm⁻¹.

Elemental Analysis

Sulfur, potassium, and sodium were determined by scanning electron microscopy combined with energy dispersive analysis of X-rays (SEM-EDAX) as described previously.¹⁵ Nitrogen and sulfur were also determined by conventional analytical techniques, and sodium and potassium by atomic absorption spectrometry.

Acid-Base Titration

Titration of free sulfonate groups was used to verify their presence in the "precursor" polymer and to quantify the derivatization reactions. In all cases the polymer was acidified prior to titration by treating a solution of the polymer in DMF with excess 1 M HCl at 0°C. After stirring overnight the acidified polymer was precipitated, washed, and dried. Molecular weight determination confirmed that this treatment did not cause significant chain scission. Titration of the acidified polymer was carried out in DMF containing 0.1 M LiBr. The titrant was 0.025 M triethylamine (TEA) in DMF standardized by titration with 0.1 M HCl in DMF. The polymer titration endpoint was monitored using a potentiometer.

Molecular Weights

Molecular weights were determined by size exclusion chromatography (SEC). Four Waters Ultrastaygel columns with pore sizes of 10^3 , 10^4 , 10^4 , and 10^5 Å, and a differential refractive index detector were used. The operating temperature was 80°C and the mobile phase was DMF containing 0.1 M LiBr. The sample volume was 200 μ L and the polymer concentration was approximately 0.2 g/100 mL. With a flow rate of 1 mL/min a typical chromatogram showed a retention volume of 40 mL. The system was calibrated with TSK polystyrene standards obtained from Toyo Soda Manufacturing Co Ltd., Tokyo. All molecular weight data are reported as polystyrene equivalent molecular weights.

Mechanical Testing

Tensile stress versus strain data were obtained using an Instron Tensile Testing System, Model TT-D. Polyurethane films were prepared from a 5% w/v solution in DMF. Multiple layers were cast in Teflon molds in order to provide films of adequate thickness for testing according to the ASTM D412-80 standard. The film molds were maintained in a dry glove

bag during the entire casting procedure to avoid the presence of moisture.

The solvent was allowed to evaporate for 48 h between "layers," and casting was continued until films of approximately 0.5 mm were obtained (8–9 layers). The final films were dried in an air oven at 60°C for 24 h and then in a vacuum oven at 25°C for an additional 24 h. Samples for mechanical testing were cut using an ASTM dumbbell die (size D) according to the ASTM D412-80 code. A 10-lb load cell and a strain rate of 1 in/min were used in these measurements.

Differential Scanning Calorimetry (DSC)

DSC scans were obtained using a Dupont Instruments 910 differential scanning calorimeter. Samples for DSC experiments were prepared as for the tensile stress-strain measurements. The sample weight was 10 ± 2 mg. The specimens were scanned from -100 to 250°C at a rate of $5^\circ\text{C}/\text{min}$. The samples were initially cooled to -100°C using liquid nitrogen. On reaching 250°C , the samples were rapidly cooled to room temperature and then to -100°C prior to making a second scan from -100 to 250°C . This second scan allows observations of the material after its microstructure has been altered by the initial heating. In this study the glass-transition temperature (T_g) is reported as a temperature range. Transitions observed in the interval between the T_g and the hard segment melt temperature are reported as the midpoint of the range, and the hard segment melt transition is reported as the onset temperature of the transition.

Water Uptake

The investigation of water solubility and water uptake behavior was carried out to provide an indication of the bulk hydrophilic character of the polymers. Water uptake experiments consisted of equilibrating solid samples of the polyurethanes in water. Films of about 0.5-mm thickness were prepared from a 5% w/v solution in DMF as described for tensile property measurements. Polymer film samples (about 1 g) were weighed accurately and incubated in 25 mL distilled water for 30 days at 25°C , after which they were filtered and blotted to remove adherent water and then weighed. These swollen samples were then cut into 2-mm wide \times 1-cm long strips and placed in sample vials containing 100 mL distilled water. The vials were placed in an oven at 70°C for 2 days. They were then cooled and held at room temperature for 3 days prior to refiltering, re-

blotting, and reweighing. The data were recorded as weight percent water uptake.

RESULTS AND DISCUSSION

Conversion of Sulfonate to DDA and PEOMe Derivatives

The sulfonate content of the polyurethane ionomer BDDS-1.4 and the degree of DDA and PEO incorporation into the derivatized polymers were determined by titration of free sulfonate groups with TEA. These data are shown in Table I. According to the titration data, all of the available sulfonate groups of BDDS-1.4 were converted to the C₁₂ alkyl or PEO derivatives.

Molecular Weights

The molecular weight data (Table I) show that the incorporation of the C₁₂ and PEO side chains in the hard segment did not cause significant change. Thus neither cross-linking nor degradation of the chains appears to have occurred to any significant extent. The fact that the molecular weight did not change may seem at odds with the fact that two PEO chains (molecular weight 550) or two C₁₂ chains (molecular weight about 180) were apparently added per repeat unit of the chain, and thus a measurable increase in molecular weight would have been expected. However it is possible that the hydrodynamic volumes of the polymers did not change significantly with the grafting of these relatively short side chains.

Infrared Spectra

Hydrogen bonding is an important interaction that influences phase separation behavior in polyurethanes. Infrared spectroscopy is amenable to the study of hydrogen bonding, and several investigations¹⁶⁻¹⁸ have used this method to estimate the fraction of hydrogen bonded carbonyl groups in

polyurethanes. The N—H stretching region around 3400 cm⁻¹ and the carbonyl stretching region around 1700 cm⁻¹ are of interest. However "free" and hydrogen bonded NH groups are difficult to distinguish via the 3400 cm⁻¹ band¹⁸ so our analysis is focused on the carbonyl stretch. When urea and urethane groups are in proximity to each other, as is the case for the hard segment domains of polyurethanes, hydrogen bonding is usually quite significant and the carbonyl peaks are shifted to a lower wavenumber. FTIR data in the 1700 cm⁻¹ region are shown in Figure 1. The bands in this region reflect the behavior of the urethane carbonyl groups in the vicinity of different functional groups of the hard segment. If we take the bands at 1700 and 1735 cm⁻¹ as indicating H-bonded and non-H-bonded carbonyls, respectively,¹⁶⁻¹⁸ then we see increased hydrogen bonding in the derivatized polymers compared to the precursor polymer. Given the bulkiness of the side chains in the derivatized polymers this observation is somewhat surprising. It may be that the sulfonate groups located in the hard segment of BDDS-1.4 inhibit hydrogen bonding of carbonyls either between or within chains because the sulfonate groups themselves will impose steric constraints due to possible ion pair aggregation. Also the DDA-derivatized polymer appears to have a lower ratio of hydrogen bonded to normal carbonyls than the PEOMe-derivatized polymer. This may be related to the greater flexibility of the PEO compared to the hydrocarbon chains, resulting in less steric hindrance to hydrogen bonding.

DSC

Figures 2-4 show DSC thermograms for PPO 1025 and the polyurethanes BDDS-1.4, BDDS-1.4-PEOMe, and BDDS-1.4-DDA. Curves are shown for the "original" materials and for samples that were quenched following the initial DSC experiment and then reheated. The thermogram data and their interpretation in terms of structure are summarized

Table I Chemical and Molecular Weight Data for Polyurethanes

Polymer	Conversion of Sulfonate to Derivative ^a (%)	Free Sulfonate Content (mol/g polymer)	<i>M_w</i>	<i>M_w/M_n</i>
BDDS-1.4	—	$(2.2 \pm 0.3) \times 10^{-4}$	77,000	1.3
BDDS-1.4-DDA	100 ± 20	—	72,000	1.4
BDDS-1.4-PEOMe	100 ± 20	—	80,000	1.4

^a Determined by titration with triethylamine.

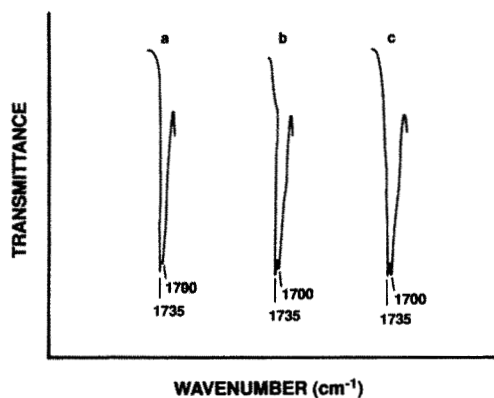


Figure 1 FTIR spectra of polyurethanes in the vicinity of 1700 cm^{-1} : (a) BDDS-1.4; (b) BDDS-1.4-DDA; (c) BDDS-1.4-PEOMe.

in Table II. Pure PPO (Fig. 2) shows only one transition (-70°C), which is assumed to be the glass transition. The interpretations for the polyurethanes follow those given for similar systems by Hesketh et al.¹⁹ The transition at -10 to -41°C is assigned to the soft segment T_g . The remaining transitions in order of increasing temperature are attributed, respectively, to dissociation of short-range order in the hard domains (35 – 115°C), dissociation of long-range order in the hard domains (130 – 190°C), and hard domain crystalline melting (205 – 216°C).

The degree of phase separation in a segmented polyurethane material may be assessed by the temperature at which the glass transition occurs and by the sharpness of the transition. In particular, changes in T_g of the soft segment phase relative to that of the corresponding pure PPO used in the synthesis of the prepolymer are of interest. In the present case PPO of molecular weight 1025 was used.

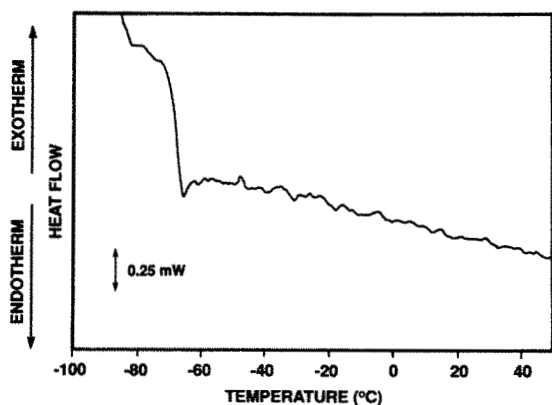


Figure 2 DSC thermogram for polypropylene oxide of molecular weight 1025.

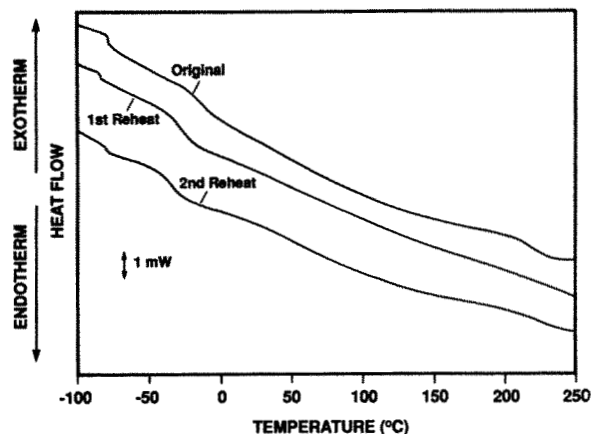


Figure 3 DSC thermogram for polyurethane BDDS-1.4.

As can be seen in Figure 2, the T_g for this material is approximately -70°C , and because it is relatively pure, the transition is sharp, occurring over a range of about 4°C . The degree of crystalline order within the hard segment can be assessed by the sharpness of the hard segment melt temperature (T_{HSM}). This transition gives a measure of packing and ordering in the hard segment microdomains.

The thermogram transitions in Figure 3 for the BDDS-1.4 polymer show changes associated with thermal history. In the initial scan, the polymer exhibits a glass transition at about -20°C , a melt temperature near 213°C , and a short-range order transition at about 115°C , which may reflect sulfonate group interactions within ion pair aggregates. Rapid cooling after initial heating presumably locks in the "melt" state of the material, and the first reheat thermogram in Figure 3 shows a slightly reduced T_g

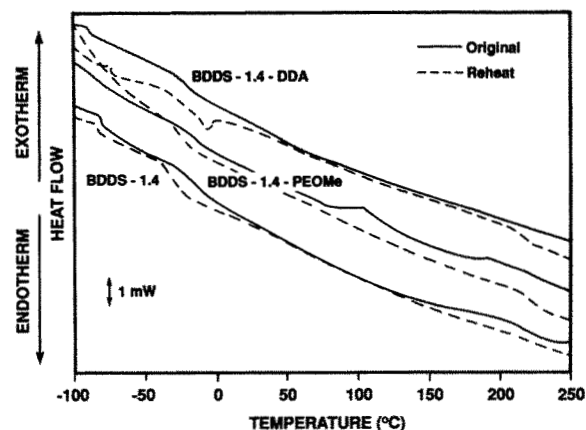


Figure 4 DSC thermograms for BDDS-1.4, BDDS-1.4-PEOMe, and BDDS-1.4-DDA.

Table II Thermal Transitions From DSC Thermograms

Polymer	Soft-Segment Glass Transition	Short-Range Order Transition	Long-Range Order Transition	Hard-Segment Melt Temperature
BDDS-1.4	-20 to 7 (S)	115 (M)	—	213 (S)
BDDS-1.4 R	-35 to -20 (S)	—	140 (VW)	205 (VS)
BDDS-1.4 R2	-41 to -25 (S)	35 (M)	131 (S)	210 (S)
DDA	-25 to -7 (M)	64 (W)	—	—
DDA R	-36 to -8 (VS)	—	—	211 (M)
PEOMe	-25 to -10 (S)	100 (VS)	190 (S)	—
PEOMe R	-30 to -17 (S)	—	—	216 (M)

Data in °C. VS, very strong; S, strong; M, medium; W, weak; VW, very weak; R, reheat run; R2, second reheat run.

value indicating that hard segment mixing into the soft segment matrix has been reduced. The phase separation process appears to be dependent on thermal history, suggesting that perhaps the mechanical properties of these materials could be improved by annealing. Heating of the polymer apparently reduces ordering in the hard segment domains because the short-range order, long-range order, and melt transitions are all weak in the reheat thermograms. This does not necessarily mean that ordered structures cannot reform, but suggests that their rate of formation, involving ionic interactions, hydrogen bonding, and crystallization, is much slower than the rate of quench cooling.

For the curve labeled second reheat, the polymer was cooled to room temperature following the second DSC scan and maintained at 25°C for an extended period. Under these conditions the hard segment domain structure is expected to reform, and both short- and long-range order transitions and possibly a melt transition should be apparent. The data show a T_g onset value of -41°C, that is even lower than for the first reheat experiment, suggesting an even greater degree of microphase separation. Relatively strong short-range order, long-range order, and melt transitions for the hard segment are also present in the second reheat thermogram.

Figure 4 shows DSC data for the BDDS-1.4 polyurethanes derivatized with DDA and PEOMe. The original curve for BDDS-1.4-DDA could be interpreted as showing enhanced phase separation compared to BDDS-1.4 because the onset of the glass transition occurs at -25°C compared to -20°C for BDDS-1.4. The presence of C_{12} alkyl chains thus appears to facilitate the formation of hard and soft segment domains. On the other hand, the width of the glass transition is greater in the DDA derivatized material suggesting increased phase mixing. This apparent paradox may be due to the mixing of some

of the C_{12} side chains into the soft segment matrix, thus broadening the T_g range. The presence of pendant alkyl chains in the hard segment appears to inhibit ordering in the hard segment domains because there is no observable transition in the T_{HSM} range, whereas BDDS-1.4 shows a strong hard segment melt transition.

The reheat thermogram for BDDS-1.4-DDA shows a number of unique features. The onset of the glass transition occurs at -36°C compared to -25°C in the original thermogram; however the glass transition is increased considerably in width (28 compared to 18°C) and in magnitude. The decrease in glass transition onset temperature indicates enhanced separation of hard and soft segment domains. At the same time there appears to be "contamination" of the soft segment phase, causing an increase in the width of the glass transition. An explanation that could accommodate these apparently conflicting data would be to postulate the formation of a third microphase consisting primarily of C_{12} chains. The driving force for the formation of this phase would be the same as that for classical polyurethane microphase separation. The hard segment of the polyurethane is highly polar and is expected to be incompatible with the C_{12} alkyl side chains, even more than with the polyether chains of the soft segments. Thus the incorporation of these long alkyl chains should increase the polar/nonpolar incompatibility and enhance the driving force for hard segment domain formation. Under the conditions used to prepare the original samples, the ability of the system to respond to this driving force may be limited. However as shown in Figure 3 for BDDS-1.4, phase separation may be increased by annealing. For BDDS-1.4-DDA, domain structuring apparently occurred during the first heating and quenching as indicated by the appearance of a melt transition at 211°C in the reheat thermogram. The appearance

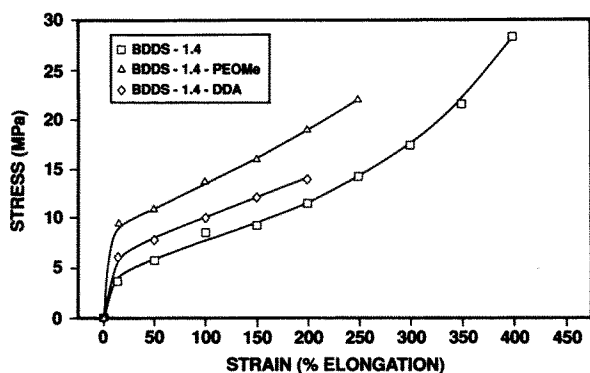


Figure 5 Tensile stress-strain behavior of polyurethanes.

of a well-defined melt temperature following a single "heat treatment" was unexpected based on the behavior of the BDDS-1.4 polymer. Additional support for the formation of a third (C_{12}) microphase is provided by the first order transition observed in the reheat thermogram at -5°C , which could be associated with the "melting" of the C_{12} microphase. Thus considered as a whole, the DSC data suggest that on heating, the hydrocarbon chains may form a third microphase having a high concentration of C_{12} chains with some admixture of soft segment. Contamination of the soft domains by C_{12} chains may be responsible for the increased width of the glass transition in the reheat thermogram.

Some of the considerations discussed for polymer BDDS-1.4-DDA are also applicable to polymer BDDS-1.4-PEOMe. The original thermogram for PEOMe (Fig. 4) reveals very strong transitions at 100 and 190°C , yet no melt transition is observed. The onset of the soft segment glass transition occurs at -25°C compared to -20°C for the precursor polymer with the width of the glass transition similar to that of BDDS-1.4. Therefore the incorporation of PEOMe chains appears to increase phase separation (as for C_{12}) but does not "contaminate" the soft segment phase (in contrast to C_{12}). Yet even

with improved phase separation there is no evidence of hard segment crystallization as in BDDS-1.4 and BDDS-1.4-DDA. This observation supports the hypothesis suggested by the infrared data that the PEOMe chains interfere with hard segment packing. These effects would be expected to yield a material having a lower tensile strength and ultimate elongation than the precursor polymer BDDS-1.4. Hydrogen bonding interactions between the PEOMe chains and the hard segments may also account for the strong transitions at 100 and 190°C .

The reheat thermogram for PEOMe shows a lower T_g than the original. The transitions at 100 and 190°C are not observed and, if as proposed these reflect H-bonding of PEOMe in the hard segment domains, these structures appear to be broken down in the first heating cycle and do not reform prior to the second cycle. As was the case for DDA, a hard segment melt transition is observed in the reheat thermogram, again indicating that annealing improves hard segment packing.

Tensile Properties

Tensile stress strain curves for the three polyurethanes are shown in Figure 5 and tensile data are listed in Table III. Chain extension of PPO prepolymers with BDDS compared to the unsulfonated analog methylene dianiline has been shown to increase tensile strength but to have very little effect on initial modulus and elongation.²⁰ The increased tensile strength may be due in part to an increase in ionic interactions in the hard segment domains resulting from ion pair aggregate formation.

The DDA and PEOMe derivatized materials show substantial changes in initial modulus, elongation at break, and tensile strength relative to the precursor polymer BDDS-1.4. The initial modulus of the DDA derivatized material is higher than that of BDDS-1.4. It is apparent that this is not due to increased ionic interactions because the substituent is a 12-carbon alkyl chain. The enhanced initial

Table III Tensile Stress-Strain Data for Polyurethanes

Polymer	Tensile Strength (MPa)	Modulus at 5% Elong (MPa)	Elongation at Break (%)
BDDS-1.4	28	3.6	380
DDA	15	5.9	210
PEOMe	21	9.5	250

Relative standard deviations calculated from five tests for each material are as follows: tensile strength, $\pm 10\%$; modulus, $\pm 15\%$; elongation, $\pm 12\%$.

modulus may be a result of van der Waals interactions and entanglements among the alkyl side chains themselves. Such an explanation implies the formation of a third phase as already discussed in relation to the DSC data. The original DSC curve for the DDA polymer shows no melt transition and suggests that the hard segment phase in the original polyurethane film is not highly structured. A material with a lower tensile strength is thus to be expected. Reduced cohesion within the hard segment domains may also cause a decrease in ultimate elongation. Figure 5 confirms this interpretation because both tensile strength and ultimate elongation are lower for the DDA polymer than for BDDS-1.4.

In contrast to the present study, Grasel et al.¹² did not find that hydrocarbon chains grafted to the hard segment of polyurethanes caused an increase in initial modulus. It may be that alkyl chains of a particular length are required to achieve this effect. Grasel et al. used C₂ and C₁₈ alkyl side chains; in the present work C₁₂ chains were used. It seems likely that very short chains would not provide enough interaction, and longer chains would not allow for separation of hard segment from the side chains because entanglements would be too difficult to overcome.

The PEOMe derivatized material also shows increased initial modulus, reduced tensile strength, and reduced ultimate elongation compared to the precursor polymer. Polymer PEOMe has the highest initial modulus of the three materials studied and this may reflect the capacity of the PEO chains to form hydrogen bonds with the hard segments. The molecular weight of the PEOMe residue is 550, corresponding to about 12 ethylene oxide units and providing many hydrogen bonding possibilities. Although the PEOMe polymer shows relatively high initial modulus, its tensile strength is lower than that of the precursor. The DSC data (Fig. 4) again suggest that the PEO chains "disrupt" the microdomain structure of the original cast film since no melt transition is observed.

Interactions With Water

The water uptake experiments were intended to measure the capacity of the polyurethane ionomer and its derivatized forms to absorb and retain water. It was anticipated that these measurements would provide additional information on the microstructure of the materials. Initial experiments were carried out at room temperature over a period of 30 days. Additional uptake over 2 days at 70°C was then measured. The materials did not show further water uptake at longer times.

The data are summarized in Table IV. The samples were taken from the same films that were prepared for stress-strain and DSC measurements. Polymer MDA, a nonfunctionalized polyurethane synthesized using methylene dianiline rather than BDDS as chain extender, was included for the purpose of assessing the effects of sulfonate groups on water absorption. At 25°C the BDDS-1.4 polymer showed higher absorption than the nonionic polymer MDA, although the difference was not as great as might have been expected.

It is possible that many of the sulfonate groups in BDDS-1.4 are "buried" in the microdomain structure and are not readily accessible for hydration. Hydration presumably requires the breakup of ion pair aggregates in the hard segment domains that appear to be strongly cohesive according to the DSC data. As was shown by the DSC measurements, the hard segment structure of BDDS polyurethanes can be relaxed by heating. It was expected, therefore, that continuation of the water absorption experiment at an elevated temperature would result in significant additional water uptake by the BDDS-1.4 polymer. As shown in Table IV, the water uptake for BDDS-1.4 increased about 20-fold while that of the nonsulfonated MDA polymer increased only by a factor of two relative to the values at room temperature.

The effect of microdomain structure on water uptake is also apparent for the BDDS-1.4-PEOMe and

Table IV Water Uptake of Polyurethanes

Polymer	Weight Percent Water Uptake 30 Days, 25°C	Weight Percent Water Uptake 2 Days, 70°C
MDA	6	9
BDDS-1.4	19	240
DDA	77	800
PEOMe	69	1500

BDDS-1.4-DDA polymers. The DSC data for these polymers showed that the hard segment microdomains are much less cohesive and structured than in BDDS-1.4. The greater water absorption of these two polymers at room temperature supports this interpretation.

The level of water uptake observed for BDDS-1.4-DDA at 70°C is perhaps surprisingly high because it could be argued that the presence of C₁₂ hydrocarbon chains would reduce the ultimate hydration of the material. As can be seen it showed greater water uptake than BDDS-1.4. It is clear that the mechanism of water uptake must differ significantly in the two polymers. The wet DDA polymer was observed to be very weak, and upon removal from the experimental cell, the absorbed water flowed rapidly out of the sample. In the swollen state, when immersed, the DDA material lost its shape, whereas the BDDS-1.4 material retained its original shape. These observations suggest that the water within the swollen DDA polymer may be mostly bulk, not structured or bound water. The polymer undoubtedly has a tendency to swell, and probably hydrates to some extent via the sulfonamide groups, but the pendant C₁₂ chains appear to prevent permanent water retention.

Polymer BDDS-1.4-PEOMe shows higher water absorption than DDA. This is not surprising since PEO is itself water soluble. In addition, the water-swollen polymer showed a material "strength" comparable to the BDDS-1.4 polymer after water uptake and retained its water after being removed from the experimental cell. These observations suggest that, unlike polymer BDDS-1.4-DDA, the PEOMe-containing material possesses a certain degree of water structuring in the hydrated state.

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REFERENCES

1. M. D. Lelah and S. L. Cooper, *Polyurethanes in Medicine*, CRC Press, Boca Raton, FL, 1986.
2. D. Lee, R. A. Register, C. Yang, and S. L. Cooper, *Macromolecules*, **21**, 998–1004 (1988).
3. D. Dieterich, W. Keberle, and H. Witt, *Angew. Chem. Internat. Ed.*, **9**, 40 (1970).
4. A. Eisenberg and M. King, *Ion Containing Polymers: Physical Properties and Structure*, Academic Press, New York, 1977.
5. L. Holliday, *Ionic Polymers*, Applied Sci. Publ. Ltd., England, 1975.
6. E. B. Yeager, et al., *Electrochem. Soc. Proc.*, **83**, 3 (1983).
7. A. Eisenberg, *Amer. Chem. Soc. Adv. Chem. Ser.*, **187**, 123 (1980).
8. M. Pineri and A. Eisenberg, *Structure and Properties of Ionomers*, NATO ASI Series C, Vol. 198, Reidel Publ. Company, 1987.
9. W. Y. Asu and T. D. Gierke, *Macromolecules*, **15**, 1032 (1982).
10. K. A. Mauritz and C. E. Rogers, *Macromolecules*, **18**, 483 (1985).
11. A. Eisenberg and H. L. Yeager, *Amer. Chem. Soc. Symp. Ser.*, **180**, Chap. 8 (1982).
12. T. G. Grasel, J. A. Pierce, and S. L. Cooper, *J. Biomed. Mater. Res.*, **21**, 815 (1987).
13. A. Takahara, A. Z. Okkema, H. Wabers, and S. L. Cooper, *J. Biomed. Mater. Res.*, **25**, 1095 (1991).
14. J. P. Santerre, P. ten Hove, N. H. Vanderkamp, and J. L. Brash, *J. Biomed. Mater. Res.*, **26**, 39 (1992).
15. J. P. Santerre and J. L. Brash, *Macromolecules*, **24**, 5497 (1991).
16. M. M. Coleman, D. J. Skrovanek, J. Hu, and P. C. Painter, *Macromolecules*, **21**, 59 (1988).
17. H. Ishihara, I. Kimura, K. Saito, and H. Ono, *J. Macromol. Sci. Phys.*, **B10**, 591 (1974).
18. V. W. Srichatrapimuk and S. L. Cooper, *J. Macromol. Sci. Phys.*, **B15**, 267 (1978).
19. T. R. Hesketh, J. W. C. Van Bogart, and S. L. Cooper, *Polym. Eng. Sci.*, **20**, 190 (1980).
20. J. P. Santerre and J. L. Brash, to appear.

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