

Synthesis of Surface-Modifying Macromolecules for Use in Segmented Polyurethanes

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SYNOPSIS

Polyurethanes are one of the most important classes of thermoplastic elastomers and have been widely used in medical-device manufacturing as well as in other applications. However, their function can be limited, particularly under environmental conditions that render them susceptible to hydrolysis. Using polymeric additives that are hydrolytically stable may be one approach to modifying the surface of polyurethanes for the purpose of improving their hydrolytic resistance without compromising their structural features. In this paper, the development of a series of novel fluorine-containing polyurethane surface modifying macromolecules (SMMs) is described and their synthesis conditions are investigated. The material structure and mixing properties of the synthesized SMMs with base polyurethanes was dependent on the reactant stoichiometry and concentration for the SMM components, as well as the reaction temperature and the amount of catalyst used in the SMM synthesis. This study describes the use of low surface energy components (fluorinated tails) which showed selective migration towards the surface when added to a polyester-urea-urethane. These novel macromolecules generated a nonwetable surface while not significantly altering the apparent bulk structure of the base polymer. The advancing and receding contact angle results indicated that the surface of these modified polyurethanes showed wettability characteristics similar to that of Teflon.TM The differential scanning calorimetry thermograms for the mixtures of the SMM with the polyurethane showed that, at 5% w/w SMM in the base polyurethane, the thermal transitions were similar to that of the native base polyurethane, indicating that the additives had no detectable effect on the polyurethane structure.

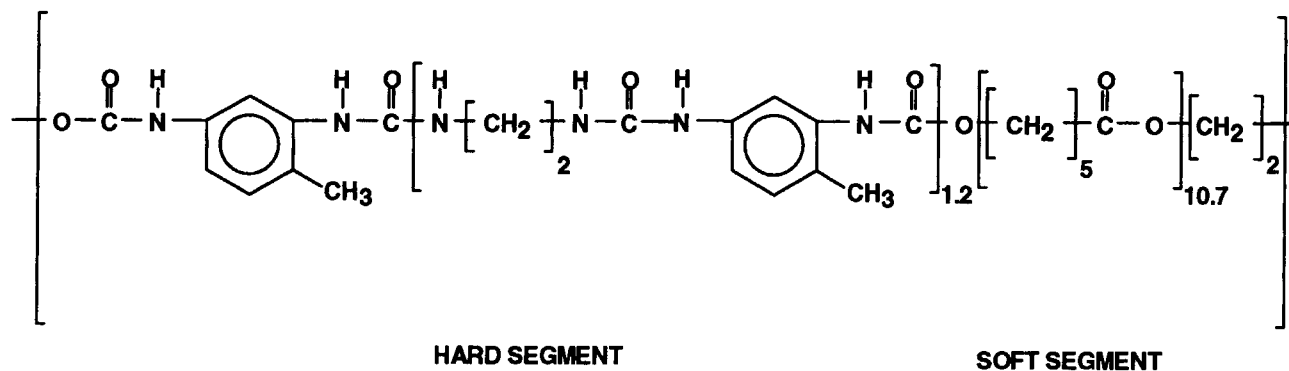
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INTRODUCTION

Polyurethane elastomers have a long history of applications as thermoplastic elastomers.^{1,2} A typical polyurethane elastomer is a block (or segmented) copolymer of the type (AB)_n, and is composed of alternating hard and soft segments that are generally not chemically compatible. This incompatibility leads to phase separation and the creation of microdomains in which hard block domains are dispersed in the matrix of the soft segment.³ The unique chemical structure of polyurethanes yields elasto-

mers with high tensile strength, good lubrication properties, abrasion resistance, ease of handling (extruding, bonding, etc.), and moderate "biocompatibility."^{4,5} Although polyurethanes used in applications requiring all of the above properties have been successful for short-term use, the long-term function of the materials still remains a problem.⁵ In biomedical applications, the materials are subjected to the hostile biological environment which is established in part by the foreign nature of the implant materials relative to the body. This hostile environment has been directly linked to the body's inflammatory response system and can lead to material biodegradation, along with the eventual failure of the device.⁶ The consequences of material deg-

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Base Polyester-urea-urethane

Figure 1 Synthesis of the base polymer TDI/PCL/ED.

radiation inside the body include the loss of the materials' tensile strength and the formation of surface cracks.^{7,8} Several studies have been undertaken to identify the specific mechanisms of degradation for polyurethanes and it has been found that hydrolytic and oxidation processes are key *in vivo* mechanisms involved in the material breakdown.^{8,9}

A legitimate approach to altering the surface chemistry and thereby stabilizing polyurethanes is by the use of additives. In previous work, Ward and colleagues¹⁰ demonstrated that this method was efficient for improving blood/material interactions because only a small wt % of additive was required to modify the surface properties, while the bulk properties remained unchanged. Ratner and Yoon¹¹ blended Advawax®, a stearamide used as an extrusion lubricant for processing polyurethanes, into commercial Pellethane as a means of altering its surface chemistry. A C_{1s} spectrum obtained from X-ray photoelectron spectroscopy analysis showed that the surface of the polymer mixture appeared to be almost identical to that of the Advawax® alone. The new surface became a hydrocarbon-rich environment which was believed to reduce platelet adhesion and subsequent clot formation when exposed to blood.¹¹ Brunstedt¹² mixed an antifoam agent, Methacrol 2138F, into a base polyether-urea-urethane which had the same composition as the biomedical polyurethane, Biomer™. The results indicated that with loading of this additive, the degree of protein adsorption was significantly reduced.¹²

However, the effectiveness of surface-active additives to enhance the biocompatibility of a material in the local *in vivo* environment has been debated,

since many additives such as antioxidants, plasticizers, etc., can leach out of the polymer. For example, Ratner and Yoon¹¹ found that Advawax® was easily extracted from polyurethane substrates. In some cases the leaching of plasticizers can lead to further concerns of toxicity.⁴ In addition, it is possible that these additives can unintentionally behave as fillers, initiators, or even crosslinkers, thus changing the mechanical performance of the polyurethane.¹³

In the present work, surface modifying macromolecules (SMMs) have been synthesized in an effort to produce a material that can be blended with segmented polyurethanes to alter the surface chemistry of the polyurethane while leaving the bulk phase relatively unchanged. The SMMs contain two segments which differ in their compatibility with the base polymer. The segment with less polymer compatibility provides a driving force for migration of the SMM toward the surface, while the compatible portion links the SMM to the base polymer via noncovalent interactions and physical entanglements. By designing and synthesizing the SMMs tailored to the base polymer, it is anticipated that the polymer mixture will contain the SMM chemistry at or close to its surface, thereby altering its biostability and/or biocompatibility.

EXPERIMENTAL

Synthesis of the Base Polyurethane

The base polymer to which the SMM was added was a polyester-urea-urethane, referred to as TDI/PCL/ED (see Fig. 1). TDI/PCL/ED was

synthesized using 2,4-toluene diisocyanate (TDI, obtained from Eastman Kodak, Rochester, NY), polycaprolactone diol 1250 (PCL, obtained from Aldrich Chemical Company, Milwaukee, WI), and ethylene diamine (ED, obtained from Aldrich). Prior to the synthesis, TDI was vacuum-distilled at 70°C and 0.025 mmHg. PCL was degassed for 24 h at 40°C and 0.5 mmHg, while ED was distilled under atmospheric pressure. The solvent used in the synthesis was dimethyl sulphoxide (DMSO), which was vacuum-distilled at 45°C and 0.5 mmHg within 24 h of use.

TDI/PCL/ED was synthesized by a conventional two-step procedure in a controlled atmospheric glove box containing dried nitrogen gas. The complete details of the synthesis are provided in previous work.¹⁴ The first step involved the reaction of TDI with PCL in DMSO for 2 h, over the temperature range of 60–70°C. The second step, the chain extension step, was carried out at room temperature with ED. The reaction stoichiometry of TDI : PCL : ED was 2.2 : 1 : 1.2. The polymerization product was precipitated with distilled water and dried in a 50°C oven for 48 h. In order to further purify the polymer, it was redissolved using DMSO and precipitated again. After washing the polymer 3 times in distilled water, the material was dried in a 50°C oven for 48 h and further dried in a vacuum oven for another 24 h. The final polymer was stored in the dark at 4°C until required.

Synthesis of SMMs

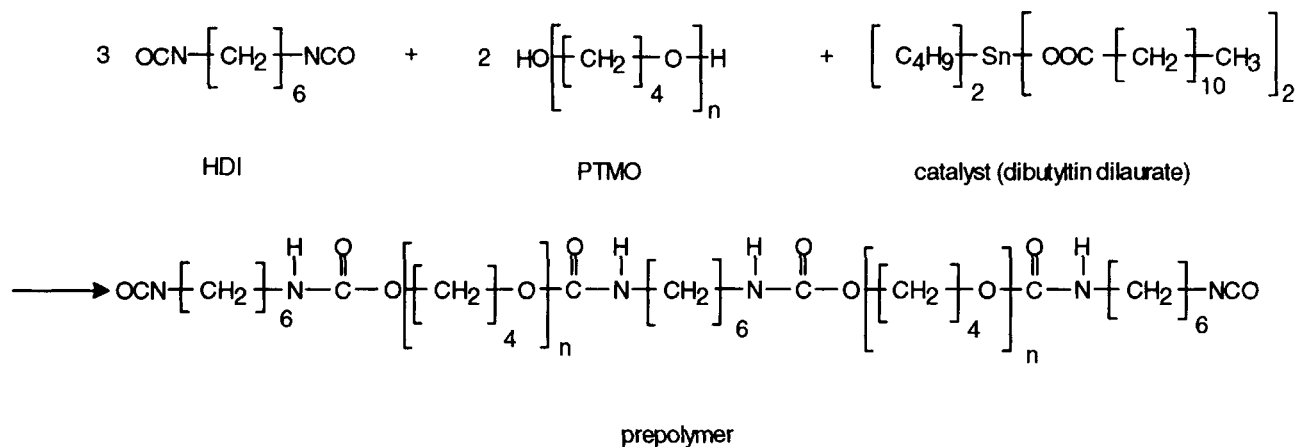
The SMMs were synthesized using 1,6-hexanediisocyanate (HDI, obtained from Aldrich). This particular diisocyanate was selected primarily on the basis of favorable carcinogenicity reports relative to classical diisocyanates such as TDI and 4,4'-methylenebisphenyl diisocyanate.¹⁵ Two polyols were used for the synthesis: polypropylene oxide of molecular weight 1000 (PPO, Aldrich), and polytetramethylene oxide of molecular weight 1000 (PTMO, Dupont, Mississauga, Ont., Can.). The synthesis pathway of a typical SMM is shown in Figure 2. SMMs were synthesized using a similar prepolymer method to the one used for TDI/PCL/ED, however the final step differed in that a chain extension was not carried out. Instead, a mono-functional fluorinated alcohol, BA-L (Van Waters & Rogers, Montreal, Que., Can.) was used to cap the prepolymer.

Prior to the synthesis, HDI was vacuum-distilled at 70°C and 0.025 mmHg, while PPO or PTMO was vacuum-degassed at 40°C and 0.1 mmHg overnight. BA-L was distilled into three fractions. The first fraction, called BA-L (Low), was a clear liquid distilled at 102°C and atmospheric pressure. The second fraction, BA-L (Int), was a white semi-solid material distilled between 70 and 80°C under a vacuum of 0.01 mmHg pressure. The last fraction, referred to as BA-L (High), was distilled between 80 and 100°C under a vacuum of 0.01 mmHg as a very pale yellow solid. The solvent used in the SMM synthesis was *N,N*-dimethylacetamide (DMAC, Aldrich). Because of the low reactivity of HDI with the polyols, dibutyltin dilaurate was used as a catalyst in the reaction. Table I provides the SMM nomenclature that is used throughout this paper. An alphanumeric code is used in which the first alpha sequence refers to the polyol used, the numerical sequence refers to the reagent stoichiometry, and the final letter refers to the fraction of the fluoro-alcohol contained in the additive.

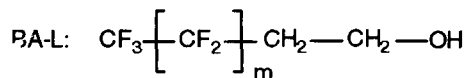
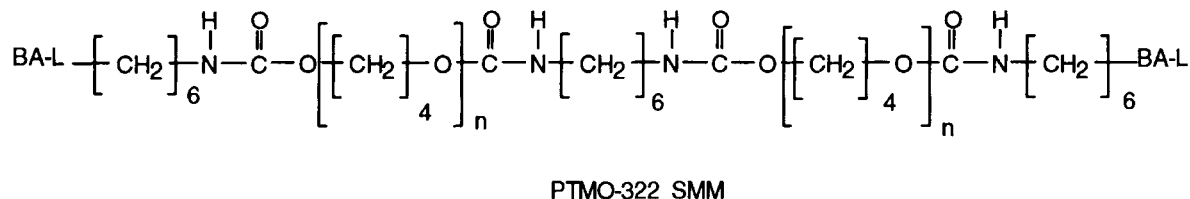
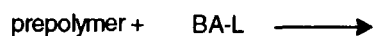
Table II contains the mass of reagents and volume of solvent used for each synthesis. In the first reaction step, HDI was added to the polyol solution and the catalyst. The reaction was maintained within a range of 60 to 70°C for 2 h, and then cooled to 45°C over a 15-min period. Following this, the BA-L was added to the products of the first step (i.e., the prepolymer) and the mixture allowed to react overnight. The polymer was then precipitated in distilled water and further washed in analytical chromatography grade 1,1,2-trichlorotrifluoroethane (obtained from BDH, Toronto, Ont., Can.) to remove any residual BA-L. After washing 3 times, the polymer was dried in a 50°C oven for 48 h, followed by drying in a vacuum oven for another 48 h.

Twelve different chemical formulations of the SMM reagents were used in this study. These were selected in order to evaluate the effect of the prepolymer size and the length of the fluoro-alcohol chain on the SMM's ability to perform as a surface modifying agent within the polyurethane. Following preliminary characterization of the above materials, five SMMs (PPO-212L, PTMO-322I, PPO-322I, PTMO-322H, and PPO-322H) were selected for continued studies and to evaluate the reproducibility of the synthesis while controlling solvent volume, the amount of catalyst, and temperature profile. For these latter materials, the solvent volume for the prepolymer reaction step was set at 130 mL, the

STEP 1



STEP 2



$m = \text{odd number from 3 to 17}$

Figure 2 Synthesis of a surface-modifying macromolecule (SMM).

amount of catalyst was restricted to 42.5 mg, and the temperature profile was maintained within 60 to 70°C.

Molecular Weight Determination

The molecular weights were determined by gel permeation chromatography methods, which were described previously.⁹ The operating temperature was

80°C and the mobile phase was *N,N*-dimethylformamide containing 0.05M LiBr. The sample size was 200 μL and the polymer concentration was approximately 0.2 g/100 mL. If the sample was not dissolved by the mobile phase solution at room temperature, heating was applied. Polystyrene standards were used to generate a calibration curve; subsequently the molecular weight values are reported here as polystyrene equivalent molecular weights.

Table I Example of SMM Nomenclature

Example PPO-322I	
PPO	Poly(propylene oxide) 1000 is the polyether used in this SMM synthesis. Another possible polyether includes PTMO.
322	The target mole ratio of HDI : PPO : BA-L (Int) is 3 : 2 : 2. Another possible stoichiometry includes 2 : 1 : 2.
I	The intermediate fraction of BA-L is used here. Other fractions include "L" and "H"; all are defined in the text.

Elemental Analysis

SMM samples were sent to Guelph Chemical Laboratories Ltd., (Guelph, ON) for fluorine elemental analysis. The following method was used. A sample was combusted with sodium peroxide in an oxygen rich atmosphere using a Schoniger oxygen flask with distilled water as the absorbing medium. An aliquot of the resulting solution (after filtration) was titrated

with thorium nitrate using alizarin red S as an indicator. The volume of required titrant was then used to determine the percentage of fluorine in the sample.

Differential Scanning Calorimetry (DSC)

DSC was used to characterize the thermal transitions of the polyurethanes and subsequently to assess the occurrence of microphase separation. The DSC equipment used in this work (model number 910, Dupont Instruments) was located in Dr. David Cooney's laboratory at the National Research Council of Canada, Institute for Environmental Chemistry, Ottawa, Ontario, Canada. DSC films were cast from 10% wt/wt solutions of TDI/PCL/ED or TDI/PCL/ED with SMM in DMAC. Solutions were filtered through a 0.5- μm poly(tetrafluoroethylene) filter in order to remove particles and then poured into wells of a TeflonTM sheet. The solvent was evaporated off in an oven at 50°C for 48 h and then further dried in a vacuum oven for another 48 h. The final sample was approximately 0.5 mm thick. The sample weight of the DSC specimens was approximately 6 ± 2 mg. The polymer was pre-cooled to -160°C using liquid nitro-

Table II Materials and Amounts Used in SMM Synthesis

SMM	HDI (g)	PTMO/PPO (g)	BA-L (g)	Catalyst (μL)	DMAC in Prepolymer (mL)
SMM1 (PTMO-432I)	2.24	10.0	4.0	80	70
SMM2 (PTMO-212L)	3.36	10.0	9.0	60	70
SMM3 (PTMO-322L)	2.52	10.0	5.0	60	70
SMM4 (PTMO-212H)	1.68	5.0	4.5	40	60
SMM5 (PTMO-212I)	1.68	5.0	4.5	40	60
SMM6 (PPO-212L)	3.36	10.0	9.0	80	130
SMM7 (PPO-322I)	2.52	10.0	5.0	60	130
SMM8 (PTMO-322H)	2.52	10.0	5.0	60	130
SMM9 (PPO-322H)	2.52	10.0	5.0	60	130
SMM10 (PTMO-322I)	2.52	10.0	5.0	60	130
SMM11 (PTMO-432L)	2.24	10.0	4.0	100	70
SMM12 (PTMO-432H)	2.24	10.0	4.0	80	100

gen. Data were recorded from -160°C to 220°C for the pure TDI/PCL/ED and SMM/base polymer mixtures. Data collection for the pure SMMs was carried out between -160°C and 120°C for PPO-containing SMMs, and from -160°C to 150°C for PTMO-containing SMMs. Following heating, the samples were rapidly cooled to room temperature, then cooled to -160°C prior to performing a second scan. This second scan allowed for a further investigation of the polyurethane's internal structure after its original structural features had been relaxed by heating. Unless otherwise stated, a third scan was run in order to confirm the position of the thermal transitions on the thermogram. DSC thermograms were obtained for 2 batches of the same SMM formulation.

Contact Angle Measurement

Contact angle measurements were carried out by measuring water drop contact angles at the material/air interface. The results provide information on the relative hydrophilicity of the material surface. Polyurethane surfaces were prepared by a dip-coating technique. Prior to coating, glass slides were cleaned with chromic acid and were subsequently coated with a polymer solution and dried in an oven at 50°C for 12 h. Four coatings were needed to generate an optically smooth surface. Prior to taking measurements, the samples were allowed to cool to room temperature. The coating solutions consisted of 10% polymer in DMAC ((total weight of SMM and TDI/PCL/ED polymer)/weight of DMAC). The SMM concentrations of the TDI/PCL/ED solutions were 2.5% and 5% (SMM/base polymer).

The contact angle measurements were obtained using a Contact Angle Goniometer (Rame-Hart Inc.). Ultrapure water, 5 to $10\ \mu\text{L}$, was pumped from a micro-syringe onto the surface of the film. Advancing and receding angles were measured by increasing or decreasing the volume until the three-phase boundary moved over the surface. The advancing angle measurements reflected the hydrophobic character of the material while the receding angle was more characteristic of the hydrated state of the surface. In order to obtain reproducible results, care was taken to avoid vibration and distortion of the drop during volume changes. Twenty readings were obtained for every sample and standard errors were calculated using the student *t*-test where $P < 0.05$ indicated a significant difference. Measurements were taken for the different batches of each SMM formulation.

RESULTS AND DISCUSSION

Polymer Synthesis and Bulk Properties

The SMMs were synthesized so that they contained a polyurethane compatible soft-segment and a hydrophobic fluorine component which would be incompatible with the base polymer. The soft-segment of the SMM was selected to encourage a permanent anchoring of the SMM in the TDI/PCL/ED, following their mixing. The fluorine tails were selected for their ability to carry the SMMs to the surface and expose their chemically resistant fluorine chains out from the surface. The latter process was driven by the thermodynamic incompatibility of the fluorotail with the TDI/PCL/ED polymer as well as the tendency toward establishing a low surface energy at the mixture's surface. If an appropriate balance between anchoring and surface migration is achieved, the SMM should remain stable at the surface of the polymer while simultaneously altering the surface properties.

Table III lists the weight-average molecular weight and the fluorine content for 12 SMM formulations. In all cases, the measured molecular weight was greater than the value predicted by the reaction stoichiometry. The ultimate molecular weight value of the SMM is primarily determined by the size of the prepolymer generated in the first step of the reaction. This is because the fluorine-containing reactant is monofunctional and theoretically cannot allow for further increases in the molecular weight beyond its own addition to the prepolymer. In order to control the size of the prepolymer, a stoichiometric excess of HDI was added to the prepolymer synthesis. Hence, if the mixture contains n moles of polyol, then $n + 1$ moles of HDI are added to favor the formation of an isocyanate-terminated prepolymer.

It is also noted in Table III that the fluorine contents for the various SMMs are significantly lower than anticipated values, based solely on reactant stoichiometries. Several explanations for the lower theoretical fluorine content and high molecular weights exist. One possibility is that, during the BA-L capping procedure, unreacted hydroxyl groups from the polyol reacted with the HDI end-capped prepolymer. In fact, when comparing the hydroxyl groups of BA-L with those of the polyols, it can be hypothesized that the one associated with the BA-L molecule might be less reactive due to the electro-negativity of the fluorine atoms adjacent to the hydroxyl group. An assessment of the reaction kinetics

Table III Polystyrene Equivalent Weight-average Molecular Weight and Fluorine Content of SMMs

SMM	M_w	Polydispersity	Fluorine Content
SMM1 (PTMO-432I)	1.1×10^5	2.0	NF
SMM2 (PTMO-212L)	3.0×10^4	1.5	7.98
SMM3 (PTMO-322L)	2.4×10^5	1.8	NF
SMM4 (PTMO-212H)	9.7×10^4	2.1	0.72
SMM5 (PTMO-212I)	1.4×10^5	3.1	0.10
SMM6 (PPO-212L)	2.2×10^4	1.3	12.44
SMM7 (PPO-322I)	4.8×10^4	1.6	3.95
SMM8 (PTMO-322H)	6.1×10^4	2.0	0.71
SMM9 (PPO-322H)	2.6×10^4	1.6	5.11
SMM10 (PTMO-322I)	5.0×10^4	1.7	4.97
SMM11 (PTMO-432L)	1.8×10^5	2.0	NF
SMM12 (PTMO-432H)	7.1×10^4	1.7	3.28

NF, Not found; M_w : Weight-average molecular weight.

for the PPO and BA-L molecules with the prepolymer will be required in order to confirm this hypothesis.

A second explanation for the lower fluorine is based on the chemical incompatibility of BA-L with the prepolymer (i.e., nonpolar vs. polar). As a result of this incompatibility, BA-L may be partially excluded from the reaction zone of the HDI end-capped prepolymer. This could yield a continuing reaction of free hydroxyls on the polyol with diisocyanate end-capped prepolymers. Furthermore, in the case where reactant concentrations are elevated, an amplification of this effect could be anticipated. Evidence of this possibility is apparent when molecular weight values for SMMs containing similar initial reagent stoichiometries but different reaction volumes (see Table II) are compared. In reference to the data in Table III, it was found that for SMM3 (PTMO-322L) and SMM8 (PTMO-322H), which were synthesized using similar reactant stoichiometries, the PTMO-322H which was synthesized with a higher solution volume had a higher fluorine content and lower molecular weight. In a similar manner, it was observed that SMM1 (PTMO-432I), which was synthesized in 70 mL of solvent, had a higher molecular weight and lower fluorine content than those of SMM12 (PTMO-432H), which was synthesized in 100 mL of solvent. There is little evidence in the literature to support the effect of solvent volume on the solution synthesis of polyurethanes; however, Potts and coworkers¹⁶ and Gao and colleagues¹⁷ made similar observations in their synthesis of hexachlorocyclotriphosphazene and poly(ethylene glycol), respectively.

The heat source for this synthesis work was a stirrer/hot plate, which made precise temperature control difficult. While in all cases the temperature was controlled within the range of 60–70°C, the temperature profile during the 2-h prepolymer reaction period did vary for each batch synthesis (see Fig. 3). It is not clear to what extent this affected the prepolymer product; however, since Wang and coworkers,¹⁸ have indicated the importance of temperature on catalyzed systems, it was possible that this also contributed to the variable molecular

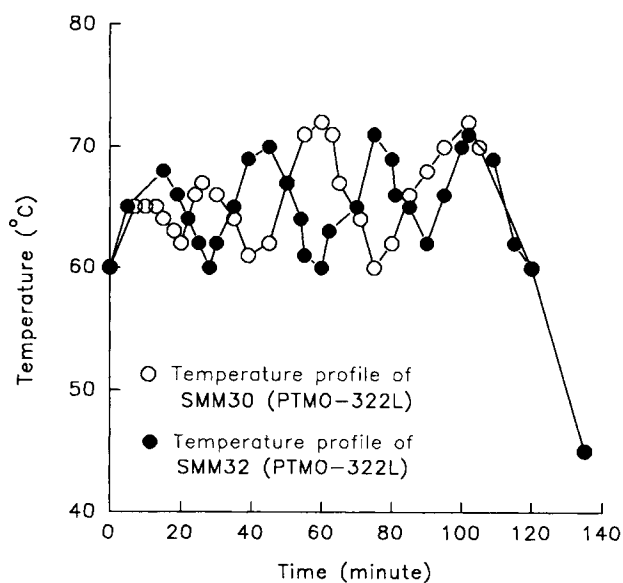


Figure 3 Reaction temperature profile for the synthesis of PTMO-322L.

weights and the range of fluorine content observed for the initial 12 SMMs.

It is interesting to note that the SMMs containing PPO as the soft-segment generally had lower molecular weight values than those containing PTMO. It has been reported in studies by Rand and colleagues¹⁹ that the primary hydroxyl groups of the polyether (such as in the PTMO) react more rapidly with a diisocyanate than do the secondary hydroxyl groups (as found in PPO) because of the hindrance of the methyl side chain in the latter case. The enhanced reactivity of PTMO with HDI, coupled with the previous factors discussed, would further reduce the incorporation of BA-L into the SMM. In addition, Wang and Lyman's work²⁰ confirmed that, in a prepolymer synthesis, PTMO led to longer prepolymer chains and more free diisocyanate than did reactions with PPO. Any BA-L reacting with free HDI molecules would form relatively lower molecular weight polymers that would likely be washed out of the polymer in the post-synthesis steps.

In addition, the data in Table III show that SMMs which contain a low fluorine content are also characterized with a low molecular weight. This further indicates that the most significant contribution to the SMM's molecular weight was the size of the prepolymer chain and not the size of the fluorine tail, since the addition of the BA-L was a chain-termination step. This trend was most noticeable with the three largest SMMs—SMM1 (PTMO-432I), SMM3 (PTMO-322L) and SMM11 (PTMO-432L)—which did not show any measurable fluorine content.

It was hypothesized that SMMs containing BA-L (High) should have a higher fluorine content than SMMs synthesized with BA-L (Int) and BA-L (Low) when the prepolymer chains were equivalent. However, the experimental results showed no clear trend in this regard. For example, SMM8 (PTMO-322H) had a much lower fluorine content than that of SMM10 (PTMO-322I). This contradiction of the theoretical predictions may again be explained by some of the unanticipated differences in the reaction kinetics of the various reagents.

Based on the above observations, five SMMs were selected for further characterization. The three SMMs that contained PPO (PPO-212L, PPO-322I, and PPO-322H) were chosen because of the lower PPO reactivity which seemed to allow for greater control of the prepolymer reaction and a less competitive reaction with the hydroxyl groups of the BA-L molecule. Two of the PTMO analogs of these

materials (PTMO-322I, PTMO-322H) were also selected in order to compare the effect of the soft-segment component on the SMM properties. Limited characterization studies were done with the PTMO-212L analog of PPO-212L because of problems related to obtaining smooth-cast films from its mixture with TDI/PCL/ED.

Table IV contains the average molecular weight and fluorine content for 4 to 5 batches of each of the above five formulations. Based on the standard error data, it was observed that PPO-322I, PTMO-322I, and PPO-212L showed the best reproducibility. It is hypothesized that the poor reproducibility of the PTMO-322H and PPO-322H were in part associated with the relative reactivity of the high BA-L fraction with the prepolymers in comparison with the other two fractions. BA-L (High) contains the largest fluorine tail ($-(CF_2)_n$, $n = 11-17$), and the molecule may be selectively excluded from the reactive isocyanate due to the chemical incompatibility of this long hydrophobic chain with the relatively hydrophilic prepolymer chain. In such a case, prepolymer chains with free hydroxyl groups can compete for free isocyanate groups on the prepolymer chains. This exclusion can lead to less-effective capping and greater batch-to-batch variability for the resulting SMMs.

Differential Scanning Calorimetry

The thermal transitions of the five SMMs selected for characterization along with the thermograms of their SMM-TDI/PCL/ED polymer mixtures were obtained by DSC. This information was used to determine whether the presence of SMM in TDI/PCL/ED influenced the bulk microdomain structure, as well as to determine the structural state of pure SMM materials. TDI/PCL/ED mixtures containing 5% SMM were selected for the studies, since there was concern that the DSC instrument would not be sensitive to changes in thermal transitions when the SMM concentration was lower than this. This value was based on work by Theocaris and Kefala,²¹ who found that a 5% additive concentration was detectable by a DSC measurement. Figures 4 to 8 show the DSC data for two repeat batches of the five SMM formulations.

In Figure 4, both SMM34 (PTMO-322I) and SMM36 (PTMO-322I) show similar PTMO glass transition temperature (T_g) ranges (from -74.47°C to -61.69°C), as well as similar melting temperatures for the high-ordered PTMO segments (be-

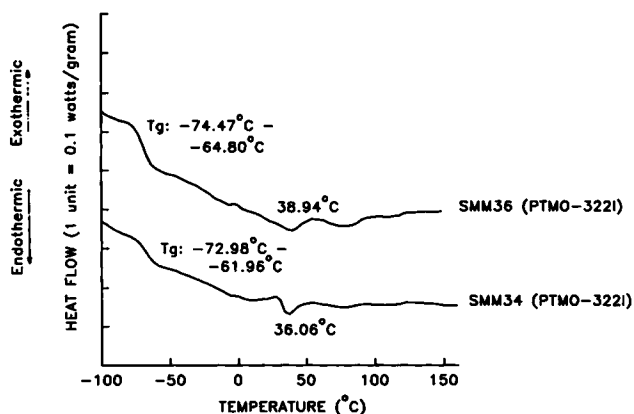
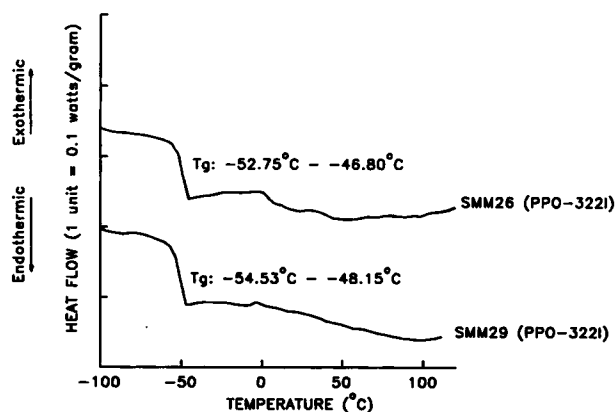
Table IV The Mean Weight-average Molecular Weight and Fluorine Content of Resynthesized SMMs

SMM	Number of Batches	Mean Molecular Weight	Mean Fluorine Content (%)
SMM13 (PTMO-322I)	5	$(4.6 \pm 0.53) \times 10^4$	5.50 ± 1.21
SMM15 (PTMO-322I)			
SMM25 (PTMO-322I)			
SMM34 (PTMO-322I)			
SMM36 (PTMO-322I)			
SMM14 (PPO-322I)	4	$(3.3 \pm 0.41) \times 10^4$	9.37 ± 1.70
SMM16 (PPO-322I)			
SMM26 (PPO-322I)			
SMM29 (PPO-322I)			
SMM19 (PPO-212L)	4	$(1.6 \pm 0.16) \times 10^4$	18.87 ± 2.38
SMM24 (PPO-212L)			
SMM37 (PPO-212L)			
SMM39 (PPO-212L)			
SMM17 (PTMO-322H)	4	$(5.5 \pm 0.81) \times 10^4$	3.83 ± 1.80
SMM20 (PTMO-322H)			
SMM23 (PTMO-322H)			
SMM43 (PTMO-322H)			
SMM9 (PPO-322H)	4	$(4.63 \pm 2.55) \times 10^4$	4.63 ± 2.55
SMM18 (PPO-322H)			
SMM21 (PPO-322H)			
SMM22 (PPO-322H)			

tween 36.06 and 38.94°C). Both SMM29 (PPO-322I) and SMM26 (PPO-322I) showed a higher T_g range (from -52.75°C to -48.15°C) (Fig. 5) than that of the PTMO-322I SMMs (Fig. 4). This may be due to the fact that the T_g value of pure PPO (-70°C²²) is lower than that of pure PTMO (-79.8°C, unpublished data from our laboratory). The lack of an ordered soft-segment melt transition can be explained by the presence of the side-chain methyl group in

PPO, which hinders packing and crystallization of the chain segments.²³ The structural character of these two SMMs was also reflected by their physical appearance: the PPO-322I SMM was a tacky powder, whereas the PTMO-322I SMM was a soft, fibrous material.

DSC data for SMM37 (PPO-212L) and SMM39 (PPO-212L), shown in Figure 6, revealed the most complicated thermograms of the five SMMs. They

**Figure 4** DSC thermograms of PTMO-322I (SMM34 and SMM36).**Figure 5** DSC thermograms of PPO-322I (SMM26 and SMM29).

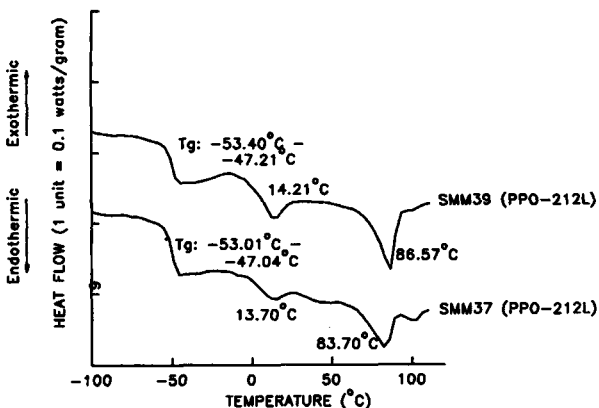


Figure 6 DSC thermograms of PPO-212L (SMM37 and SMM39).

displayed one T_g as well as two sharp melting temperatures. The T_g of this polymer ranged from -53.40°C to -47.04°C . The similarity of the range to that of PPO-322I (SMM29) indicated that the polyol was the dominant factor in determining the T_g of these SMMs. The presence of two melting temperatures indicated that the SMM stoichiometry could influence its structural nature. The two melting points observed in PPO-212L are believed to indicate a higher order in the microstructure of this SMM which may be induced by the proximity of the two fluorine tails as a result of the short SMM chain length. The PPO segments, meanwhile, are not believed to be involved since they did not crystallize.

Both PTMO-322H SMMs and PPO-322H SMMs (Figs. 7 and 8, respectively) had T_g s similar to their BA-L (Int) analogs, i.e., PTMO-322I and PPO-322I. This again showed that the T_g was highly dependent on the type of polyol used. However, these two BA-

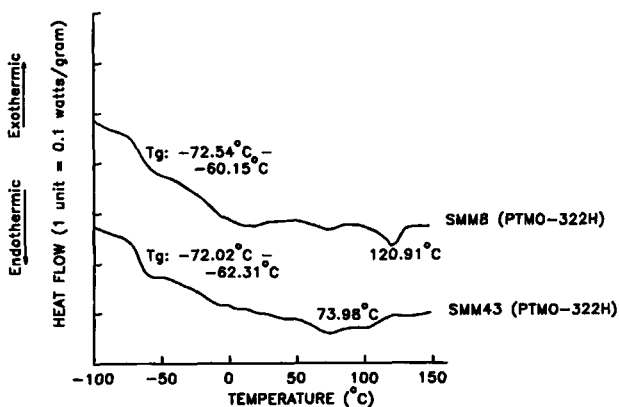


Figure 7 DSC thermograms of PTMO-322H (SMM8 and SMM43).

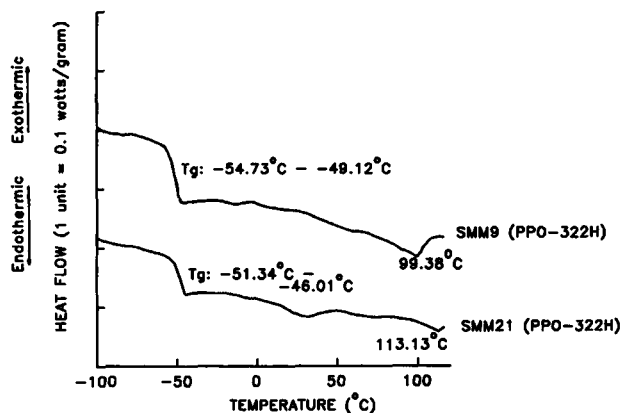


Figure 8 DSC thermograms of PPO-322H (SMM9 and SMM21).

L (High) SMMs displayed several other transitions which did not appear in the thermograms for the BA-L (Int) analogs. The increased size of the fluorine tail is believed to be partly responsible for the formation of these new structures. The precise nature of those structures and the relative distribution of the hydrophobic tails around the prepolymer components will require further study.

Figure 9 contains the DSC thermograms for TDI/PCL/ED and a mixture of the SMM PPO-212L, with TDI/PCL/ED. TDI/PCL/ED has a T_g range between -47.79°C and -36.73°C which was similar to values previously reported for this polymer.⁹ Although pure PPO-212L showed a very complicated DSC thermogram, the mixture of 5% PPO-212L in TDI/PCL/ED revealed a T_g range similar to that of the TDI/PCL/ED without SMM. This would suggest that, at this concentration of SMM, the macromolecules were not evenly distributed throughout

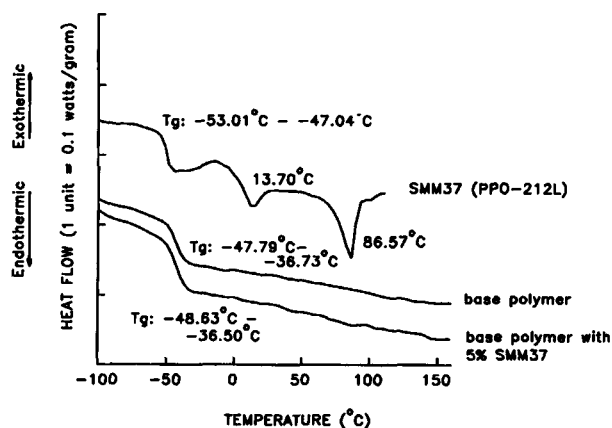


Figure 9 DSC thermograms of TDI/PCL/ED, SMM37 (PPO-212L), and their mixture.

the bulk material, but rather had migrated to the surface of the polymer and had little impact on the bulk phase microstructure. The thermograms for the mixtures of TDI/PCL/ED with the other formulations were also identical to that of the pure base material.

Contact Angle Measurement

Table V contains contact angle values for two repeat batches of each SMM formulation. During the preparation of films for contact angle measurements, it was noted that the ease of coating the polymer solutions with SMMs on the glass slides was highly dependent on the polymer concentration in the casting solution. Specifically, the SMM-TDI/PCL/ED mixtures were difficult to cast when the total polymer matrix concentration was lower than 10% w/w (polymer in DMAC). However, there was no difficulty associated with coating films of the pure base polymer, even at a polymer solution concentration of 2% w/w. The difference in observed behavior between the mixtures and the base polymer is believed to be due to the presence of the fourth phase (i.e., SMM) during the casting process. Since the SMM is an amphiphilic molecule, it can effec-

tively behave as a surfactant whereby its hydrophobic tails are incompatible with the hydrophilic glass. In the case where the total concentration of the polymer in the casting solution was too low, the base polymer matrix layer would not be thick enough to mask the SMM-enriched layer from the glass. As a result of the tendency of the SMM to exist at the interface between the polyurethane and the glass, the SMM would effectively drive the polymer away from the glass until the total energy of the system was minimized, thus forming a discontinuous film. If the total polymer concentration was increased to 10% enough base polymer became available to cover the glass, thereby providing a three-phase system (air-SMM-base polymer) at the air interface and making it possible to cast a continuous film.

The advancing angle of the pure TDI/PCL/ED was 77.3° whereas its receding angle was 39.6°. By comparison, the contact angle values for the surface of the SMM-polyurethane mixtures were significantly higher ($P < 0.05$), indicating that the SMM was present in an enriched layer on or near the polymer-air interface. The fact that the receding contact angles were consistently higher in the mixtures as compared with the pure TDI/PCL/ED indicates further that, even after reorientation occurs

Table V Contact Angle Results

Polymer or SMM Mixture	Concentration of SMM (wt %)	Advancing Contact Angle (°)	Receding Contact Angle (°)	Hysteresis (°)
TDI/PCL/ED	0	77.3 ± 0.4	39.6 ± 0.6	36.7 ± 0.3
SMM36 (PTMO-322I)	2.5	99.1 ± 0.2	68.7 ± 0.8	30.4 ± 0.9
	5.0	107.4 ± 0.5	81.4 ± 0.6	25.4 ± 0.7
SMM34 (PTMO-322I)	2.5	92.4 ± 0.6	67.8 ± 0.4	21.9 ± 0.7
	5.0	105.9 ± 0.7	79.8 ± 1.1	26.1 ± 0.8
SMM26 (PPO-322I)	2.5	106.1 ± 0.6	48.4 ± 0.6	58.0 ± 0.8
	5.0	116.2 ± 0.6	54.3 ± 0.8	62.2 ± 1.0
SMM29 (PPO-322I)	2.5	107.8 ± 0.4	52.0 ± 0.5	45.9 ± 0.5
	5.0	114.0 ± 0.4	53.9 ± 0.5	50.1 ± 0.7
SMM39 (PPO-212L)	2.5	102.5 ± 1.2	75.9 ± 1.8	27.2 ± 2.1
	5.0	109.1 ± 1.1	77.2 ± 1.3	19.9 ± 1.2
SMM37 (PPO-212L)	2.5	80.0 ± 0.8	57.2 ± 0.7	22.8 ± 1.1
	5.0	86.6 ± 0.6	59.5 ± 0.7	26.8 ± 0.8
SMM20 (PTMO-322H)	2.5	113.5 ± 0.5	91.5 ± 0.8	21.0 ± 0.7
	5.0	115.8 ± 0.5	101.9 ± 0.3	13.9 ± 0.6
SMM43 (PTMO-322H)	2.5	113.8 ± 0.4	99.4 ± 0.3	14.4 ± 0.5
	5.0	115.6 ± 0.4	105.2 ± 0.6	10.4 ± 0.5
SMM9 (PPO-322H)	2.5	99.9 ± 0.6	56.9 ± 0.9	43.1 ± 1.0
	5.0	110.0 ± 0.5	61.7 ± 0.3	50.4 ± 0.8
SMM21 (PPO-322H)	2.5	103.6 ± 0.8	52.4 ± 0.8	51.1 ± 1.0
	5.0	113.1 ± 0.8	56.5 ± 0.8	56.5 ± 0.7

due to the change in environment (from air to aqueous surroundings), hydrophobic segments related to the SMM remain at the interface. In addition, it is shown that both the advancing and receding contact angle increases with increasing SMM content in the TDI/PCL/ED film.

It is interesting to note that the receding angles of PTMO-322I and PTMO-322H mixtures were all significantly higher than those of the PPO-322I and PPO-322H analogs. This may be attributed to the enhanced ability of PTMO segments to crystallize where the PPO segments cannot. The presence of crystallized segments will enhance the SMMs' stability within the polymer matrix, following the exposure to an aqueous media. As well, this difference has been in part attributed to the fact that the PTMO-SMMs have higher molecular weights and longer chains than the PPO-SMMs. The longer chains increased the number of interactions with the TDI/PCL/ED soft-segment and also assisted in stabilizing the SMMs within the polymer matrix. Once established through casting, the stabilized SMM/TDI/PCL/ED matrix reduced the degree of chemical group mobility (i.e., reorganization of hydrophobic fluorine groups away from the surface and mobilization of polar groups at the aqueous interface) when the environment changed with exposure to water during the contact angle measurement.

The increase in matrix stability was reflected in the hysteresis data (i.e., difference in advancing and receding contact angles) for the PTMO-containing SMM materials and PPO-containing materials. As shown in Table V, the PPO-SMM mixtures always displayed greater hysteresis than their PTMO-SMM counterparts. The work of Freij-Larsson and colleagues¹³ showed that an additive with less hysteresis would be less susceptible to leaching. Therefore one may postulate that, for TDI/PCL/ED, the PTMO formulation would be favored in any long-term application. An earlier study by Tingey and Andrade²⁴ showed that the advancing contact angle of a polyurethane with fluorinated diols and PTMO as soft-segment was approximately 125°; however, the hysteresis was as great as 85°. This agrees with the hypothesis that it is the soft-segments in polyurethanes which are responsible for the segment reorganization once the material is exposed to another medium.²⁵ Tingey's result then proves the benefit of incorporating formulations of fluorinated SMMs into the polyurethane mixtures, since the latter macromolecules appear to form a relatively stable uniform layer which modifies the polyurethane soft-segments.

Tests were performed to verify the reproducibility of the contact angle measurements for SMMs synthesized from different batches. The value of advancing and receding contact angles for four of the SMMs were very similar, however the results for the two different batches of PPO-212L SMMs differed somewhat. It was previously noted that this polymer contained a very high fluorine content and as a result casting continuously smooth films was difficult. This difficulty could explain the observed differences.

In conclusion, the polymeric SMMs synthesized in this work can significantly alter the surface chemistry of segmented polyurethanes. In this case, the SMMs migrated to the surface of the polymer mixture, yielding a new hydrophobic surface. The advancing and receding contact angles for the PTMO formulation showed significant increases over the base polymer, comparable to contact angle values obtained for pure Teflon® (116° for advancing contact angle and 92° for receding contact angle²⁶). Simultaneously, the thermal transitions of TDI/PCL/ED, measured by DSC, which are an indication of bulk structure, did not change with the addition of 5% SMMs to the base polyester-urethane. This would imply that the polyurethane-SMM mixture retained most of the structure which defines the polyurethane's elastomeric nature but yet had surface characteristics similar to Teflon™. This new surface may have all the attributes of perfluoro-carbon chains and therefore be significantly more stable with respect to oxidation and hydrolysis, demonstrate low fouling properties, and display increased heat resistance.²⁷

The authors acknowledge the financial support of the Ontario Center for Material Research and the Natural Science and Engineering Research Council. The authors also express their thanks to the Ontario Ministry of Health for Faculty funding through the Career Scientist Program.

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Received November 20, 1995

Accepted March 18, 1996