A Mass Spectrometry Analysis of Hard Segment Length Distribution in Polyurethanes

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ABSTRACT: Matrix-assisted laser desorption ionization (MALDI) mass spectrometry was utilized to determine the hard segment length distribution in poly(urea−urethane)s. Although hard segment length is expected to vary with water content in the initial formulations, the actual distribution is rather similar for all samples analyzed. A more detailed analysis, however, revealed that the principal difference is in the region corresponding to hard segments with greater than eight urea repeat units. This finding has implications for both in the origin of phase separation behavior and the mechanical performance of phase separated heterogeneous polymers. The similarity in hard segment distribution suggests that phase separation behavior in these polyurethane foams cannot be due solely to the orientational entropic contribution. The presence of these long hard segments, although not extensive (7% of the total number fraction), may contribute significantly to mechanical performance. MALDI also revealed the presence of side products. The amount of cyclic species, either isocyanurate or cyclic hard segments, varied from 2 to 4% for foams with different urea contents.

Introduction

Despite numerous studies of polyurethane copolymers consisting of soft and hard segment units, a number of fundamental issues remain unanswered. These thermoelastic systems have tremendous commercial value and present opportunities to study fascinating aspects of chemistry, physics, and engineering. The soft block is usually a multifunctional polyether or polyester. Hard blocks, or hard segments, are typically composed of aromatic units and tend to segregate into domains. To a large extent, formation and organization of hard domains depend on the chemical structure of the hard blocks and the processes that occur during phase separation.[1]

One area of polyurethane research involves the formation and properties of structural foams. In our laboratory, particular emphasis was devoted to open cell foams. These cellular solids are composed of an interconnected network of solid struts, which form edges of cells. The development of the microstructure within the struts is extremely complex. Hard segments form in situ through reactions between isocyanates and water and segregate into domains in order to stabilize the overall structure.[2] The soft segment or elastic component is usually is a trifunctional polyether. As hard segment polymerization and phase separation proceed, there is a concurrent increase in viscosity due to chemical cross-linking. The situation is further complicated by a rapid rise in temperature to 140−150 °C because of heat released by the chemical reactions.[2,3]

Although polyurethanes are among the most studied materials, the parameters, which govern the evolution of morphology, are difficult to define because of the many factors that require consideration. The miscibility of water, isocyanates, and polyethers is crucial in formation of hard segments. Further development of phase-segregated morphology depends not only on the kinetics of phase separation, which relates to the hard segment length, but also on the viscosity rise that accompanies cross-linking of the soft segments. Characterization methods such as infrared spectroscopy, transmission electron microscopy, X-ray, and in-situ modulus measurements have been extensively used to probe polyurethane structure.[3−14]

Polyurethane phase separation is generally believed to be due to chemical immiscibility between hard and soft segments. Previous studies of a polyurethane comprised of a rigid MDI/butanediol hard segment and a flexible poly(propylene oxide) soft segment revealed that hydrogen bonding between a urethane N−H group and an ether oxygen was actually stronger than between the N−H group and a carbonyl.[15] In fact, even polyurethanes that do not hydrogen bond still phase separate.[16−18] To account for polyurethane phase separation, the entropic contribution from chain orientation of rigid molecules must also be considered.[19,20] Both theoretical and experimental studies have shown that as hard segment length increased, the volume fraction of hard segments dispersed in the soft matrix decreased; i.e., samples with longer hard segments had significantly higher degrees of phase separation.[19,20] Hard segment length is therefore a crucial parameter in governing the phase separation behavior of polyurethanes under conditions of thermodynamic equilibrium. However, hard segment lengths and length distributions are usually unknown in polyurethane foams. A relatively new technique, matrix-assisted laser desorption ionization (MALDI) mass spectrometry, provides for the direct characterization of hard segment mass and mass distribution, which may be important factors controlling morphology.

MALDI time-of-flight (MALDI-TOF) mass spectrometry circumvents a major obstacle to the mass spectrometric analysis of large molecules—sample volatility. As traditional mass spectrometry techniques ionize molecules in the gas phase, they are consequently limited to analysis of small molecules.[21−23] In MALDI, a light-absorbing matrix mediates ionization of the analyte.

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Matrix choice is hence crucial. [22−28] Whereas other mass spectrometry techniques induce fragmentation, MALDI provides analysis of intact molecules.[21,23,24] The matrix facilitates a moderate energy transfer to sample molecules, avoiding analyte fragmentation that would accompany desorption if the energy were absorbed directly by the sample.[22−24] Following desorption, the analytes travel across a flight tube to a detector. The resulting sample spectrum is a plot of signal intensity versus mass per charge (m/z). Since charges of one are typical in MALDI, the peaks correspond to molecular masses.[22−25,29]

In this study, two series of polyurethane films based on the polymer in water-blown polyurethane foams were prepared with different hard segment content at various temperatures. The details of sample preparation and morphological characterization have been reported.[1] Synthesis at low reaction temperature (50 °C) yielded a phase-separated morphology. A phase-mixed structure developed in films prepared at high temperatures (150 °C). These differences were assigned to varying rates of phase separation and chemical cross-linking as a function of reaction temperature. Chemical cross-linking prevailed at high reaction temperatures, kinetically trapping a phase-mixed state. At low temperatures, the rate of phase separation was faster than cross-linking. Although a number of characterization techniques have been employed in the examination of sample composition, phase-separated morphology, and resultant mechanical properties, a remaining crucial aspect is the uncertainty in hard segment distribution which may in fact dictate both the morphology and resultant properties. As we shall demonstrate, MALDI can address this particular point. It is also important to analyze a seldom-considered aspect of polyurethanes, i.e., the formation of branched side products. Because excess isocyanate is generally needed in the synthesis of polyurethanes, the possibility exists that allophanate, biuret, and isocyanurate can form. As these structures are branched, they have the potential to disrupt packing within hard domains. Additionally, the trifunctional nature potentially provides extra cross-links that could impede phase separation. MALDI-TOF mass spectrometry can differentiate the number of repeats in a hard segment and some of the side products. This technique can thus be used to evaluate the impact of hard segment mass distribution and side products on polymer morphology. Our results are presented in this report.

Experimental Section

Hydrolysis Procedure. Since these polyurethanes are chemically cross-linked, it is not possible to determine molecular weight in the intact molecule. Recently, however, a procedure to selectively cleave the urethane bond connecting hard and soft segments was reported.[30] Preferential hydrolysis of the urethane is based partly on the reactivities of urethane, ether, and urea linkages to basic conditions and partly on the fact that the polyether soft segment is more easily swollen than the hard domains. Urea linkages within the hard domains are consequently much less accessible. This procedure allows recovery of intact hard segments.[30] Because the hydrolyzed hard segments are soluble, MALDI mass spectrometry can be used to determine the mass distribution of the molecules and reveal hard segment length.

The original procedure described hydrolysis of foam, which is very permeable.[30] To facilitate penetration of reactants into polyurethane film samples, pieces of film were milled into small particles at liquid nitrogen temperatures. As in the original study, foams prepared using the same formulation as the film samples were cut into small pieces before hydrolysis.[30] A solution of 5 g of sodium hydroxide in 50 mL of water was poured into a poly(tetrafluoroethylene) flask. A 50 mL aliquot of 1-butanol and 1 g of sample were then added. The flask was attached to a water-cooled condenser equipped with a nitrogen purge and placed in an oil bath maintained at 100 ± 2 °C. The reaction proceeded with stirring for 24 h, the time it takes for a polyurethane to reach the maximum level of hydrolysis.[30] After 24 h, methanol (80−100 mL) was added to the mixture until a single phase formed. The solution was then centrifuged for 25 min at 8000−10 000 rpm. The liquid was decanted, and the precipitate was filtered, washed with 150−200 mL of methanol, and dried.

After hydrolysis, the polyether soft segment should be completely detached from the hard segments, giving the structure in Figure 1. Figure 2 presents the infrared spectrum of the hard segments recovered from a foam formulated to have an average of six ureas per chain. The infrared spectrum of the original material is given in a previous publication.[1] Bands marked with an asterisk are from residual solvent. The CH stretching bands, which are mostly due to groups in the soft segment, are no longer present. Moreover, the urethane carbonyl bands in the 1700 cm^{-1} region disappear, leaving just

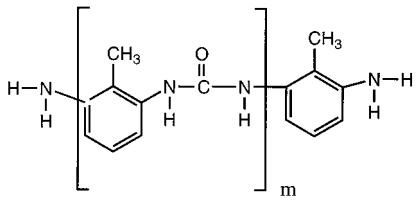

Figure 1. Structure of hard segment after hydrolysis.

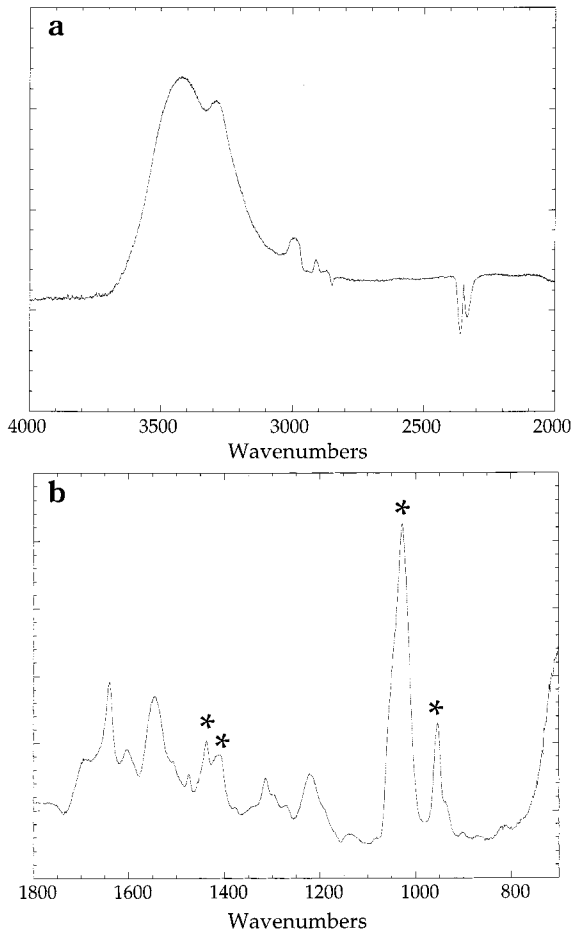

Figure 2. Transmission infrared spectrum of hard segments recovered from 6-foam after hydrolyzing for 24 h. The film was cast onto a KBr window from DMSO solution. (a) NH stretching region; (b) carbonyl stretching region.

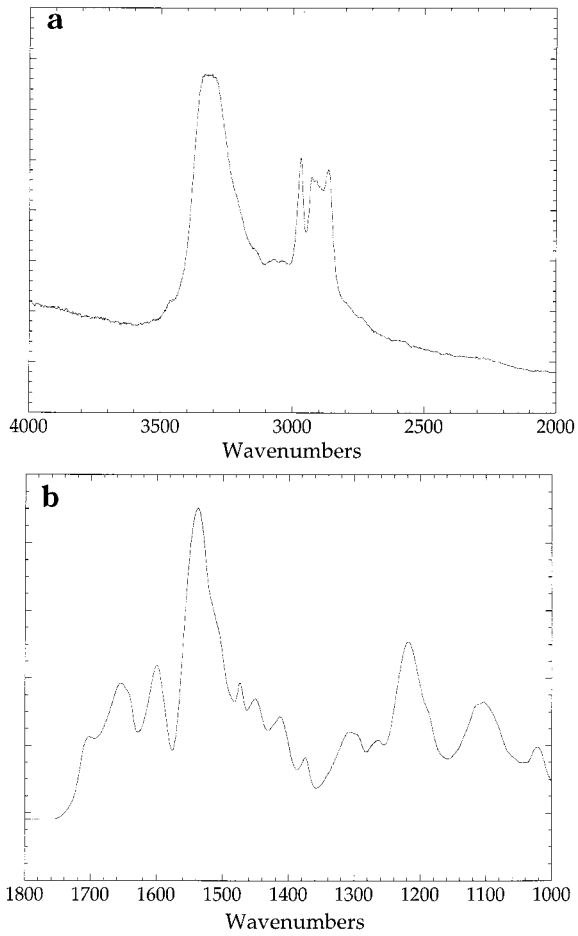

Figure 3. Transmission infrared spectrum of soluble hard segments recovered from 6-50 film after hydrolyzing for 24 h. The film was cast onto a CaF_2 window from DMSO solution. (a) NH and CH stretching region; (b) region containing carbonyl stretching.

urea carbonyl bands. It is evident from this spectrum that the urethane bonds have been hydrolyzed.

Materials Studied. Samples studied have been described elsewhere.[1] In this paper, film samples are designated $x-T$, where x is the stoichiometric number of ureas per chain and T is the isothermal reaction temperature. In some cases, portions of the hydrolyzed sample (~3%) could not be dissolved. Infrared spectra and MALDI mass spectrometry data are therefore indicative of the soluble portions of the sample. An infrared spectrum of the soluble portion of a hydrolyzed film formulated to have six ureas/chain and synthesized at 50 °C (Figure 3) shows, in contrast to the hydrolyzed foam, some evidence of CH stretching bands. This suggests that insolubility of the hydrolyzed film is due to incomplete hydrolysis, most likely because of lower permeability of the reactants into the grains in comparison with the foam. As grain size was not controlled, some samples had fine grains while others had coarse. If hydrolysis is incomplete due to particle size, the mass spectrometry data should be illustrative of the sample as a whole.

Mass Spectrometry. In these experiments, the urea hard segments were dissolved in a 50/50 (v/v) solution of DMSO and THF at a concentration of 4×10^{-3} g/mL. A saturated solution of the matrix, dithranol, was prepared using the same solvent system. The matrix and sample solutions were mixed in equal volume and cast onto a stainless steel target. Because dithranol oxidizes rapidly in air and DMSO evaporates very slowly, it was necessary to aid the drying process with an airgun set on low heat. Each spectrum is a sum of 200 shots, unless otherwise noted. All data interpretations are based on an average of either four or five spectra, each collected from a different film cast from the same solution. A Bruker Reflex

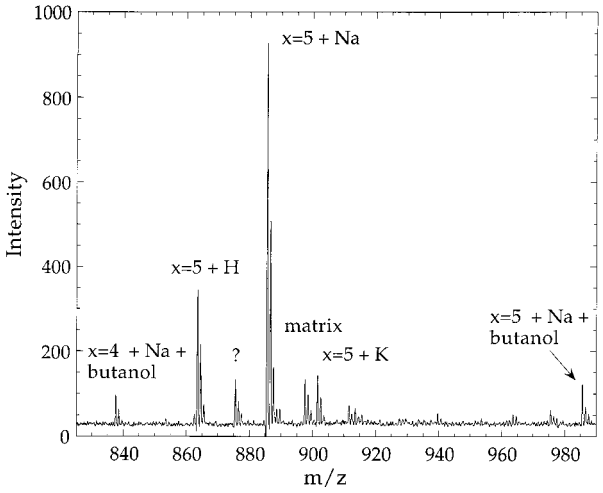

Figure 4. Portion of a MALDI mass spectrum of a polyurethane foam formulated to have six ureas per chain on average. Region around $x = 5$.

Table 1. Masses of Linear Hard Segments

no. of repeats	original molecule	H adduct	Na adduct	K adduct
0	122	123	145	161
1	270	271	293	309
2	418	419	441	457
3	566	567	589	605
4	714	715	737	753
5	862	863	885	901
6	1010	1011	1033	1049
7	1158	1159	1181	1197
8	1306	1307	1329	1645
9	1454	1455	1477	1493
10	1602	1603	1625	1641
11	1750	1751	1773	1789
12	1898	1899	1921	1937

III MALDI-TOF spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm) was operated in reflectron mode. The operating laser power was set 2−4% higher than threshold. All peaks at masses higher than the matrix (i.e., higher than 600 Da) were selected for analysis. Within the region populated with matrix peaks, only dominant peaks or those identified as sample peaks were integrated.

Results and Discussion

The accuracy and high resolution of MALDI mass spectrometry make it an ideal technique for determining the mass distribution of polyurethane hard segments. However, the success of mass spectrometry lies in assigning peaks in the mass spectra. Normally, molecules are found intact as adducts with H, Na, or K in MALDI experiments.[23,29] As shown in Figure 4, all of these can be observed for $x = 5$. The hydrolysis conditions make it possible for butanol to exchange with polyol.[30] In this case, 100 Da will be added to the expected mass. These are observed as well.

The expected masses for linear hard segments after hydrolysis are presented in Table 1, along with the masses of chains with adducts. (For Na counterion, the mass is then calculated as $148x + 145$.) It should be noted that the data are tabulated chains according to number of urea repeat units, x, and not TDI units. For instance, five repeat units correspond to a hard segment with six aromatic rings, counting the one involved in a urethane bond. This identification scheme was used for comparison with the formulated number of urea repeats per chain.

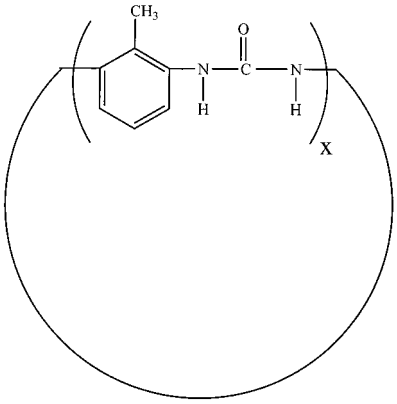

Figure 5. Chemical structure of cyclic hard segment.

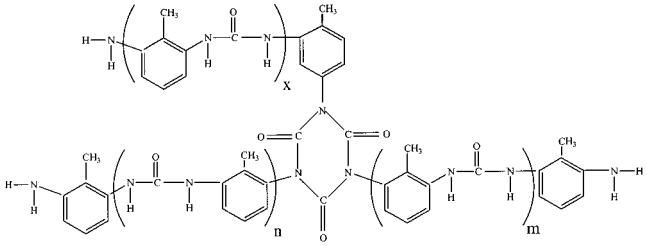

Figure 6. Chemical structure of isocyanurate after hydrolysis.

Table 2. Masses of Isocyanurates (Cyclic)

no. of repeats	original molecule	H adduct	Na adduct	K adduct
0	444	445	467	483
1	592	593	615	631
2	740	741	763	779
3	888	889	911	927
4	1036	1037	1059	1075
5	1184	1185	1207	1223
6	1332	1333	1355	1371
7	1480	1481	1503	1519
8	1628	1629	1651	1667
9	1776	1777	1799	1815
10	1924	1925	1947	1963
11	2072	2073	2095	2111
12	2220	2221	2243	2259

Unfortunately, because the masses overlap, allophanate and biuret, products of side reactions, cannot be distinguished from linear hard segments. However, it is possible to distinguish cyclic structures such as cyclic hard segments (Figure 5) and isocyanurates (Figure 6) from the linear and branched hard segments, hereafter referred to as a group as noncyclic hard segments. Within the cyclic chains, differentiation is not possible. Masses of isocyanurate (Figure 6) listed in Table 2 are calculated using the expression $148(n + m + x) + 467$ for sodium counterion. Masses of cyclic structures listed in Table 3 are calculated using the expression $148x + 23$ for sodium counterion. Therefore, cyclic structures can be attributed to either isocyanurate (Figure 7), cyclic hard segments (Figure 5), or both.

As shown in Tables 2 and 3, the sodium adduct of a cyclic structure with added butanol has the same nominal mass as a proton form of a noncyclic chain. For instance, a cyclic isocyanurate with four repeats in sodium form has a mass of 1059 Da. With butanol added, the mass is 1159 Da, the same as the protonated form of a linear hard segment with seven repeats. To distinguish these species, the sample/matrix solution was doped with potassium. Both the sodium and the protonated noncyclic structures should shift to the

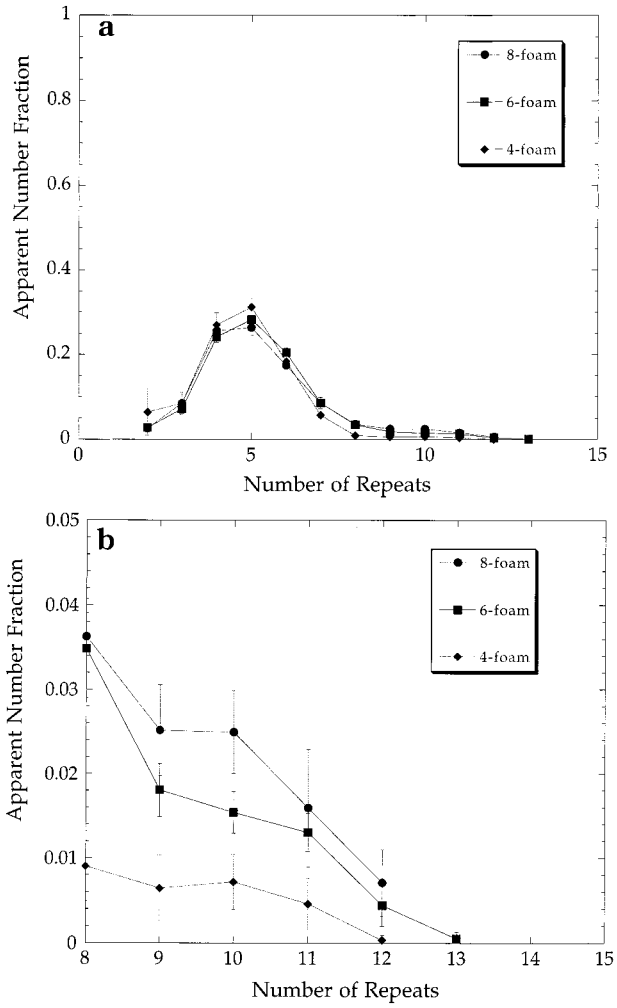

Figure 7. Mass distribution curves for noncyclic hard segments in foams with varying urea contents as determined by MALDI mass spectrometry. Each curve is an average of five distributions.

Table 3. Masses of Cyclic Hard Segments

no. of repeats	original molecule	H adduct	Na adduct	K adduct
0	0	0	0	0
1	148	149	171	187
2	296	297	319	335
3	444	445	467	483
4	592	593	615	631
5	740	741	763	779
6	888	889	911	927
7	1036	1037	1059	1075
8	1184	1185	1207	1223
9	1332	1333	1355	1371
10	1480	1481	1503	1519
11	1628	1629	1651	1667
12	1776	1777	1799	1815

noncyclic potassium position. The sodium adduct of the cyclic/butanol structure should shift to its potassium adduct. There was, however, no evidence of the potassium form of the cyclic/butanol molecule. Therefore, it was concluded that the peaks at 419, 567, 715, 863, 1011, 1159, etc., are the proton adducts of the noncyclic structures, not the sodium adducts of cyclic structures that had exchanged with butanol.

With proper assignment of masses, the relationship between hard segment length distribution and morphology may be determined. Water content has historically been used to control hard segment length in polyure-

Table 4. Sum of Number Fractions of Hard Segments with Nine or More Urea Repeats in Foam Samples

sample	sum[a]
4-foam	0.019
6-foam	0.051
8-foam	0.073

[a] Values are from average curves.

thane foams; it has been assumed that increasing the amount of water, with a concomitant adjustment in isocyanate, leads to longer hard segments.[1,2] The effect of water content (urea content) on hard segment distribution is illustrated in Figure 7. In this figure, the number fraction of noncyclic hard segments was calculated by dividing the total intensity of each species (all ions and all isotopes) by the total intensity of all noncyclic hard segments (all ions and all isotopes). These calculations do not include any cyclic species, so the apparent number fraction in the figure represents the distribution of the noncyclic hard segments. Plots of number fraction versus number of urea repeats, x, are shown for foams with 3.54 pphp water ($x = 4$), 5.31 pphp water ($x = 6$), and 7.5 pphp water ($x = 8$), which correspond to hard segment weight fractions of 0.28, 0.35, and 0.42, respectively.[1] It has been reported that the MALDI mass spectra of foams do not change with water content, i.e., the urea content, [30] which seems true at first inspection of data in Figure 7. As these foams were formulated to have different hard segment lengths, it is surprising that hard segments with five urea repeats predominate in all samples. In addition, long chains with as many as 14 repeats exist, despite the fact that the composition used should yield averages ranging from 4 to 8 urea units. Chains with as few as 1 or 0 urea repeats, i.e., soft segments linked by 2 or 1 TDI units, should exist. As these short hard segments appear in a mass region filled with matrix peaks, they cannot be distinguished.

The most significant differences found for samples of different water contents appear in the region of high mass (Figure 7b). The foam with the highest water content, 8-foam, has the highest fraction of chains with more than nine repeats; 4-foam, that with the lowest water content, has the fewest number of these hard segments. The sums of the number fractions of hard segments with $x \geq 9$ are given in Table 4. Approximately 7% of the hard segments in 8-foam have at least nine urea repeats. Only 2% of the hard segments in 4-foam are of this length.

From Figure 7, it is apparent that increasing the water content of a foam does not actually increase the average hard segment length, although it increases the overall hard segment composition. The amount of water controls the number of long hard segments. By increasing the quantity of water in a foam formulation, certain chains grow longer at the expense of the majority. In other words, the additional water is not equally distributed among the growing hard segments. Had the water been evenly allotted to each segment, the lengths of all hard segments and the average value would increase.

The relative amount of cyclic species in the foams can be calculated using MALDI. Figure 8 shows that cyclic species in foams have no more than six TDI units. In this case, similar to the data presented in Figure 7, the number fraction in Figure 8 was calculated by dividing the intensity of a specific cyclic species (all ions and all isotopes) by the sum of all cyclic peak intensities (all

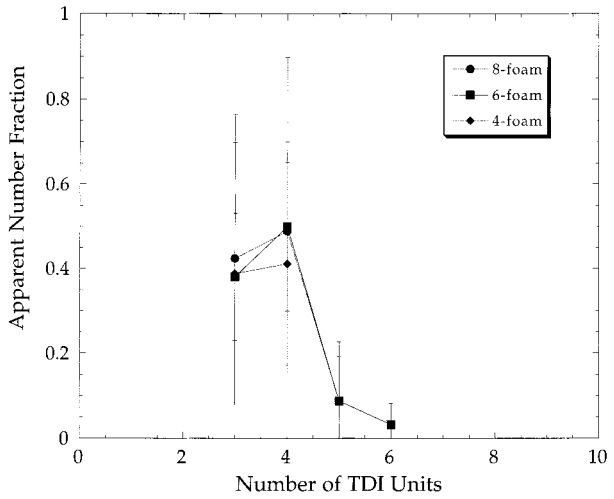

Figure 8. Mass distribution curves for cyclic hard segments in foams with varying urea contents (hydrolyzed for 1 day) as determined by MALDI mass spectrometry. Each curve is an average of five distributions.

Table 5. Percentage of Sample Peaks in Foams That Correspond to Cyclic Structures

sample	% cyclic
4-foam	1.8
6-foam	3.9
8-foam	2.2

ions and all isotopes). As evident from Figures 6 and 7, a cyclic structure with six TDI groups corresponds either to an isocyanurate with three urea repeats or to a cyclic hard segment with six urea repeats. Previous studies attribute the cyclic species to cyclic urea hard segments and exclude the possibility of isocyanurate on the basis that no cyclic structures with large masses were observed.[30] In line with this notion is the decreasing probability of ring formation with increasing ring size because of difficulties in the end groups finding and reacting with each other.[31] Since isocyanurates are still capable of growth, these chains should grow to a higher molecular weight. Most likely these cyclic structures are cyclic hard segments which have no reactive ends and cannot grow to large masses. The amount of cyclic species observed in the foams in Figure 8, expressed in Table 5 as a percentage of the total intensity of sample peaks, is in the range of the amount of cyclic oligomers formed during polymerization of polyurethanes and polyureas.[32]

MALDI mass spectrometry data for the film formulated to six ureas per chain and synthesized at 50 °C are similar to the analogous foam, as illustrated in Figure 9. The data presented here are calculated as the ones shown in Figure 7. In both samples as shown in Figure 9, most hard segments contain five repeat units, although hard segments with as many as 14 repeat units exist. The amount of hard segments containing more than nine urea repeats is comparable with 5.1% in the foam and 6.2% in the film. The similarity in the curves suggests this to be a suitable analytical method for films, despite the small amount of insoluble material found for the prepared films. Again, if the hydrolyzed film material lacks solubility because of incomplete hydrolysis due to penetration rate, the soluble portion of the sample should be representative of the whole. The impact of hard segment mass distribution on film morphology, described in our previous publication,[1] can therefore be evaluated by this technique. We made the

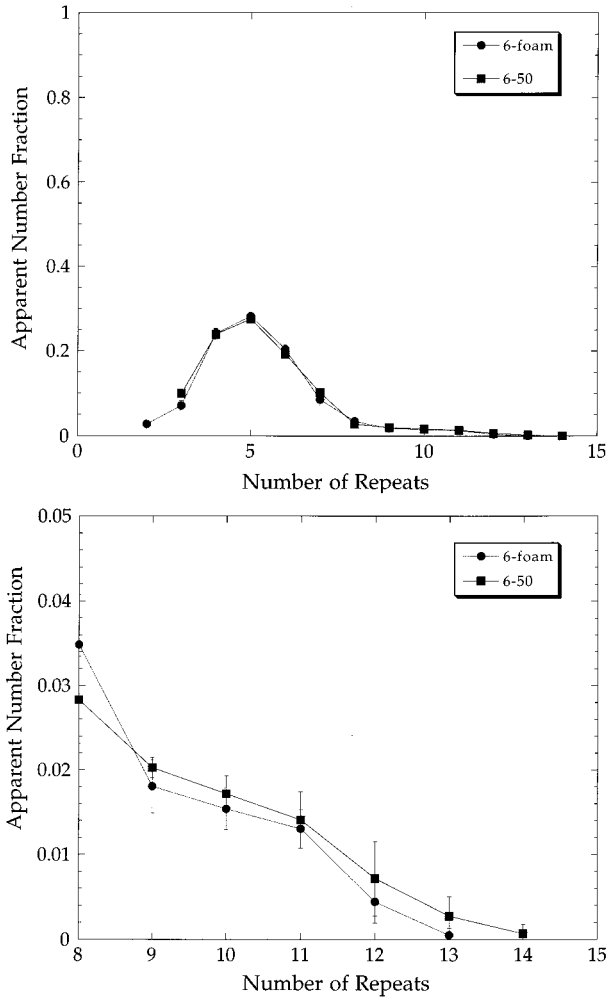

Figure 9. Comparison of foam and film (synthesized at 50 °C) formulated to have six ureas per chain.

suggestion that hard domain morphology was dominated by the rate of chemical cross-linking relative to that of phase separation. If so, then hard segment length may not be as important a factor as for the equilibrium case.

Conclusions

MALDI mass spectrometry has been used to characterize the mass distribution of hard segments in poly(urea−urethane) foams and films. In agreement with previous studies,[30] the average hard segment mass (length) does not vary with water content. However, a detailed inspection of the mass curves indicates differences in the amount of long hard segments. Increasing the water content in a poly(urea−urethane) formulation leads to a larger portion of long hard segments, even though the average number of ureas per chain does not change. Controlling hard segment length distribution is thus not trivial. From previous studies[12,15,19,20] hard segment length is known to control the equilibrium degree of phase separation. In the case of the polyurethanes studied here, in which polymerization, phase separation, and chemical cross-linking compete, hard segment length may be less important in determining the final morphology. Using MALDI, we can evaluate its effect on the morphologies previously observed.

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