Characterization of Polyester−Polyurethane Soft and Hard Blocks by a Combination of MALDI, SEC, and Chemical Degradation

Renata Murgasova, Eric L. Brantley, and David M. Hercules*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

Hartmut Nefzger

Bayer AG, PU-Research, Geb. A 608, 41538 Dormagen, Germany

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ABSTRACT: Size exclusion chromatography and matrix-assisted laser desorption ionization mass spectrometry (SEC/MALDI) coupled with selective degradation reactions have been applied for characterization of polyurethane soft and hard blocks. A series of model PUR's were prepared from 4,4′-diphenylmethane diisocyanate (MDI) and poly(butylene adipate) (pBA)−polyols with molecular weights of 1000 and 4000 Da. The weight ratio of the pBA polyols was varied: 1:3, 1:1, and 3:1; the amount of MDI was adjusted accordingly. In these model PUR systems no additional chain extender was added in addition to that in the polyester soft segments (butanediol), as a consequence their Flory distribution was used. Therefore, the model systems only have a minimum of so-called hard segments (oligo urethanes consisting of MDI and butanediol). Molecular weights of soft blocks, liberated by isocyanatolysis using phenyl isocyanate and measured by SEC/MALDI, showed reasonable agreement with those estimated from tandem light scattering and SEC (MALS/SEC). The increase in molecular weights observed with increasing amounts of pBA4000 indicated that selective degradation combined with SEC/MALDI is sensitive to the polymer soft block composition. Polydispersity indices (PDs), determined for the soft blocks recovered from phenyl isocyanate degradation, were lower than those expected on the basis of reaction theory. Partial acid-catalyzed hydrolysis was applied to determine the hard block chain length distribution for polyester-based PUR samples having different amounts of MDI. MALDI spectra of the degraded products provided proof for a degradation mechanism proposed in the literature. The results presented here demonstrate that applying partial acid hydrolysis to polyester−polyurethane generates exclusively a series of hydroxy-terminated oligomers, which can be identified as former hard segments of the polyester−polyurethane elastomer. The methodology hydrolyzes selectively all ester bonds while leaving the urethane groups containing hard segments completely intact, thus providing an additional tool for the complete characterization of polyurethanes.

Introduction

Polyurethanes are in principle prepared by the exothermic polyaddition reaction of polyisocyanates, polyol molecules, and short chain diol(s) or diamine(s) (chain extender). Many different kinds of polyurethane materials are produced from a relatively small variety of isocyanates and a broader range of hydroxy-terminated polyols with different functionalities and molecular weights. Polyols typically contain ester or ether repeat units in their chains and thus are designated polyester or polyether polyols. In the PUR elastomer chain, polyols with a glass transition below the temperature range of their use (so-called soft blocks) alternate with more rigid and in many cases crystallizable units (hard blocks), typically made up of oligo urethanes or ureas, often with aromatic groups and a chain extender. Because of physical immiscibility of hard and soft segments, these building blocks of polyurethanes phase separate on a microscopic scale. Phase separation behavior, as well as thermal and mechanical properties of the resulting PUR, depends on chemical nature and the length distribution of the constituent soft and hard blocks. Determination of hard and soft segment length and length distribution is a difficult and challenging analytical problem. Standard methods such as size exclusion chromatography (SEC), light scattering, viscosimetry, osmometry, nuclear magnetic resonance (NMR), and infrared spectroscopy (IR) provide inadequate information about these complex polymer systems.

Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry[1] is becoming an increasingly important technique for characterization of the average molecular weights, oligomer repeat units, and end groups of polymers. Currently, MALDI−TOF operating in the reflector mode with time lag focusing can yield isotopically resolved mass spectra, which are extremely rich in information, allowing detailed analysis of a variety of homopolymers and copolymers. While useful, MALDI continues to struggle with polymer samples having broad polydispersity (PD). MALDI alone yields precise molecular weight values when PD is below ∼1.2. To overcome MALDI polydispersity discrimination, a sample with broad dispersity can be fractionated by analytical or preparative SEC, yielding fractions with very narrow distributions, which can be analyzed subsequently by MALDI.[2] The coupling of MALDI to SEC provides advantages to both techniques. SEC provides MALDI with simplified, narrow PD samples and therefore improves the capability to detect minor species. The molecular weights of SEC fractions measured by MALDI can be used effectively to calibrate the SEC system to give absolute values for the average molecular weight. In addition, at lower *m*/*z* values, the mass spectrometer provides significant compositional information.[3]

* To whom correspondence should be addressed.

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Table 1. Composition of Poly(butylene adipate) (pBA)-Based Polyurethanes (PUR)

sample	pBA1000 [wt %]	pBA4000 [wt %]	MDI [wt %]
pBA1000-PUR	80.5		19.5
pBA(3:1)-PUR[a]	62.6	20.8	16.6
PBA(1:1)-PUR[a]	43.3	43.3	13.4
PBA(1:3)-PUR[a]	22.5	67.4	10.1
pBA4000-PUR		93.6	6.4

[a] Samples are represented by the ratio of pBA1000:pBA4000.

Although chemical treatment of polyurethanes has been widely studied, primarily with regard to recycling and polymer stability,[4−6] in the present report chemical degradation reactions form the basis for investigation of the structure of PURs. Alkaline and acid hydrolysis has been used in the characterization of PURs of unknown composition.[7] High-performance liquid chromatography (HPLC) was used to study the hydrolysis of aromatic biuret or allophanate groups of polyester−polyurethanes.[8] Acid-catalyzed partial hydrolysis of polyester-based PURs effectively cleaves the polymer only at the ester bonds of the soft blocks, leaving the oligourethanes (which form the hard blocks) available for analysis.[9] Recently, a procedure based on preferential base-catalyzed hydrolysis, which allows recovery of intact hard segments, was reported.[10]

Our previous work[11] on a series of PURs containing simple polyether (polytetrahydrofuran) and polyester (poly(butylene adipate)) soft blocks has shown that MALDI combined with SEC and selective chemical degradation can provide information about the soft block oligomer distribution in the PUR chain. However, a number of questions still exist. The present report is a continuation of this work.

The present study, SEC/MALDI in combination with selective degradation reactions, has been applied to characterization of polyurethane soft *and* hard blocks. A series of model PURs were prepared from 4,4′-diphenylmethane diisocyanate (MDI) and a mixture of two poly(butylene adipate) (pBA) diol-terminated polesters (polyols) having molecular weights of 1000 and 4000 Da. The weight ratio of the pBA polyols was varied from 1:3, 1:1, to 3:1; the share of MDI was adjusted accordingly. The molecular weights and polydispersities of mixed soft blocks, liberated via phenylisocyanatolysis, were estimated by MALDI/SEC and multiangle light scattering (MALS)/SEC. Acid-catalyzed partial hydrolysis was used to recover the hard blocks, so that the complete characterization of pBA−PURs was possible.

Experimental Section

Materials. All polymers were supplied by Bayer Corp. (Pittsburgh, PA). The details of synthesis are reported elsewhere.[11] These include a series of model PURs based on 4,4′-diphenylmethane diisocyanate (MDI) and poly(butylene adipate) (pBA)−polyol.

The soft blocks were composed of several binary pBA polyester mixtures with number-average molecular weights (M_n) of 1042 Da (pBA1000) and 3679 Da (pBA4000). For simplicity, no additional chain extender was used. The weight ratio of the pBA polyols was varied as shown in Table 1; the MDI was adjusted accordingly. To account for some loss of reactive NCO groups, the index (ratio of moles of NCO and OH groups) used was 1.03. On the basis of the weight ratios of pBA1000 and pBA4000, the PUR samples with mixed soft blocks will be further referred to as pBA(1:3)-PUR, pBA(1:1)-PUR, and pBA(3:1)-PUR.

Hard block analysis was performed on two commercial PUR samples (A and B), prepared from pBA polyol (pBA2000) (M_n = 2011 Da) with different amounts of MDI. Sample A had 33 wt % hard block, while sample B contained 65 wt % MDI. Butanediol was used as the chain extender in both cases. M_n values for the raw polyol material (pBA 1000, pBA2000, and pBA4000) were determined by end group titration.[11]

Chemical Degradation. *Phenylisocyanatolysis.* Phenyl isocyanate was used to degrade PURs with compositions shown in Table 1. Degradation of these polymers was conducted under the same conditions as reported previously.[11] 4.4 mL of phenyl isocyanate (Aldrich Chemical Co., Milwaukee, WI) was added to 4.0 g of PUR in a three-neck flask. The reaction proceeded in an inert atmosphere (N_2) at 160 °C for 3.5 h. After the reaction mixture was cooled to room temperature, 6.8 g of dibutylamine (Aldrich Chemical Co., Milwaukee, WI) in 20 mL of THF was added dropwise, not allowing the temperature to exceed 25 °C. The solution was poured into a dish and allowed to evaporate overnight. Purification was carried out by washing the solid raw product with ether. The ether was removed from the solid by filtration, and the product was air-dried. The ether soluble part was recovered from the filtrate by evaporation under vacuum.

Acid-Catalyzed Partial Hydrolysis. Samples A and B (50 mg) were suspended in a 0.25 M HCl solution in a dimethyl sulfoxide (DMSO)/water (91.6/8.2 vol %) mixture. The samples were then kept in a 70 °C thermostatic bath for 48 h, and the final degradation products were neutralized with $NaHCO_3$ and filtered through 0.45 μm Millipore filters. The details of this preparation have been described by Chapman.[9]

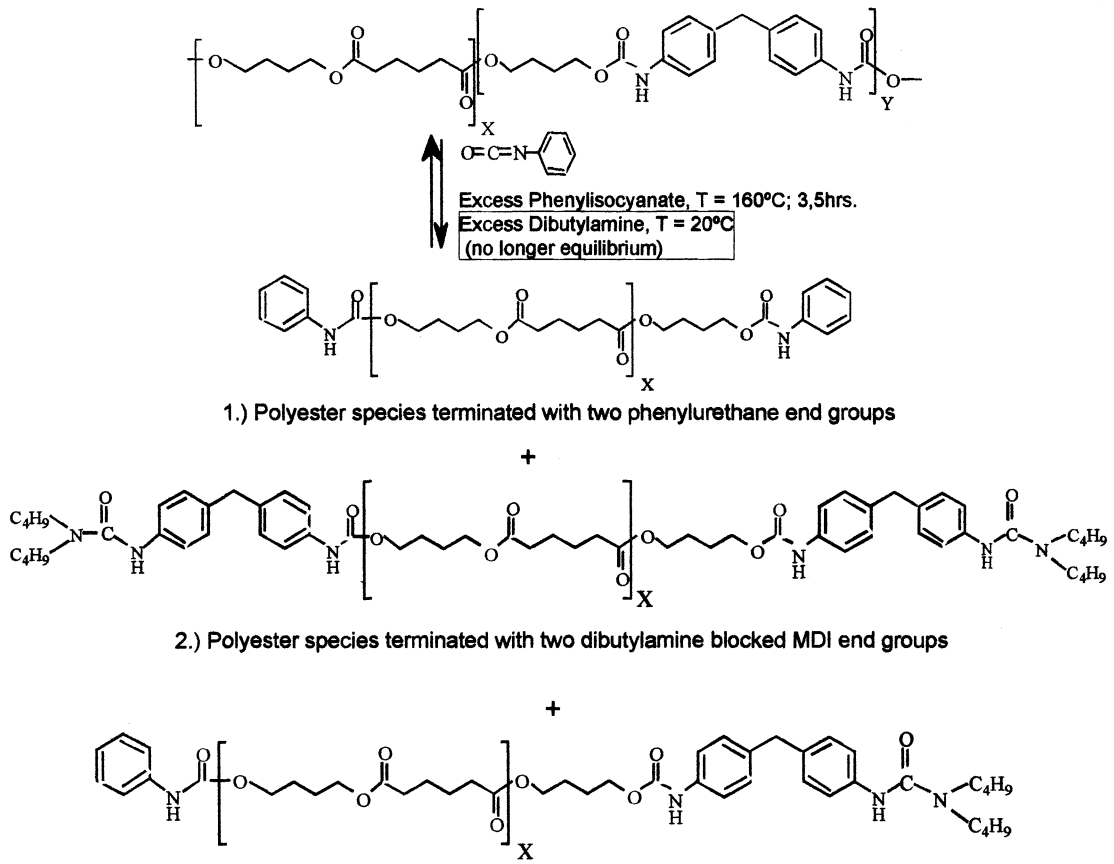
MALDI−MS Analysis. All MALDI spectra were acquired using a Voyager-DE STR, MALDI−TOF mass spectrometer from Applied Biosystems (Framingham, MA). The instrument was equipped with a N_2 laser emitting at 337 nm. Spectra were acquired in the positive-ion mode using the reflectron. The acceleration voltage was 25 kV. Typically, 125−225 single-shot mass spectra were summed to give a composite spectrum. PURs (see Table 1) degraded with phenyl isocyanate were dissolved in tetrahydrofuran (THF) (HPLC grade, Fisher Scientific, Pittsburgh, PA) at 10 mg/mL. The dithranol (Fluka, Buchs, Switzerland) matrix solution was prepared by dissolving 30 mg in 1 mL of THF; matrix and polymer solutions were mixed in a 5:2 ratio. To aid sample ionization, the MALDI target was prespotted with 2 mg/mL NaI in methanol and allowed to air-dry. A 1−2 μL aliquot of the polymer/matrix mixture was deposited on top of the NaI and air-dried.

For MALDI analysis of hydrolyzates A and B in a DMSO/water mixture, the matrix used was dihydroxybenzoic acid (DHB) (Aldrich Chemical Co., Milwaukee, WI) in *N*,*N*-dimethylformamide at 30 mg/mL. The layer deposition technique gave the best results; the sample was first allowed to evaporate on the sample target after prespotting with NaI methanol solution. After evaporation, the matrix solution was deposited on top and allowed to dry at room temperature. All data were processed using the GRAMS/386tm software.

SEC Analysis. For soft block analysis, SEC was performed on a Jordi Gel DVB mixed bed column (250 × 10 mm) (JORDI Associate, Inc. Bellingham, MA) with a refractive index detector from Knauer (Berlin, Germany) at ambient temperature. THF (HPLC grade, Fisher Scientific, Pittsburgh, PA) plus 2% CH_3CN was used as the eluent at a flow rate of 0.5 mL/min. Polystyrene standards from Polymer Laboratories (Amherst, MA) with molecular weights ranging from 580 to 195 900 Da and at concentrations of 10 mg/mL were used for calibration of the SEC system. A 100 μL aliquot of polymer solution with a concentration of 10 mg/mL was injected. For SEC fractionation, 40−50 fractions (0.2 mL) were collected manually in test tubes and evaporated to dryness overnight. A 25−50 μL aliquot of dithranol solution (30 mg/mL in THF) was added prior to MALDI analysis.

MALDI was used to determine M_n and M_w values for each fraction. Elution times of the fractions from SEC and molecular weight values (M_n and M_w) from MALDI were used to create MALDI/SEC calibration curves. The elution times for M_n and M_w were determined by the SEC software (PL Logical version

Scheme 1. Phenyl Isocyanate Degradation Reaction of pBA-PUR



1.) Polyester species terminated with two phenylurethane end groups

2.) Polyester species terminated with two dibutylamine blocked MDI end groups

3.) Polyester species terminated with one dibutylamine blocked MDI and one phenylurethane end group

6.01, Polymer Laboratories, Amherst, MA), and M_n and M_w values were obtained from the MALDI/SEC calibration curves for the analyte.

MALS/SEC measurements were carried out using a Wyatt OPTILAB 903 RI and a Wyatt miniDAWN multiangle light scattering detector (MALS) (Wyatt Technology Corp., Santa Barbara, CA). The same experimental conditions as described above for conventional SEC with concentration RI detector were followed with polymer solutions, except the flow rate of the mobile phase was kept at 1.0 mL/min. To determine the molecular weight of each polymer sample, a specific refractive index increment (d*n*/d*c*) was measured off-line using a Wyatt OPTILAB 903 RI detector. Data were processed by a Wyatt software package (ASTRA, version 4.72.03; DNDC, version 5.20).

For hard block analysis, SEC (Waters 150 modular SEC system with Millenium Data System) was performed with a UV detector working at 254 nm. A series of 10^5, 10^3, 10^2, and 50 Å columns (Polymer Laboratories) were used. The mobile phase was dimethylformamide at the flow rate of 0.8 mL/min. The injected volume of sample solution was 50 μL.

Results and Discussion

Soft Block Analysis. Chemical degradation, in particular hydrolysis, has been widely used for analysis of PUR systems. The susceptibility of polyurethanes to degradation depends on the stability of the functional groups under the reaction conditions used. Polyethers are known to have high hydrolytic stability, while polyesters are more susceptible to acid/alkaline hydrolysis.[12] Acid hydrolysis, however, may induce side reactions[13] and may or may not proceed to completion.[14] On the other hand, alkaline hydrolysis must be performed in a stainless steel apparatus rather than in glass to avoid silicate contaminants.[15] As we reported earlier,[11] ethanolamine applied to polyether-based PURs and phenyl isocyanate applied to polyester-based PURs can be used successfully to cleave urethane linkages leaving the polyol soft segments intact. As far as molecular weights and polydispersities are concerned, MALDI analysis reveals almost 100% coincidence for a polyether soft segment (pTHF, polytetrahydrofuran), but in the case of a polyester soft segment (pBA, poly(butylene adipate)), this value was less than 100%.

In the present study, pBA−PURs with mixed soft blocks (see Table 1) were degraded with phenyl isocyanate and free NCO groups were end-capped with dibutylamine prior to analysis, preventing them from undergoing further reaction. The systematic variation of the soft segment composition from a pure 1000 Da polyester gradually to a 4000 Da polyester should provide information about the accuracy of the methodology employed. On the basis of knowledge of the mechanism for phenyl isocyanate degradation of polyester-based PURs, shown in Scheme 1, three individual series of species would be expected: polyester species terminated with two phenylurethane end groups, polyester species terminated with dibutylamine blocked MDI end groups, and polyester species terminated with one dibutylamine blocked MDI and one phenylurethane end group. In addition, there will also be several low molecular weight species, based on the reaction of MDI and phenyl isocyanate with dibutylamine, as shown in Scheme 1.[11]

Figure 1 shows details of the MALDI spectrum of degraded pBA(3:1)-PUR as a representative example. Although the MALDI spectra are rather complex due to the presence of several series of oligomer ions,

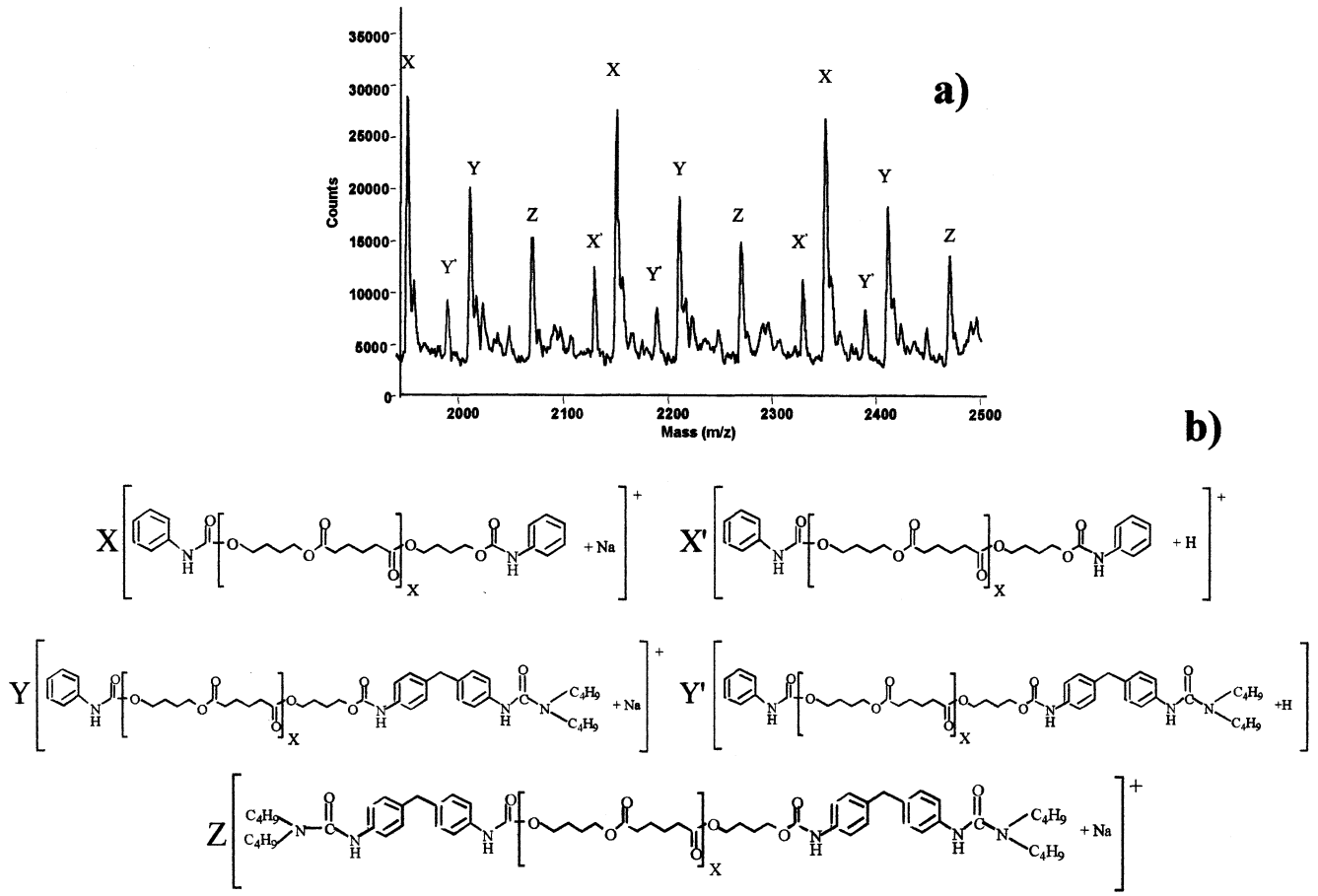


Figure 1. Ions observed in MALDI spectra of pBA-PURs degraded using phenyl isocyanate. The enlarged detail of the MALDI spectrum of the degraded pBA(3:1)-PUR is shown in (a); structures of ions marked in the spectrum are shown in (b).

interpretation of the spectra can address several issues concerning the chemistry of the pBA-PUR degraded products. In each series, mass spectral peaks differ by 200 mass units, which can be attributed to the butylene adipate monomer unit. The main peaks of the spectrum (labeled X) represent the *N*-phenyl isocyanate terminated polyesters cationized with Na^+. The series of lower intensity peaks (labeled Y and Z) can be identified as the mixed *N*-phenyl isocyanate/MDI and MDI terminated, sodiated polyesters. The lowest intensity peaks X′ and Y′ can be assigned to the protonated forms of the X and Y oligomer series. Oligomer ions seen in the spectra of degraded pBA-PUR are exclusively products based on hydroxyl-terminated polyesters. This is qualitatively what should be expected because typically alcohol functions form the reactive groups for polyaddition of polyester−polyols with isocyanates. The presence of MDI terminated species aids in hard block identification. From the quantitative point of view, however, the end-group distribution along with generation of protonated oligomer ions lowers the absolute ion yields for individual series, thus reducing the sensitivity. Carboxyl-terminated and/or cyclic nonreactive pBA species were not observed by MALDI, most likely as a consequence of their low concentration.

Figure 2 shows stacked MALDI spectra for five pBA-PUR degraded samples. MALDI spectra are apparently biased against higher mass oligomers, since the normal distribution of for example the pBA4000 would result in an abundance of peaks above *m*/*z* 4000. This is a common phenomenon that has been widely documented for polydisperse synthetic polymers.[16] The reason for

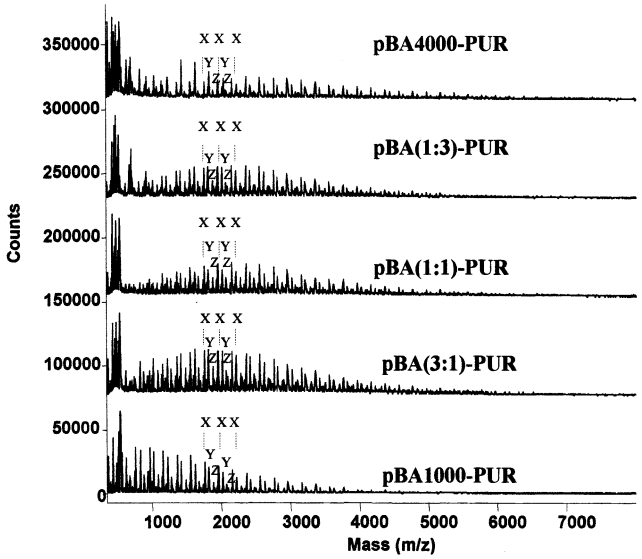


Figure 2. Stacked MALDI spectra for pBA-PUR samples degraded using phenyl isocyanate. Structures of ions marked in the spectra are shown in Figure 1b.

bias toward lower mass oligomers in the MALDI spectra of polydisperse polymers lies in both the MALDI ionization process and the instrument. The ionization efficiency is not the same for all molecules and is usually lower for higher masses. This means that all ions seen in the gas phase actually do not necessarily represent those in the original sample. The detector response is also molecular weight dependent. Overall, the discrimination in ionization, transmission, and detection causes

Table 2. Method Comparison for pBA-PUR Soft Block Analysis

	MALDI			SEC/MALDI			MALS/SEC		
sample	M_n	M_w	PD	M_n	M_w	PD	M_n	M_w	PD
pBA4000-PUR	2956	4055	1.37	4349	6943	1.6	5038	7557	1.5
pBA(1:3)-PUR	2681	3575	1.33	3528	6065	1.72	4658	6662	1.4
pBA(1:1)-PUR	2583	3429	1.33	3192	5324	1.67	4050	6075	1.5
PBA(3:1)-PUR	2435	3174	1.3	2583	4125	1.6	2677	4284	1.6
pBA1000-PUR	1952	2604	1.33	2273	3180	1.4	2343	3187	1.4

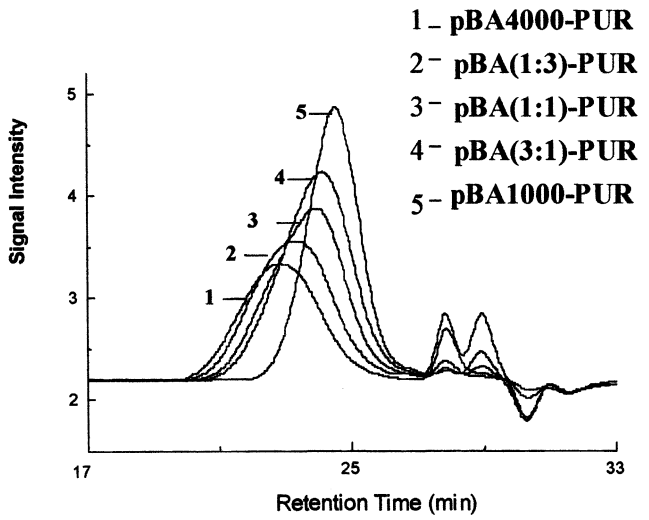


Figure 3. SEC traces for pBA-PUR samples degraded with phenyl isocyanate. Retention time decreases with increasing amount of the pBA4000 polyol in the PUR sample.

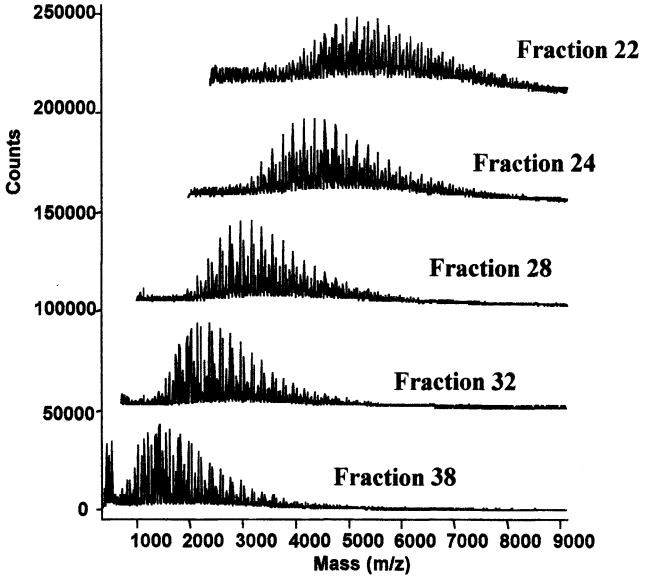


Figure 4. MALDI spectra of selected SEC fractions from phenyl isocyanate degraded pBA(3:1)-PUR.

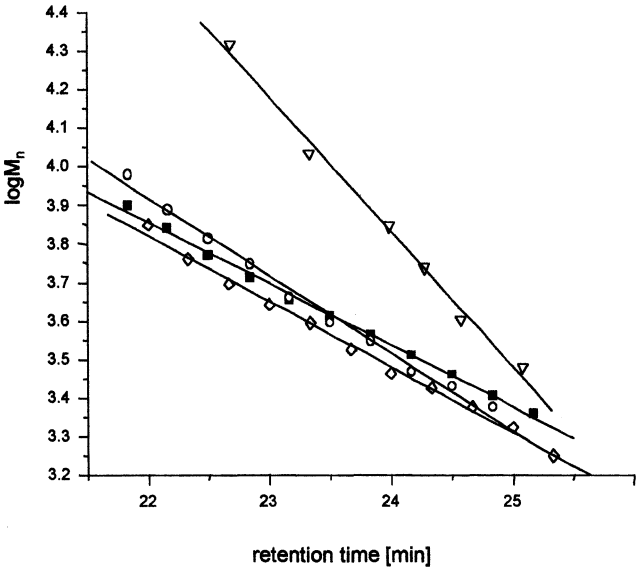


Figure 5. MALDI/SEC calibration curves for pBA4000-PUR (squares), pBA(1:1)-PUR (circles), and pBA1000 (diamonds) degraded using phenyl isocyanate. The points of the SEC calibration curve based on PS standards are marked with triangles.

the high mass signal often to be lost in the noise of the baseline.

MALDI M_n, M_w, and PD values shown in Table 2 were calculated by $M_n = \sum N_i M_i / \sum N_i$, $M_w = \sum N_i M_i^2 / \sum N_i M_i$, and PD $= M_w/M_n$, where M_i is the mass and N_i is the signal intensity of the ith oligomer in the distribution. Comparison of the MALDI molecular weight values with values estimated by other techniques used in this study will be discussed further.

While the MALDI mass spectrometer operates by counting the number of ions falling on the detector, SEC detects the concentration of polymers by weight. SEC is an entropically controlled separation technique in which molecules are separated in an ideal case on the basis of hydrodynamic volume, which is a relative measure of molecular weight and depends simultaneously on chemical composition. To obtain absolute molecular weight values by SEC, either the exact relationship between hydrodynamic volume and molecular weight for a given polymer must be known or molecular weight-sensitive detectors need to be employed. Nevertheless, SEC traces of the five degraded pBA-PUR samples show their maxima in the order pBA4000-PUR < pBA(1:3)-PUR < pBA(1:1)-PUR < pBA(3:1)-PUR < pBA1000-PUR. In other words, retention time decreases with an increasing fraction of pBA4000 in the degraded sample (Figure 3). The observed trend supports the fact that the degradation procedure used worked well in all cases.

In MALDI the mass axis is independent of the nature of the materials being analyzed. Therefore, similar to light scattering and viscosimetry, MALDI can be used as an SEC detector for absolute molecular weight measurements. In addition, compared to light scattering and viscosimetry, oligomer resolution can be achieved by MALDI. To circumvent MALDI discrimination due to polydispersity and to calibrate the SEC system, selected SEC fractions with a PD of approximately 1.05 were analyzed by MALDI (see Figure 4). With a variety of known MALDI M_n and M_w values (up to 10 000 Da) and corresponding retention times, excellent linear curve fits with correlation coefficients (R^2) greater than 0.996 were obtained. Figure 5 shows the striking difference between the MALDI/SEC calibration curves for degraded pBA4000-PUR, pBA(1:1)-PUR, pBA1000-

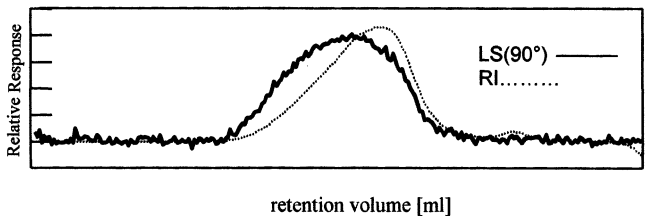


Figure 6. 2D-SEC response for pBA(1:1)-PUR degraded using phenyl isocyanate.The light scattering (LS) detector signal is shown as the solid line; the refractometer (RI) signal is shown as the dotted line.

PUR, and the SEC calibration curve based on PS standards. The lines that define the molecular weight/retention time plot obtained for degraded pBA-PURs differ in slope but fall in the same general region. This indicates that solvent/solute interactions of degraded products in THF are not the same. In other words, their hydrodynamic volume changes with mass in a different manner. This may be due to differences in the end group distribution of these low molecular weight oligomers. Examination of the MALDI spectra supports this assumption, as the signal intensities for the individual oligomer series vary from sample to sample (see Figure 2).

The combined SEC/MALDI method for determination of soft block molecular weights and polydispersities yields much more reasonable M_n and M_w values than MALDI alone (see Table 2). SEC/MALDI M_w values are around 20%−70% higher than the corresponding MALDI values. Also, the expected increase in molecular weight with an increasing fraction of pBA4000 is observed. SEC based on calibration with narrow distribution polystyrene standards gives relative M_w values that are 2−4 times higher than the corresponding SEC/MALDI values. On the basis of reaction conditions and theory,[17] PDs for degraded pBA-PURs were expected to be higher (around 2) than those estimated by the combined SEC/MALDI technique.

MALS/SEC provides absolute molar masses without use of calibration standards, making it an ideal tool for comparison with SEC/MALDI. MALS/SEC M_w, M_n, and PD values for degraded pBA1000-PUR and pBA(3:1)-PUR samples (see Table 2) are in fairly good agreement with the corresponding SEC/MALDI values. MALS/SEC M_w values for samples with higher amounts of pBA4000 are around 10% higher than the corresponding SEC/MALDI values. PD values estimated by MALS/SEC are lower than those obtained by SEC/MALDI. The higher M_w values and lower polydispersities estimated by MALS/SEC can be attributed to a limitation of the tandem technique of light scattering and SEC for the determination of lower masses at low concentration since, for a given concentration c, the scattered light signal is proportional to cM_w.[18] Indeed, simultaneous monitoring by MALS and the RI detector for the degraded pBA(1:1)-PUR sample fractionated by SEC column (Figure 6) shows a decrease in the light scattering signal at higher retention volumes by MALS compared to the RI signal. In addition, the two-dimensional response indicates that the MALS detector is more sensitive to higher mass oligomers than the RI detector. Also, the one influencing factor, which must be taken into account in terms of the precision of MALS/SEC molecular weight determination, is the possibility

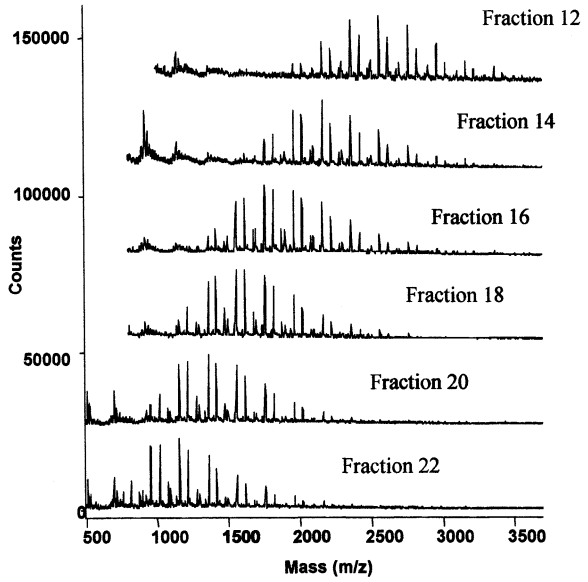


Figure 7. MALDI spectra of selected SEC fractions from reaction byproducts of phenyl isocyanate degraded pBA(3:1)-PUR.

of variation of dn/dc values over a molecular weight range that may be due to the relatively wide variety of end groups in the pBA-PUR degradation products. Variation in oligomer signal intensities from fraction to fraction as seen in Figure 4 is supportive of this assumption.

As reported recently,[11] the purification procedure used might influence the pBA soft block recovery. The purification procedure is based on washing the solid degradation product with ether to remove reaction byproducts. Small pBA oligomers, however, may be selectively removed during the washing step. To determine whether this is possible, reaction byproducts from the pBA(3:1)-PUR degraded sample were recovered from ether and subsequently analyzed by MALDI/SEC. Mass spectral analysis of selected SEC fractions, which are shown in Figure 7, proved that the low mass pBA(3:1)-PUR degraded products are the same series of oligomer ion peaks as those shown in Figure 1. The SEC/MALDI calibration curve of reaction byproducts from the pBA-(3:1)-PUR degraded sample gave the M_w value of 1968 Da and the PD value of 1.07. The results indicate that the purification procedure contributes to the MALDI/SEC discrimination against lower oligomer masses, and the further refinement of the purification procedure is necessary. It is also quite obvious that this influence is to a certain degree random in nature and therefore is a source of experimental error.

Hard Block Analysis. Selective hydrolysis is an additional tool that allows complete characterization of polyester-based polyurethanes. Alkaline or acid hydrolysis selectively cleavages polyester soft segments, leaving the hard segments intact. Recently, alkaline hydrolysis was utilized to determine the hard segment length distribution in polyester based poly(urea−urethane)s using IR and MALDI mass spectrometry.[19] In the present study, we used acid hydrolysis, as originally proposed by Chapman,[9] to selectively degrade soft blocks in pBA(2000)-PUR samples to liberate hard blocks for further MALDI and SEC analysis. Scheme 2 shows the expected reaction mechanisms for partial hydrolysis of the polyester-based PURs, forming hydroxyl-terminated species. MALDI spectra of hydrolyz-

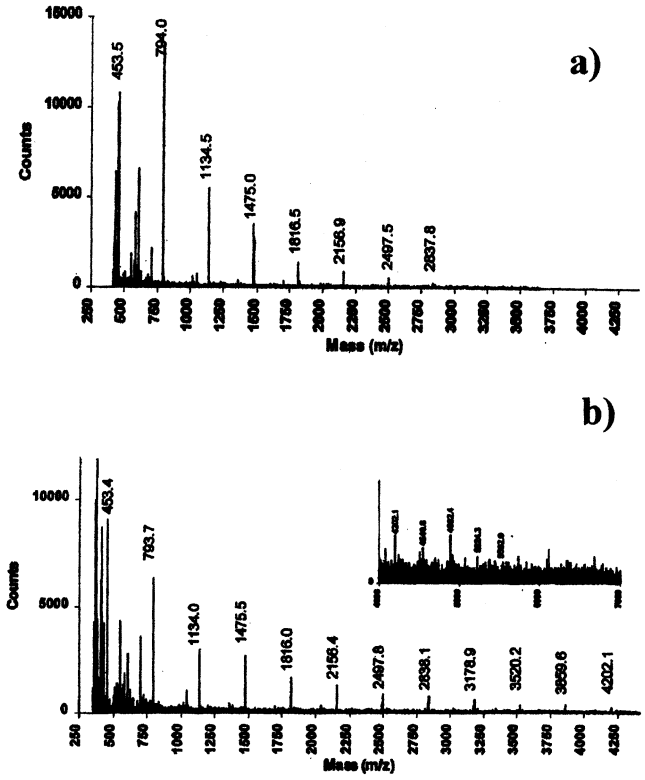
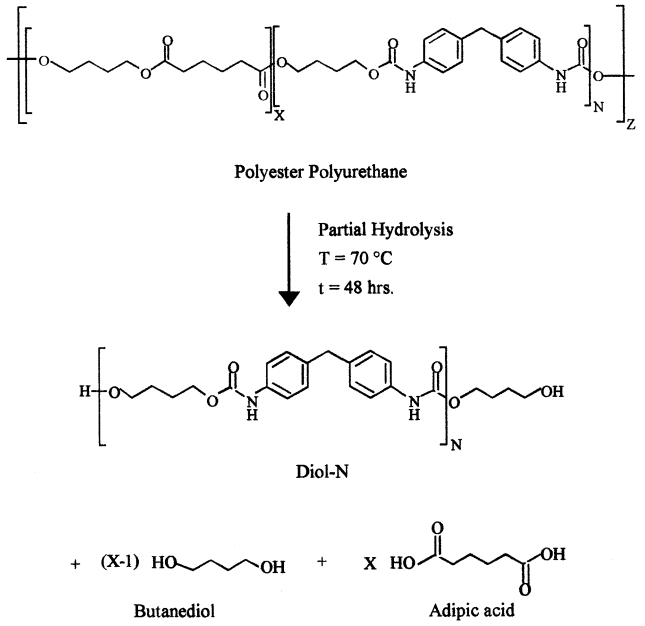


Figure 8. MALDI spectra of partially hydrolyzed pBA(2000)-PUR. The spectrum for hydrolyzate A (33 wt % MDI) is shown in (a); the spectrum for hydrolyzate B (65 wt % MDI) is shown in (b). The enlarged detail of the high mass region for the hydrolyzate B spectrum is shown as an inset.

Scheme 2. Partial Hydrolysis of pBA-PUR



ate A with 33 wt % MDI in the original sample and hydrolyzate B with 65 wt % MDI showed a relatively wide range of oligomer distributions (Figure 8). The oligomer peaks in the spectra are separated by 340 Da, which corresponds to the mass of the diol-N repeat unit. As shown in Scheme 2, the diol-N species are a series of linear oligomers of hydroxyl-terminated all-urethane group-containing fragments, originating from the partially hydrolyzed elastomers. The MALDI spectrum of hydrolyzate A **(**33 wt % MDI**)** indicates hard block

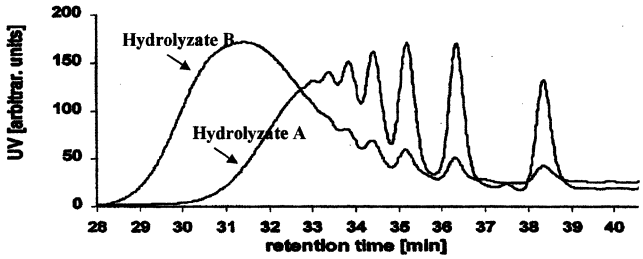


Figure 9. SEC traces of hydrolyzed pBA(2000)-PUR samples using the UV detector (254 nm).

masses of up to almost 3000 Da, corresponding to $N = 8$. For hydrolyzate B **(**65 wt % MDI**),** the mass distribution of the hard segments is broader, and the peak series extends well beyond 5000 Da, or $N = 14$, and with some imagination even up to 7000 Da ($N = 20$**)** (see inset in Figure 8). In both cases, neither free polyol nor polyol attached to the hard block was detected by MALDI. In both MALDI spectra, only a few low-intensity peaks, mainly in the *m*/*z* range between 500 and 700, cannot be identified with certainty. Most likely these peaks originate from additives present in the commercial pBA-PUR material. Nevertheless, MALDI results provide support for the highly selective nature of the acid degradation method as well as direct proof for the molecular structure of the fragments proposed in Scheme 2.

Comparison of the MALDI spectra with SEC traces illustrates the advantage of MALDI for analysis of the hard block length distribution over the currently used SEC method. While the MALDI technique is capable of distinguishing between oligomer ions with N ranging from 1 to 14 (see Figure 8), the SEC traces of hydrolyzates A and B show a series of approximately seven peaks for each sample (see Figure 9). Loss of oligomer resolution is observed for higher masses. In addition, the chemical structures of the individual peaks can easily be elucidated from the MALDI spectra.

The comparison between MALDI data and the theoretical masses for the diol-N oligomer series was also performed based on the following equation:

$$M(\text{diol-N}) = nM(\text{ru}) + M(\text{eg}) + 23 = n \times 340.38 + 113 \quad (1)$$

where n is the number of a repeat unit (ru) and M(ru) and M(eg) are the masses of the repeat unit and the end group, respectively; additionally, 23 mass units are added for sodium attachment to each oligomer.

Table 3 shows a good agreement between the theoretical data calculated using eq 1 and the experimental MALDI data from Figure 8. In addition, the mass increments determined for both hydrolyzates are very close to the values expected from the reaction mechanism.

Conclusions

Two selective chemical degradation reactions combined with MALDI and SEC were applied for characterization of polyester-based PURs. Phenyl isocyanate, which selectively cleaves PUR chains at urethane linkages, was applied for liberation of mixed soft blocks, which consisted of pBA polyol mixtures with molecular weights of 1000 and 4000 Da of varying weight ratios. The combined SEC/MALDI method for determination of soft block molecular weights and polydispersities

Table 3. Comparison of MALDI Data with Theoretical Masses; Determination of the Mass Increment

	hydrolyzate B			hydrolyzate A	
N	mass (theor)	mass (expt)	increment (expt)	mass (expt)	increment (expt)
1	453.4	453.4		453.5	
2	793.8	793.7	340.3	794.0	340.5
3	1134.1	1134.0	340.3	1134.5	339.5
4	1474.5	1475.5	341.5	1475.0	340.5
5	1814.9	1816.0	340.5	1816.5	341.5
6	2155.3	2156.4	340.4	2156.9	340.4
7	2495.6	2497.8	341.4	2497.5	340.6
8	2836.0	2838.1	340.3	2837.8	339.3
9	3176.4	3178.9	340.8		
10	3516.8	3520.2	341.3		
11	3857.1	3859.6	339.4		
12	4197.5	4202.1	342.5		
13	4537.9	4540.8	338.7		
14	4878.3	4882.4	341.6		
15	5218.7	5224.4	342.0		
16	5559.0	5562.0	337.4		
			av 340.6 ± 1.3		av 340.3 ± 0.7

yields more reliable M_n and M_w values than either technique alone. SEC/MALDI M_w values correspond with those estimated by MALS/SEC within experimental error. Lower polydispersities estimated by MALS/SEC compared to SEC/MALDI values can be attributed to a limitation of the tandem technique of light scattering and SEC for determination of lower masses at low concentrations. The observed increase in molecular weight with increasing share of pBA4000 indicates that selective degradation combined with SEC/MALDI is sensitive to the polymer soft block composition.

Partial acid hydrolysis was applied to determine the hard block chain length distribution for polyester-based PURs. The MALDI spectra of degraded products provided proof for the proposed degradation mechanism. The results presented here demonstrate that applying partial acid hydrolysis to polyester−polyurethanes generates exclusively a series of hydroxy-terminated oligomers. These oligomers can be identified as former hard segments of the polyester−polyurethane elastomer. This methodology hydrolyzes selectively all ester bonds while leaving the urethane groups containing hard segments completely intact, thus providing an additional tool for the complete characterization of polyurethanes.

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