Experimental Determination of Sequence Length Distribution of Hard Segments in Polyester–Polyurethanes

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Received March 28, 1994; Revised Manuscript Received September 14, 1994®

ABSTRACT: A new analytical procedure based on selective acid hydrolysis was developed to measure the chain length distribution of hard segments (HSCLD) of polyester–polyurethanes. It was tested with polymers made from 4,4′-methylenebis(phenyl isocyanate), 1,6-hexanediol, and α,ω-dihydroxypoly(hexamethylene adipate) with number-average molecular weight 2200. Heating samples with 0.25 M HCl solution in dimethyl sulfoxide with 8.2% water for 36 h leads to nearly complete hydrolysis of the ester groups, leaving the urethanes largely unaffected. The resulting mixture of oligomers can be analyzed by size exclusion chromatography, using dimethylformamide at room temperature as the solvent. Experimentally measured HSCLDs were most often very different from those theoretically predicted for homogeneous reaction.

Introduction

Cooper and collaborators[1] have shown the importance of microphase separation in the establishment of the unique properties of segmented polyurethanes. Several researchers have since then prepared model polymers with well-known hard and soft segment length distributions and proved their outstanding influence in thermal and mechanical properties.

Solutions for chain length distribution[2] and for the sequence length distributions in batch reactors of the linear polycondensation of three monomers have long been known from different probabilistic approaches[3–5] or Monte Carlo simulation.[6–10] A kinetic approach was developed by ourselves[11] and confirms the results obtained by Peebles.[2,3] Under homogeneous conditions, the sequence length follows the most probable distribution.

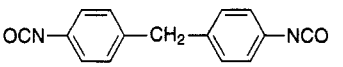
The extremely complex problem of describing the process of coupling chemical reaction and microphase separation is far from complete solution in spite of some attempts. A weak point about modeling studies of polyurethane formation is the absence of information about the underlying chemical structure of polymers. Current physical characterization methods show the consequences of microphase separation but do not actually measure segment length distributions.

A recent study[12] on the relative rates of hydrolysis in weakly acidic conditions of urethanes, esters, ethers, amides, and other compounds found a striking stability difference between urethanes and ester groups. That stability difference was exploited by us to selectively destroy the ester groups of a segmented polyurethane, yielding a mixture of oligomers containing intact hard segments. Analysis by size exclusion chromatography allowed the hard segment length distribution to be measured.

This work was intended as a starting point for the much more complex study of the industrial manufacturing processes of polyurethanes. There was no way of actually measuring sequence length distributions in segmented polyurethanes, so that the novel analytical procedure developed here, albeit specific to polyester–polyurethanes, is a step forward.

Table 1. Chemical Formulas of the Materials Used

Isocyanate



4,4′-methylenebis(phenyl isocyanate) (MDI)

Polyester diol

$HO\text{-}(CH_2)_6[OOC(CH_2)_4COO(CH_2)_6]n\text{-}OH$

α,ω-dihydroxypoly(hexamethylene adipate) (PE 31)

Chain Extender

$HO\text{-}(CH_2)_6\text{-}OH$

1,6-hexanediol (HD)

Experimental Section

Materials. The segmented polyester–polyurethanes were prepared in a single step by reacting MDI with PE 31, a 2200 number-average molecular weight polyester diol derived from adipic acid and 1,6–hexanediol (HD) as chain extender. The MDI (Hoechst Portuguesa) was purified by heating at 60 °C for 2 h and filtering through a heated filter. Its purity was determined by the standard di-*n*-butylamine titration and found to be over 99.5%. PE 31 (Hoechst Portuguesa) was degassed overnight under vacuum at 70 °C. Its number-average molecular weight was determined by hydroxyl acetylation. The amount of carboxyl end groups is below 0.03 mol/kg. The HD (Hoechst Portuguesa) was used as received.

The recipes of the polyurethanes used in this study are summarized in Table 2.

Selective Hydrolysis. The samples of segmented polyester–polyurethanes (100–150 mg) were dissolved in a 0.25 M HCl solution in dimethyl sulfoxide with 8.2% water. The details of preparation have been described by Chapman.[12] Samples were then placed in a thermostatic bath, and the final solution was neutralized with sodium hydrogen carbonate.

To optimize reaction conditions, different temperatures were employed, namely, 60, 70, and 80 °C. The time for apparently complete ester hydrolysis was measured.

Gel Permeation Chromatography. The apparatus was a Gilson high-performance liquid chromatograph equipped with a UV detector (Model 116) working with UV absorption at 280 nm. At this wavelength, the response is only due to the phenyl urethane groups. A Phenogel 10 500A column (600 × 7.8 mm) was used. The mobile phase was dimethylformamide (DMF) at a flow rate of 1 mL/min. The injected volume of sample solution was 20 μL.

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® Abstract published in *Advance ACS Abstracts,* November 1, 1994.

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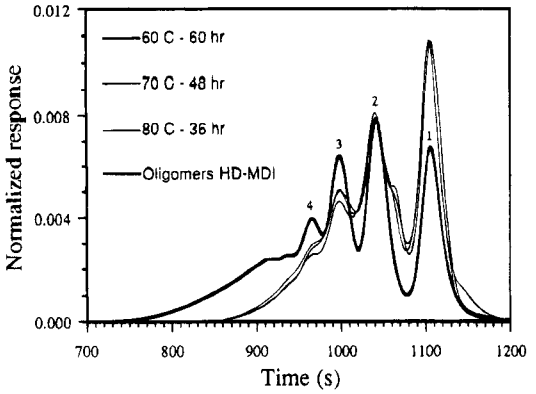

Figure 1. Chromatograms of hydroxyl-terminated oligomers in a prepolymer and in hydrolysates of the industrial polyester–polyurethane 200HD: (1) 1 MDI residue + 2 HD residues; (2) 2 MDI residues + 3 HD residues; (3) 3 MDI residues + 4 HD residues; (4) 4 MDI residues + 5 HD residues.

Table 2. Recipes of Polyurethane Systems Used

polymer name	molar ratio extender/MDI	molar ratio polyester diol/MDI	hard segment wt frac (%)
60HD	0.490	0.510	12.6
70HD	0.525	0.477	14.2
90HD	0.570	0.437	16.4
200HD	0.684	0.334	23.7

The samples for the GPC trials were obtained by dilution with DMF of the resulting hydrolysis solution. The identification of the individual peaks was made by comparison with the chromatogram of hydroxy-terminated oligomers in a prepolymer.

Proton and Carbon-13 NMR. The spectra were obtained on a JEOL 400 MHz FT-NMR spectrometer operating at 100.5 MHz for carbon). The solid product for the NMR trials was obtained by precipitation with water of the resulting oligomers followed by centrifugation. This procedure was repeated several times. The starting polymer sample was run as a solution of 40 mg in 0.8 mL of $CDCl_3$, and the hydrolysis products were run as a solution of 20 mg in 0.8 mL of DMSO-d_6.

Results and Discussion

Gel Permeation Chromatography. Oligomers prepared by reaction between MDI and an excess of HD that were submitted to the acid hydrolysis were found to be hydrolytically stable. Peak positions in those oligomers were at the same places as the hydrolysis products of the polyester–polyurethanes (see Figure 1).

Homemade software was used to fit by least squares the observed chromatographic trace by a sum of Gaussian peaks, with variable heights and widths as needed.

According to Chapman,[12] about 0.25% of the urethane linkages of di-*n*-butyl 4,4′-methylenebis(phenylcarbamate) are hydrolyzed at 70 °C after 36 h in the acidic solvent media used. Within this lapse of time (see Figure 2) almost complete hydrolysis of the ester groups is observed. We have confirmed that no appreciable hydrolysis of hard segments occurs at 80 °C even after 48 h (see Figure 3). This higher temperature can be used to accelerate the hydrolysis, and then only 36 h is necessary to achieve complete hydrolysis of the ester groups. A still higher temperature was not tried because of excessive pressure rise (tube breakage) as well as an increased amount of hydrolysis of the urethane linkages (which should be kept below 1%), causing then a detectable error in the estimated HSCLD.

Proton and Carbon-13 NMR. Previous studies[13–17] helped to establish the peak assignments shown in Tables 3–5. The carbon-13 NMR spectrum confirmed the structure of the starting material and matched the expected product for the hydrolyses: a hard segment structure based on MDI and 1,6-hexanediol. No ester carbonyls appear, so complete degradation of the polyester diol was achieved, and the units of MDI are joined by urethane links with the diol. The phenyl ring/$NCOOCH_2$ group ratio is 1.00/1.00, so we conclude once more that no appreciable cleavage occurred at the urethane linkages.

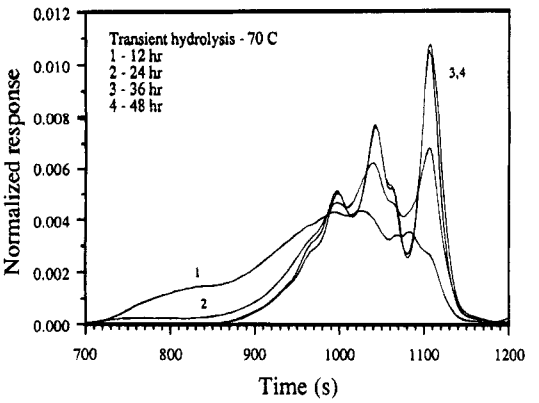

Figure 2. Transient hydrolysis of an industrial segmented polyester–polyurethane.

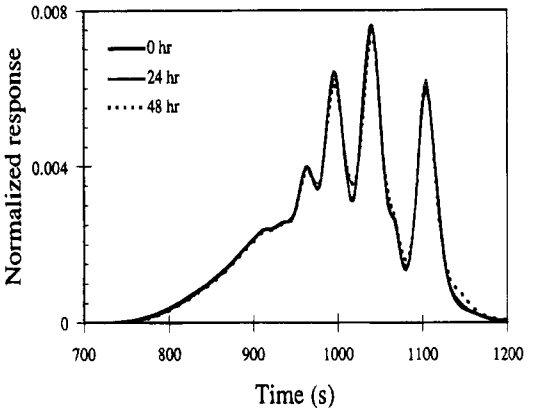

Figure 3. Transient hydrolysis of hydroxy-terminated oligomers at 80 °C.

Table 3. Carbon Assignments for the Starting Polymer (200HD) before Hydrolysis

δ/ppm	assignment	δ/ppm	assignment
173.3	C13	64.9 + 64.1	C7 + C12
153.8	C6	40.4	C1
137.2	C2	33.75	C14
135.9	C5	28.61 + 28.35	C8 + C11
129.2	C3	25.44	C9 + C10
118.7	C4	24.25	C15
79.9	$CDCl_3$		

Table 4. Proton Assignments for Hydrolysis Products

δ/ppm	peak type	integral area	assignment
9.5	singlet	6.36	–NH–
7.36 + 7.34	doublet	18.06	CH-4
7.09 + 7.08	doublet	17.54	CH-3
4.04	triplet or multiplet	18.23	D1
3.78	singlet	9.60	CH_2-1
3.42	singlet	203	impurity (H_2O)
3.38	triplet	10.4	D6
2.55	singlet	129	impurity
2.50	multiplet		DMSO-d_6
2.21	triplet or multiplet	1.00	not assigned
1.66–1.57	multiplet	17.12	D2
1.51		1.69	not assigned
1.45–1.30	multiplet	37.11	D3 + D4 + D5

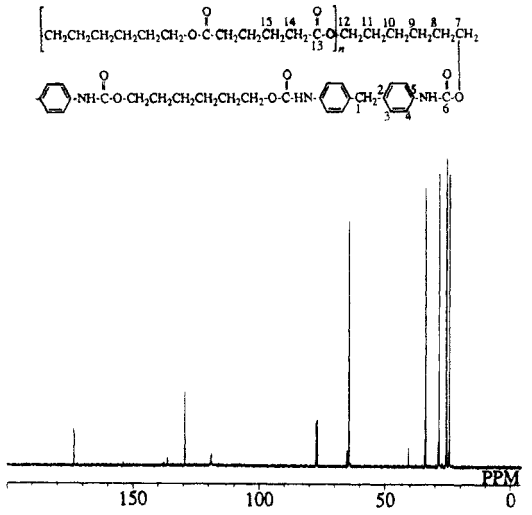

Figure 4. Carbon-13 NMR spectrum for the starting polymer (200HD) before hydrolysis.

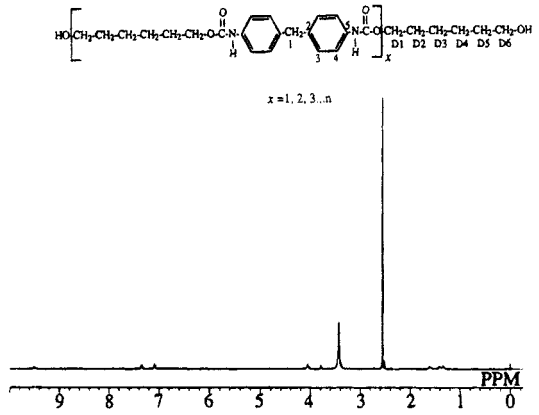

Figure 5. Proton NMR spectrum for the hydrolysis products.

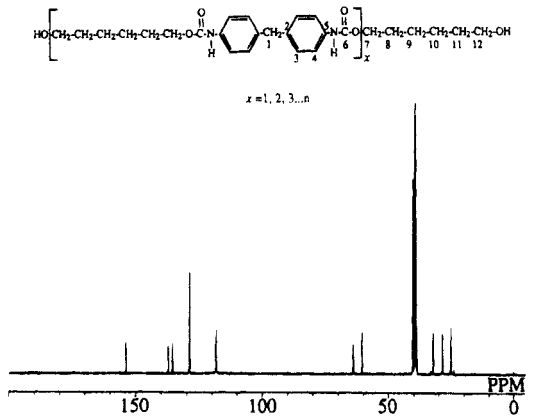

Figure 6. Carbon-13 NMR spectrum for the hydrolysis products.

Table 5. Carbon Assignments for Hydrolysis Products

δ/ppm	assignment	δ/ppm	assignment
153.5	C6	60.5	C12
137.0	C2	40.3	C1
135.3	C5	39.4	DMSO-d_6
128.7	C3	32.3	C11
118.2	C4	28.4	C8
63.9	C7	25.1	C9 + C10

Comparison between GPC and NMR Results. The results obtained by GPC and NMR are in good agreement. The relative numbers of hydrogen atoms are shown in Table 6 (relative to the MDI and urethane-CH_2 protons).

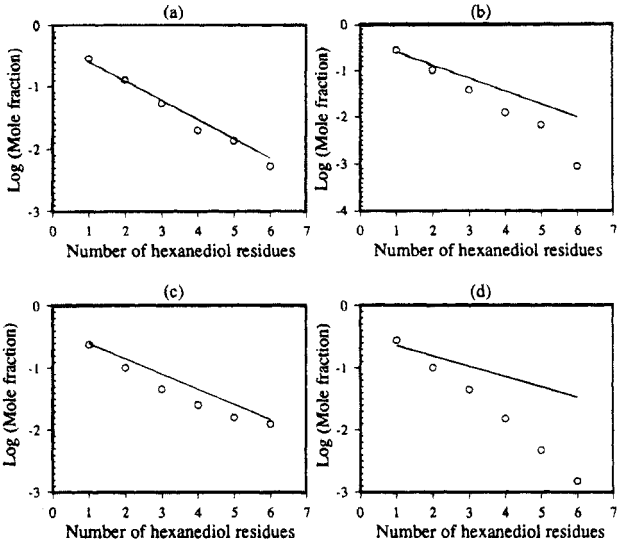

Figure 7. Comparison between theoretical (homogeneous reaction) and experimentally observed chain length distributions: (a) 60HD; (b) 70HD; (c) 90HD; (d) 200HD.

Table 6. Numbers of Hydrogen Atoms Calculated by GPC and NMR

	MDI-CH_2	phenyl-H	NCOOCH_2	HOCH_2	total CH_2
NMR	2.12	7.85	4.02	2.30	18.29
GPC	2.00	8.00	4.00	2.31	18.93

Table 7. Comparison between Theoretical (Homogeneous Reaction) Slopes of Relationships log(mole fraction) vs Number of Extender Units with Experimentally Observed Values and Average Error between Predicted and Experimental Mole Fractions of Sequences

polyurethane	obsd slope	theor slope	average error in predicted mole fractions of sequences
60HD	−0.3426	−0.3098	0.1557
70HD	−0.4723	−0.2798	0.4938
90HD	−0.2591	−0.2444	0.2955
200HD	−0.4697	−0.1649	0.6334

Comparison of Experimental Chain Length Distribution of Hard Segments with Theoretical Predictions for Homogeneous Reaction. Theoretical mole fractions are calculated according to our model[11] assuming that end groups are fully converted and that homogeneous conditions prevail (macro- and micromixing phenomena do not control the buildup of sequences). Experimental number chain length distributions of hard segments (shown in Figure 7) are roughly geometrical for the lowest members. This is what theory predicts for homogeneous reaction. However, the measured slopes of the relationships log(mole fraction) vs number of hexanediol residues are only in a rough agreement with predicted ones for the polymers with a lower amount of hard segments (see Figure 7 and Table 7); the average error in predicted sequence mole fractions is 16%. The sample with the second lowest amount of hard segments (70HD) shows a large difference between the observed HSCLD and the one predicted for homogeneous reaction. However, no simple pattern of these discrepancies seems to arise from our data, as shown by the behavior of the next sample (90HD). For the sample with the highest amount of hard segments (200HD), there is a particularly large discrepancy of slope with predictions for homogeneous reaction, a much lower amount of higher sized hard segments being observed. This seems to point unambiguously to an influence of phase separation of hard segments, their

segregation causing a fall of the probability of their growth relative to a homogeneous system.

Further research involving other chemical systems and accompanying morphological studies using, for instance, small-angle X-ray scattering are needed to gain a better insight into these effects.

Acknowledgment. Financial support by JNICT (Project PMCT/C/MPF/502/90) and the European Commission (Brite-Euram Project BREU-0077/C/SMA) is gratefully acknowledged as well as the precious support given by Prof. J. Bordado and Hoechst Portuguesa. We also thank Dr. D. J. Hourston and Dr. Keith Dillingham (Polymer Centre, Lancaster University) for help with the NMR studies.

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