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NOTE

Sequence Analysis of Polyether-Based Thermoplastic Polyurethane Elastomers by ^{13}C NMR

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Introduction

Thermoplastic polyurethane elastomers (TPUs) are materials of great technological interest due to the good mechanical behavior that they are able to display in a wide interval of temperatures.[1−3] These polymers are usually obtained from mixtures of long and short chain diols, and aromatic or aliphatic diisocyanates, applying either the *one-shot* or the *prepolymer* method.[4−6] The resulting polyurethane chain is made of soft and hard segments that are more or less interacting depending on the level of miscibility between the phases, which is the main factor determining the final properties of the material.[7−9] These past years a good amount of research has been devoted to understand the correlation between microstructure and properties of segmented polyurethanes.[10,11] Some researchers have tried to obtain these polyurethanes with different microstructures by changing the reaction procedure.[12−14] Others have studied their microstructure using complicated methods based on the hydrolysis of the polymer and subsequent analysis of the hydrolyzed products by size exclusion chromatography.[15] However, as far as we know, no work using NMR to determine the microstructure of these polymers has been published to date in the accessible literature.

In this Note we would like to report on the analysis of the microstructure of segmented polyurethanes by ^{13}C NMR making use of the signals arising from nonprotonated aromatic carbons which appear to be sensitive to dyads sequence distribution. The polyurethanes here studied were obtained from poly(tetramethylene glycol) (PTMG) as macrodiol soft segment, 1,4-butanediol (BD) chain extender, and 4,4′-methylenediphenyl diisocyanate (MDI) as hard segment. The results obtained in this work provide a relatively simple and reliable method to determine the microstructure of MDI-based thermoplastic polyurethanes by means of the NMR technique.

Experimental Section

The segmented polyurethanes abbreviated as BD$_x$PTMG$_y$MDI, where x and y denote the molar ratio of chain extender and macrodiol, respectively, were prepared by the *one shot* method in a 100 mL round-bottom flask equipped with a mechanical stirrer. x moles of BD (Sigma-Aldrich, 99%) chain extender and y moles of PTMG macrodiol (Sigma-Aldrich, $M_n = 1000$) were mechanically stirred and heated at 130 °C. At this temperature $x + y$ moles of MDI diisocyanate (Sigma-Aldrich, 98%) was added, and the reaction was left to proceed for 1 min. After that the mixture was observed to be very viscous and difficult to stir. Then the reaction was continued by placing the reaction mixture in an oven at 120 °C for 3 h. The resulting polyurethanes were characterized without further purification. Segmented polyurethanes with x to y ratios of 3:1, 1:1, and 1:3 in addition to the homogeneous polyurethanes fully made of BD or PTMG were prepared by this method.

Intrinsic viscosity of the polyurethanes was measured in *N,N*-dimethylformamide (DMF) at 25 °C in an Ubbelohde viscosimeter. For each sample four dilutions with different concentrations were measured. The thermal behavior of the polymers was examined by differential scanning calorimetry (DSC) with a PerkinElmer DSC Pyris 1 instrument calibrated with Milli-Q water, indium, and zinc. DSC data were obtained from 4 to 6 mg samples at heating and cooling rates of 10 °C min^{-1} under nitrogen circulation. The T_g of the polyurethanes was measured from amorphous samples at a heating rate of 20 °C min^{-1}. Thermogravimetric analysis (TGA) was carried out with a PerkinElmer TGA-6 thermobalance at a heating rate of 10 °C min^{-1} under a nitrogen flow rate of 20 mL min^{-1}.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 80.0 ± 0.1 °C, operating at 300.1 and 75.5 MHz, respectively. The segmented polyurethanes (10 mg for ^{1}H and 50 mg for ^{13}C NMR) were dissolved in 0.7 mL of 1,1,2,2-tetrachloroethane-d_2, and chemical shifts were internally referenced to tetramethylsilane (TMS). ^{1}H NMR spectra were recorded with 2.3 μs (30°) pulse width, 3.4 s acquisition time, 6 s relaxation delay, and 4.9 kHz spectral width. 128 scans were collected with 32K data points and Fourier transformed (FT) with 16K data points. For ^{13}C NMR spectra, the pulse and spectral widths were 4.3 μs (90°) and 18 kHz, respectively, and the acquisition time and relaxation delay were 1.8 and 2 s, respectively. From 5000 up to 15 000 FIDs were acquired with broadband proton decoupling, with 64K data points and FT with 128K providing a digital resolution of 0.27 Hz per point. Integration of the overlapping signals was made by Lorentzian deconvolution of the spectra using the Bruker 1D WIN-NMR computer software. 2D ^{1}H−^{1}H homonuclear (COSY) and ^{13}C−^{1}H heteronuclear shift correlation (HETCOR) spectra were recorded by means of the *cosy* and *hxco*, respectively, pulse sequences implemented in the Bruker NMR instrument package.

Results and Discussion

The synthetic procedure followed in this work for the preparation of BD$_x$PTMG$_y$MDI segmented polyurethanes and BDMDI and PTMGMDI polyurethanes is shown in Scheme 1. They were obtained by the *one shot* method with good yields as a white to transparent yellowish solid. Their average molecular weights determined by viscosity measurements ranged from 28 400 to 55 100 g mol^{-1} (Table 1).

Both composition and microstructure of segmented polyurethanes were determined by NMR. For illustration, ^{1}H and ^{13}C NMR spectra of BD$_{50}$PTMG$_{50}$MDI are shown in Figure 1. Chemical assignments were accomplished by the *cosy* and *hetcor*

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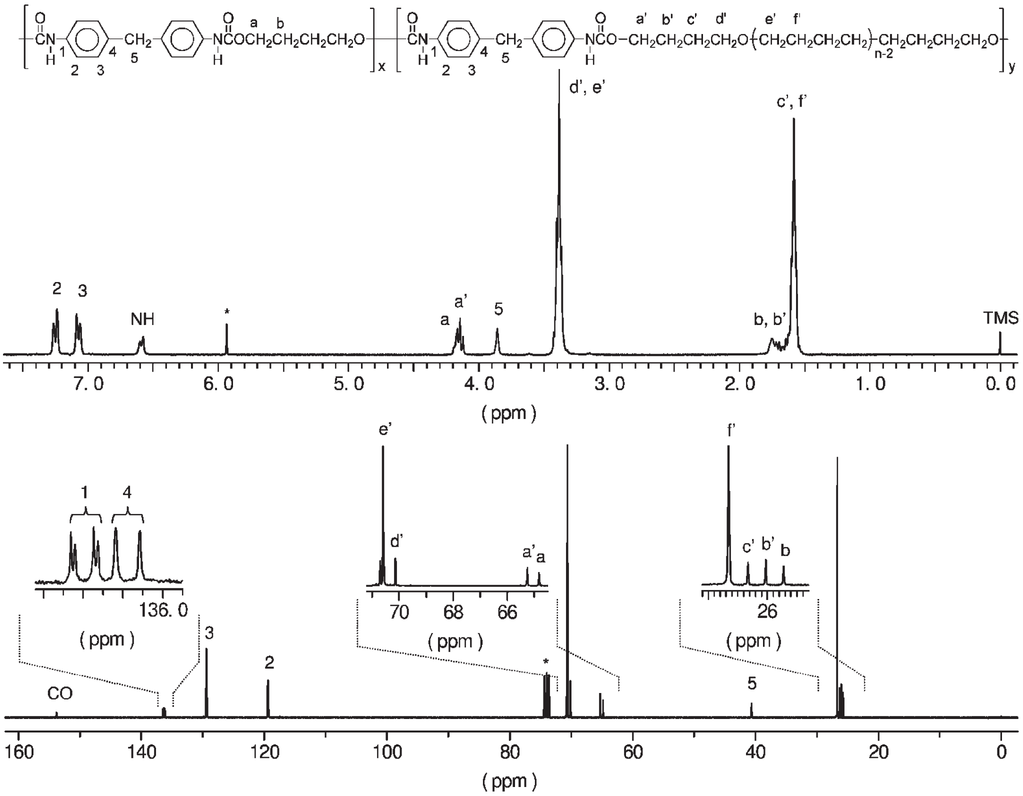
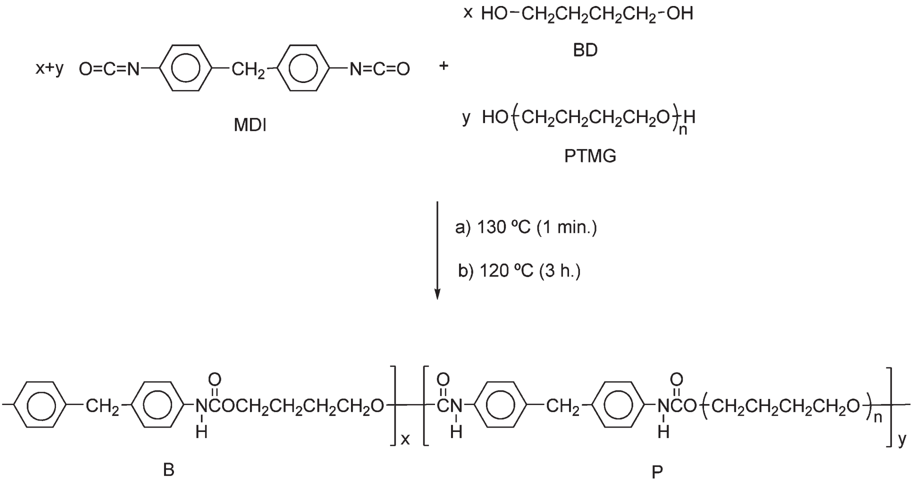


Figure 1. 300.1 MHz ^{1}H NMR (top) and 75.5 MHz ^{13}C NMR (bottom) spectra of BD$_{50}$PTMG$_{50}$MDI recorded in $Cl_2CDCDCl_2$ at 80 °C. (*) Signals of solvent.

Scheme 1



BD$_x$PTMG$_y$MDI

^{1}H–^{1}H and ^{1}H–^{13}C homo- and heteronuclear shift correlation 2D NMR spectra. Composition of polymers was determined by integration of ^{1}H NMR peaks at 4.15 ppm corresponding to a, a′ methylenes of BD and PTMG units, respectively, and the signal at 3.4 ppm corresponding to d′ and e′ methylenes of PTMG unit. The polyurethanes showed slightly lower content in BD than the feed, indicating that small amounts of this diol were evaporated during the reaction.

^{13}C NMR spectra showed splitting for the nonprotonated aromatic carbons of MDI segments in the *ipso* position relative to urethane group (carbon 1). This splitting of the signal that appeared around 136.4 ppm was due to sequence distribution at the level of dyads. Figure 2 shows the ^{13}C NMR spectra of this region for polyurethanes with different compositions with indication of the peak assignments for the different dyad types. The assignment of different dyads was accomplished by comparison of NMR spectra with that of PTMGMDI polyurethane where only PP dyads are feasible. BP or PB dyads show two peaks of equal intensity, and the fourth peak is therefore assigned to BB dyads. No comparison could be made with BDMDI because unfortunately this polyurethane was insoluble in the solvent used for the NMR analysis.

By integration of these peaks the molar ratio of different dyads was estimated, and the number-average sequence lengths of B

Table 1. Molecular Weights and Thermal Properties BD_xPTMG_yMDI Polyurethanes

	molecular weights		DSC				TGA		
polyurethane	$[\eta]^a$	M_v^a	T_g^b (°C)	T_c^c (°C)	T_m^d (°C)	ΔH_m^d (J g^{-1})	$^oT_d^e$ (°C)	$^mT_d^e$ (°C)	RW^e (%)
BDMDI	0.85	51 900	108.3	150	217	25.4	321	**340**/368/517	22
$BD_{75}PTMG_{25}MDI$	0.82	49 100	−9.9	88	171/208	1.7/23	337	**356**/371/427	8
$BD_{50}PTMG_{50}MDI$	0.76	43 500	−28.4		162	7.1	345	375/**426**	7
$BD_{25}PTMG_{75}MDI$	0.88	55 100	−43.1				361	382/**425**	5
PTMGMDI	0.58	28 400	−54.1				365	386/**425**	6

[a] Intrinsic viscosity (dL g^{-1}) measured in *N,N*-dimethylformamide at 25 °C. M_v calculated using $K = 8.52 \times 10^{-4}$ and $a = 0.636$ Mark−Houwink constants taken from ref 19. [b] Glass transition temperature from melt-quenched samples determined by DSC at 20 °C min^{-1}. [c] Crystallization temperature measured by DSC at cooling from the melt at 10 °C min^{-1}. [d] Melting temperature and enthalpy determined by DSC on the first heating at 10 °C min^{-1}. [e] Onset (10% of weight loss) and maximum rate decomposition temperatures (main peak in bold) and residual weight at 600 °C determined by TGA under inert atmosphere.

Table 2. Experimental[a] and Theoretical[b] (in Parentheses) Sequence Distribution and Randomness of BD_xPTMG_yMDI Polyurethanes

	composition^c		dyads (mol %)			number-average sequence length		randomness
polyurethane	X_B	X_P	BB	BP + PB	PP	$\bar{n}_B$	$\bar{n}_P$	B
$BD_{75}PTMG_{25}MDI$	70.8	29.2	43.3	43.7	13.0	3.0	1.6	0.96
			(50.1)	(41.4)	(8.5)	(3.4)	(1.4)	(1.00)
$BD_{50}PTMG_{50}MDI$	45.2	54.8	20.1	45.6	34.3	1.9	2.5	0.92
			(20.5)	(49.5)	(30.0)	(1.8)	(2.2)	(1.00)
$BD_{25}PTMG_{75}MDI$	22.3	77.7	4.7	30.1	65.2	1.3	5.3	0.96
			(5.0)	(34.6)	(60.4)	(1.3)	(4.5)	(1.00)

[a] Experimental values were obtained from integration of ^{13}C NMR peaks using the equations mentioned in the text. [b] Theoretical values were calculated on the basis of a random distribution using the polyurethane compositions given in this table. [c] Calculated from the oxymethylene signals in the ^1H NMR spectra.

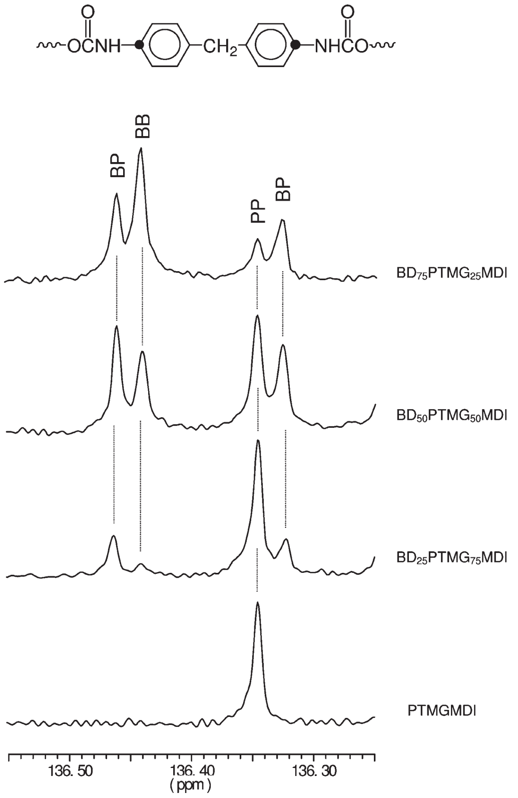


Figure 2. Comparison of ^{13}C NMR spectra of polyurethanes in the aromatic region showing the splitting for the nonprotonated carbons.

and P units, as well as the degree of randomness, could be calculated using the following expressions:[16]

$$\bar{n}_B = \frac{N_{BB} + \frac{N_{BP}}{2}}{\frac{N_{BP}}{2}} \qquad \bar{n}_P = \frac{N_{PP} + \frac{N_{BP}}{2}}{\frac{N_{BP}}{2}} \qquad B = \frac{1}{\bar{n}_B} + \frac{1}{\bar{n}_P}$$

^{13}C NMR spectra could be quantitatively used since for calculations we are using the same type of nonprotonated aromatic carbons for the four different dyads which can be assumed to have similar spin−lattice relaxation times (T_1) and nuclear Overhauser effects (NOE). This assumption is strongly supported by the fact that polyurethane compositions calculated by ^{13}C NMR using such signals were in good agreement with those obtained from ^1H NMR. As it can be observed in Table 2, the experimental values are in good agreement with the theoretical ones calculated for a statistical copolymer, indicating that these polyurethanes have a random distribution of diols in the polymer. It can be assessed from these values that the hydroxyl groups of BD and PTMG display similar reactivity. Otherwise, a blocky microstructure should be generated unless *transurethanization* reactions have taken place, which is largely unexpected at the temperatures used for the reaction.[17,18]

In order to corroborate the results obtained by NMR, the thermal properties were evaluated, and results are summarized in Table 1. These polymers showed good thermal stability as observed by TGA. The T_g of the polymers increased continuously with the content of BD in the polyurethane from −54 to 108 °C. These values are in full agreement with a random distribution of diols in the segmented polyurethanes. Samples with high contents of hard segments, where the number-average sequence length of B units is above 1.9, were able to crystallize showing melting temperatures between 162 and 217 °C, the values increasing with the content in hard segments.

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Supporting Information Available: ^1H−^1H and ^1H−^{13}C homonuclear (cosy) and heteronuclear (hetcor) shift correlation 2D NMR spectra of $BD_{50}PTMG_{50}MDI$. This material is available free of charge via the Internet at http://pubs.acs.org.

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