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The Determination of Hard Segments in Polyurethane Elastomers by High Performance Liquid Chromatography

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Summary

Reverse phase HPLC methods are elaborated for the characterisation of polyurethane elastomers. The quantitation of urethane groups after aminolysis, as well as the determination of basic hard segments and qualitative hard segments size distribution after hydrolysis in dimethylsulfoxid (DMSO) are described. The methods are ilustrated with diphenylmethane-p,p'-bis(4-octanoiloxybutylcarbamate) (U1) as model compound and three different polyurethane formulations.

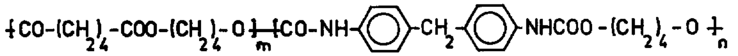
Introduction

Elastomeric polyurethanes (PU) are segmented copolymers composed of soft rubbery segments (polyesters or polyethers) joined by hard glassy segments (HS), containing urethane linkage. The microphase separation of these dissimilar blocks produces regions of hard block concentrations (domains) which act as very minute filler particles, resulting a self-reinforced and physically cross-linked polymer (LAWANDY and HEPBURN 1980, LILAONITKUL and COOPER 1979).

The hard blocks, which usually constitute about 30-50 % by weight of the total polymer, are formed by the reaction of a diisocyanate, such as p,p'methylenedi(phenylisocynate) (MDI), with a low molecular weight diol such as 1,4-butanediol (BD) (REDMAN 1978).

Since the physical and mechanical properties of these polymers are determined to a great extent by the type and concentration of hard segments, their medium length and size distribution (GOYERT and HESPE 1978, NOSHAY and McGRATH 1977), analytical methods used for their determination are of special interest.

In the present work high performance liquid chromatographic (HPLC) methods are described which allows :
- determination of basic HS structure
- quantitation of urethane structure
- qualitative analysis of HS size distribution in PU elastomers, having the general formula :



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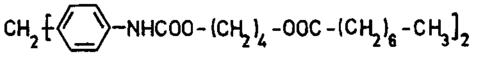
Materials and Procedures

All chemicals were of AR grade, unless otherwise stated. MDI (UPJOHN) was hot-filtered before use. Poly(butylene adipate)diol (PAB), $\bar{M} \sim 2000$ was synthetized in our laboratory by melt polycondensation.

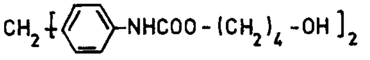
A mixture of 4-hydroxybutyl octanoat (HBO) with 1,4-butanediol dioctanoat (BDO) was obtained by esterification of octanoic acid with excess BD, excess which had been removed by several washings with water.

Diphenylmethane-p,p'-bis(4-octanoiloxybutyl carbamate)


U1

was synthetized from the HBO-BDO mixture and MDI at room temperature. Succesive recrystallization of the resulted precipitate from CH_3OH/H_2O and CH_3CN/H_2O gave a white crystalline product, MP=91°C.

Diphenylmethane-p,p'-bis(4-hydroxybutyl carbamate)


U2

was prepared by selective cleavage of ester group of U1 in DMSO. Under the conditions described below (VINSON et all 1966) the urethane linkage is not affected (LÖCSEI).
To 0.5 mmol (0.34 g) U1 dissolved in 40 ml DMSO, 8 ml KOH 0.5 N was added, kept 15 min. at room temperature, diluted with water, the precipitate filtered, washed with water, recrystallized from aqueous methanol and dried (MP=133-134°C)

Benzyl N-phenylcarbamate was prepared from phenylisocyanate and benzylalcohol and recrystallized from aqueous methanol, MP= 76.8°C (MUKAIYAMA and HOSHINO 1956 MP= 76°C).

The structure of these compounds was proved by elemental analysis, IR and ^1H-NMR, and the purity cheked by HPLC.

PU elastomers with various PAB/BD/MDI molar ratios (PU-1 = 1:2.4:3.4 ; PU-2 = 1:2:3 ; PU-3 = 1:0.6:1.6) were obtained by hand mixing a quasi-prepolymer (13 % NCO) on basis of PAB and MDI with a tertiary amine catalysed blend of PAB and BD and curing it 2 h at 120°C.

For the determination of the amount of urethane structure, the PU was aminolysed with ethanolamine (EA) (SCHRÖDER 1963, LÖCSEI et all 1982), by refluxing 0.1 g PU in 10 ml EA for 1 h. The resulted diamine, i.e. 4,4'-diaminodiphenylmethane (MDA) was determined by RP-HPLC using toluene as internal standard.

The apparatus used was a Waters Model ALC/GPC 244 liquid chromatograph with two pumps Model 6000 A , a Model 660 solvent programmer, UV detector Model 440 at 254 nm and an injector U6K all from Waters.

The chromatographic conditions were as follows :
Column micro-Bondapak C_{18} (30 cm x 3.9 mm), eluent 75 % (v/v) methanol/water in the isocratic mode, flowrate 1.5 ml/min.,

time of analysis 5 min. 5 μl of a solution obtained from 0.1 g of the aminolysis product in 10 ml methanol which contained toluene as internal standard were injected. The method of peak height ratios was used for quantitation.

In order to quantitate the basic HS structure (i.e. U2) and to qualitatively determine the segment size distribution the PU was hydrolized under the same conditions as described previously (synthesis of U2). The reaction mixture was neutralized with HCl 0.5 N, then 1.o g of the solution was diluted with 10 ml DMF which contained the internal standard benzyl N-phenylcarbamate, and 5 μl were injected.

The chromatographic conditions were :
Column micro-Bondapak C_{18} (30 cm x 3.9 mm), gradient concave (7 with Model 660 solvent programmer) for 12 min from 68 % methanol/water (v/v) to 100 % methanol, flowrate 1.5 ml/min. Chromatograms of the three PU formulations after hydrolysis in DMSO are shown in Fig. 1.

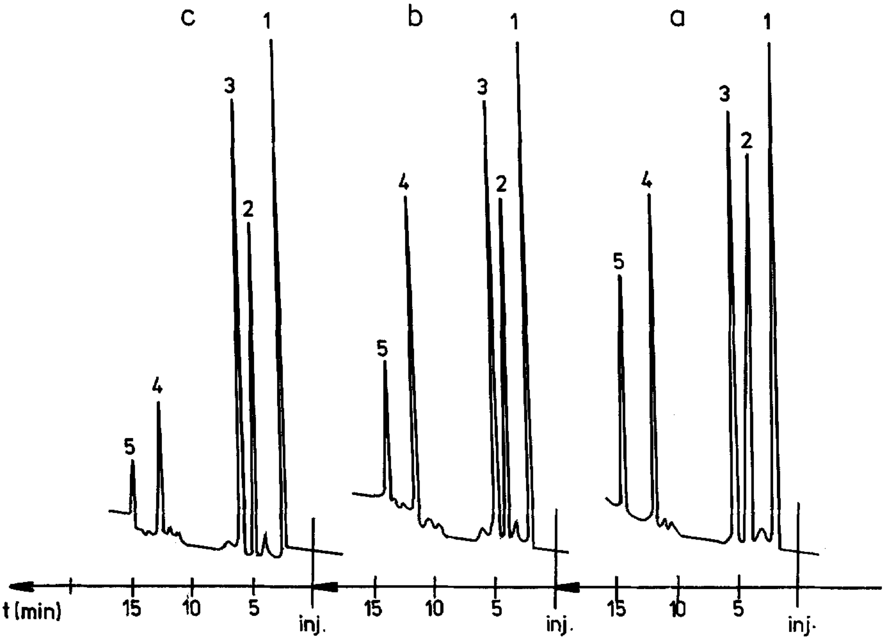


Fig. 1
Rp-gradient elution-HPLC of three polyurethane formulations
a. PU 1 ; b. PU 2 ; c. PU 3
Peak identification : 1 - solvent peak ; 2 - U2 that means a sequence of BD-MDI-BD ; 3 - benzyl N-phenylcarbamate (IS); 4 - "dimer D" a sequence BD-MDI-BD-MDI-BD ; 5 - "trimer T" a sequence BD-MDI-BD-MDI-BD-MDI-BD.
Chromatographic conditions , see text

Results and Discussion

TABLE 1

Results of MDA and U2 Determinations in Urethane Samples

Compound	mmol MDA/g		Recov.%	mmol U2/g		Recov.%
	Calcul.	Found		Calcul.	Found	
U1	1.465	1.450	99.0	1.465	1.436	98.0
PU-1	1.091	1.066	97.7	-	0.105	-
PU-2	1.004	1.025	102.1	-	0.100	-
PU-3	0.627	0.636	101.4	-	0.186	-

The data represents the media of three determinations and the relative standard deviation of the whole method did not exceed 5 %.

The methods allow, as can be seen from Table 1, to obtain important data for the characterization of a polyurethane (PU)elastomer. It is possible to quantitate the percent of diisocyanate present as "monomer" (U2), per total diisocyanate found as equivalent MDA. For PU-1 this is 9.8% while for PU-3 it is 29.2%.

The different HS size distributions (Fig.1), even if we could not quantitate them, because of the difficulty to obtain D and T, are important fingerprints, which can be very useful for investigating some correlations between size distribution and preparation methods or properties.

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