THERMOPLASTIC POLYURETHANE ELASTOMERS FOR POTENTIAL BIOMEDICAL USE: SYNTHESIS OF α,ω–DI(HYDROXY)POLYISOBUTYLENE AS MACRODIOL FOR THE PREPARATION OF POLYURETHANES

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INTRODUCTION

Polyurethane (PU) is a synthetic polymeric material, which is synthesized by the polyaddition reaction of dioles with diisocyanates. The good mechanical properties[1b] and their relatively good biocompatibility[1a, b] make the PUs to the most used biomaterials. For that reason polymeric materials based on PU have a great utilization in the manufacturing of medical implants.[1a, b]

Keywords: polyurethane, cationic polymerization, polyisobutylene, ^{1}H-NMR

GOALS

The aim of this study is to develop a synthesis method for PUs based on macrodiols with excellent hydrolytic/oxidative stability. We started our investigations with a commercially available polycarbonate (PC) because it has a relatively good resistance to hydrolysis.[2] In order to increase the biostability a small amount of polydimethylsiloxane (PDMS)[3] was added as comacrodiol. As the polyisobutylene (PIB) moiety exhibits hydrolytic and oxidative stability[4], it is to be expected that PUs based on PIB should have the same properties. Because a PIB-macrodiol is not commercially available, it seemed appropriate to perform the synthesis in our laboratory.

RESULTS: SYNTHESIS AND CHARACTERIZATION OF PUs USING POLYCARBONATE DIOL (PC) AS SOFT SEGMEN

Table 1. Synthesis of PUs based on (PC) and 4,4'-diphenylmethanediisocyanate (MDI).

PU	R-PDMS-R (%)	R	Chain extender	Hard segment (%)
1	10	OH	1,4-butanediol	35
2	5	OH	1,4-butanediol	35
3	5	OH	1,4-butanediol	40
4	5	OH	1,4-butanediamine 1,5-pentanediol	35
5	5	OH	1,5-pentanediol	35
6	5	NH_2,3000 g/Mol	1,4-butanediol	35
7	5	NH_2,5000 g/Mol	1,4-butanediol	35
8	-	-	1,4-butanediol	35

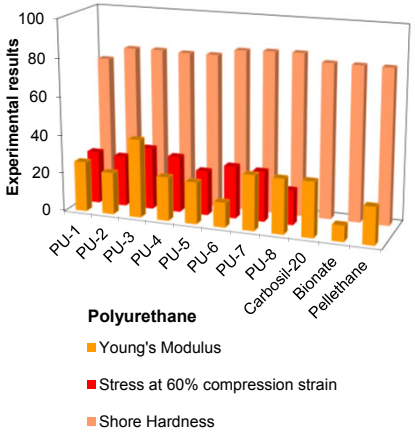


Fig 1. Mechanical properties of synthesized PUs.

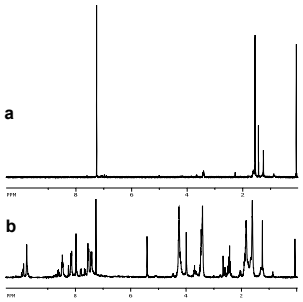


Fig. 2. ^{1}H NMR spectra of Pellethane 55D.
a) bevor hydrolytic/oxidative test in 65% HNO_3
b) after hydrolytic/oxidative test in 65% HNO_3

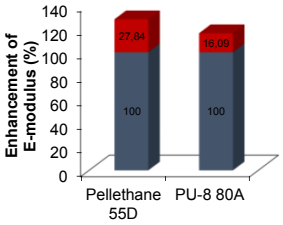
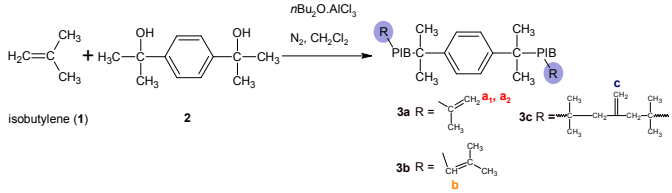


Fig.3. Hydrolytic/oxidative tests. 1 h reaction time in 35% HNO_3

RESULTS: SYNTHESIS OF HO-PIB-OH

Table 2. Optimization of polyisobutylen synthesis.[a]



entry	$AlCl_3$/nB_2O (mmol)	2 (mmol)	time (h)	t (°C)	H_2O (mMol)	conversion[d] (%)	PIBend-group composition 3a:3b:3c	Mn[e] (g/Mol)
1[b]	18.8/15.6	1.1	3[15]	-40	16.6	53	1:0.04:0.008	1056
2[c]	18.8/16	11	5	-60	16.6	35	1:0:0	2515
3[c]	16/16	5	5	-40	0.55e-3	58	1:0.03:0.03	1168
4[c]	16/11.8	5	5	-40	0.55e-3	60	1:0.09:0.03	2120

[a] 534.6 mmol (50 ml) **1**; [b] 150 mL CH_2Cl_2 were used as a solvent; [c] 200 mL CH_2Cl_2 were used as a solvent; [d] determinated gravimetrically; [e] determinated by ^{1}H NMR spectroscopy.

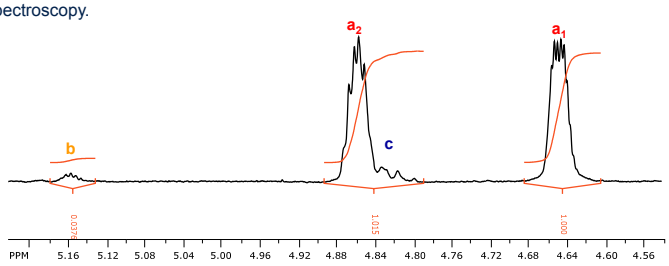


Fig. 4. Olefinic part of the ^{1}H NMR spectrum (mixture **3a, 3b** and **3c**).

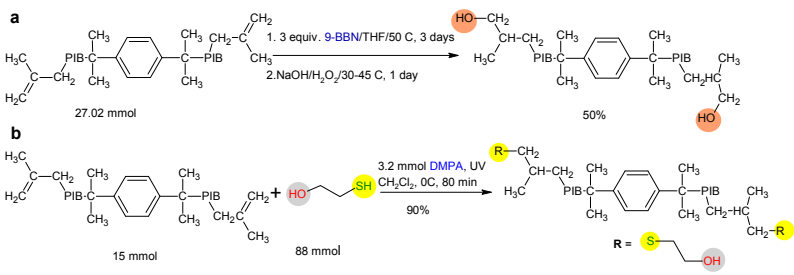


Fig. 5. Functionalization of polyisobutylene **a)** *via* hydroboration/oxidation **b)** *via* thiol-ene click chemistry.

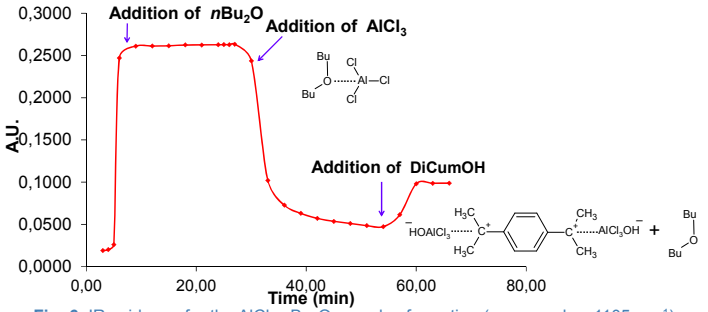


Fig. 6. IR evidence for the $AlCl_3$.nBu_2O complex formation (wavenumber 1105 cm^{-1}).

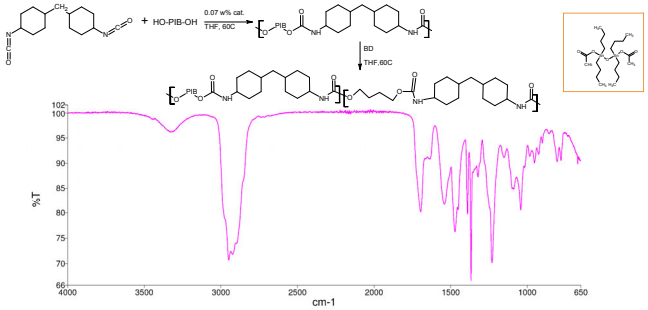


Fig. 7. Reactivity test of HO-PIB-OH towards 4,4'-diisocyanatodicyclohexylmethan (H_{12}MDI).

CONCLUSIONS

- 8 PC-PUs were synthesized and characterized.
- *exo*-terminated PIB was synthesized using H_2O/$AlCl_3$.nBu_2O/DiCumOH as initiating system.
- two strategies for the synthesis of HO-PIB-OH were successfully developed.
- PIB-PU has a good reactivity towards H_{12}MDI.

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