



**PHYSICAL CHEMISTRY 2014**

12<sup>th</sup> International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry

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The Conference is dedicated to the  
25. Anniversary of the Society of Physical Chemists of Serbia

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September 22-26, 2014  
Belgrade, Serbia



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PHYSICAL CHEMISTRY 2014

*12th International Conference on  
Fundamental and Applied Aspects of  
Physical Chemistry*

*Organized by  
The Society of Physical Chemists of  
Serbia*

*in co-operation  
with\_*

*Institute of Catalysis Bulgarian Academy of Sciences*

*Boreskov Institute of Catalysis of Siberian Branch of the Russian Academy  
of Sciences*

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## THERMOPLASTIC POLYURETHANES BASED ON POLY(DIMETHYLSILOXANE): STRUCTURE AND THERMAL BEHAVIOR

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### ABSTRACT

Segmented polyurethanes are an important class of thermoplastic elastomers which have potential use as a biomaterial. Biostability, biocompatibility and some other features of polyurethanes can be improved by the introduction of poly(dimethylsiloxane) in the polymer chain. A series of novel thermoplastic polyurethanes was synthesized by two-step polyaddition reaction in solution from 4,4'-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BD) and poly(propylene oxide)-*b*-poly(dimethylsiloxane)-*b*-poly(propylene oxide) (PPO-PDMS). The content of PPO-PDMS (i.e. soft segment) was varied between 40 and 90 wt%. The influence of PPO-PDMS content on the structure and thermal properties of copolymers was investigated by FTIR, <sup>1</sup>H and 2D NMR spectroscopy, as well as by DSC analysis.

### INTRODUCTION

Thermoplastic polyurethanes (TPUs) are linear segmented copolymers consisting of a high molecular weight macrodiol, called the soft segment (SS), and a diisocyanate and low molecular weight diol, which form the hard segment (HS). Thermodynamic incompatibility between SS and HS results in a phase separated structure [1]. The introduction of poly(dimethylsiloxane) (PDMS) macrodiol, into the polyurethane structure provides some good properties of prepared materials, such as: low surface energy, excellent thermal, oxidative and hydrolytic stability, flexibility and biocompatibility [2]. The aim of this work was to investigate the effect of soft segment content on the structure and thermal properties of the synthesized TPUs.

### EXPERIMENTAL

Poly(propylene oxide)-*b*-poly(dimethylsiloxane)-*b*-poly(propylene oxide) (PPO-PDMS) (from ABCR,  $M_n = 2900$  g/mol) was dried over molecular

sieves before use. 4,4'-Diphenylmethane diisocyanate (MDI) (Aldrich, purity > 98 %) was used as received. 1,4-Butanediol (BD) (Aldrich) was purified by vacuum distillation. Tetrahydrofuran (THF) (Moss Hemoss) and *N,N*-dimethylacetamide (DMAc) (Merck) were distilled before use. The catalyst was stannous octanoate (Sn(Oct)<sub>2</sub>) (Aldrich).

A two-step polymerization was employed to synthesize novel TPUs. Firstly, the isocyanate terminated prepolymer was prepared by the reaction between the PPO-PDMS and MDI in solution of DMAc/THF, at 80 °C for 40 min in nitrogen atmosphere, and in presence of catalyst. Then, solution of BD in DMAc/THF was added to the –NCO terminated prepolymer, at the same temperature and the reaction was proceeded for 10 hours. The last two numbers in the name of the sample represent the weight percent of the HS.

FTIR spectra were recorded using Nicolet 6700 FTIR spectrometer.

NMR experiments were collected on Bruker Avance 500 spectrometer. The <sup>1</sup>H NMR (at 500 MHz) and 2D NMR spectra (HSQC, HMBC and ROESY) of copolymers were measured using DMSO-*d*<sub>6</sub> as the solvent.

Differential scanning calorimetry (DSC) was conducted using a DSC Q1000V9.0 Build 275 thermal analyzer. The copolymers were analyzed under a nitrogen atmosphere in the temperature range from -90 to 230 °C at a heating and cooling rate of 10 and 5 °C/min, respectively.

## RESULTS AND DISCUSSION

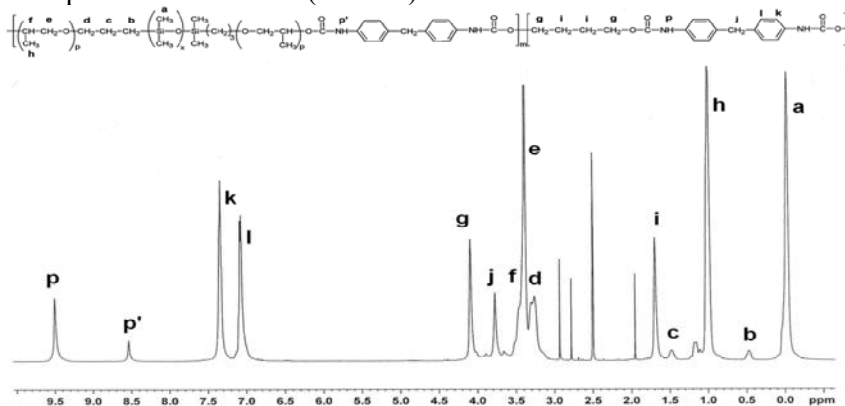
The molecular structure of the copolymers was confirmed by FTIR spectroscopy. Characteristic absorption bands appeared at 3330 cm<sup>-1</sup> ( $\nu_{\text{N-H}}$ ), 2970 and 2895 cm<sup>-1</sup> ( $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}$  of C-H), 1705 cm<sup>-1</sup> ( $\nu_{\text{C=O}}$ ), 1600 and 1415 cm<sup>-1</sup> ( $\nu_{\text{C=C}}^{\text{arom}}$ ), 1540 cm<sup>-1</sup> (amide II) and 1230 cm<sup>-1</sup> (amide III), 1020 and 1080 cm<sup>-1</sup> ( $\nu_{\text{Si-O-Si}} + \nu_{\text{C-O-C}}$ ) and 810 cm<sup>-1</sup> ( $\rho_{\text{C-H}}$  in SiCH<sub>3</sub>).

The molecular structure of the TPUs was also investigated by <sup>1</sup>H NMR spectroscopy. In <sup>1</sup>H NMR spectra (Figure 1), the signals of the –SiCH<sub>3</sub> protons appeared at 0.03 ppm. All methylene protons, derived from propylene groups connected to PDMS, can be observed at 0.47, 1.48 and 3.26 ppm. The protons at 1.69 and 4.09 ppm originated from the central and terminal methylene groups from the BD. The signal of methylene protons from the MDI residue appeared at 3.77 ppm. The protons at 7.08 and 7.34 ppm were from the aromatic ring and at 8.53 and 9.50 ppm were from the urethane –NH group present in the HS and SS. Also, the signals of the methyl, methylene and methine protons from the poly(propylene oxide) residue appeared at 1.00, 3.38 and 3.40 ppm, respectively.

The composition of the TPUs was determined from the <sup>1</sup>H NMR spectra. The values for the weight fraction of the SS ranged from 38.5 to 88.6%,



which are in relatively good agreement with the values predetermined from the composition of the feed (Table 1).



**Figure 1.**  $^1\text{H}$  NMR spectra of the PU-PPO40 copolymer

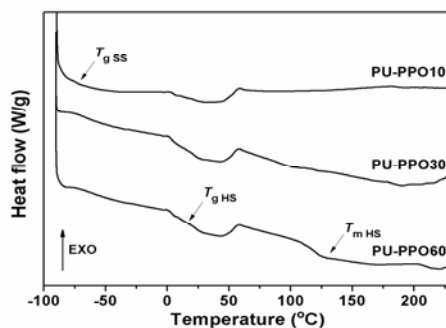
The assignments of the carbon and proton resonances in the structures were also confirmed by two-dimensional NMR spectroscopy. The chemical shifts of some overlapped and/or barely visible signals in  $^1\text{H}$  NMR spectra can be solved with COSY, HSQC and ROESY spectra. The overlapped signals *f*, *e* and *d* in the  $^1\text{H}$  NMR spectrum were determined and separated using HSQC correlations. Also, from HMBC spectra it can be concluded that MDI is incorporated into SS and HS.

**Table 1.** Composition and some DSC data of the TPU

Sample	wt% SS (in feed)	wt% SS NMR	$T_{\text{gHS}}$ ( $^{\circ}\text{C}$ )	$T_{\text{mHS}}$ ( $^{\circ}\text{C}$ )	$T_{\text{gSS}}$ ( $^{\circ}\text{C}$ )
PU-PPO10	90.3	88.6	14.7	-	-73.2
PU-PPO20	82.0	77.8	14.9	-	-69.1
PU-PPO30	69.8	65.9	14.9	-	-64.6
PU-PPO40	60.1	60.4	14.8	118.4	-66.0
PU-PPO50	47.8	47.9	14.8	130.5	-64.5
PU-PPO60	39.9	38.5	14.8	131.7	-64.4

The obtained DSC thermograms are shown in Figure 2 and results are summarized in Table 1. The DSC curves show transitions which correspond to the melting temperatures of HS ( $T_{\text{mHS}}$ ), glass transition temperatures of the HS ( $T_{\text{gHS}}$ ) and SS ( $T_{\text{gSS}}$ ). The  $T_{\text{mHS}}$  of TPUs ranged from 118 to 132  $^{\circ}\text{C}$ , and increased with decreasing content of PPO-PDMS segment. The  $T_{\text{mHS}}$

was observed only in sample with lower SS content. The  $T_{gHS}$  were similar for TPUs and their values were approximately 15 °C. The  $T_{gSS}$  that correspond to the PPO units in SS, were between -73 and -65 °C, and increased with decreasing content of SS.



**Figure 2.** DSC thermograms (second heating run) of TPUs with different content of PPO-PDMS

## CONCLUSION

In this work, novel TPU copolymers based on PPO-PDMS were prepared by two-step polyaddition reaction in solution. The multiblock structure and composition of the obtained copolymers were confirmed by FTIR,  $^1\text{H}$  and 2D NMR spectroscopy. DSC analysis showed that TPUs exhibit two glass transition temperatures, one corresponding to the hard segment and the second to the PPO units in soft segment, and a melting temperature of hard segment.

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