



**PHYSICAL CHEMISTRY 2010**

**10th International Conference on  
Fundamental and Applied Aspects of  
Physical Chemistry**

Proceedings

---

**The Conference is dedicated to the  
100th Anniversary of the academician Pavle Savić birthday  
and  
20th Anniversary of the Society of Physical Chemists of Serbia**

---

**21-24 September 2010  
B E L G R A D E**

**ISBN 978-86-82475-17-0**

**Title:** Physical Chemistry 2010. (Proceedings)

**Editors:** S. Anić and Ž. Čupić

**Published by:** Society of Physical Chemists of Serbia, Studentski trg 12-16  
P.O.Box 47, 11158 Beograd, 218, Srbija

**Publisher:** Society of Physical Chemists of Serbia

**For Publisher:** S. Anić, President of Society of Physical Chemists of Serbia

**Printed by:** “Jovan” Printing and Publishing Company; 200 Copies;

Number of pages 16 + 388, **Format:** B5; Printing finished in September  
2010.

**Text and Layout:** “Jovan”

*200 - Copy printing*

*The Society of Physical Chemists of Serbia*

*in co-operation with*

*Institute of Catalysis, Bulgarian Academy of Sciences*

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

*Faculty of Physical Chemistry, University of Belgrade, Serbia*

*Institute of Chemistry Technology and Metallurgy, University of  
Belgrade, Serbia*

*Vinča Institute, University of Belgrade, Serbia*

*Institute of General and Physical Chemistry, Serbia*

### **International Organizing Committee**

**Chairman:** S. Anić (Serbia)  
**Vice-chairman:** N. Stepanov (Russia)  
B. Adnađević (Serbia)

#### **Members:**

M. Gabrovska (Bulgaria), N. Cvijetićanin (Serbia), T. Grozdić (Serbia),  
D. Jovanović (Serbia), M. Lalić (BiH), D. Marković (Serbia), B. Milosavljević  
(USA), N. Miljević (Serbia), M. Mojović (Serbia), N. Ostrovski (Serbia), C. Pona  
(Italy), B. Simonović (Serbia), D. Stanisavljev (Serbia), A. G. Stepanov (Russia),  
V. Vasić (Serbia), N. Vukelić (Serbia), V. Vukojević (Sweden)

### **International Scientific Committee**

**Chairman:** Ž. Čupić (Serbia)  
**Vice-chairmans:** V. N. Parmon (Russia)  
M. Franko (Slovenia)  
V. Vasić (Serbia)

#### **Members:**

A. Antić-Jovanović (Serbia), G. Bačić (Serbia), R. Cervellati (Italy), R. Compton  
(United Kingdom), V. Gaspar (Hungary), M. Jeremić (Serbia), A. L. Kawczyński  
(Poland), Lj. Kolar-Anić (Serbia), S. Kuchanov (Russia), R. Leblanc (USA),  
S. Mentus (Serbia), S. Milonjić (Serbia), Lj. Morozova-Roche (Sweden),  
D. Moscone (Italy), J. Nedeljković (Serbia), Z. Noszticzus (Hungary), M. Perić  
(Serbia), V. Petruševski (Macedonia), M. Plavšić (Serbia), G. Smulevich (Italy),  
G. Schmitz (Belgium), I. Schreiber (Czech), P. Ševčík (Slovakia), N. Stepanov  
(Russia), M. Trtica (Serbia), D. Veselinović (Serbia)

### **Local Executive Committee**

**Chairman:** B. Adnađević  
**Vice-chairmans:** S. Blagojević  
A. Ivanović

#### **Members:**

A. Abu Rabi-Stanković, P. Banković, N. Begović, S. N. Blagojević,  
N. Cvjetičanin, M. Daković, A. Đerić, A. Ignjatović, Lj. Ignjatović, A. Jović,  
J. Krstić, S. Kuprešak, D. Lončarević, J. Maksimović, V. Marković, M.  
Milenković, M. Milojević, Z. Mojović, B. Nedić, I. Pašti, N. Pejić, A. Popović-  
Bjelić, M. Petković, N. Potkonjak, D. Ranković, R. Ranković, M. Stević,  
I. Stojković, B. Šljukić, M. Vujković

# NOVEL CROSSLINKED POLYURETHANES BASED ON HYPERBRANCHED POLYESTER

M. V. Pergal<sup>1</sup>, J. Džunuzović<sup>1</sup>, M. Kićanović<sup>3</sup>, V. Vodnik<sup>2</sup> and S. Jovanović<sup>4</sup>

<sup>1</sup>*ICTM-Center of Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia*

<sup>2</sup>*Institute of Nuclear Science "Vinča", P. O. Box 522, 11001 Belgrade, Serbia*

<sup>3</sup>*Holding Institute of General and Physical Chemistry, Studentski trg 12-16, Belgrade 11000, Serbia*

<sup>4</sup>*Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia*

## Abstract

The polyurethane (PU) elastomers based on hydroxy-terminated hyperbranched polyester (BH-20) and 4,4'-methylenediphenyl diisocyanate (MDI) as hard segments and hydroxyl-terminated ethylene oxide-poly(dimethylsiloxane)-ethylene oxide (PDMS-EO) as soft segment, were synthesized and examined in this work. The obtained results show that sol fraction decreases and thermal stability increases with increase of the hard segment content.

## Introduction

Crosslinked polyurethanes (PUs) have numerous applications such as coatings, elastomers, sealants, foams and adhesives due to their unique properties and great efforts have been made in chemistry and physics of PUs. PU elastomers showed excellent mechanical and elastic properties, but lower thermal stability. Their thermal stability can be improved by introduction of PDMS segments in PU backbone. The properties of PU elastomers are depending on the molecular weight of the soft segment as well as on the chemical structure of all components. The use of hyperbranched (HB) polymers as crosslinker of PUs has attracted large scientific attention over the last years, because of their unique structure and properties and simple synthetic procedure [1-3].

In this work, the influence of the content of macrodiol on the structure, swelling and thermal properties of crosslinked PUs based on ethylene oxide-poly(dimethylsiloxane)-ethylene oxide, was investigated. Crosslinking agent was hydroxy-functional aliphatic HB polyester of the second pseudo generation (BH-20, Boltorn<sup>®</sup>).

## Experimental

The PU networks were synthesized by catalyzed two-step polymerization in solution (NMP/THF) using PDMS-EO ( $\bar{M}_n = 1200 \text{ g mol}^{-1}$ ), 4,4'-methylenediphenyl diisocyanate (MDI) as monomers and BH-20 ( $M_n = 1340 \text{ g/mol}$ , functionality  $f_n = 12$ ) as crosslinking agent. The molar NCO/OH ratio was 1.05. The PU prepolymer was synthesized in an argon atmosphere by reacting PDMS-EO with excess MDI. Then the prepolymer was reacted with BH-20.

Reaction was carried out in reaction vessel at 40 °C for 1 h. The obtained mixture was then cast in Teflon® dish and heated in oven at 80 °C for 50 h and 1 h at 110 °C. The crosslinked samples were obtained as brown films.

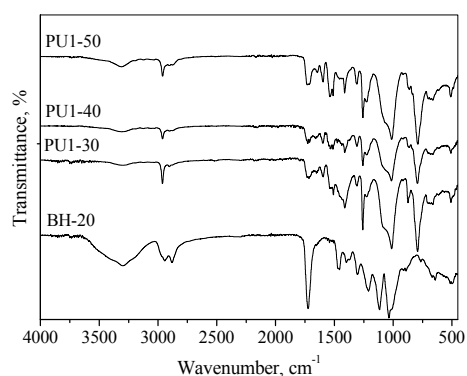
IR spectra of the crosslinked PUs were recorded on ATR NICOLET 380 FTIR spectrometer. Swelling behavior of square samples was investigated in toluene at room temperature. The thermal stability of samples was determined by thermogravimetric (TG) analysis, using TGA Q500 V6.3 Build 189 instrument in nitrogen atmosphere, at heating rate of 10 °C/min.

## Results and Discussion

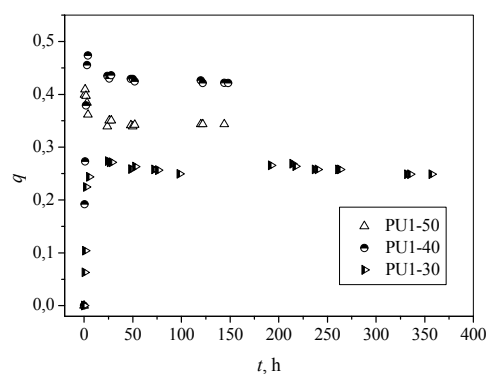
Some important properties of the synthesized PU networks are listed in Table 1. The soft segments content, SSC, was varied in the range from 30 to 50 wt. %. The chemical structure of PUs was determined by IR spectroscopy. The characteristic stretching frequencies for PUs appear at 3310  $\text{cm}^{-1}$  ( $\nu_{\text{N-H}}$ ), 1533  $\text{cm}^{-1}$  ( $\nu_{\text{C-N}} + \delta_{\text{N-H}}$ , amide III), 1259  $\text{cm}^{-1}$  ( $\nu_{\text{C-N}} + \delta_{\text{N-H}}$ , amide II), 1733  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ester), 1710  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ urethane), 1598  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$  arom), 1015 and 1080  $\text{cm}^{-1}$  ( $\nu_{\text{C-O}} + \nu_{\text{Si-O-Si}}$ ). In the IR spectra of PU samples the isocyanate  $-\text{N}=\text{C}=\text{O}$  band (2260  $\text{cm}^{-1}$ ) and hydroxyl group (3000  $\text{cm}^{-1}$ ) from BH-20, were not detected.

**Table 1.** The soft segments content, SSC, maximum swelling degree,  $q$ , and characteristic temperatures of thermal degradation of crosslinked PUs.

Sample	SSC, wt. %	$q_{\text{max}}$	Sol fraction, %	$T_{10}$ , °C	$T_{50}$ , °C	$T_{\text{max}}$ , °C
PU1-30	30	0.3	4.5	287	356	302/415/563
PU1-40	40	0.5	8.3	278	341	299/336/406/560
PU1-50	50	0.4	10.3	283	335	292/324/423/554



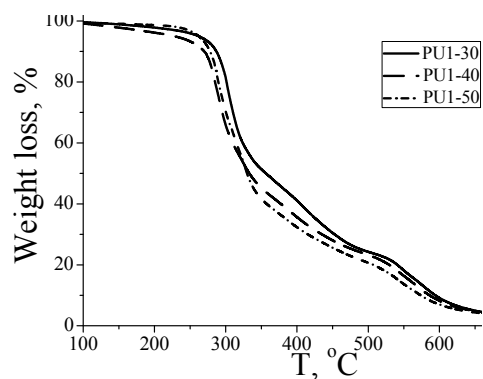
**Fig.1.** IR spectra of crosslinked PUs.



**Fig.2.** The change of the swelling degree,  $q$ , with time for crosslinked PUs.

The results obtained by investigation of swelling behavior of the synthesized crosslinked PUs in toluene at room temperature are presented in Table 1 and Fig. 2. Values of the swelling degree,  $q$ , were calculated using

conventional gravimetric method, equation  $q = (m-m_0)/m_0$  and values of the sample weights before,  $m_0$ , and after swelling,  $m$ . The sample weight was measured periodically, and the change with time was recorded. After reaching the maximum weight, the samples started losing weight because of the extraction of the sol fraction until constant values were obtained. The obtained sol fraction increases from 4.5 to 10.3 % with increasing soft segment content.



**Fig.3.** TG curves of investigated crosslinked PUs, determined in nitrogen atmosphere, at heating rate of 10°C/min.

From the results presented in Fig. 3 it can be observed that the thermal degradation of these crosslinked PUs is a three-step process in nitrogen. This is clearly demonstrated from the characteristic temperatures obtained from thermogram derivative curves (Table 1.). The thermal degradation of polyurethanes first goes via decomposition of urethane bonds, followed by breakage of the soft segment. Further decomposition in the region between 500 and 600 °C correlates with the aromatic content in polyurethanes [4]. The  $T_{10}$  value is considered to represent the beginning of degradation. The degradation of the PUs commences between 278 and 287 °C. Also, the temperature of 50 weight % loss ( $T_{50}$ ) of the PUs increases with increasing content of hard segments.

## Conclusions

The results presented in this work show that content of macrodiol have significant influence on the properties of PU networks. Thermal stability decreased with increase of macrodiol content. At the same time, as the content of PDMS-EO increase the determined sol fraction of these samples also increased.

## References

- [1] A. S. Nasar, M. Jikei, M. Kakimoto, E. Polym. J., 2003, **39**, 1201-1208.
- [2] L. Okrasa, P. Czech, G. Boiteux, F. Mechin, J. Ulanski, Polymer, 2008, **49**, 2662-2668.
- [3] P. A. Gunatillake, G. F. Meijs, S. J. McCarthy, R. Adhikari. J. Appl. Polym. Sci., 2000, **76**, 2026-2040.
- [4] Z. S. Petrovic, Z. Zavargo, J. H. Flynn, W. J. Macknight, J. Appl. Polym. Sci., 1994, **51**, 1087-1095.