



PHYSICAL CHEMISTRY 2012

¹¹th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Under the auspices of the
University of Belgrade

Proceedings

The Conference is dedicated to
Professor Ivan Draganić

September 24-28, 2012
Belgrade, Serbia

ISBN 978-86-82475-27-9 <i>Volume 1</i> ISBN 978-86-82475-28-6 <i>Volume II</i>

Title: PHYSICAL CHEMISTRY 2012 (Proceedings)

Editors: S. Anić and Ž. Čupić

Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia

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: 6+ 497; **Format:** B5; Printing finished in September 2012.

Text and Layout: “Jovan”

200- Copy printing

ORGANIZERS

PHYSICAL CHEMISTRY 2012

*11th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

*Under the auspices of the
University of Belgrade*

*Organized by
The Society of Physical Chemists of
Serbia*

*in co-operation
with*

Institute of Catalysis Bulgarian Academy of Sciences

*Boriskov Institute of Catalysis of 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

Faculty of Pharmacy, University of Belgrade, Serbia

COMMITTEES

International Organizing Committee

Chairman: S. Anić (Serbia)

Vice-chairmans: M. Gabrovska (Bulgaria)

V. A. Sadykov (Russia)

B. Adnadjević (Serbia)

Members: Z. Cherkezova-Zheleva (Bulgaria), N. Cvjetičanin (Serbia), S. N. Blagojević (Serbia), M. Daković (Serbia), T. Grozdić (Serbia), Lj. Ignjatović (Serbia), D. Jovanović (Serbia), N. Jović-Jovičić (Serbia), M. Kuzmanović (Serbia), D. Marković (Serbia), N. Kovačević (Serbia), J. Marković-Dimitrić (Serbia), B. Milosavljević (USA), Š. Miljanić (Serbia), N. Miljević (Serbia), A. Milutinović-Nikolić (Serbia), M. Mojović (Serbia), Z. Mojović, (Serbia), N. Ostrovski (Serbia), I. Pašti (Serbia), C. Pona (Italy), B. Simonović (Serbia), D. Stanisavljev (Serbia), B. Šljukić (Serbia), N. Vukelić (Serbia), V. Vukojević (Sweden)

International Scientific Committee

Chairman: Ž. Čupić (Serbia)

Vice-chairmans: V. N. Parmon (Russia)

S. Rakovsky (Bulgaria)

Members: A. Antić-Jovanović (Serbia), G. Bačić (Serbia), R. Cervellati (Italy), R. Compton (UK), V. Dondur (Serbia), Biljana Gaković (Serbia), V. Gaspar (Hungary), S. Gorodsky (Russia), V. Goussev (France), K. Hedrih (Serbia), Florou Heleny (Greece), M. Jeremić (Serbia), A. L. Kawczyński (Poland), Lj. Kolar-Anić (Serbia), V. Kuntić (Serbia), S. Mentus (Serbia), S. Milonjić (Serbia), Š. Miljanić (Serbia), Lj. Morozova-Roche (Sweden), P. Misaelides (Greece) M. Perić (Serbia), M. Plavšić (Serbia), V. Sadykov (Russia), G. Schmitz (Belgium), I. Schreiber (Czech), P. Sevcik (Slovakia), Natalia Skorodumova (Sweden), Dalimil Snita (Czech), N. Stepanov (Russia), D. Todorović (Serbia), M. Trtica (Serbia), V. Vasić (Serbia), D. Veselinović (Serbia), M. Zdujić (Serbia)

Local Executive Committee

Chairman: B. Adnadjević

Vice-chairman: S. Blagojević

Members: A. Abu Rabi-Stanković, P. Banković, N. Begović, J. Dostanić, A. Đerić, A. Ignjatović, A. Ivanović, A. Jović, D. Lončarević, J. Krstić, J. Maksimović, M. Milenković, S. Maćešić, V. Marković, B. Nedić, M. Petković, A. Popović-Bjelić, N. Potkonjak, D. Ranković, M. Stević, I. Stojković, M. Žunić

Honorary Committee

Nikola Hajdin,	President of Serbian Academy of Sciences and Arts
Branko Kovačević,	Rector of University of Belgrade
Radivoje Mitrović	Secretary of State for Education and Science
Vera Dondur	President of the Council for Scientific and Technological Development
Vladimir Bumbaširević	Dean of the Faculty of Medicine of University of Belgrade
Paula Putanov,	Member of Serbian Academy of Sciences and Arts
Momčilo Ristić,	Member of Serbian Academy of Sciences and Arts
Ankica Antić Jovanović,	Honorary President of Society of Physical Chemists of Serbia

POLY(URETHANE-SILOXANE) NETWORKS BASED ON HYPERBRANCHED POLYESTER: MECHANICAL AND THERMAL PROPERTIES

M. V. Pergal¹, J. V. Džunuzović¹, R. Poręba², M. Špírková²

¹*ICTM-Center of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia,* ²*Institute of Macromolecular Chemistry AS CR, v.v.i., Nanostructured Polymers and Composites Department, Heyrovského nam. 2, 16206 Praha 6, Czech Republic*

Abstract

Mechanical and thermal properties, hardness as well as degree of microphase separation of novel poly(urethane-siloxane) networks based on hyperbranched polyester of the fourth pseudo generation were investigated using a variety of experimental methods. According to the combined results obtained from DSC and DMTA experiments, these networks exhibit two glass transition temperatures, of the soft and hard segments, and one secondary relaxation process. The results showed increase of crosslinking density and microphase separation and improvement of mechanical properties with decreasing content of soft ethylene oxide-poly(dimethylsiloxane)-ethylene oxide segment.

Introduction

Polyurethanes (PUs) are considered as one of the most useful class of polymers in coating applications. Contrary to other polymers, PUs have the advantage of using many available reactants as well as superior elastomeric properties. The careful design of PU structure is crucial to obtain good mechanical properties and adhesive strength of the coatings [1]. Macrodiol can play an important role to improve these properties. Poly(dimethylsiloxane) (PDMS) is attractive due to several advantages such as low surface tension, unique flexibility, low glass transition temperature, high thermal stability and good water resistivity. In the last few years, the PDMS has been used in PUs synthesis to improve the properties such as thermal stability, adhesive strength, shape memory properties and water resistance. Recently PU with PDMS has been proposed as a component of marine coating due to its smooth surface, to protect the coating from the fouler attachment. Due to the low surface energy of the PDMS, the PU coating is enriched by Si and makes the surface very smooth. The use of hyperbranched polyester (HBP) as crosslinker for the synthesis of PUs based on PDMS leads to the formation of networks with good chemical resistance and thermal properties [2].

In this work, mechanical and thermal properties, as well as hardness of PU networks based on aliphatic Boltorn[®] hyperbranched polyester of the fourth pseudo generation were investigated using DSC, DMTA, and hardness measurements.

Experimental

The PU networks were synthesized by two-step polymerization in solution (NMP/THF) using α,ω -dihydroxy-(ethylene oxide-poly(dimethylsiloxane)-ethylene oxide) (EO-PDMS-EO, ABCR), 4,4'-methylenediphenyl diisocyanate (MDI, Aldrich) and hyperbranched aliphatic polyester of the fourth pseudo generation with average hydroxyl functionality of 23 (BH-40, Perstorp Specialty Chemicals AB) [2]. The soft EO-PDMS-EO content was varied from 15 to 40 wt.%. In samples with digit numbers, the number shows the EO-PDMS-EO weight content.

Dynamic mechanical thermal analysis (DMTA) of samples was carried out on ARES G2 Rheometer (TA Instruments) in the temperature range from -135 to 180 °C, at strain 0.1 %. Differential scanning calorimetry (DSC) was performed on DSC Q1000V9.0 Build 275 thermal analyzer in the temperature range from -90 to 200 °C, at a heating rate of 10 °C/min. The hardness measurements of the PU films were performed on a Shore A apparatus (Hildebrand, Germany).

Results and Discussion

The influence of soft segment content on the viscoelastic properties of the polyurethane networks was investigated by dynamic mechanical thermal analysis of selected samples. Three peaks can be observed in the temperature dependence of G'' (Fig. 1), indicating existence of microphase separation of PUs.

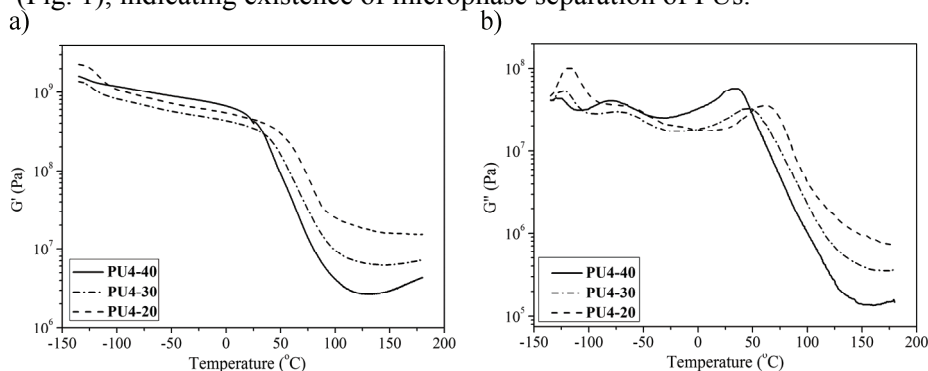


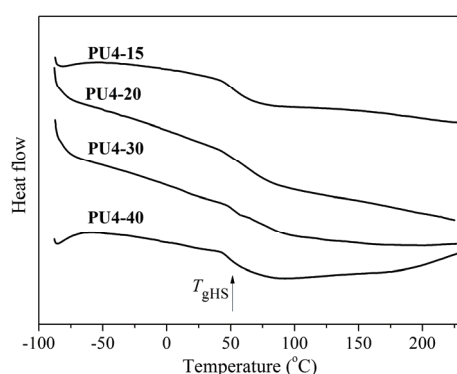
Figure 1. Storage (G') and loss (G'') moduli of the PUs vs. temperature at 1 Hz and a heating rate of 3 °C/min.

From the Fig. 1 it can be observed that all investigated PUs show T_g of the soft EO-PDMS-EO segment, T_{gSS} , in the temperature range between -126 and -118 °C, due to the well phase separation of PDMS. Peak observed in the region between -80 and -67 °C is associated with the subglass relaxation process and is probably a consequence of the movement of the part of the chain which contains urethane groups connected to the Boltorn[®] HBP (BH-40). The third peak detected in the region between 35 and 61°C is ascribed to the glass transition temperature of the hard segments (MDI-HBP), T_{gHS} , (Table 1). From DMTA results, value of G' for PU samples is higher than values of the loss modulus in the whole investigated temperature region. This observation indicates that cohesion and stability of the PU network is not destroyed under investigated experimental conditions.

Table 1. Results of DSC, DMTA and hardness of PU networks

Sample	G''			$\nu \times 10^4$ (mol/cm ³)	T_{gHS} (DSC) (°C)	Hardness (Shore A)
	T_{gSS} (°C)	T_2 (°C)	T_{gHS} (°C)			
PU4-40	-126	-80	35	9.08	49	94
PU4-30	-124	-72	47	18.48	54	96
PU4-20	-118	-67	61	44.40	56	98

Values of the crosslinking density, ν can be easily calculated from the rubbery plateau moduli and are summarized in Table 1. Crosslinking density of the synthesized PUs decreases with increasing soft EO-PDMS-EO content. The increase of the crosslinking density increased hardness of PUs from 94 to 98 Shore A (Table 1), which is in agreement with DMTA results.

**Figure 2.** DSC thermograms (second run) of the selected synthesized PUs.

Thermal properties of the synthesized PUs were also examined by DSC (Fig. 2). A T_g of synthesized PUs decreases with increasing EO-PDMS-EO content from 56 to 49 °C (Table 1). Higher T_g of PUs is attributed to increased hydrogen bonding and crosslinking density of samples.

Conclusions

DMTA results revealed existence of microphase separation of PUs due to presence of EO-PDMS-EO. Two thermal transitions were detected by DMTA and they depend on the soft segment content. The first one (at -126 to -118 °C), corresponds to the glass transition of soft segments. The second transition, located at 35 to 61 °C, well detectable by DSC and DMTA, corresponds to the glass transition of hard segments. The second relaxation peak is located in the temperature region -80 to -67 °C. The results showed that the decrease of EO-PDMS-EO content enhanced microphase separation, improved mechanical properties and hardness of PUs.

Acknowledgments

This work was financially supported by the Ministry of Education and Science of the Republic of Serbia (No. 172062) and the Grant Agency of the Czech Republic (No. P108/10/0195).

References

- [3] E. Žagar, M. Žigon, Prog. Polym. Sci, 2011, 39, 53-88.
- [4] M. V. Pergal, J. V. Džunuzović, M. Kićanović, V. Vodnik, M. M. Pergal, S. Jovanović, Russ. J. Phys. Chem. A, 2011, 85, 2251-2256.