



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

CONTENTS

Volume 1

Organizers	V
Committees	VI
Sponsors	VIII
Professor Ivan Draganić	IX
Plenary lectures	1
Chemical Thermodynamics	35
Spectroscopy, Molecular Structure, Physical Chemistry of Plasma	65
Kinetics, Catalysis	137
Nonlinear Dynamics	225
Electrochemistry	301
Biophysical Chemistry, Photochemistry, Radiation Chemistry	337
Radiochemistry, Nuclear Chemistry	
Material Science	415

Volume II

Solid State Physical Chemistry	505
Macromolecular Physical Chemistry	515
Environmental Protection	
Forensic Sciences Pharmaceutical Physical Chemistry	557
Phase Boundaries	667
Complex Compounds	681
General Physical Chemistry	707
Geophysical Chemistry	719
Education, History	731
Food Physical Chemistry	743
Free Topic	783
Index	791

J-06-P

POLY(URETHANE-ESTER-SILOXANE) NETWORKS

J. V. Džunuzović¹, M. V. Pergal¹, V. V. Vodnik²

¹*ICTM-Center of Chemistry, University of Belgrade, Studentski trg 12-16, 11000
Belgrade, Serbia*

²*Institute of Nuclear Science "Vinča", University of Belgrade, P. O. Box 522,
11001 Belgrade, Serbia*

Abstract

The waterproof performance and formation of hydrogen bonds in polyurethane (PU) networks based on Boltorn[®] hyperbranched polyester of the third pseudo generation (BH-30), α,ω -dihydroxy-(ethylene oxide-poly(dimethylsiloxane)-ethylene oxide) (EO-PDMS-EO) and 4,4'-methylenediphenyl diisocyanate (MDI) were studied in this work. Obtained results revealed that as the content of EO-PDMS-EO decreases, the degree of microphase separation increases, while the water resistance of the prepared PU networks decreases.

Introduction

The application of hyperbranched polyesters (HBP) or PDMS macrodiols for the preparation of polyurethanes has gained great attention over the last years, since these polymers have properties which can be applied to improve and modify performances of PUs for specific applications [1,2]. Besides, it has been shown that the combination of both, PDMS macrodiol and HBP, can also be used for the synthesis of PU networks [3]. Such networks are good candidates for coating applications, because numerous end functional groups in HBP provide fast curing and formation of highly crosslinked system with good mechanical properties, while the presence of PDMS improves thermal and surface properties and brings elasticity in such material, due to its low glass transition temperature. The aim of the present work is the investigation of the influence of EO-PDMS-EO content on the water resistance and the extent of hydrogen bonding in the polyurethane networks synthesized using Boltorn[®] hyperbranched polyester of the third pseudo generation, EO-PDMS-EO and MDI.

Experimental

PUs based on BH-30, EO-PDMS-EO and MDI were synthesized according to the procedure described elsewhere [3]. The last two numbers in the name of PUs represent EO-PDMS-EO content. FTIR spectra of the synthesized PUs were recorded using ATR NICOLET 380 FTIR spectrometer. Water absorption of the synthesized PUs was determined at room temperature by their immersion for 48 h in distilled water. The water contact angles of the synthesized PUs were determined on Krüss DSA100 instrument, using the sessile drop method, at 22 °C.

Results and Discussion

The chemical structure of PUs was examined by FTIR spectroscopy. In the FTIR spectra of PUs (Figure 1a) absorption bands characteristic for the amide II and

amide III vibrations (1258 cm^{-1} and 1537 cm^{-1}), overlapped bands of Si-O-Si and C-O-C groups (1015 and 1080 cm^{-1}), Si-CH₃ linkage (790 cm^{-1}), symmetric and asymmetric -CH₂- and -CH₃ (2961 , 2903 and 2875 cm^{-1}), aromatic C=C (1596 and 1412 cm^{-1}) and H-bonded -NH stretching vibration (3306 cm^{-1}) are visible. The formation of urethane bonds was confirmed from the absence of isocyanate peak at 2260 cm^{-1} .

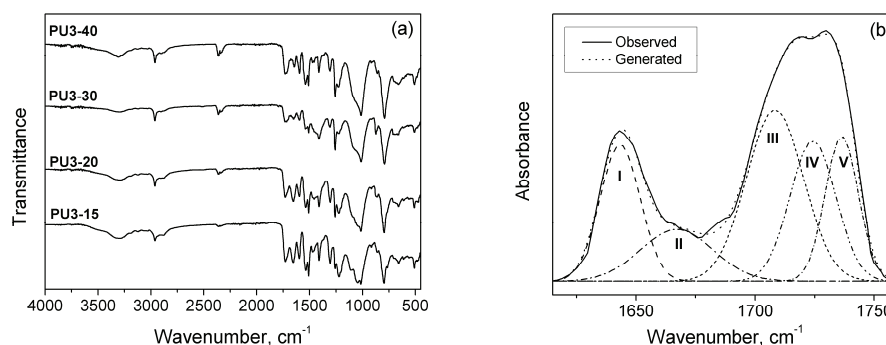


Figure 1. (a) FTIR spectra of PUs and (b) curve-fitting FTIR spectra of PU3-40.

Table 1. Curve fitting results of the C=O stretching regions from the PUs FTIR spectra.

Sample	Area I (CO _{ester-H} bonding) ₂ %	Area II (CO _{order urethane-H} bonding) ₂ %	Area III (CO _{disorder urethane-H} bonding) ₂ %	Area IV (CO _{free} ester) ₂ %	Area V (CO _{free} urethane) ₂ %
PU3-40	16.7	14.2	31.3	22.3	15.5
PU3-30	19.7	17.2	25.9	22.2	15.0
PU3-20	21.5	38.4	10.1	16.8	13.2

To investigate the extent of hydrogen bonding in the synthesized PUs and to obtain individual spectral bands and areas in the overlapping spectra of C=O region, the Gaussian deconvolution method (OriginPro 8) was applied. The absorbance region of the C=O groups of PU3-40 is given in Figure 1b, while curve fitting results for selected PUs are listed in Table 1. Five absorbance peaks were observed in the C=O region corresponding to the: H-bonded C=O groups from ester bonds (1645 cm^{-1}), H-bonded urethane C=O groups in ordered hard domains (1680 cm^{-1}), H-bonded urethane C=O groups in disordered domains (1710 cm^{-1}), free C=O groups from ester bonds (1725 cm^{-1}) and free urethane C=O groups (1735 cm^{-1}) [4]. As the content of EO-PDMS-EO decreases, the possibility for H-bonding between urethane groups and H-bonding between urethane and ester carbonyl groups generally increases, while the fraction of H-bonding between -NH urethane and ether oxygen from EO-PDMS-EO, free ester and free urethane C=O decreases. It can be concluded that ordering of the hard segment domains, i.e. the tendency of H-bonds formation between hard segments is more pronounced in samples with lower EO-PDMS-EO content, resulting in higher degree of microphase separation.

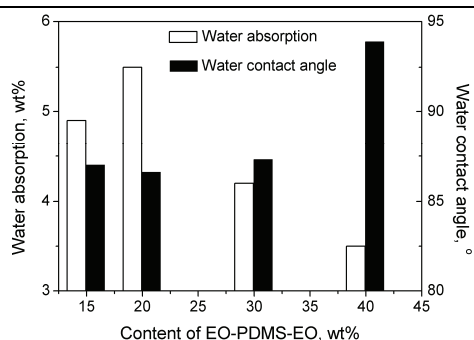


Figure 2. Values of the water absorption and water contact angles of the PU networks.

The waterproof performance of the PU networks was investigated by measuring their water absorption and water contact angle and obtained results are given in Figure 2. The weight percent of the water absorption decreases while the water contact angle increases as the EO-PDMS-EO content increases, due to the hydrophobic character of PDMS and possible migration of the EO-PDMS-EO to the surface of PUs.

Conclusions

The presented results revealed that the tendency of H-bonds formation between hard segments in prepared PU networks decreases with increasing EO-PDMS-EO content. The increase of EO-PDMS-EO content also induced better water resistance of PUs.

Acknowledgments

This work was financially supported by the Ministry of Education and Science of the Republic of Serbia (Project No. 172062).

References

- [1] P. K. Maji, A. K. Bhowmick, *J. Polym. Sci. Part A Polym. Chem.*, 2009, 47, 731-745.
- [2] R. Hernandez, J. Weksler, A. Padsalgikar, J. Runt, *Macromolecules*, 2007, 40, 5441-5449.
- [3] J. V. Džunuzović, M. V. Pergal, S. Jovanović, V. V. Vodnik, *Hem. Ind.*, 2011, 65, 634-644.
- [4] Z. S. Petrović, J. Ferguson, *Prog. Polym. Sci.*, 1991, 16, 695-836.

CIP Volime II

CIP - Каталогизacija у публикацији
Народна библиотека Србије, Београд

544(082)

621.35(082)

66.017/.018(082)

MEĐUNARODNA konferencija iz fundamentalne i
primenjene fizičke hemije (11 ; 2012 ;
Beograd)

Physical Chemistry 2012 : proceedings.
#Vol. #2 / 11th International Conference on
Fundamental and Applied Aspects of Physical
Chemistry, September 24-28, 2012, Belgrade ;
[editors S.[Slobodan] Anić and Ž.[Željko]
Čupić ; organized by Society of Physical
Chemists of Serbia ... et al.]. - Belgrade :
Society of Physical Chemists of Serbia, 2012
(Belgrade : Jovan). - VI str., 499-782 str. :
ilustr. ; 24 cm

"The Conference is dedicated to Professor
Ivan Draganić" --> nasl. str. - Tiraž 200. -
Bibliografija uz svaki rad. - Registar.

ISBN 978-86-82475-28-6

1. Društvo fizikohemičara Srbije (Beograd)

a) Физичка хемија - Зборници b)

Електрохемијско инжењерство - Зборници c)

Наука о материјалима - Зборници

COBISS.SR-ID 193433356