

dye-doped polyurethane resins



Tamara Bezrodna¹, Vira Nesprava¹, Oleksandr Roshchin¹, Oksana Antonenko², Lyudmila Kosyanchuk², Tetiana Gavrilko^{*1,3}, Jan Baran³, and Marek Drozd³

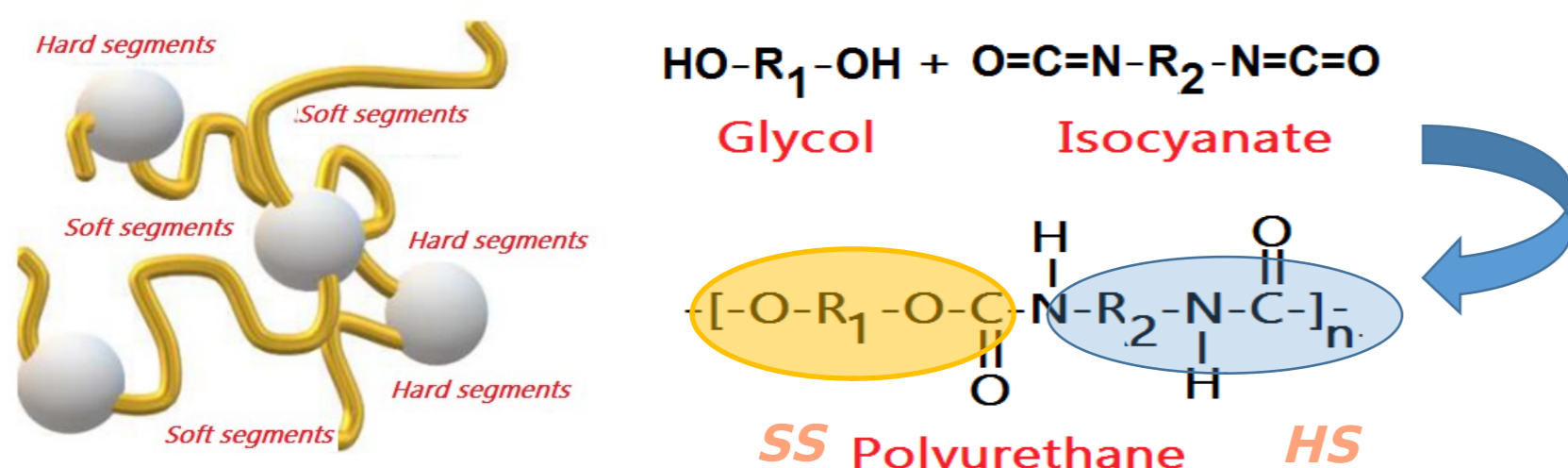
¹Institute of Physics NASU, 46 Nauki Ave., 03680 Kyiv, Ukraine; ²Institute of Macromolecular Chemistry NASU, 48 Kharkivske Ave., 02160 Kyiv, Ukraine; ³Institute of Low Temperatures and Structure Research PAN, 2 Okolna Str., 50-422 Wroclaw, Poland
*Corresponding author: gavrilko@gmail.com

INTRODUCTION

Polyurethanes are extremely versatile polymers widely used in medicine, electronics, and the automotive and food packaging industries. They are produced of a wide range of organic units that allows controllable modification of their properties. Due to their homogeneity and high optical transparency they are recently intensively studied as dye-doped media for the development of tunable solid-state dye lasers [1-2]. Polyurethane-based solid state dye laser elements must withstand high temperatures and be resistant to dynamic heat build-up under laser irradiation. The dyes for doping the polymer matrices are selected by their PL emission wavelength, PL quantum yield and photo-stability. The dyes are known to affect the polymer matrix [3-4], in particular, its mechanical properties and thermal stability, however, there are no detailed analysis on this matter in the literature so far.

MATERIALS AND METHODS

Polyurethanes are segmental macro-molecular chains that contain hard segments (HS) formed of isocyanates with chain extenders, and soft segments (SS) comprising polyols.

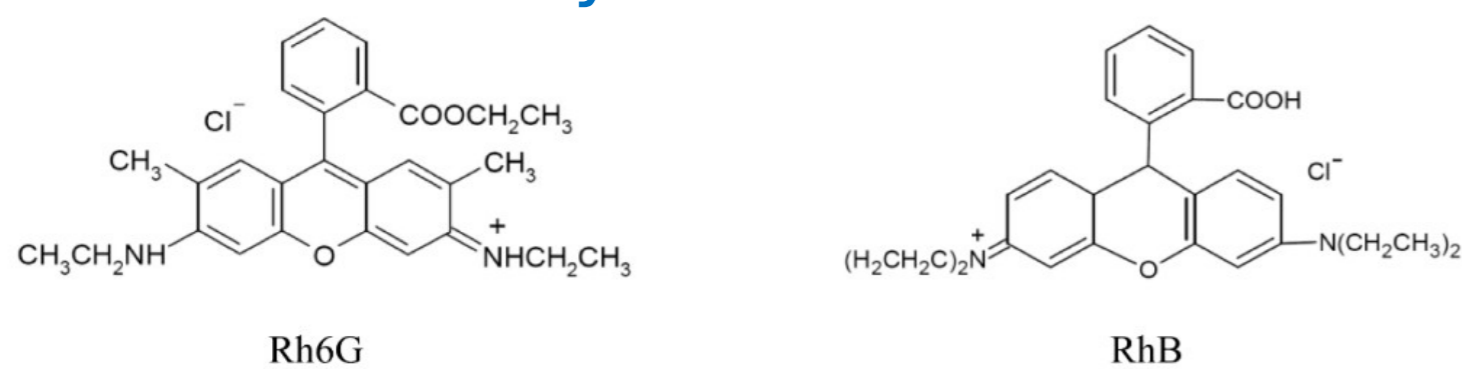


Polyurethanes under study

Two polyurethanes intended for use as a gain media in solid-state dye laser were employed:

- aliphatic polyurethane (PU)** synthesized by a two-stage polymerization process of toluene diisocyanate and poly-oxypropylene glycol hardened by trimethylol propane,
- polyurethane acrylate (PUA)** obtained by radical photo-polymerization of oligourethane acrylate and benzoin isobutyl ester.

Dyes used



Two cationic xanthene-type dyes, rhodamine 6G (Rh6G) and rhodamine B (RhB), differing by their reactivity, were used. The dye molecules association decreases the PL emission, which results in deterioration of lasing characteristics of the dye laser. Dye-polymer covalent bonding of RhB via COOH group is useful for that end, since it prevents the dye migration and molecular aggregation in the polymer matrix.

Experimental methods

A thermogravimetric study (TGA) in the temperature range 293 – 700°C was performed using Perkin Elmer TGA 4000 with a sensitivity of 0.1 µg at a heating rate of 10°C/min. The decomposition temperatures were defined using the corresponding peak position of the derivative thermogravimetric (DTG) curve. Molecular structure and interactions in the title compounds were studied with IR spectroscopy. IR absorption spectra were acquired using Bruker IFS-88 FT-IR spectrometer equipped with Harrick diffuse reflectance attachment, with 4 cm⁻¹ spectral resolution and 64 scans accumulated for each spectrum measurement.

THERMAL PROPERTIES

The thermal stability has a large significance for the use of dye-doped PUs in lasers. For the first time, a detailed TGA/DTA analysis of PU and PUA elastomers is presented (Fig. 1). The thermogravimetric study can give information about the presence of water in the sample and different stages of decomposition of compound. For PU and PUA resins, there is a typical three-step decomposition process. The first step below 300°C is ascribed to the evaporation of water, the second step corresponds to the decomposition of hard segments, third step is related to soft segments (ether or ester bonds). Weight loss above 400 C is related to the dye decomposition and residuals outgassing.

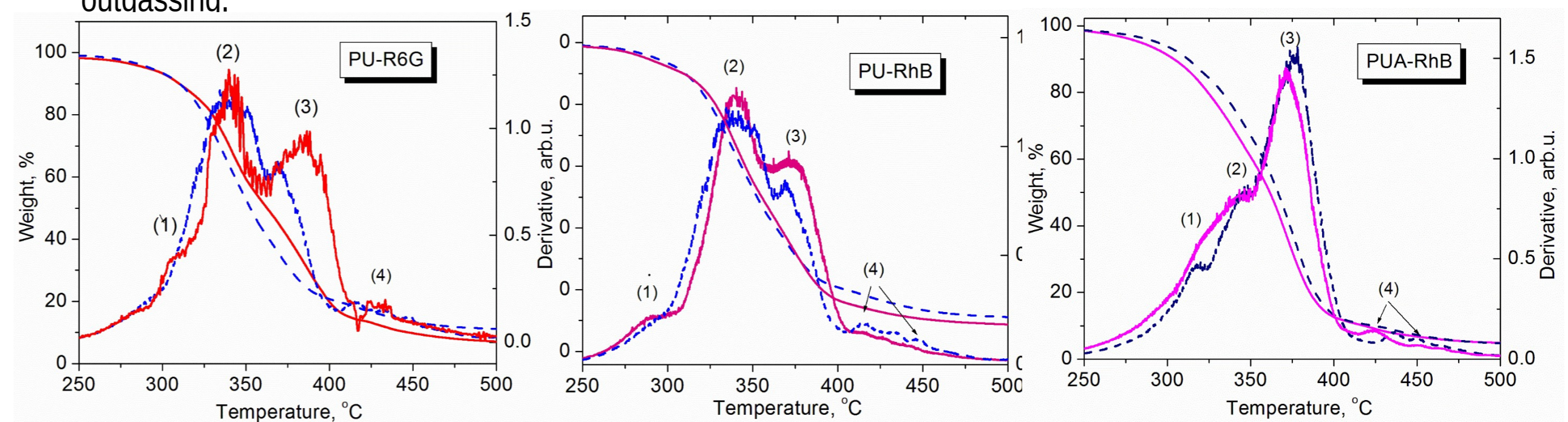


Fig. 1. TGA and DTA curves for un-doped (dash) and dye-doped (solid) PU (a,b) and PUA (c).

Sample name	Step 1		Step 2		Step 3		Step 4	
	Onset, T, °C	Weight loss, %	Onset, T, °C	Weight loss, %	Onset, T, °C	Weight loss, %	Onset, T, °C	Weight loss, %
PU	-	-	338.01	68.0163	395.14	4.3301	-	-
PU-RhB	254.52	4.8200	338.33	32.3503	370.54	20.3062	415	1.48
PU-R6G	301.2	1.94	341.4	46.69	399.4	36.1	429	1.2
PUA	-	-	377.57	73.9348	436.14	3.2659	438	0.8
PUA-RhB	-	-	371.39	78.8045	401.60	3.8683	426	1.4

It is found that a small presence of the dye molecules significantly improves the PU thermal stability (by 30-35 degrees), the effect being much smaller for PUA. This suggests that in PU the guest dye molecules are acting as a binding agent between soft- and hard-segments thus increasing the PU thermal stability.

FT-IR spectroscopy

IR-spectra (Fig. 2) were used to study molecular interactions between the guest Rh6G or RhB dyes with PU. Broadening of the spectral bands in the region 1650-1800 cm⁻¹ (Fig. 2a) and a red shift of the absorption maxima in the region of 3200-3500 cm⁻¹ (Fig. 2b) after the incorporation of guest dye molecules suggests a rearrangement of soft and hard segments, redistribution of the hydrogen bond network, possible formation of new associates with various interaction energies, and also by the appearance of new OH-groups due to the dye-polymer interaction. The effect is more noticeable for RhB dye.

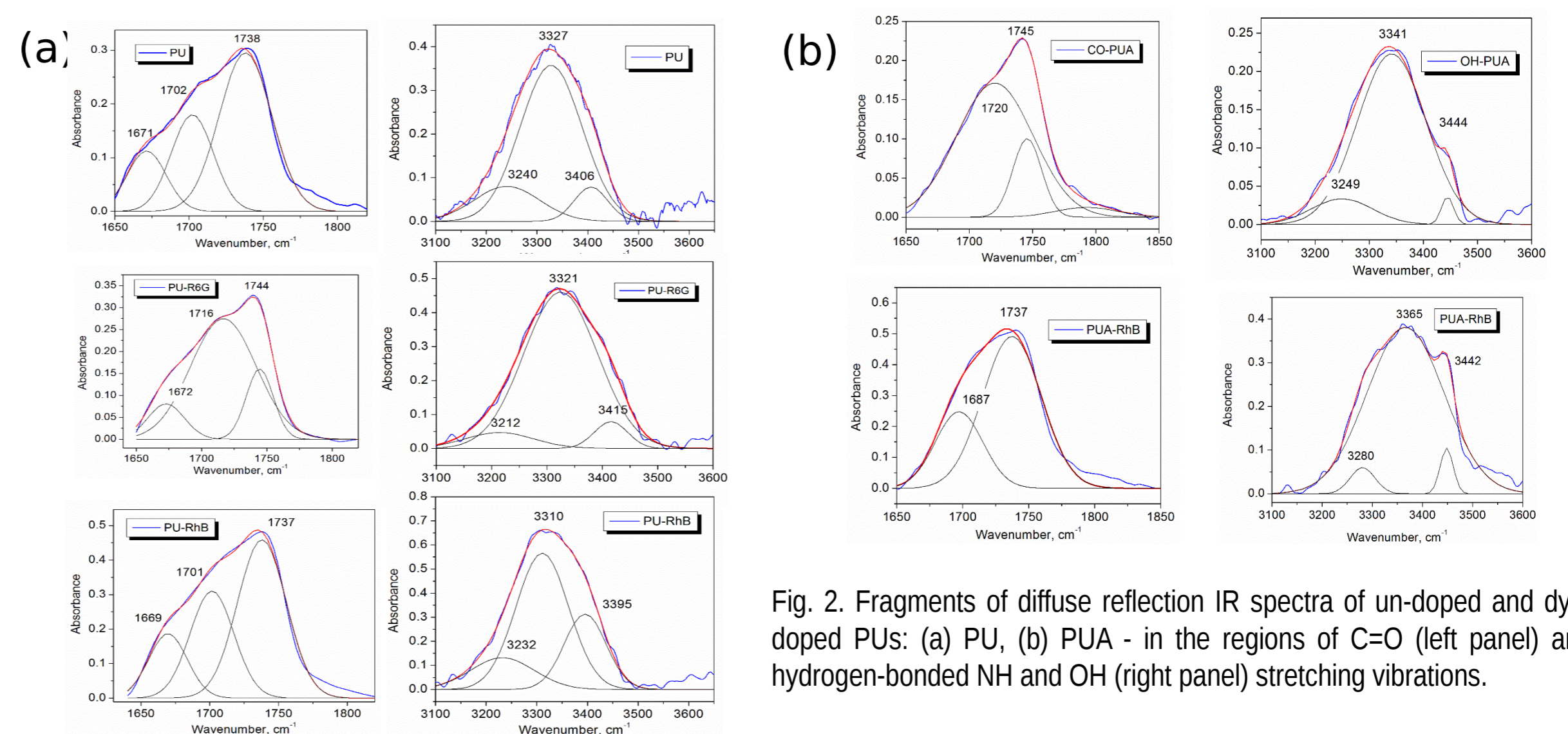


Fig. 2. Fragments of diffuse reflection IR spectra of un-doped and dye-doped PUs: (a) PU, (b) PUA - in the regions of C=O (left panel) and hydrogen-bonded NH and OH (right panel) stretching vibrations.

CONCLUSIONS

In this work, the thermal properties of polyurethane elastomers, aliphatic polyurethane (PU) and polyurethane acrylate (PUA), were studied for the first time using the detailed TGA/DTG/DSC measurements. The effect of two cationic xanthene-type dyes, rhodamine 6G (Rh6G) and rhodamine B (RhB) is demonstrated. The successful inclusion of RhB and R6G in the structure of polyurethane elastomers was confirmed by the FT-IR spectroscopy. Thermal gravimetric analysis indicated that the thermal stability of PU and PUA polyurethanes is maintained up to 338 and 378°C, respectively, where the major weight loss occurs. The introduction of RhB dye affects the polyurethane thermal properties more significantly than R6G due to effective incorporation between the polymer chains that results in redistribution of the hydrogen bond network, cross-linking and segregation of soft and hard segments, which is a crucial factor for radiation resistance of the polymers as laser active elements.

References

- V. I. Bezrodnyi, et al., *Funct. Mater.* 22 (2015) 212.
- L.F. Kosyanchuk et al., *Optical Materials* 85 (2018) 408-413.
- T. Bezrodna, V. Bezrodnyi, A. Negriyko, L. Kosyanchuk, *Optics & Laser Technology* 138 (2021) 106868.
- L. Kosyanchuk et al., *MOLECULAR CRYSTALS AND LIQUID CRYSTALS* 747 (2022) 120-130.

Acknowledgments

The authors acknowledge funding from the National Academy of Sciences of Ukraine under PAN-NASU joint research project for years 2022-2024 "Structural and spectral luminescence properties of organic compounds in nanoporous media". TG is highly grateful to Polish Academy of Sciences for the fellowship provided under the long-term program of support of the Ukrainian researchers at the Polish Academy of Sciences in collaboration with the U.S. National Academy of Sciences.