Novel photoredox catalysts based on anthracene derivatives for free radical and hybrid photosensitive resins for 3D printing technology

Magdalena Jankowska[1], Joanna Ortyl[1,2], Filip Petko[1,2], Andrzej Świeży[1,2], Paweł Niezgoda[1]

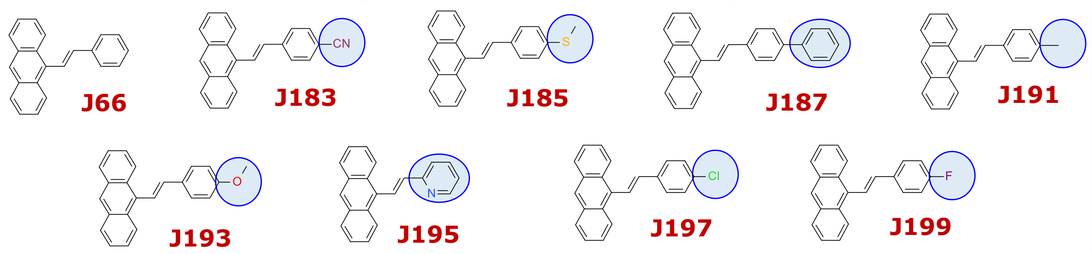
[1]*Cracow University of Technology, Faculty of Chemical Engineering and Technology, Laboratory of Photochemistry and Optical Spectroscopy, Warszawska 24, 31-155 Cracow, Poland*

[2]*Photo HiTech Ltd., Bobrzynskiego 14, 30-348 Cracow, Poland*

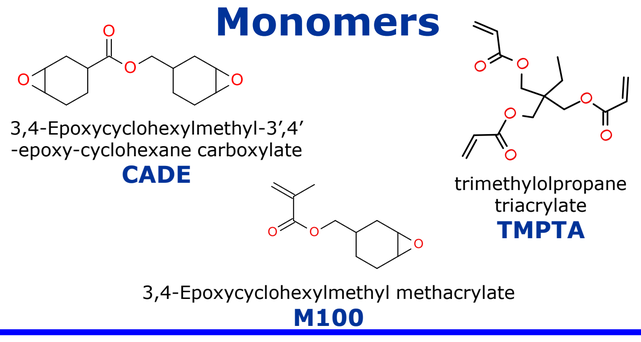
*jortyl@pk.edu.pl

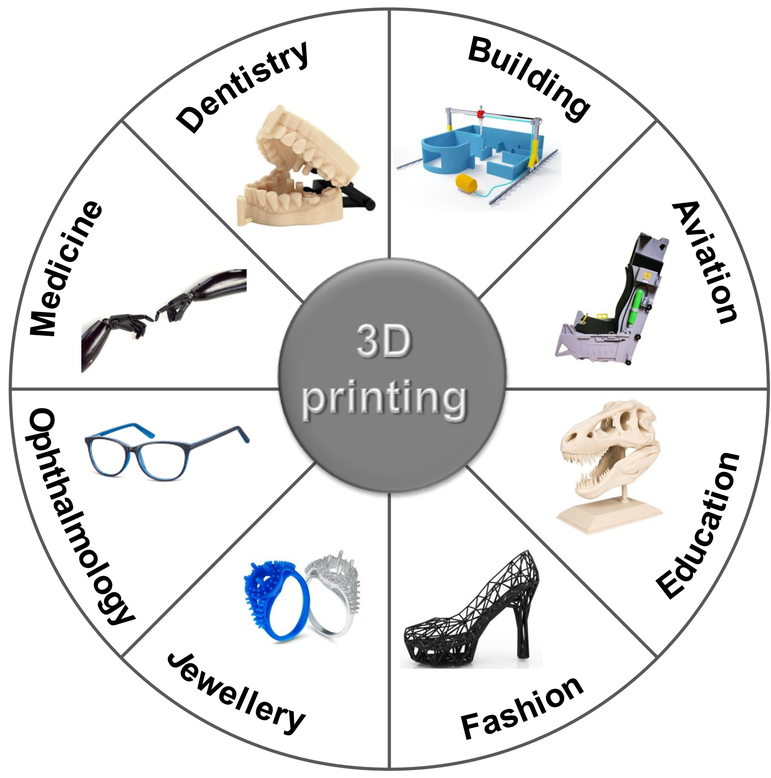
The photopolymerization is usually very fast, which is its basic advantage in practical applications, such as production of solvent-free polymer coatings applied on different products, such as furniture, car bodies, electronic components, as well as packaging materials for chemical and food industry. Photopolymerization speed and spatial resolution makes it the technique of choice in printing industry, for making prints on various surfaces, including plastics, which are difficult to print with traditional non-photocurable inks. In the industrial practice two types of photochemically initiated polymerization are most commonly used, namely radical and cationic photopolymerization. Each of them differs in terms of mechanism, and also type of monomers and initiators. The basis of widely used radical photopolymerization systems have been acrylate and methacrylate monomers, which polymerize in accordance with the radical mechanism. However, considerable disadvantage of radically polymerizing compounds is a common adverse phenomenon of oxygen inhibition, caused by the presence of atmospheric oxygen during the process of polymerization. In connection with the presence of oxygen inhibition in case of free-radical photopolymerization, much attention is currently paid to the development of the cationic photopolymerization technology. Cationic photopolymerization can be carried out in the air, which is its advantage over the free radical method. Furthermore, the cationic photopolymerization is a technique that may be used to polymerize important classes of monomers, which cannot be polymerized by free radical means, such as epoxides, vinyl ethers, propenyl ethers, siloxanes, oxetanes, cyclic acetals and formals, cyclic sulfides, lactones and lactams.

New photoredox catalysts



Monomers





Spectroscopic and electrochemical properties

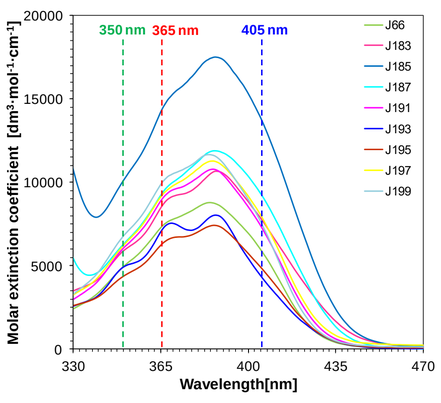


Fig.1. Absorption spectra of anthracene derivatives in acetonitryle.

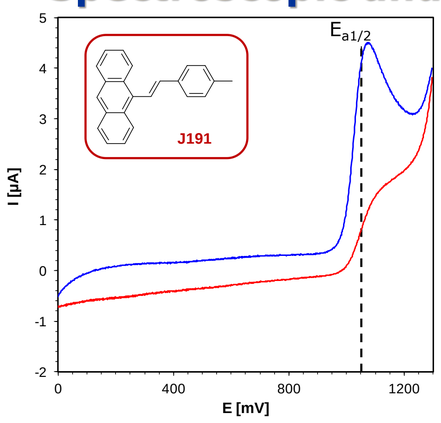


Fig.2. Cyclic voltammetry for oxidation process (CVox, vs. Ag/AgCl) experiments in ACN for J191.

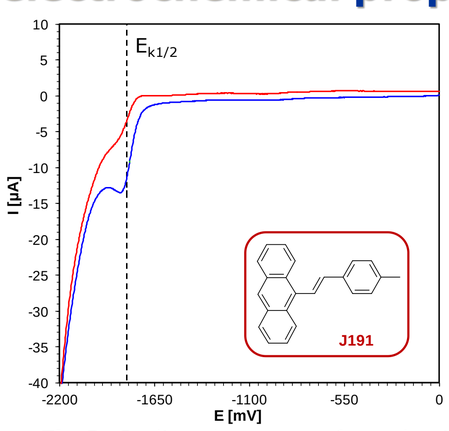


Fig.3. Cyclic voltammetry for reduction process (CVred, potential vs. Ag/AgCl) experiments in ACN for J191.

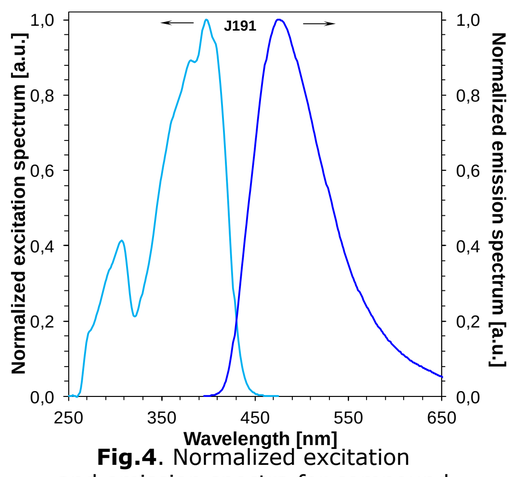


Fig.4. Normalized excitation and emission spectra for compound J191 in acetonitrile.

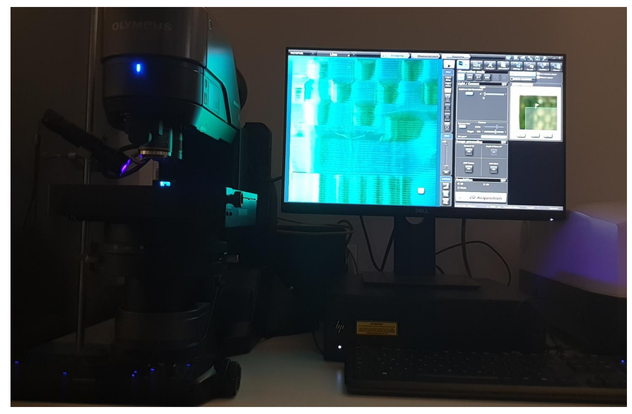


Photo 1. OLYMPUS DSX1000 Optical Microscope.

λ = 405 nm Radical photopolymerization

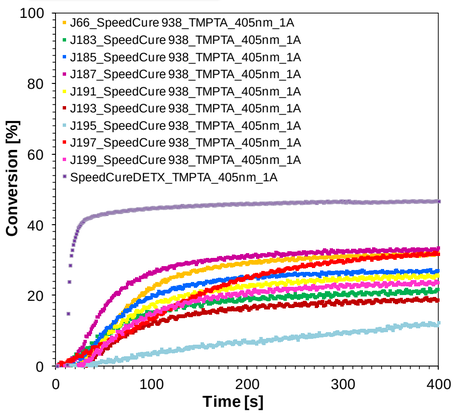


Fig.5. Kinetic profiles of radical polymerization of acrylate monomer (TMPTA) for bi-component photoinitiating system under light irradiation at 405 nm.

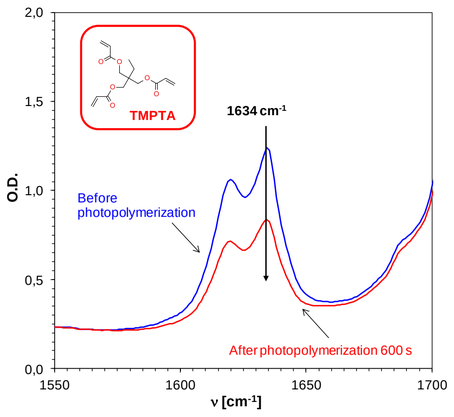


Fig.6. FT-IR spectra recorded before and after photopolymerization of TMPTA using SpeedCure 938 + J191 as photoinitiating system upon UV-LED λ_{max} = 405 nm irradiation.

λ = 405 nm Cationic photopolymerization

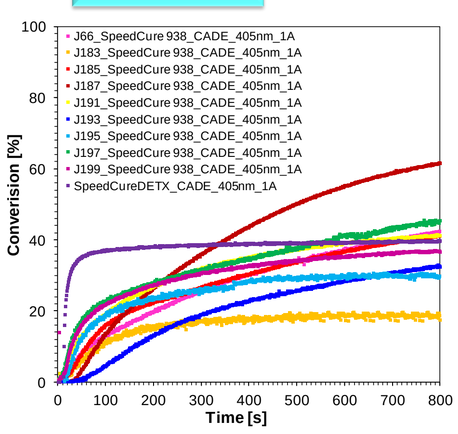


Fig.7. Kinetic profiles of cationnic polymerization of epoxy monomer (CADE) for bi-component photoinitiating system under light irradiation at 405 nm.

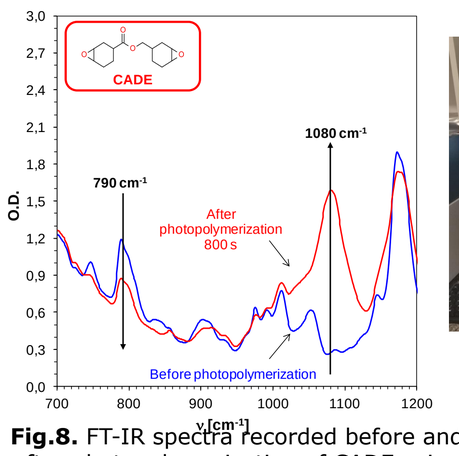
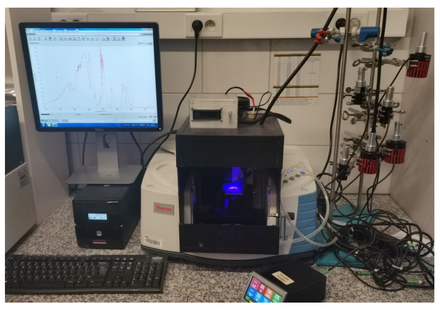


Fig.8. FT-IR spectra recorded before and after photopolymerization of CADE using SpeedCure 938 + J199 as photoinitiating system upon UV-LED λ_{max} = 405 nm irradiation.



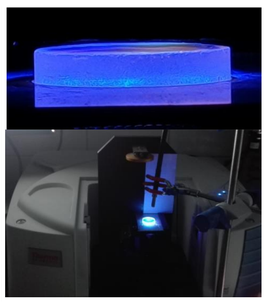


Photo 2. FT-IR Spectrophotometer (Thermo Scientific™ Nicolet™) with an attachment for kinetic measurements of photopolymerization processes with Real Time FT-IR software and samples during measurements on the BaF_2 pallet

Hybrid photopolymerization

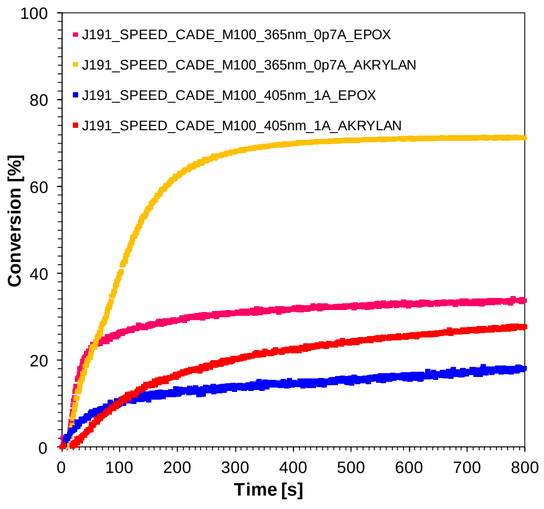


Fig.9. Kinetic profiles of hybrid polymerization of CADE and M100 monomers for bi-component photoinitiating system under light irradiation at 365 nm and 405 nm.

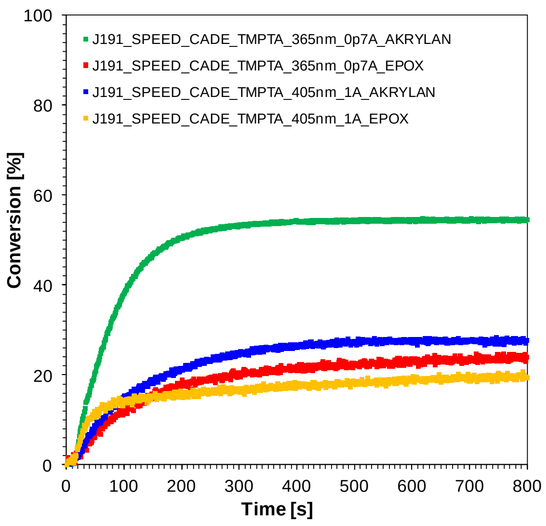


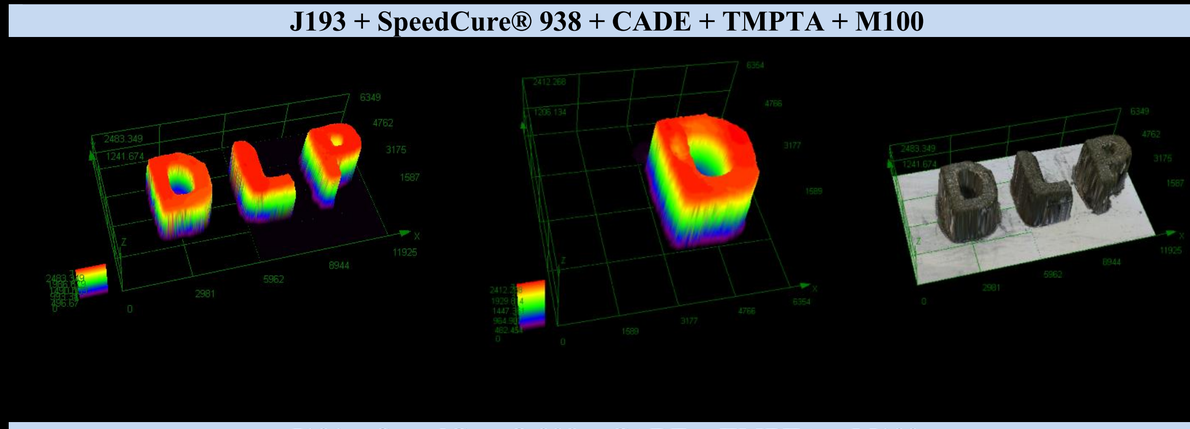
Fig.10. Kinetic profiles of hybrid polymerization of CADE and TMPTA monomers for bi-component photoinitiating system under light irradiation at 365 nm and 405 nm.

Acknowledgment

The authors are grateful to the Foundation for Polish Science (Warsaw, Poland) – **Project TEAM TECH** (Contract No. POIR.04.04.00-00-204B/16-00 – TEAM TECH/2016-2/15 – "Molecular design, synthesis and application of photoinitiator-catalysts (PICs) for photopolymerization reactions") for financial support of the research.

3D printing experiments

J193 + SpeedCure® 938 + CADE + TMPTA + M100



J191 + SpeedCure® 938 + CADE + TMPTA + M100

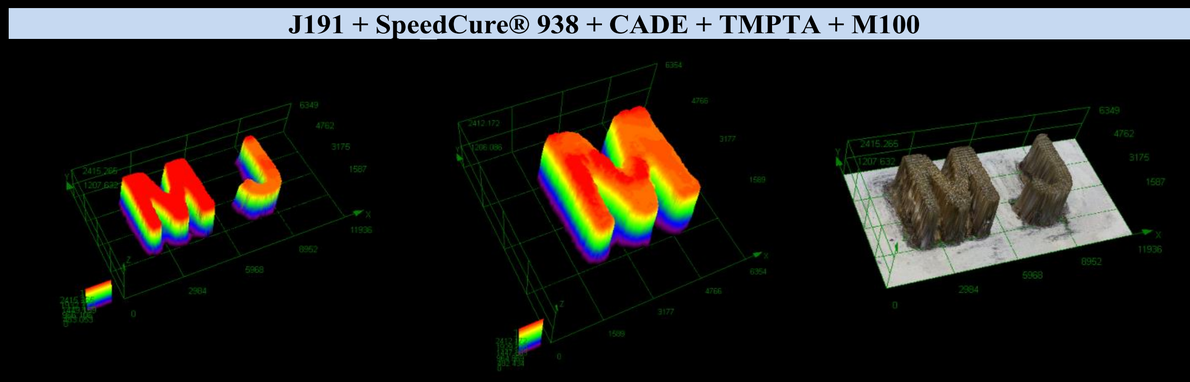


Photo 3. Printouts obtained from hybrid compositions.