

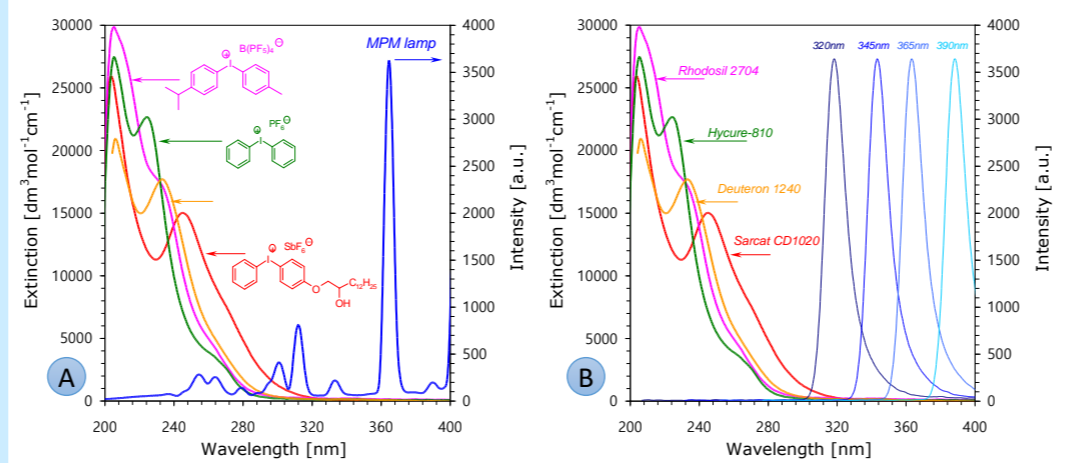
# Versatile photoinitiating systems for cationic, free radical and thiolene polymerization capable of efficient use in near UV and visible wavelengths and low light intensity

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The photopolymerization of monomers is gaining popularity as an environmentally friendly and safe method for production of the protective polymer coatings on various surfaces. The most important features of cationic polymerization are the efficiency and effectiveness of photoinitiators systems. Nowadays, all of the diaryliodonium and triarylsulfonium salts used in industry for cationic photopolymerization processes absorb UV light in the wavelength range 220-280 nm. This creates a problem, there are no efficient and simultaneously powerful UV light sources that would emit in that range. Medium pressure mercury lamps used as the UV sources emit most of the energy at the wavelength 365 nm, which is far from the absorption range of the commercial photoinitiators. Only a small fraction of energy is emitted at around 300 nm. Hence, the main problem is finding ways to shift the absorption range of the cationic polymerization photoinitiators towards 365 nm or to increase the efficiency of commercial photoinitiators by using appropriate photosensitizers. To-date derivatives of thioxanthone have been used most often for sensitization of commercial photo-initiators, but the thioxanthones cause yellowing of clear coatings. Moreover, a number of commercial photosensitizers suffer from various disadvantages, including toxicity and limited solubility in a wide variety of monomers. For these reasons, the development of novel photosensitizers is also a very important issue. **The subject of this invention is a set of new, highly efficient photoinitiating systems based on photosensitizers, for cationic, free-radical and hybrid photopolymerization processes.** The newly developed photoinitiating systems are an alternative method to increase the initiation efficiency of photopolymerization processes when medium pressure mercury lamps are used as the UV light sources or for used Vis-LEDs sources of light.



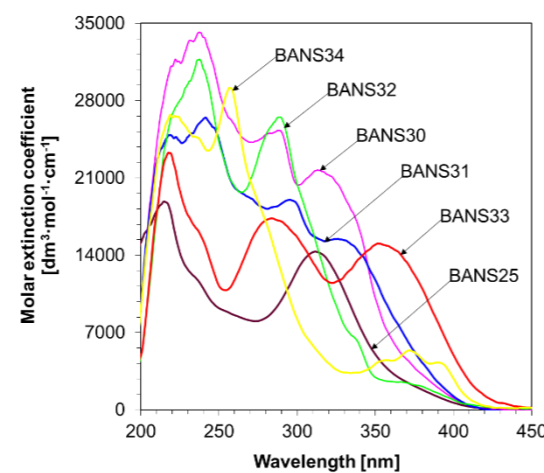
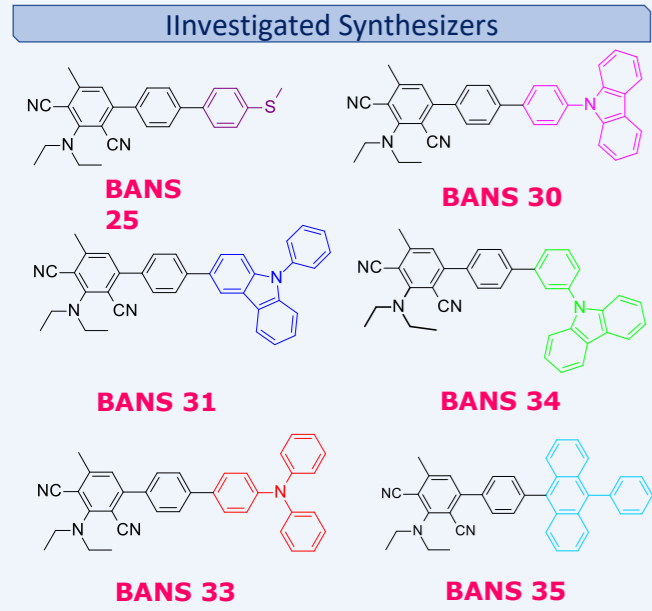
**Fig.1.** Comparison of the absorption characteristics of commercial iodonium photoinitiators with: **A-** the emission characteristics of industrial light sources (MPM lamp) and **B-** the emission characteristics of UV-LEDs.



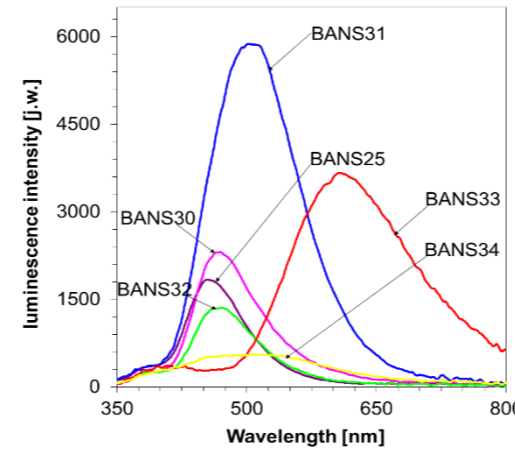
**Photo 1.** Fluorescence effect of derivatives 2-(diethylamino)-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile in acetonitrile at 320 nm wavelength

**Table 1.** Spectroscopic characteristics of 2-(diethylamino)-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile derivatives.

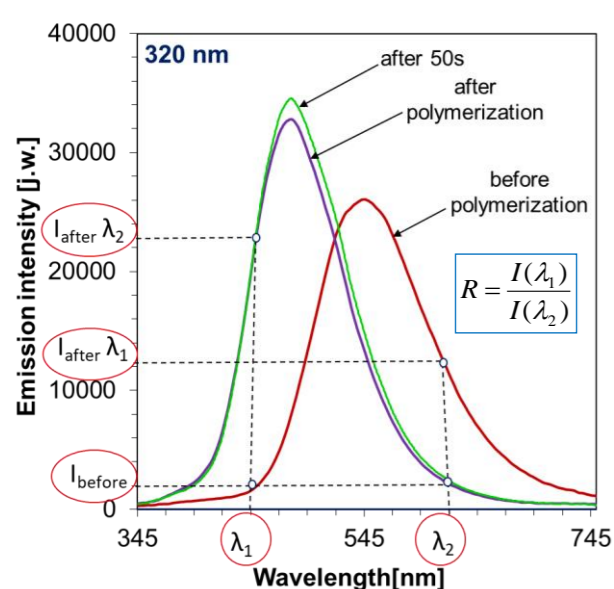
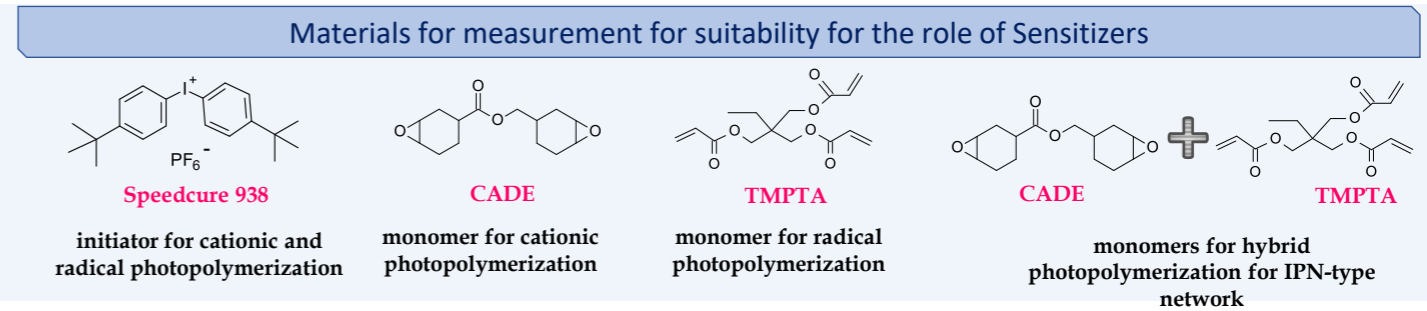
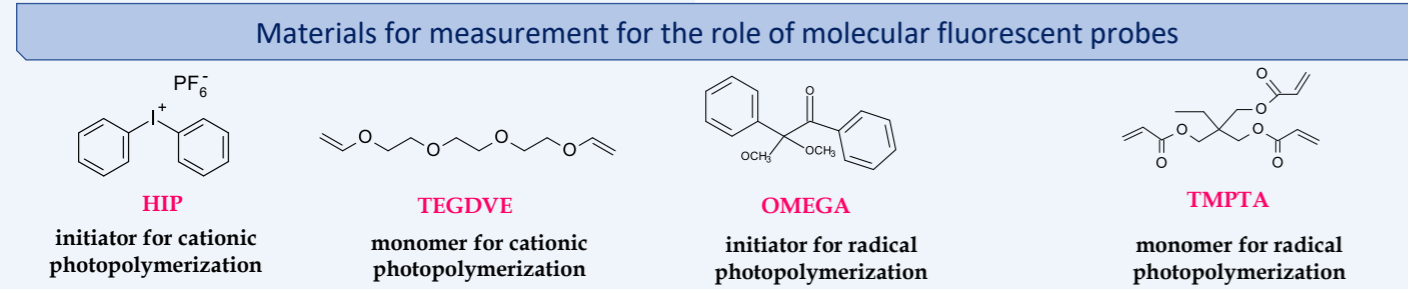
Acronym	$\epsilon$ @ $\lambda_{\text{max-ab}}$ [dm <sup>3</sup> ·mol <sup>-1</sup> ·cm <sup>-1</sup> ]	$\lambda_{\text{max-ab}}$ [nm]	$I_{\text{max-fluor}}$ ACN [nm]	$I_{\text{max-fluor}}$ ACN [j.w.]	Stokes shift [cm <sup>-1</sup> ]
			$\lambda_{\text{ex}}=320$ nm Integration time 1000 ms	$\lambda_{\text{ex}}=320$ nm Integration time 1000 ms	
<b>BANS25</b>	14339	311.5	454.8	1835	10115.0
<b>BANS30</b>	21726	313.3	469.5	2312	10619.0
<b>BANS31</b>	15490	326.3	502.0	5877	10726.3
<b>BANS32</b>	2574	360.0	471.3	1358	6559.9
<b>BANS33</b>	15070	351.7	607.4	3664	11969.7
<b>BANS34</b>	4282	389.8	508.8	555	6000.1



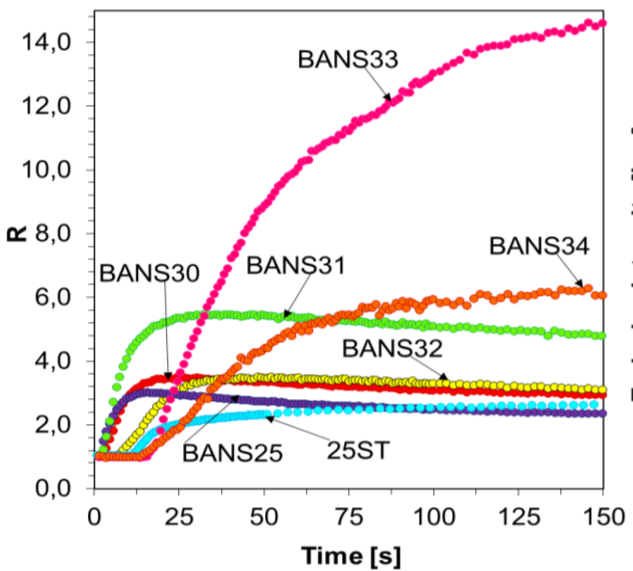
**Fig.2.** Absorption spectra for the 2-(diethylamino)-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile derivatives in acetonitrile.



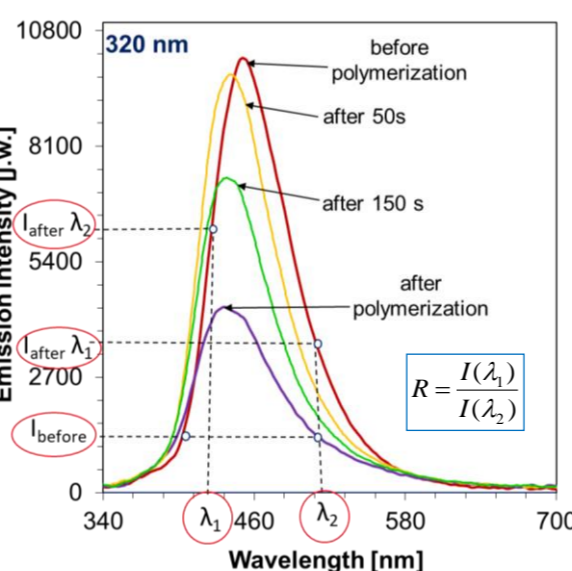
**Fig.3.** Fluorescence spectra of derivatives 2-(diethylamino)-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile in acetonitrile at 320 nm wavelength at the same time of integration.



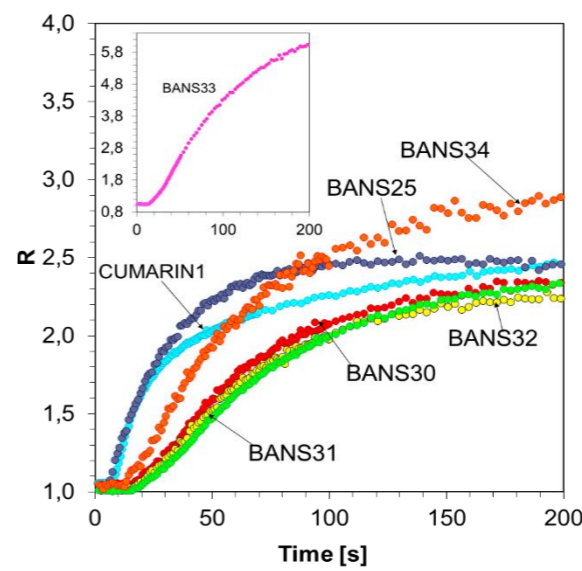
**Fig.4.** Changes in fluorescence intensity for probe BANS33 during cationic photopolymerization of triethylene glycol divinyl ether (TEGDVE).



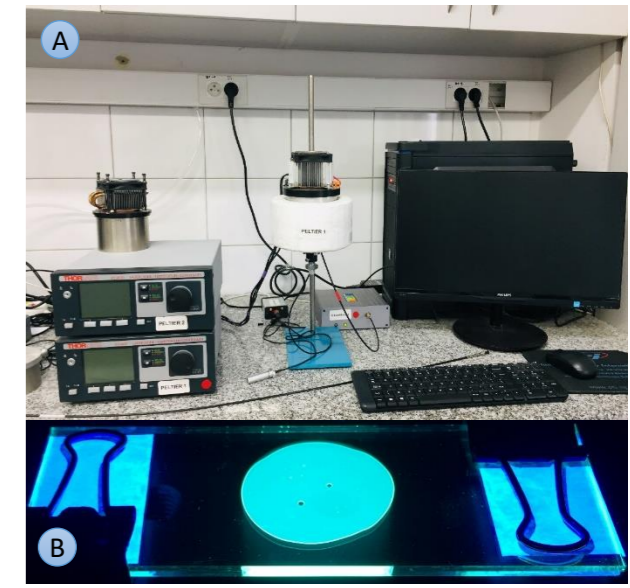
**Fig.5.** Monitoring of cationic photopolymerization of vinyl monomer (TEGDVE) by FPT method, using 320nm UV-LED as source of light.



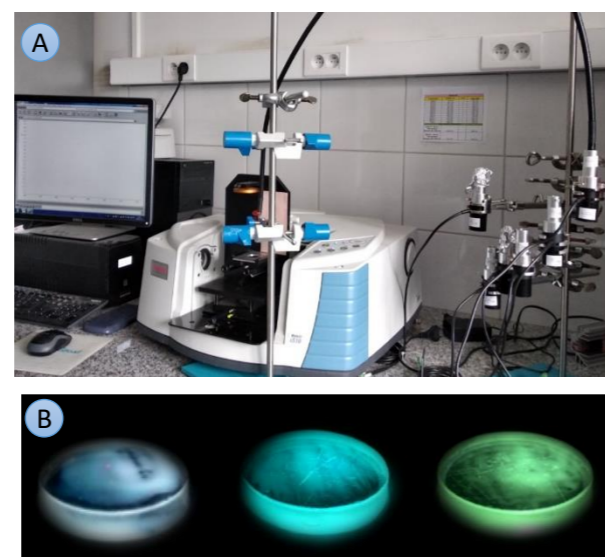
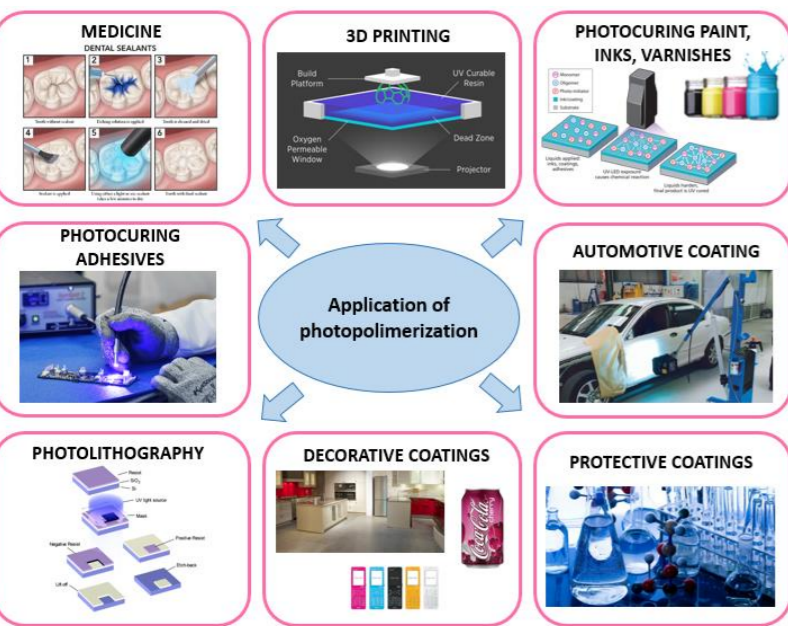
**Fig.6.** Changes in fluorescence intensity for probe BANS33 during radical photopolymerization of trimethylolpropane triacrylate (TMPTA) monomer.



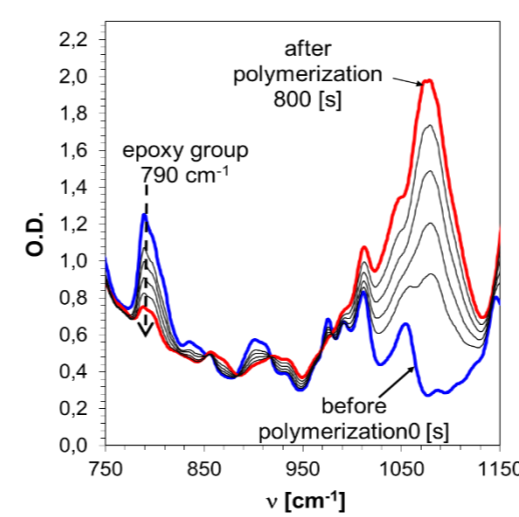
**Fig.7.** Monitoring of free-radical photopolymerization of TMPTA monomer by FPT method, using 320nm UV-LED as source of light.



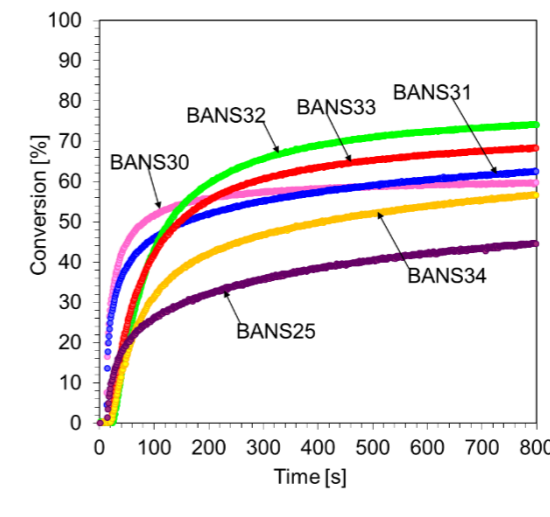
**Photo 2.** A) A stationary cure monitoring system for Fluorescence Probe Technology method was composed of a microcomputer-controlled miniature spectrometer, B) Sample during measurement.



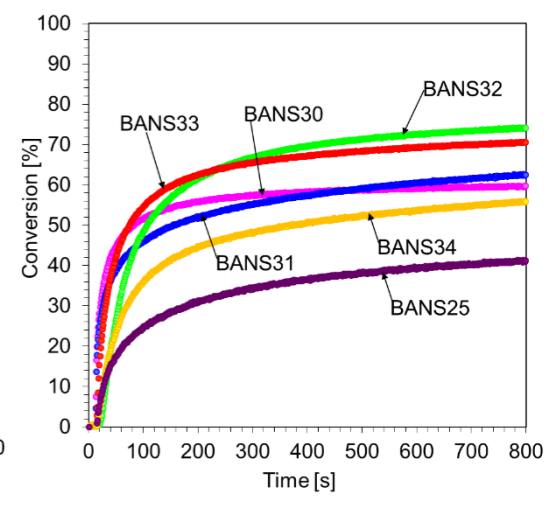
**Photo 3.** A) FT-IR Spectrophotometer (Thermo Scientific™ Nicolet™) with an attachment for kinetic measurements of photopolymerization processes with Real Time FT-IR software, B) Samples during measurement.



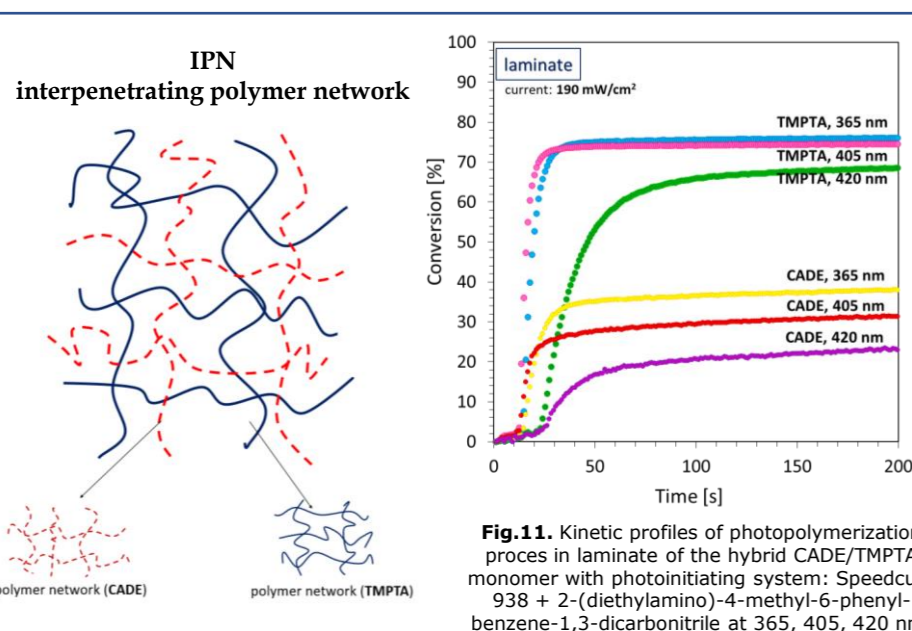
**Fig.8.** Changes in FT-IR spectrum for composition based on cationic monomer - CADE during photopolymerization with UV-LED 365 nm, using Speedcure 938 + 2-(diethylamino)-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile derivatives.



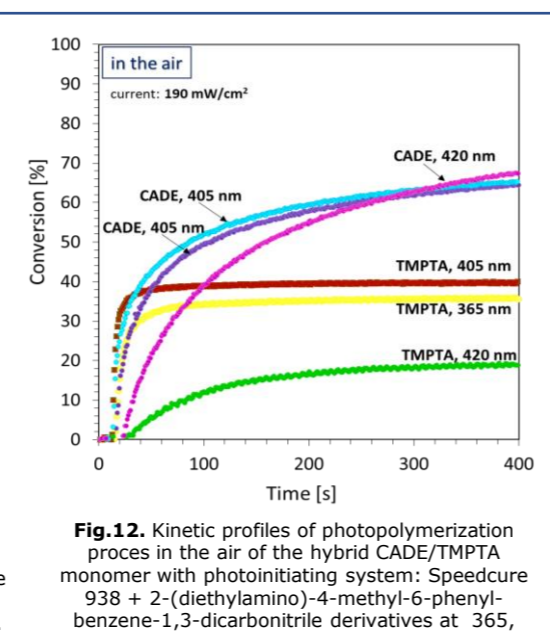
**Fig.9.** Kinetic profiles of photopolymerization process of the cationic monomer - CADE with photoinitiating system: Speedcure 938 + 2-(diethylamino)-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile derivatives at 365 nm.



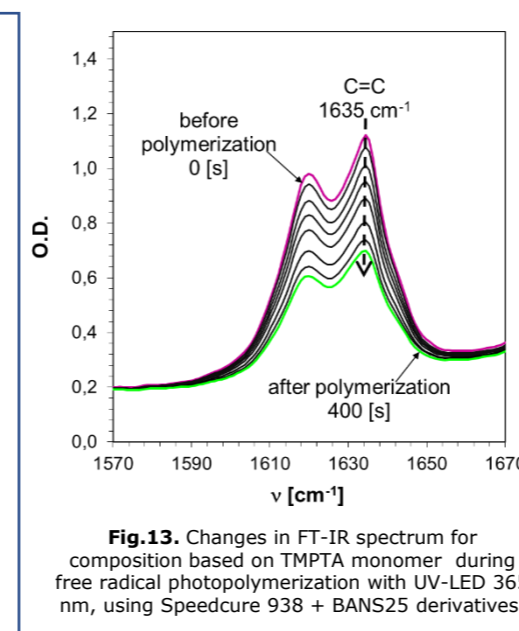
**Fig.10.** Kinetic profiles of photopolymerization process of the cationic monomer - CADE with photoinitiating system: Speedcure 938 + 2-(diethylamino)-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile derivatives at 405 nm.



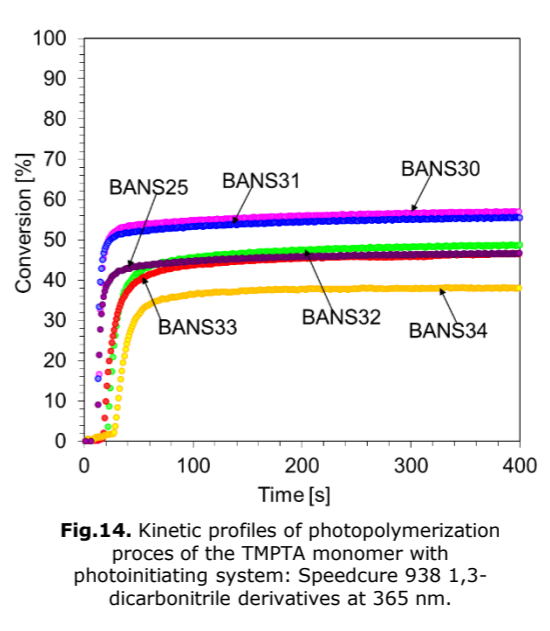
**Fig.11.** Kinetic profiles of photopolymerization process in laminate of the hybrid CADE/TMPTA monomer with photoinitiating system: Speedcure 938 + 2-(diethylamino)-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile at 365, 405, 420 nm.



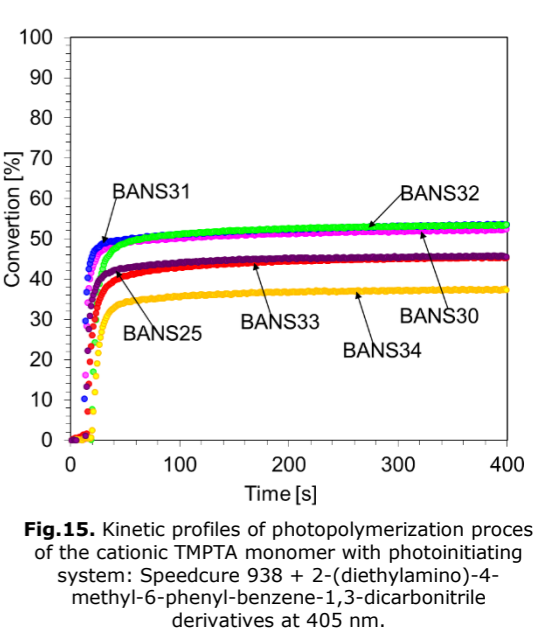
**Fig.12.** Kinetic profiles of photopolymerization process in the air of the hybrid CADE/TMPTA monomer with photoinitiating system: Speedcure 938 + 2-(diethylamino)-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile derivatives at 365, 405, 420 nm.



**Fig.13.** Changes in FT-IR spectrum for composition based on TMPTA monomer during free radical photopolymerization with UV-LED 365 nm, using Speedcure 938 + BANS25 derivatives.



**Fig.14.** Kinetic profiles of photopolymerization process of the TMPTA monomer with photoinitiating system: Speedcure 938 1,3-dicarbonitrile derivatives at 365 nm.



**Fig.15.** Kinetic profiles of photopolymerization process of the cationic TMPTA monomer with photoinitiating system: Speedcure 938 + 2-(diethylamino)-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile derivatives at 405 nm.

**The novel biphenyls are stable enough under heavy UV light exposure required for cationic, free-radical and thiol-en photopolymerization processes of monomers to enable monitoring the polymerization progress by FPT method over entire range of monomer conversions. Their good response and capability to accelerate the photopolymerization process makes them good candidates for practical applications in photocurable coatings industry as new photosensitizers as component bimolecular photoinitiating systems.**

**Acknowledgment**

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