WORKSHOP on ITALIAN-NORDIC POLYMER FUTURE
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NEW PHOTOSENSITIVE RESINS @405 nm: APPLICATIONS TO 3D PRINTING

AUDE-HÉLOÏSE BONARDI[1], SORAYA ZAHOUILY[1],CÉLINE DIETLIN[1], FABRICE MORLET-SAVARY[1], FRÉDÉRIC DUMUR[2], DIDIER GIGMES[2], SÉGOLÈNE VILLOTTE[2], JACQUES LALEVÉE[1]

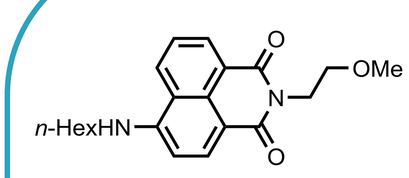
[1]Institut de Science des Matériaux de Mulhouse IS2M – UMR CNRS 7361 – UHA, 15, rue Jean Starcky, 68057 Mulhouse Cedex, France, Jacques.lalevee@uha.fr

[2]Aix-Marseille Univ., CNRS, ICR, F-13397 Marseille, France

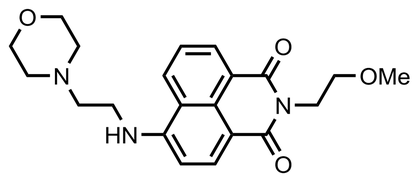
ABSTRACT

The field of 3D printing is today a hot topic. The development of new resins more efficient for such applications is today a real challenge. To this purpose, photosensitive systems are the key point to develop new high performance 3D printing system. The photopolymerization allows the transformation of mutifunctional monomer or prepolymer into highly crosslinked networks by action of light[1]. According to the literature, photopolymerization of (meth)acrylate or epoxy monomers usually requires UV-curing. As UV wavelengths are known to be noxious, the development of new free radical initiating systems upon longer (safer) wavelengths irradiation such as 405 nm is crucial.

NEW PHOTOSENSITIZERS



(1)



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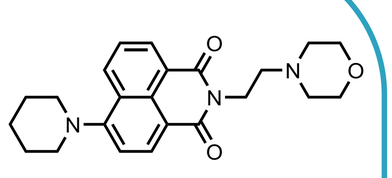

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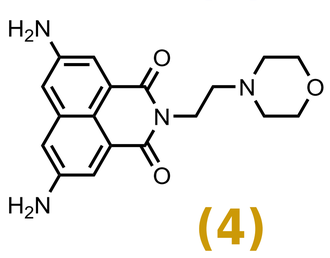

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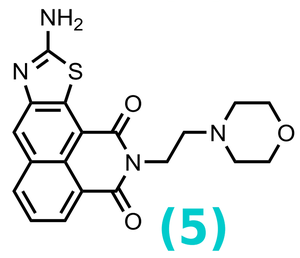

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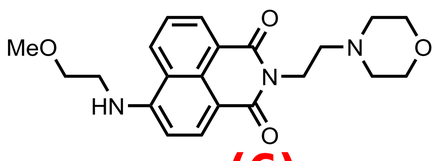

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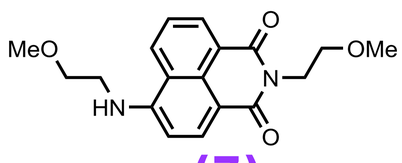
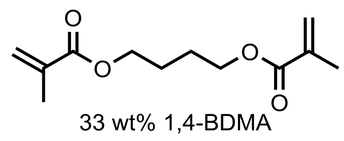


(7)

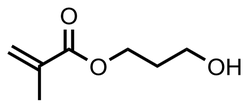
New 1,8-Naphtalimide derivatives

ADDITIVES AND MONOMER

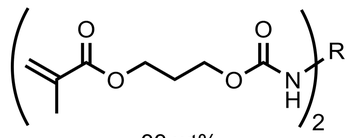
Mix MA:



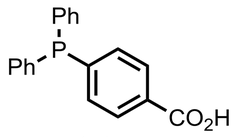
33 wt% 1,4-BDMA



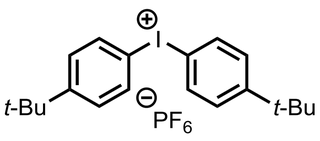
33 wt% HPMA



33 wt%



4-dppba



MECHANISM

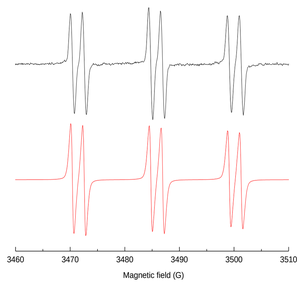
$dye^+ \longrightarrow dye^{*+} + Ph_2I^+$

$\longrightarrow dye^\bullet + Ph^\bullet + PhI$

$R^\bullet + O_2 \longrightarrow ROO^\bullet$

$ROO^\bullet + R'_3P \longrightarrow ROO\text{-}PR'_3{}^\bullet$

$ROO\text{-}PR'_3{}^\bullet \longrightarrow RO^\bullet + R'_3P{=}O$



Phenyl radicals are detected
✓ a_N= 14.3 G
✓ a_H= 2.2 G

Figure 1. ESR spectra of $Ph^\bullet$ trapped by PBN (λ = 405 nm in -*t*BuPh)**:** exp. (black) and sim. spectra (red)[2].

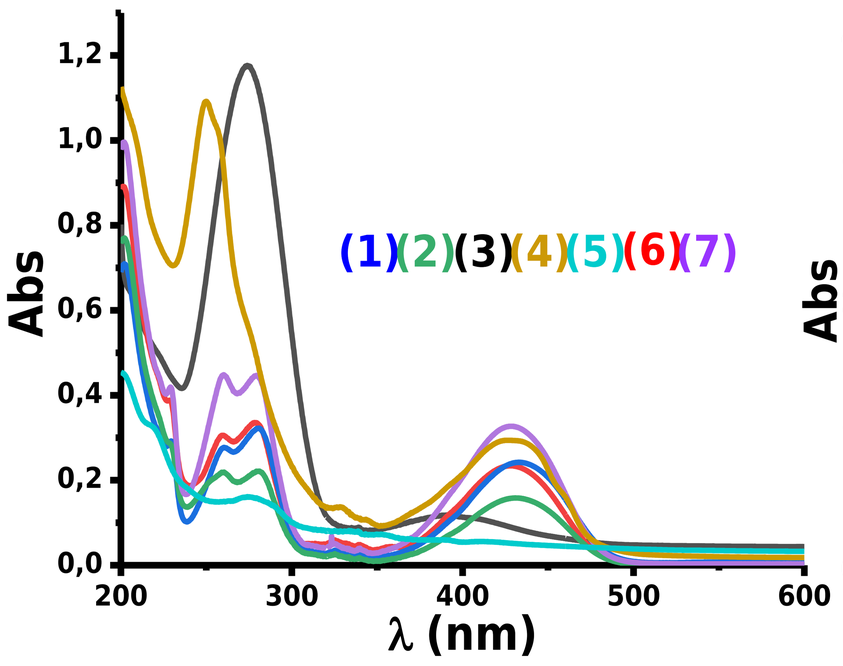


Figure 2. UV absorption spectra of the proposed 1,8-naphtalimide derivates in ACN

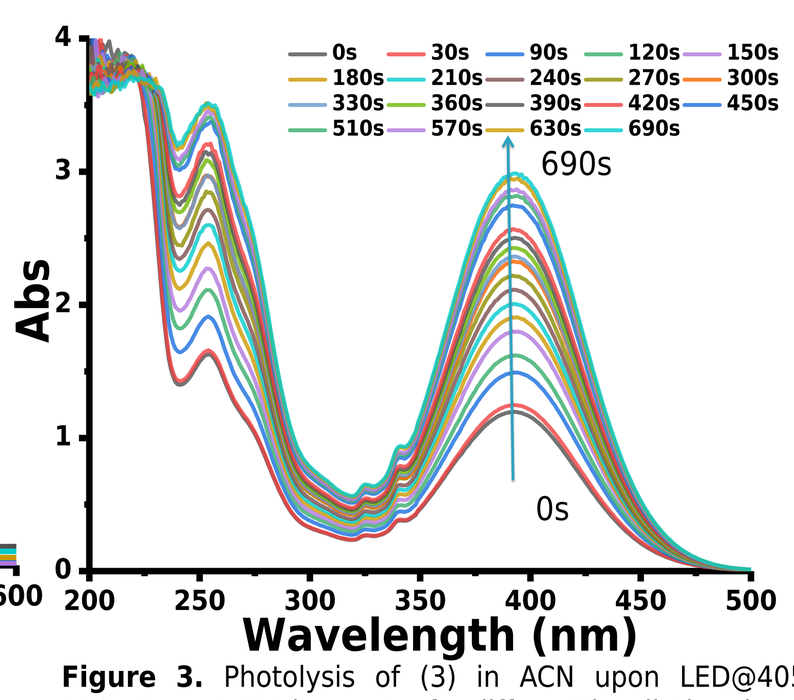


Figure 3. Photolysis of (3) in ACN upon LED@405nm, 110mW/cm²: UVvis spectra for different irradiation times

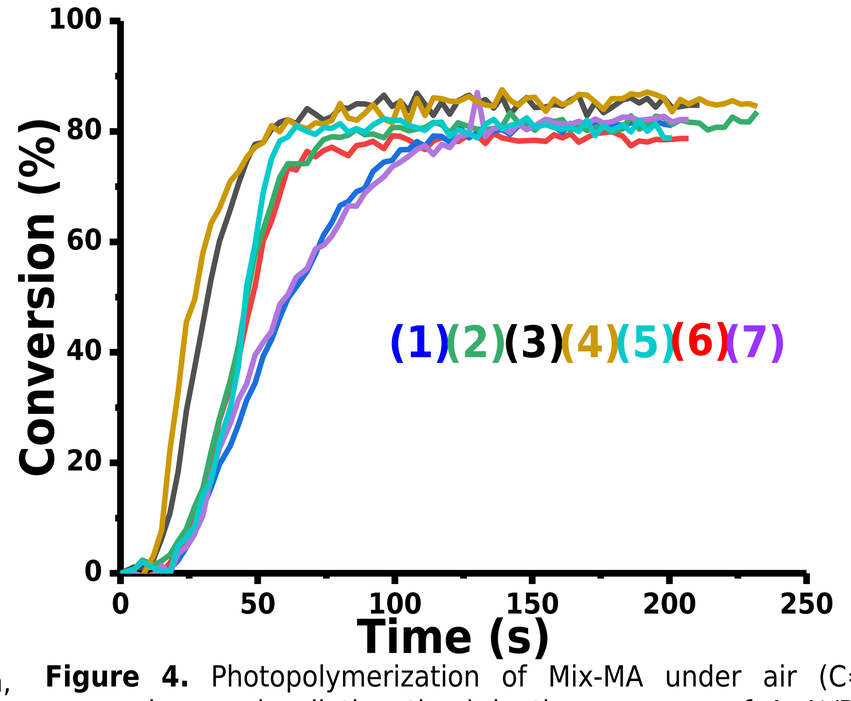


Figure 4. Photopolymerization of Mix-MA under air (C=C conversion vs. irradiation time) in the presence of Ar_2I^+/PF_6^- (3wt%), 4-dppba (2wt%) and 1,8-naphtalimide derivates (0.1wt%), LED@405nm, thickness=1,4mm

CONCLUSION AND PERSPECTIVES

-Interesting light absorption properties in the near-UV range
-Very good conversions obtained
-Fast photopolymerization upon safe irradiation conditions (faster for polymerization of larger objects)
-Compatibility with Sharebot 3D printer@405 nm (Photo 1)
-Measure of spatial resolution (in progress) (Photo 2)
-**Acknowledgments: Sharebot for the 3D printer**

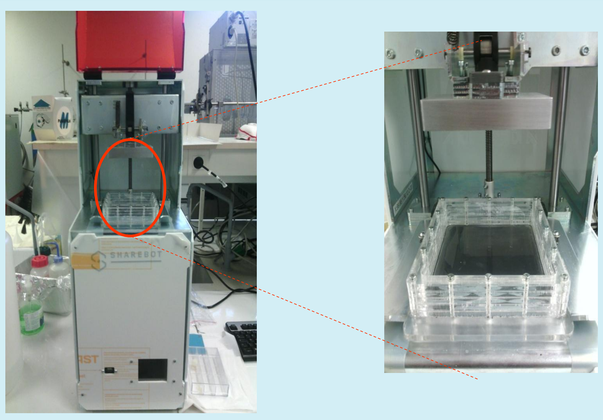


Photo 1. Sharebot 3D printer

Photo 2. Spatial resolution measurement

REFERENCES

[1] J.-P. Fouassier, J. Lalevée, *Photoinitiators for polymer synthesis: scope, reactivity and efficiency.* Weinheim: Wiley-VCH.; **2012.**

[2] M. Bouzrati-Zerelli; M. Maier; C. P. Fik; C. Dietlin; F. Morlet-Savary; J.-P. Fouassier; J. Klee; J. Lalevée; A, *Polym. Int.* **2016**, 10.1002/pi.5262.