3D printed azo-based membranes for gas permeability

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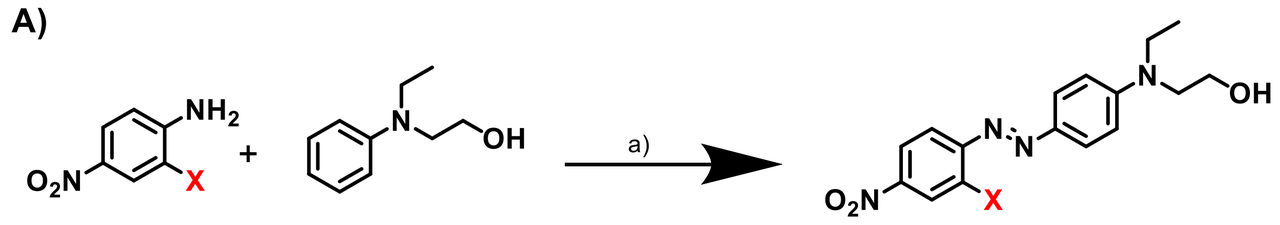
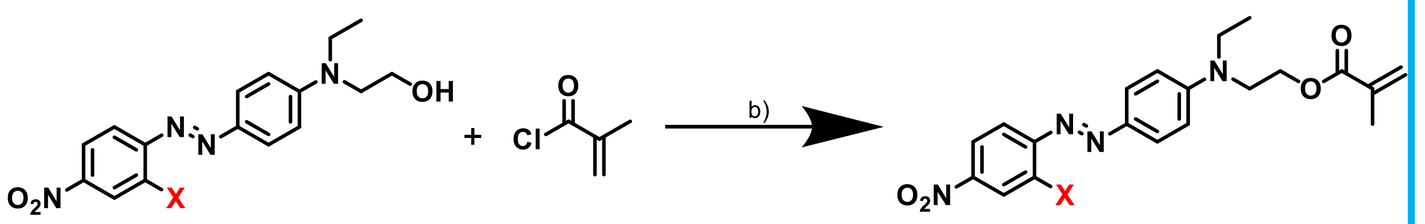
Introduction

Three-Dimensional printing (3DP) is an innovative technique, nowadays used both in industrial and academic fields. The high versatility and user-friendliness, the progressive printers' price knock off and the considerable saving of raw materials are just few advantages of these technologies. Among others, the **Digital Light Project (DLP)** printer is under investigation to widen the palette of printable formulations, producing innovative functional 3D printed devices. The exploitation of new functional materials, for example **temperature-, light- and pH-responsive polymers**, is one of the most interesting survey field [1]. **Azodyes** are typically used in the formulation to confer innovative features due to the ability to undergo ***cis/trans* isomerization under light (UV or laser) irradiation** [2]. In this work we designed, synthetized, and characterized azo benzene methacrylated monomers (Figure 1) with different groups in ortho position respect to the azo bridge, exploiting the methacrylic functional group to covalently connect the dye with the polymeric chains. It is well known in literature that the ortho position in the azodyes can interact with the polymeric matrix [3].

Synthesis and photopolymerization

A)

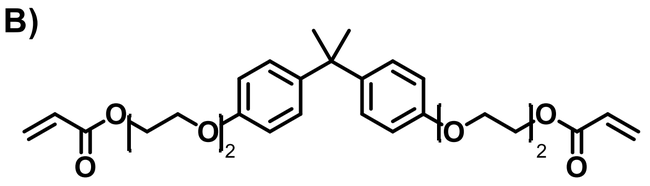




X = H, F, Cl, Br, I

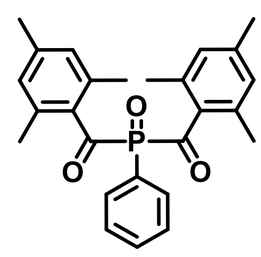
A) Schematic representation of the monomer preparation: a) $NaNO_2$, AcOH, HCl, H_2O, 0 to 5°C to rt, 4 hours. b) TEA, THF, rt, 18 hours.

B)



Bisphenol A ethoxylate diacrylate

C)

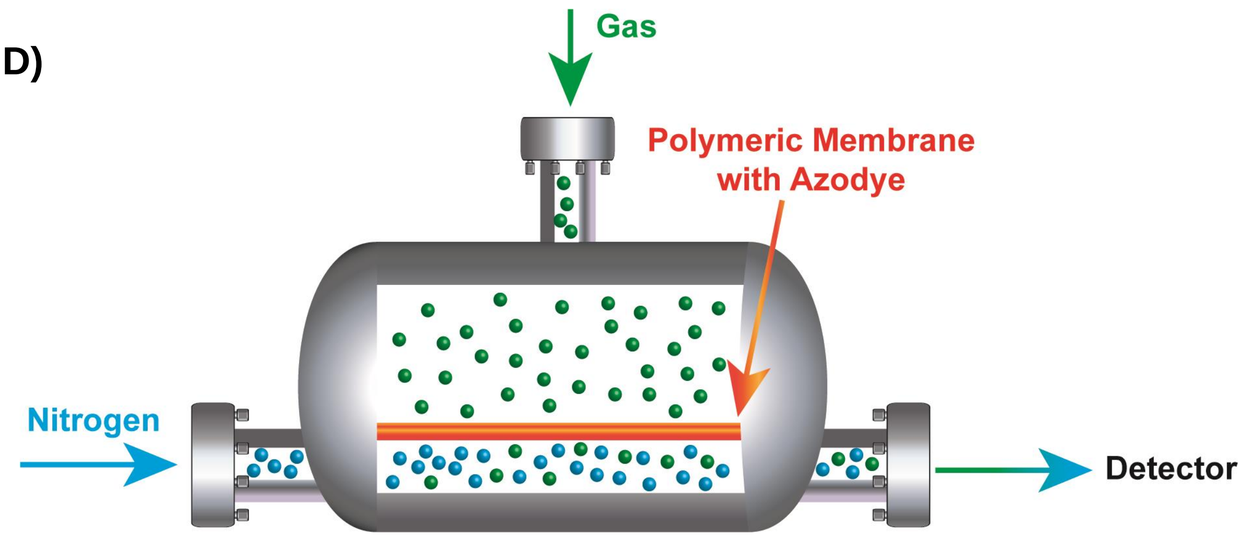


Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide

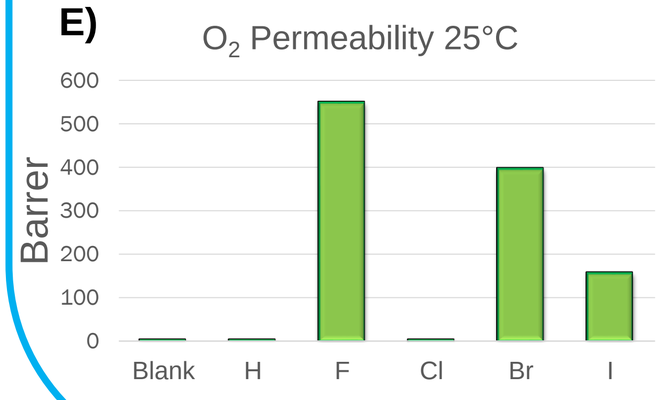
B) Monomer used in the formulation for the Digital Light Processing (DLP).
C) Photoinitiator used to start the radical polymerization.

Permeability

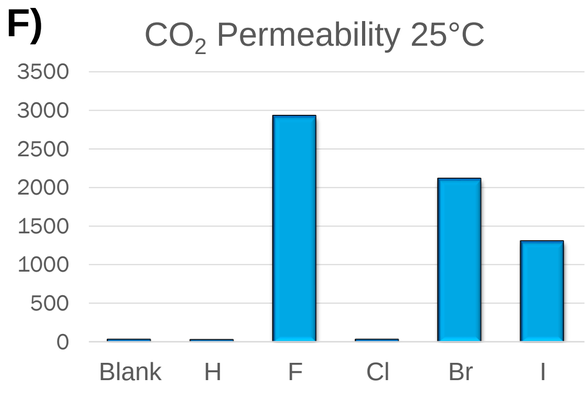
D)



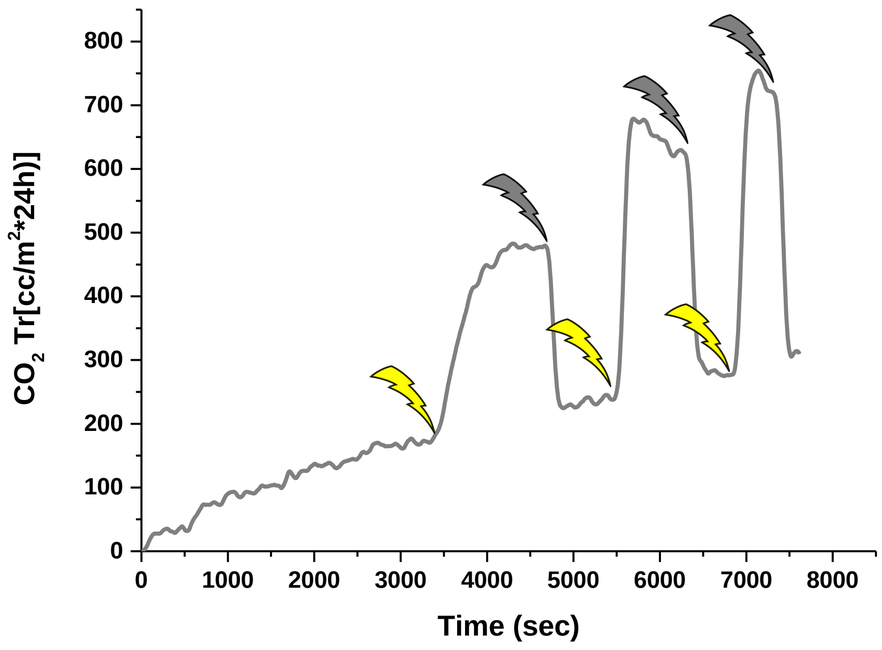
E)



F)



G)



D) Schematic representation of permeometer with polymeric azo-based membrane. Nitrogen is used as gas carrier while the analyte gas is introduced in the first chamber, it pass through the membrane and is led to the detector.

E) O_2 and **F)** CO_2 permeability trend for each sample according to the steric hindrance of the *ortho* group. **G)** The transmission rate over time for CO_2 under laser irradiation. When the laser is switched on, a rapid increase in Tr is registered, in a totally reversible and repeatable way.

Conclusion

The different transmission (Tr) rates registered for the introduced polymer are, most likely, related to the presence of the azo groups. They can increase the transmission rate of an almost totally gas impermeable polymeric membrane.

According to the steric hindrance of the ortho functional groups, different Tr values were obtained. The only functionalized samples that seem to not follow this trend are the ones with H and Cl as *ortho* groups. These samples are actually under investigation.

Under green laser irradiation (532 nm) a rapid and reversible increase in permeability of CO_2 was observed. The same behavior can't be registered for other gases. Our hypothesis of *cis/trans* laser induced isomerization is under investigation to better explain these phenomena.

[1] Z.X. Khoo, J.E.M. Teoh, Y. Liu, C.K. Chua, S. Yang, J. An, K.F. Leong and W.Y. Yeong Virtual and Physical Prototyping, 2015, 10, 103

[2] Gillono, M.; Roppolo, I.; Frascella, F.; Scaltrito, L.; Pirri, C. F.; Chiappone, A., Applied Materials Today, 2020, 18, 100470

[3] Accardo, J. V.; Kalow, J. A. Chem. Sci. 2018, 9, 5987–5993

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