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Permeability tuning of 3D printed azo-based membranes

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Introduction

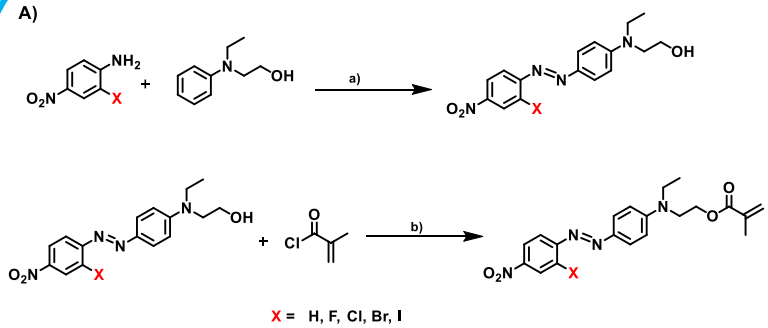
Three-Dimensional Printing (3DP) has assumed a central role in recent years both in academic and industrial fields. **Functional dyes** have been recently used to enlarge the palette of available polymers.[1] Materials able to change chemical, mechanical or optical properties, under an external stimulus, such as light, temperature or mechanical stresses, are examples of these appealing research.[2]

Here we have synthetized and characterized **azodye-functionalized polymethacrylates** for Digital Light Processing (DLP). The introduction of small amount of dye-monomers into the liquid formulation produced noticeable changes in gas permeability properties of the 3DP polymeric membranes.[3]

We tested CO_2, O_2 and H_2O permeability, noting an increase in the transmission rate (T_r) and a reduction in water permeability. Moreover, an instant rise in the CO_2 T_r can be obtained under green laser irradiation (532 nm), while no remarkable effects are obtained for other gases.

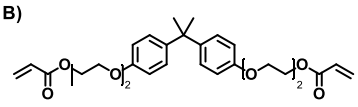
Synthesis and photopolymerization

A)



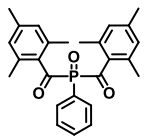
A) Schematic representation of the monomer preparation: a) $NaNO_2$, AcOH, HCl, H_2O, 0° to 5° C to rt, 4 hours. b) TEA, THF, rt, 18 hours.

B)



Bisphenol A ethoxylate diacrylate

C)

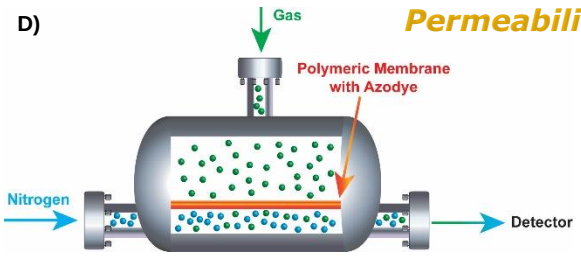


Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide

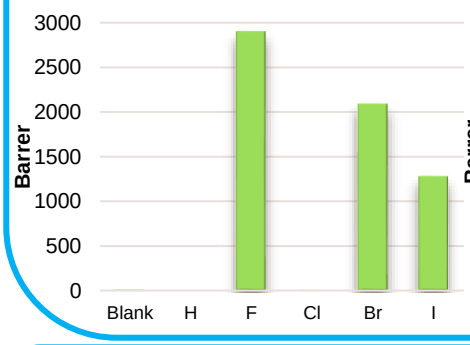
B) Monomer used in the formulation for the Digital Light Processing (DLP).
C) Photoinitiator used to start the radical polymerization.

Permeability

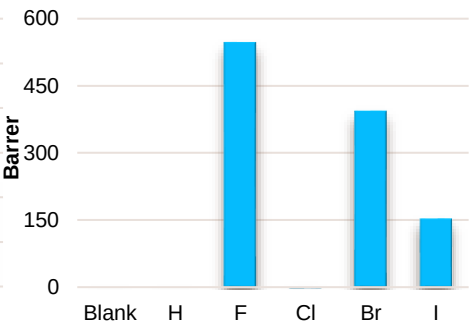
D)



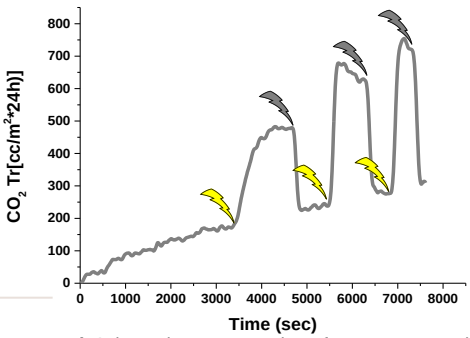
E)



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) CO_2 and **F)** O_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 T_r 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.

A possible application of these membranes is under investigation, to realize 3DP devices with different tunable gas selectivity.

[1] Layani, M.; Wang, X.; Magdassi, S. *Adv. Mater.* **2018**, *30*, 1706344.

[2] Gastaldi, M.; Cardano, F.; Zanetti, M.; Viscardi, G.; Barolo, C.; Bordiga, S.; Magdassi, S.; Fin, A.; Roppolo, I. *ACS Mater. Lett.* **2021**, *3*, 1–17.

[3] Gillono, M.; Roppolo, I.; Frascella, F.; Scaltrito, L.; Pirri, C. F.; Chiappone, A., Appl. Mater. Today **2020**, *18*, 100470.

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