

# Highly ordered honeycomb polystyrene patterns decorated with polyoxometalates for catalytic applications

Leire Ruiz-Rubio<sup>1</sup>, Beñat Artetxe<sup>2</sup>, Jagoba Martín-Caballero<sup>3</sup>, Leyre Pérez-Álvarez<sup>1,3</sup>, Santiago Reinoso,<sup>2</sup> Juan Manuel Gutierrez-Zorrilla<sup>2,3</sup>, José Luis Vilas-Vilela<sup>1,3</sup>

[1] Macromolecular Chemistry Group (LABQUIMAC), Department of Physical Chemistry, University of the Basque Country UPV/EHU, Leioa, Spain.

[2] Department of Inorganic Chemistry, University of the Basque Country UPV/EHU, Leioa, Spain.

[3] BCMaterials, Parque Científico y , Derio, Spain.

Contact@ leire.ruiz@ehu.es

Breath figure process is a cost-effective method for preparing highly ordered honeycomb patterns from polymer solutions. In this process, a polymer solution is casted onto a substrate under adequate humidity and the evaporation of the solvent cools down the solvent/air interface inducing the condensation of small water droplets.[1] The variation of the concentration, solvent and relative humidity enables the control over the formation of honeycomb patterns.[2] The fabrication of honeycomb arrays has received an increasing interest due to the potential applications of these structures in different areas, such as tissue-engineering, membranes, or catalysis.[3] In our study, honeycomb patterns have been obtained from polystyrene/poly(polystyrene-*b*-polyacrylic acid) blends. The resulting porous arrays have been decorated with polyoxometalates in order to obtain polymer films with maximized catalytic capability.

Polyoxometalates are anionic transition metal-oxo clusters of nanometric size that can act as both strong Brønsted acids and oxidation catalysts showing fast and reversible multistep redox processes without significant structural changes. The decavanadate-based  $[\text{Cu}(\text{cyclam})][\{\text{Cu}(\text{cyclam})\}_2(\text{V}_{10}\text{O}_{28})] \cdot 10\text{H}_2\text{O}$  microporous hybrid (cyclam = 1,4,8,11-tetraazacyclotetradecane) has been recently employed as catalyst for the oxidation of the highly stable, tricyclic alkane adamantane.[4] A scheme of the functional polymeric surface decorated with the Cu(cyclam)-decavanadate hybrid is shown in Figure 1.

The authors thank EG/GV (IT718-13; FRONTIERS) and MINECO (MAT2013-48366-C2-2-P) for financial support. Technical and human support provided by SGIKER (UPV/EHU) is gratefully acknowledged.

## References

- [1] A. Muñoz-Bonilla, M. Fernández-García, J. Rodríguez-Hernández, Prog. Polym. Sci. 39 (2014) 510–554.
- [2] L. Ruiz-Rubio, I. Azpitarte, N. García-Huete, J.M. Laza, J.L. Vilas, L.M. León, J. Appl. Polym. Sci. 133 (2016) 44004.
- [3] M. Hernández-Guerrero, M.H. Stenzel, Polym. Chem. 3 (2012) 563-577.
- [4] J. Martín-Caballero, A.S.J. Wéry, S. Reinoso, B. Artetxe, L. San Felices, B. El Bakkali, G. Trautwein, J. Alcañiz-Monge, J.L. Vilas, J.M. Gutiérrez-Zorrilla, Inorg. Chem. 55 (2016) 4970-4979.

## Figures

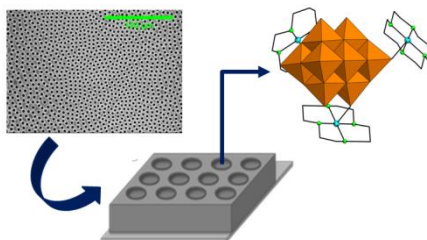


Figure 1: Poly(styrene)/Poly(styrene-*b*-acrylic acid) blend breath figures decorated with  $\{\text{Cu}(\text{cyclam})\}^{2+}$  and  $(\text{V}_{10}\text{O}_{28})^{6-}$ -units.