

EVAPORATION KINETICS IN SWOLLEN POROUS POLYMER NETWORKS

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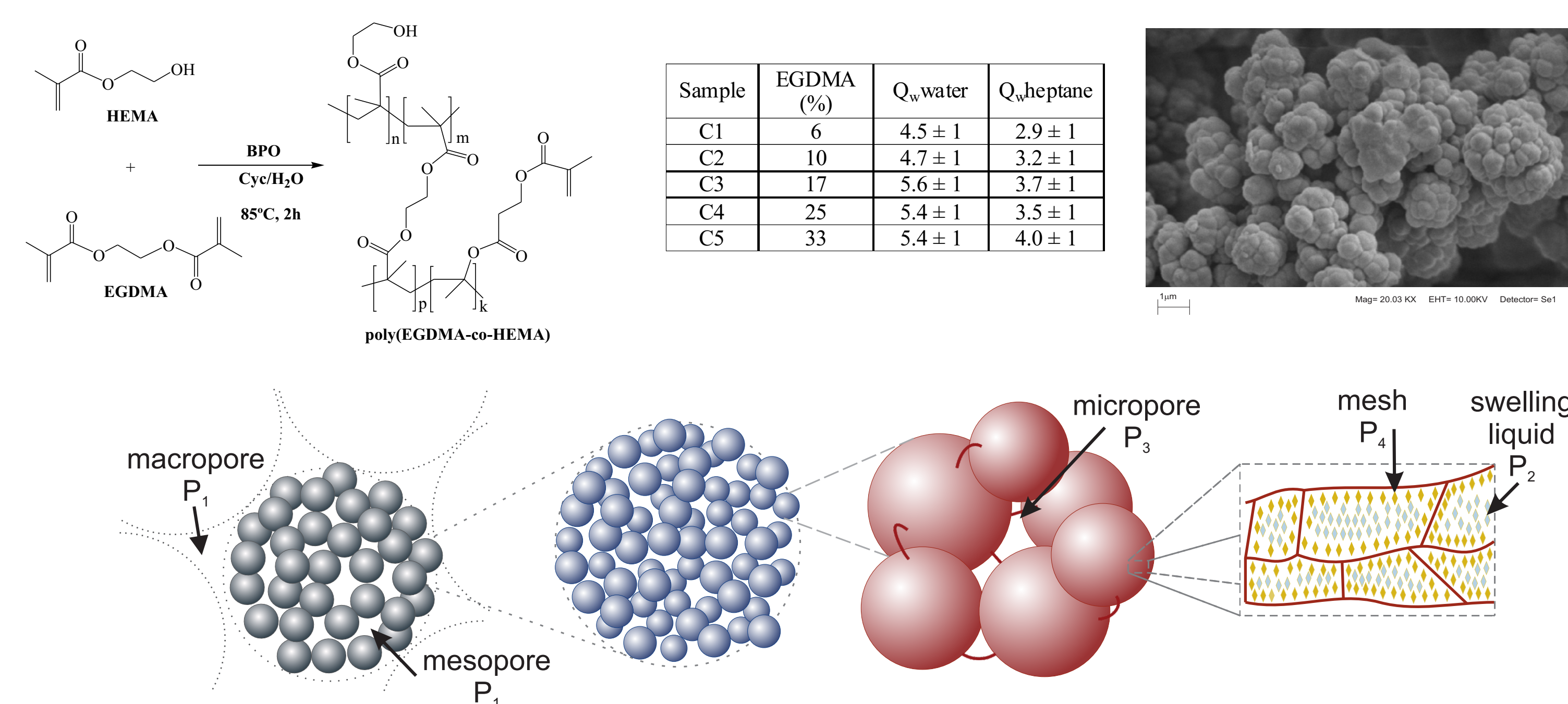
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INTRODUCTION

Polymer matrices with well defined structure and pore sizes are widely used in several areas of chemistry such as catalysis, enzyme immobilization, HPLC, adsorbents or controlled drug release. These polymers have pores in its structure both in the dry and swollen state. Although it is well known that the structures and properties greatly differ between these two states, only few methods provide information about the swollen one, even though most of the applications involve the matrices in this situation. Nuclear Magnetic Resonance (NMR) is a suitable tool for the study of the molecular dynamics of different liquids spatially confined in macro, meso and nanopores, through changes in the relaxation times. In transverse relaxation experiments, either diffusion inside the pores, or relaxation induced by the mobility restriction of the liquid near the wall, are additional sources of relaxation, which are extremely useful in the determination of structural and functional properties.

POLYMERIC NETWORKS

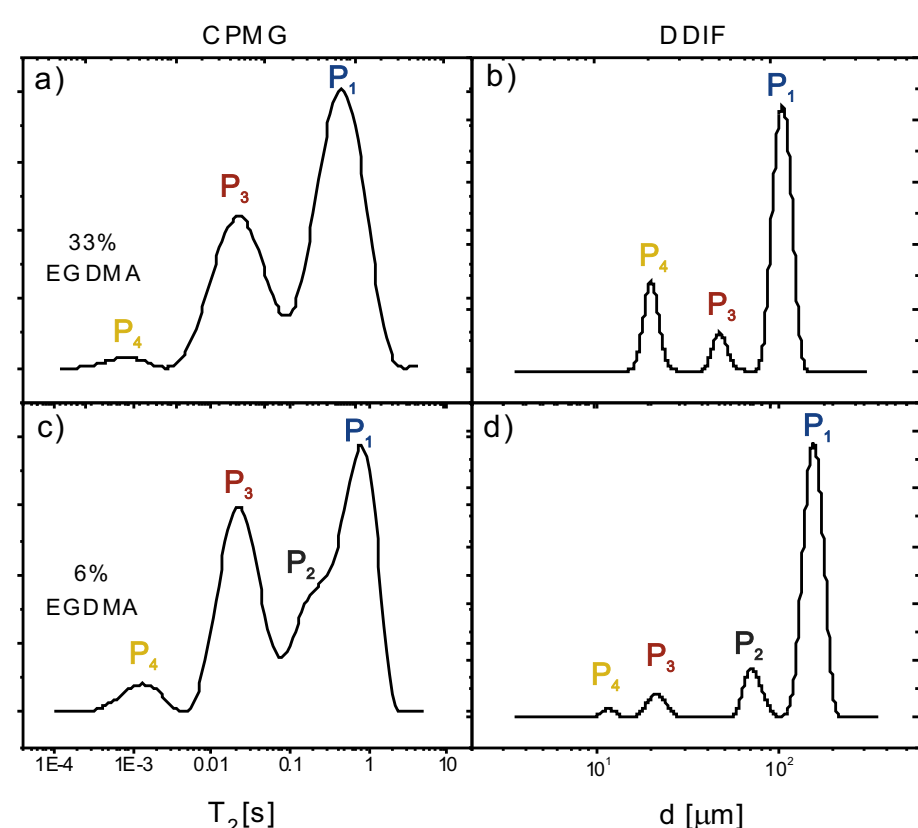
Polymers of 2-hydroxyethyl methacrylate (HEMA) cross-linked with ethylene glycol dimethacrylate (EGDMA), were synthesized varying the proportion of crosslinking between 6 and 33%. The final polymeric matrix presents macro, meso and micropores in the structure.



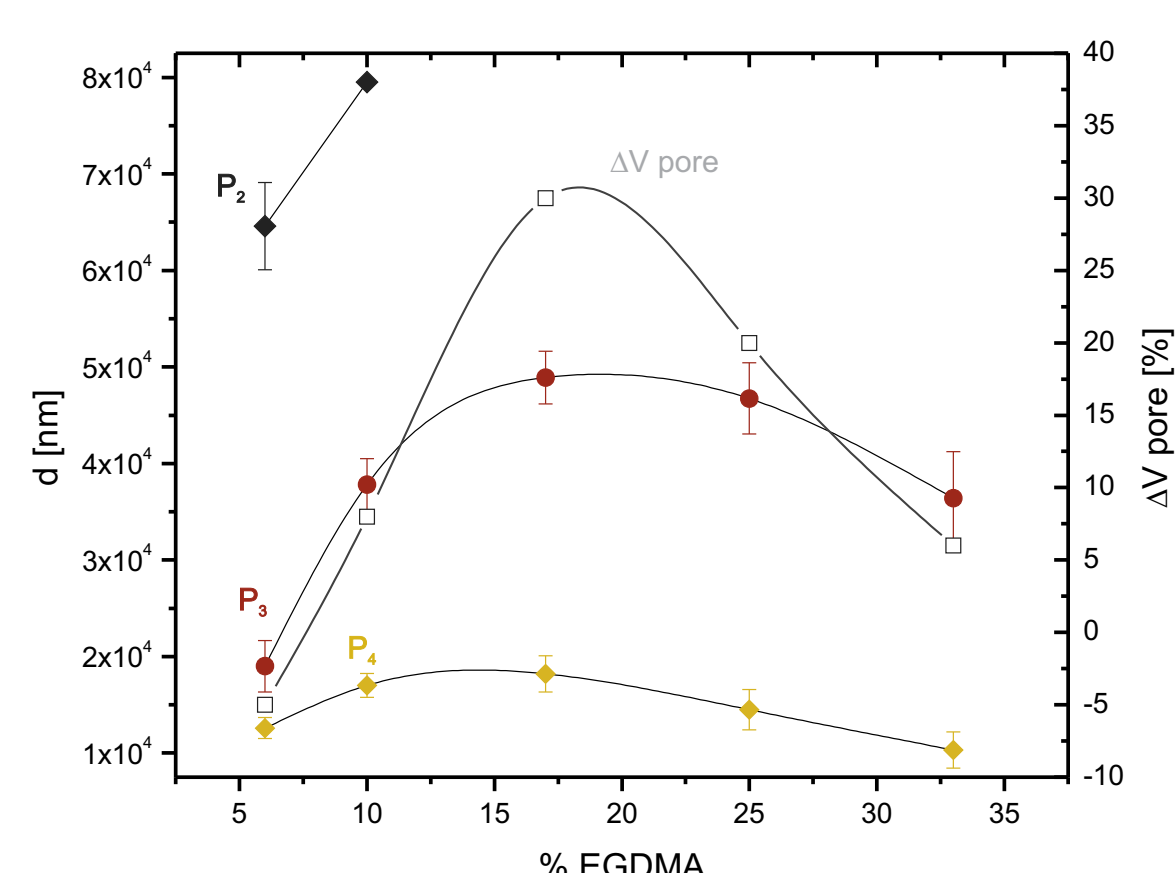
DDIF RESULTS

When a sample is placed in a magnetic field, inhomogeneities are produced inside the pores due to the susceptibility contrast between fluid and solid materials. This field pattern is referred to as internal field, which is determined by the spatial distribution of pores and thus reflects the pore structure. The spin-magnetization decay due to diffusion in the internal field (DDIF) is then dependent on the structure of the medium. Therefore, DDIF measurements provide the probe of the pore structure on the scale of the liquid molecule diffusion. The result of the DDIF measurement is a multiexponential decay. A distribution in decay times τ is obtained after an Inverse Laplace Transform (ILT). Assuming a spherical pore, a rescale is done to obtain the pore size using the diffusion constant of the liquid.

$$d = \pi\sqrt{D\tau}$$



The pore size distribution obtained from a DDIF experiment is compared to the results obtained by CPMG. In sample C5 (a,b) three populations are distinguished, corresponding to the size for mesh, micropore and macropore. Sample C1 (c,d), with the lower content of crosslinker degree, is capable of swelling. This effect is observed in the relaxation time distribution by the presence of a fourth relaxation time, between the micropore and macropore relaxation time. The figure shows the four different populations that can be assigned to water in mesh, micropore, swelling and macropore.



The results of the DDIF experiments provide the diameter variation as a function of the crosslinker degree. Mesh and micropore sizes exhibit the same behavior with a maximum at 17 % of EGDMA. It is worth to note that the micropore diameter exhibits the biggest differences when the % of EGDMA is varied, thus it can be concluded that this pore is the most sensitive to the crosslinking degree. Only sample C1 and C2 undergo swelling, thus the curve for swollen pore has exclusively two points with the same tendency. As macropore is highly dependent on the sample packing the pore size values are extremely dependent and they are not shown in the graph. Hollow symbols are obtained from gravimetric evaporation experiments and reflect an overall pore volume variation.

EXPERIMENTAL

All experiments were performed at 25 °C using a Magritek Kea2 spectrometer operating at 60 MHz for protons. 1.4 T permanent magnet (Varian EM360) was used in all the experiments.

Polymer beads were immersed in a vial containing distilled water or heptanes at room temperature for 24 h to reach the full swelling of the network. Samples of 75 mg weight were extracted from the vial and gently placed in a 5 mm outer diameter NMR sample tube. Liquids were allowed to evaporate, and transverse proton relaxation times were measured throughout the evaporation process by using a Carr–Purcell–Meiboom–Gill (CPMG) sequence with an echo time of 1 ms and 6000 echoes.

For DDIF measurements, water soaked samples were placed in a 5 mm outer diameter NMR sample holder with a sealed cap to avoid evaporation. DDIF experiments were acquired with an encoding time of 500 μ s and diffusion time ranging from 500 μ s to 4 s in 32 logarithmic increased steps.

Relaxation time and pore size distribution functions were obtained using an Inverse Laplace Transform (ILT) algorithm based on the Tikhonov regularization method provided by Victoria University of Wellington, New Zealand.

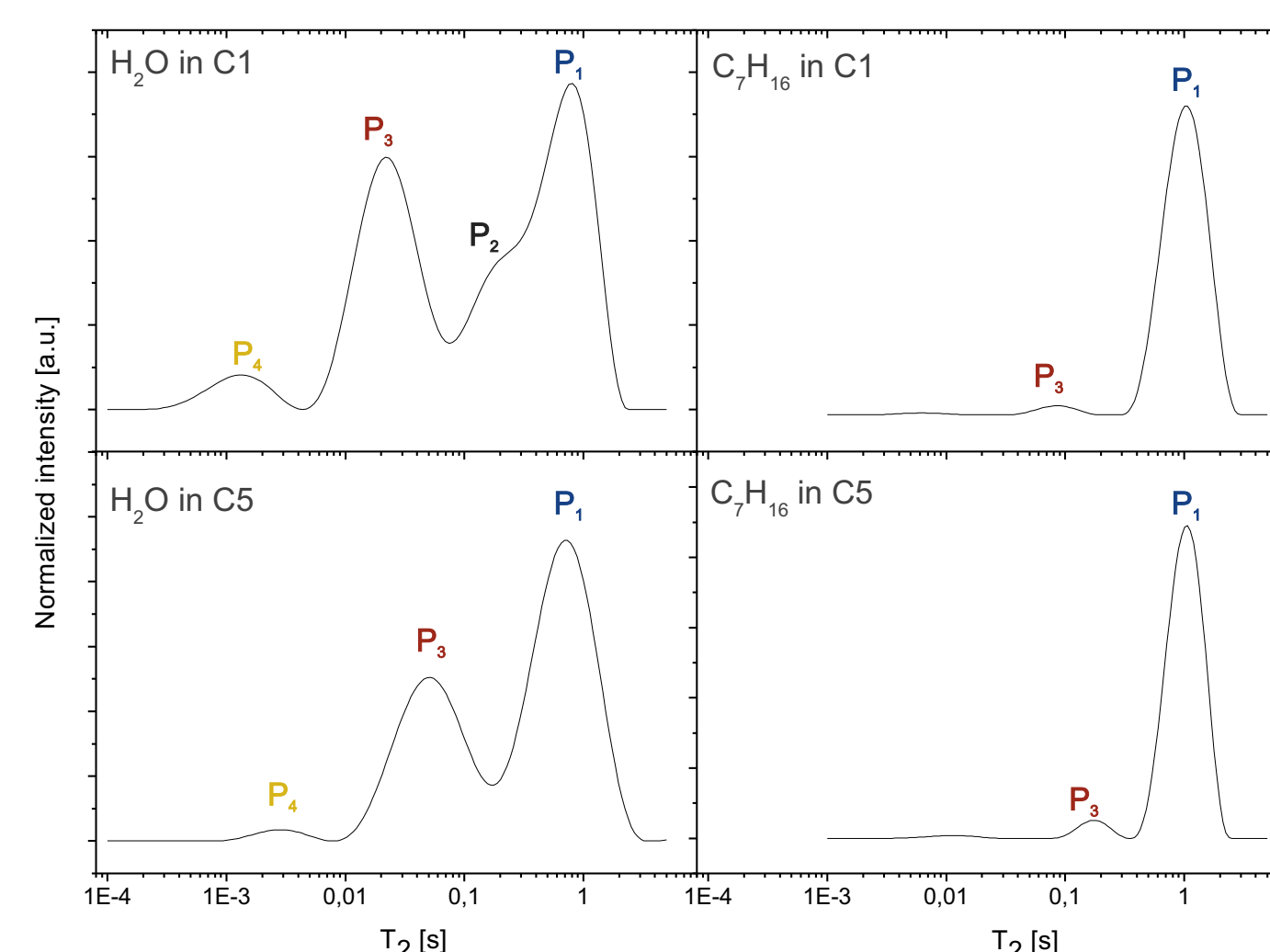
ACKNOWLEDGMENTS

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CPMG RESULTS

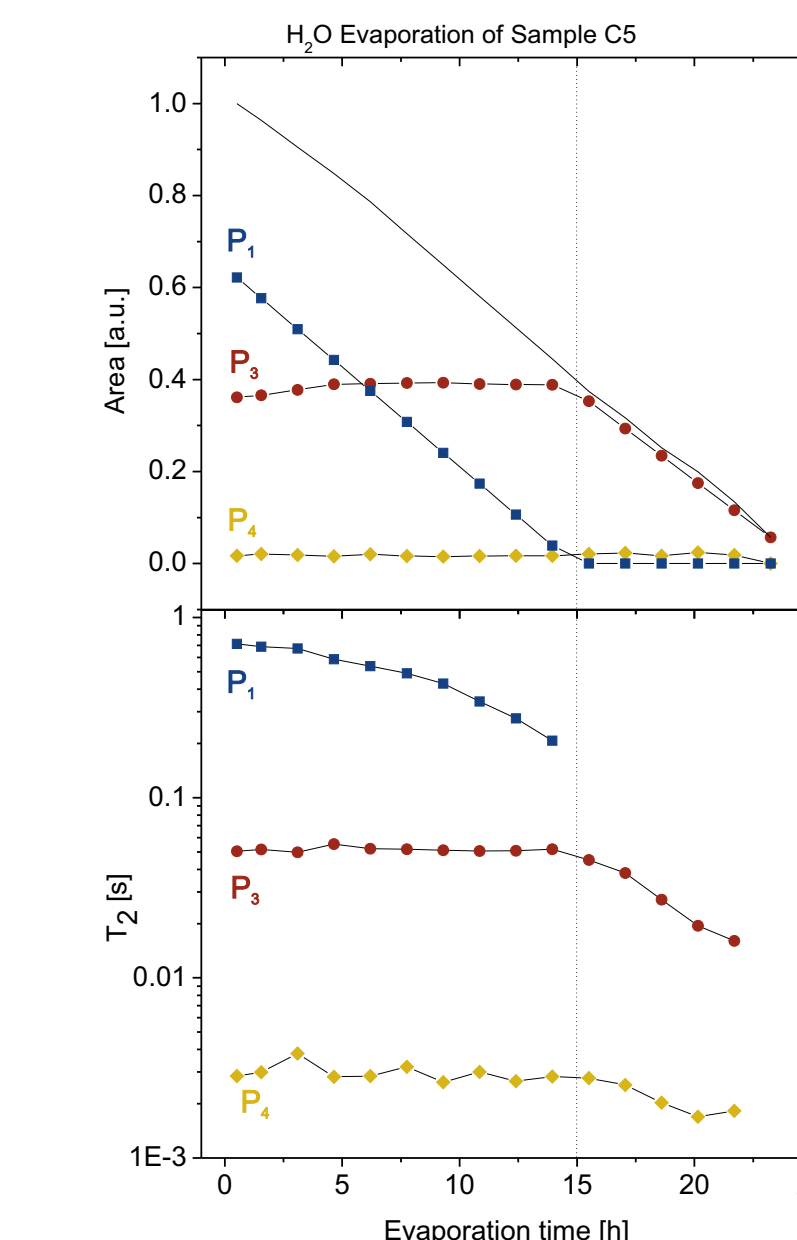
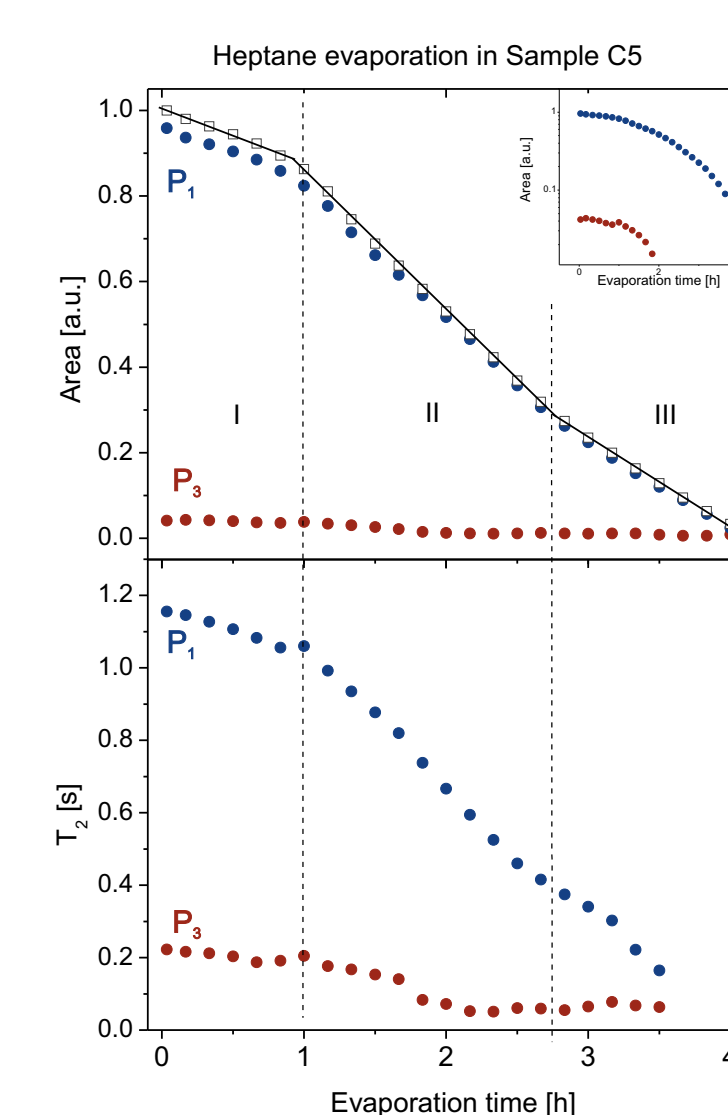
Given the polar characteristics of the matrices, heptane was used to characterize the dry state since the molecules enter in the pores but do not solvate the polymer chains. The network morphology is not altered. On the other hand, water was used to study the properties of the matrix in the swollen state.

The populations observed for water in saturated samples is in correlation to the structure of the polymer. Highest T_2 values (P_1) can be assigned to solvent in the macro and micropores, liquid in the meso pores (P_2) and adsorbed water in the polymeric mesh is assigned to population P_3 . Matrices with low crosslinker content P_2 is observed. The technique allows the discrimination between strongly adsorbed water and water between the polymeric chains.



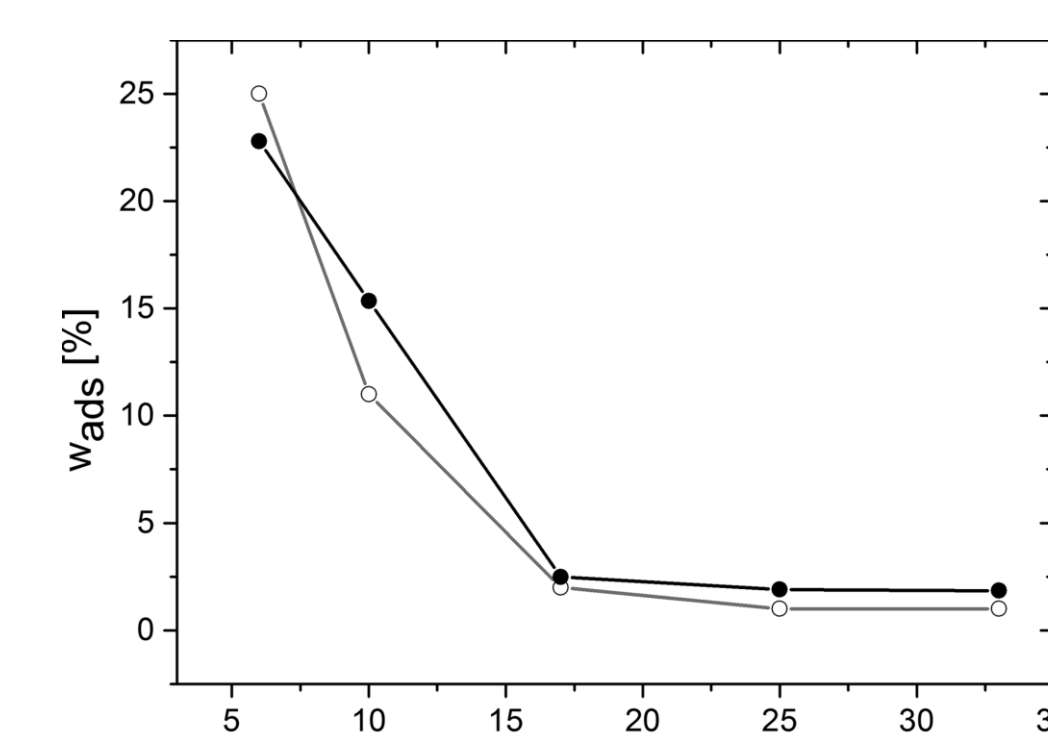
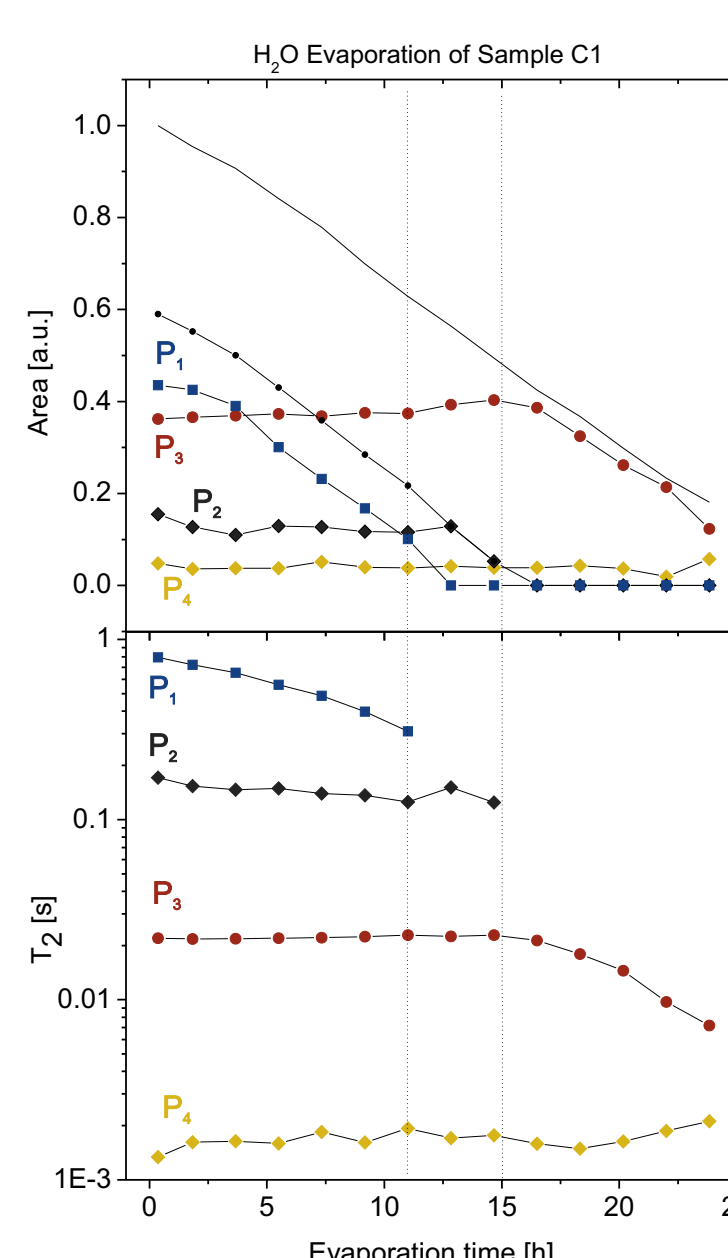
Heptane does not swell the matrix and the liquid molecules are mainly located in the macropores. A minor population is placed in the mesopores revealing that in the dry state the main contribution to the porosity of the polymer is given by the larger pore spaces.

This swelling technique also allows the observation of the variation in the distribution of pore populations as the swelling liquid evaporates. This enables to infer specific properties of each organic matrix under study.



Non-polar liquid evaporates in three clear stages. During stage I both populations change, indicating that heptane evaporates from the meso and macropore. The smaller pores dry first (stage II) and then the evaporation proceeds with the contribution of the macropore (stage III).

Water in highly crosslinked networks evaporates in steps from the bigger pores to the smaller ones. The evaporation steps are consecutive and start only when the previous pore is dry. Water adsorbed to the mesh is not removed at 25°C.



In swelling with a low amount of crosslinker, evaporation and deswelling take place. Initially water evaporates from the big pores. Once dry, the mesh shrinks and evaporation proceed in steps from the bigger pore to the small. Steps are consecutive and strongly adsorbed water does not evaporate at room temperature.

The weighting of water adsorbed by the network obtained by different methods can be compared with the areas under the relaxation time distributions corresponding to P_2 plus P_4 . The remarkable coincidence indicates that the assignment of T_2 distribution to the swollen water is correct. It is worth to note that P_2 can only be distinguished for water saturated samples C1 and C2, where the low percentage of crosslinker renders a soft network that is capable of swelling.

CONCLUSIONS

Simple NMR experiments provide information of the polymeric pore structure of different cross-linked matrices. The obtained values are very useful in the characterization of the polymeric matrices and, in contrast to the conventional techniques, this information can be obtained directly measuring either in the dry state or in the swollen state. The study in the swollen state also provides information of the structure of the microscopic mesh. These procedures represent a direct, simple, fast and non-destructive method for the determination of macromolecular properties. As previously showed all the information is in good agreement with that of the data determined other analytical techniques.

This experiment also provides information of the evaporation kinetic of liquids in the sample. A remarkable aspect, is the discrimination of the dynamics between molecules environment of microscopic resolution that is possible with this technique. Moreover, this type of experiment can be carried out in compact benchtop NMR systems, which present a negligible stray field and can be used in reduced laboratory spaces without the special conditions normally required for high field superconducting magnets. We envision that this easily applied technique will provide useful information not only on the morphology of organic porous polymeric systems but also on functionality in a wide range of applications.

REFERENCES

- 1]-Gomez, C.G., et al., Macroporous poly(EGDMA-co-HEMA) networks: Morphological characterization from their behaviour in the swelling process. *Polymer*, 2012, 53(14): p. 2949-2955.
- 2]-Sillella, E.V., et al., Evaporation Kinetics in Swollen Porous Polymeric Networks. *Langmuir*, 2014, 30(14): p. 4129-4136.
- 3]-Song, Y.Q., S. Ryu, and P.N. Sen, Determining multiple length scales in rocks. *Nature*, 2000, 406(6792): p. 178-181.