Polymer Microstructures: Modification and Characterization by Fluid Sorption

S.A.E. Boyer[S]
Tokyo Metropolitan University, Tokyo, Hachiouji-shi, Japan

M. Baba, J-M. Nedelec and J-P.E. Grolier[C]
Blaise Pascal University, Aubière, France
J-Pierre.Grolier@univ-bpclermont.fr

Polymer micro-organization can be modified by combination of the three constraints, thermal, hydrostatic and fluid sorption. In selecting the fluid's nature, chemically active or inert, and its physical state, liquid or supercritical, new "materials" can be generated. In addition, the interplay of temperature and pressure permits structure tuning of the obtained materials for specific applications. Several complementary techniques have been developed to modify, analyze and characterize the end products: vibrating wire (VW)-PVT coupling [1], thermoporosimetry, temperature modulated DSC (TMDSC) and sorptometry. Selected examples will serve to illustrate the great variety of possible applications in materials science. Typically, polymers like polyethylene (PE), poly (polyvinyldiffluoride) PVDF and fluids like, methane, or simple gas (CO_2 or N_2) can produce materials from soft gel to rigid foams.

Absorption of an appropriate fluid in a cross linked polymer leads to a swelling phenomenon. Thermoporosimetry is a calorimetric technique developed to measure the shift by confinement of thermal transition temperatures of the swelling fluids, which can be currently used solvents or mercury. Application of thermoporosimetry to a swollen cross linked polymer allows to calculate the mesh size distribution and to evaluate the degree of reticulation of the polymer. The same technique can be applied to characterize the pore size distribution in a foamed polymer.

Nanoporous sol-gel derived silica monoliths were used to calibrate the solvents used for thermoporosimetry. Careful control of the ageing procedure allowed the production of silica gel matrices with tailored textural properties. A number of solvents [2] including linear alkanes, cyclohexane, substituted benzene, CCl_4, acetone, dioxane were calibrated. Various polymers [3] like polystyrene (PS), ethylene-propylene rubber (EPR), ethylene-propylene-diene-monomer (EPDM), polybutadiene, polyisoprene, poly(dimethyle syloxane) (PDMS), cross linked by UV or gamma irradiation, by heating or ageing degradation, were characterized and their mesh size distributions calculated.

[1] S.A.E. Boyer, J-P.E. Grolier, "Simultaneous measurement of the concentration of a supercritical gas absorbed in a polymer and of the concomitant change in volume of the polymer. The coupled VW-pVT technique revisited." *Polymer*, **46**, 3737-3747 (2005).

[2] N. Billamboz, M. Baba, M. Grivet, J-M. Nedelec, "A general law for predictive use of thermoporosimetry as a tool for the determination of textural properties of divided media." *J. Phys. Chem. B.* **108**, 12032-12037 (2004).

[3] N. Billamboz, J-M. Nedelec, M. Grivet, M. Baba, "Cross-Linking of polyolefins: A study by thermoporosimetry with benzene derivatives as swelling solvents." *Phys. Chem. Chem. Phys.* **6**, 1-7 (2005).