



# Molecular confinement of solid and gaseous phases of self-standing bulk nanoporous polymers inducing enhanced and unexpected physical properties

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## ABSTRACT

In this work it is provided the first evidence of the polymer chains confinement within self-standing pore walls of nanoporous materials based on poly (methyl methacrylate) (PMMA). This was made possible by producing a series of porous samples with a wide range of pore sizes between 90 nm and 3 μm using processes combining CO<sub>2</sub> sorption, selective block copolymer swelling or homogeneous physical foaming. Mobility restrictions of the PMMA chains in the porous samples with pore size below 200 nm was consistently demonstrated with several experimental techniques, including differential scanning calorimetry, Raman spectroscopy, and broadband dielectric spectroscopy.

In addition, several scale-reduction phenomena related to the constitutive elements of the porous materials, both in the polymeric and gaseous phases, and to the porous architecture are identified. The significance of these phenomena on macroscopic electrical conductivity and permittivity of the nanoporous materials is demonstrated, and the presented observations support previous explanations of improved mechanical properties and thermal insulation of this type of nano-materials.

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## 1. Introduction

Nanoporous polymers are of great scientific and technological importance [1]. Their tunable chemistry, high surface area, and improved mechanical properties offer promising new applications in catalysis, filtration [2,3], hydrogen storage [4,5], gas separation and adsorption [6,7], energy conversion [8], and microelectronics [9,10]; while their superior thermal properties are suited for applications as high performance thermal insulators in building trade, aeronautics, or even space launch [11,12]. Several strategies have been developed for the production of these novel materials, often taking advantage of polymer blends or block copolymers self-

assembly followed by swelling or removal of a dispersed nanometric phase [13–19]. In recent years, the use of physical blowing agents (e.g. CO<sub>2</sub>) to induce the nucleation of pores inside homogeneous polymers with high chemical affinity for the blowing agent has gained popularity as this provides a pathway to exploit the unique properties of nanostructured porous polymers in advanced materials for large scale applications [19–26].

The nanometric architecture, defined by the presence of nanopores with sizes below 100 nm, provides polymeric materials with a high surface area, in which the confinement of a gaseous phase leads to a drastic reduction of thermal conductivity (i.e. the Knudsen effect already demonstrated in aerogels and porous ceramics) [27], as recently shown experimentally in bulk nanoporous materials (thick nanocellular foams) phase-separated poly (methyl methacrylate) (PMMA)-based systems [28]. Some indirect evidence of changes in the polymer phase behavior within these nanoporous materials were found, along with an enhancement of several

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mechanical properties compared to microcellular foams [29]. Such improvements were explained by a possible confinement of the polymer chains into pore walls with nanometric dimensions below 60 nm, by analogy to thin films [30]. Yet no experimental evidence exists of a relation between a hypothetical polymer chains confinement in the nanometric polymer matrix and macroscopic physical properties of bulk nanoporous polymers (i.e. self-standing samples with significant thickness of about or over 1 mm, or thousands of times thicker than the size of the pores within), in particular when materials have a closed porous structure.

## 2. Experimental section

**Materials:** Neat poly (methyl methacrylate) homopolymer (PMMA,  $T_g = 112^\circ\text{C}$ ,  $\rho = 1.18\text{ g/cm}^3$ ,  $M_w^{\text{PMMA}} \approx 83000\text{ g/mol}$ ,  $M_n^{\text{PMMA}} \approx 43000\text{ g/mol}$ ,  $I_p^{\text{PMMA}} \approx 1.9$ ) and a triblock copolymer poly (methyl methacrylate)-*co*-poly (butyl acrylate)-*co*-poly (methyl methacrylate) (MAM, 36 wt% poly (butyl acrylate),  $\rho = 1.08\text{ g/cm}^3$ ,  $M_w^{\text{MAM}} \approx 180000\text{ g/mol}$ ,  $M_n^{\text{MAM}} \approx 85000\text{ g/mol}$ ,  $I_p^{\text{MAM}} \approx 2.1$ ) were gently provided by Altuglas-Arkema Company (France) in the form of pellets.

**Fabrication of PMMA-based nanoporous polymers:** 90/10 PMMA/MAM blends containing 10 wt% of MAM were produced as follows. Both materials, PMMA and MAM, were dried in vacuum (680 mm Hg), at  $80^\circ\text{C}$  during 4 h before processing. Mixing and extrusion were carried out using a Scamex CE02 single-screw extruder ( $L/D = 28$ ,  $d = 45\text{ mm}$ ), with a temperature profile from 165 to  $225^\circ\text{C}$  at a screw speed of 60 rpm in the desired proportions. Pellets were produced using a continuous cutting machine operating at the end of the line at a constant speed of 240 rpm. In a previous work it was demonstrated that PMMA/MAM blends produced by extrusion can present a self-assembled nanostructure that acts as a pattern in the production of the porous structure [3].

In a second step, neat PMMA and 90/10 PMMA/MAM were injected into bulk solid samples ( $50 \times 15\text{ mm}^2 \times 3\text{ mm}$ ) using a small scale injection molding machine developed by DSM Xplore. The working temperature was fixed at  $240^\circ\text{C}$ , whereas mold temperature was set at  $60^\circ\text{C}$ . The injection pressure was fixed at 1 MPa. All samples were transparent and showed a good surface appearance as well as a good injection behavior, without air bubbles inside the parts (see Supplementary Information, Fig. S1).

Foaming experiments were carried out in a high pressure vessel provided by TOP Industry (France), with a capacity of  $300\text{ cm}^3$  and capable of operating at maximum temperature of  $250^\circ\text{C}$  and maximum pressure of 40 MPa. The reactor is equipped with an accurate pressure pump controller provided by Teledyne ISCO, and controlled automatically to keep the temperature and pressure at the desired values. The  $\text{CO}_2$  vessel temperature and pressure were monitored in the course of the process. Thus a collection of experiments was performed in a modified solid state foaming process. The usual solid state foaming process with amorphous polymers has three stages: the saturation (under fixed gas pressure and temperature), gas desorption during and after the pressure release (to room pressure and temperature), and foaming of the sample (at a temperature over or around the  $T_g$  of the plasticized polymer). However, the actual glass transition temperature of PMMA- $\text{CO}_2$  systems can reach values close to room temperature, even below room temperature in some particular conditions, so in this work the desorption (at room temperature) and foaming stages (also performed at room temperature) are not clearly separated.

In previous works it was established that the production of the porous structure in neat PMMA samples is obtained by a conventional gas nucleation and foaming process, whereas PMMA/MAM blends present a selective swelling of the soft phase (poly (butyl acrylate)) confined by the surrounding PMMA matrix [31].

In this study, bulk porous polymeric structures with pore sizes in the micrometric and nanometric range for neat PMMA, and only in the nanometric range for PMMA/MAM blends were obtained using  $\text{CO}_2$  as physical blowing agent (Table 1). The gas saturation process was carried out at room temperature and pressures between 10 and 30 MPa during 24 h to assure the complete dissolution of  $\text{CO}_2$  in the polymer. After this saturation process, foaming was triggered by releasing the pressure inside the vessel at a pressure drop rate between 10 and 30 MPa/min and carried out at room temperature, obtaining bulk white porous samples (see Supplementary Information, Fig. S1).

**Characterization of solid and nanoporous PMMA-based materials:** density of solid and porous polymers was determined by water-displacement method, based on Archimedes' principle. In addition, both kind of materials were analyzed by differential scanning calorimetry (DSC, Mod. 862 Mettler), Raman spectroscopy (He-Ne Horiba JY Induram Laser (633 nm), Kaiser Raman OSI head MKII, and Kaiser spectrometer OSI HoloSpec), DC electrical resistivity (Keithley 6105 Resistivity Adapter), and broadband dielectric spectroscopy (BDS, Alpha high-resolution dielectric analyzer). Porous polymers were studied by scanning electron microscope (SEM, model Quanta 200FEG, FEI) to measure the pore size, pore density, and polymer wall thickness. More details about the characterization procedures can be found in the Supplementary Information.

**Estimation of the confinement effect boundary and radius of gyration of PMMA:** some studies about the confinement effect on the chain conformation relate the appearance of this effect with the characteristics of the polymer chains under study. In particular, Kraus et al. [32] determined, both experimentally and by modeling, that the confinement effect on thin films appears when the films thickness reaches a value below six times the radius of gyration of the polymer chains. As the pore walls can be considered two-dimensional structures similar to thin films, we have estimated the pore wall thickness values where confinement effect should be noticed, using that relationship between the radius of gyration and the confinement effect, and determining the radius of gyration with the equation proposed for PMMA by Kirste et al. [33] (Equation (1)).

$$\langle r^2 \rangle = 0.096 \cdot M_w^{0.98} \quad (1)$$

Where  $M_w$  is the average molecular weight of the PMMA chains. It is obtained a value of 7.97 nm for the radius of gyration of our PMMA, and therefore the expected thickness boundary for the confinement effect should be about 47 nm.

**Analysis of the Raman spectra and selection of relative intensities:** the analysis of the Raman spectra was carried out by analyzing the evolution of four relative intensities between six peaks corresponding to vibrational modes of the pendant groups. The peaks selected in this study corresponds to 812, 968, 1452, 1736, and  $2954\text{ cm}^{-1}$  (Fig. S2, see Supplementary Information). Relative intensities under study were selected according to the following criteria: for each pair of peaks the intensity of the peak of the pendant group or vibrational mode that needs less volume is divided by the intensity of the peak of the pendant group or vibrational mode expected that needs more volume in the vibration. Pendant groups or vibrational modes that need more volume will be more sensible to the confinement (as they are going to be constrained first and before the others needing less volume), and therefore it can be expected that the studied ratios will be sensitive to the chain conformational changes, increasing when the volume that the chain can occupy is reduced. The intensity ratios under study were  $Y_{812}/Y_{968}$ ,  $Y_{812}/Y_{1452}$ ,  $Y_{1736}/Y_{1452}$ , and  $Y_{2954}/Y_{1452}$ .

For instance, in the case of the relative intensity  $Y_{812}/Y_{968}$ , the

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