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Porous Volume of Inorganic Materials and Degree of Swelling of Elastomers Monitored by DSC Measurements

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Strong analogies between inorganic porous materials and polymeric swollen gels have been demonstrated. The thermoporosimetry technique, based on the shift of the transition temperature for a confined solvent with respect to free solvent, has been applied in determining the degree of swelling in elastomers. Prior to this study, the validity of the method was demonstrated for determining the total porous volume of mesoporous silica gels. Sequential addition of solvent to the sample allows for the precise measurement of the total porous volume, and the values obtained agree well with the ones derived from gas sorption. Thermoporosimetry appears to be a very unique tool to study polymeric swollen gels and allows not only the measurement of the degree of swelling but also the mesh size distribution in a one-step easy experiment.

1. Introduction

The study of the texture of divided media has been the subject of a lot of attention during the past decades.^{1,2} Inorganic porous materials find applications in various fields such as catalysis, membranes, phase separation, or drug encapsulation, for instance. The precise knowledge of the porous volume is fundamental in this case. Whereas the pore notion is unambiguously defined in the case of inorganic materials, a quite similar notion can be defined for polymeric gels. Inorganic porous materials (powder, foam, etc.) and polymeric swollen gels have the common peculiarity that their physical properties depend on their degree of division. Polymeric materials, once aged in an appropriate solvent, tend to swell and to trap solvent inside their chains. The swollen volume can be compared with the porous volume of inorganic porous materials, and the measurement of the degree of swelling gives important information about the level of cross-linking of elastomers. As for inorganic materials, the precise measurement of the swelling ratio of elastomers is very important in understanding the behavior of these materials

To determine the porous volume, classical methods are gas sorption and mercury porosimetry. These two techniques involve a specific apparatus and take quite a long time to be carried out. The main way to determine the degree of swelling is the gravimetric method consisting of a double weighing of elastomers: dry and swollen. Because it is difficult to weigh the swollen gel without an excess of swelling solvent, this technique often leads to a high level of uncertainty concerning the final result.

The idea, investigated in this work, is the quantification of the solvent both trapped inside the network of the matrix and outside it. To do that, differential scanning calorimetric (DSC)

was used to detect and record the heat of crystallization released by the solvent when it changes states. Indeed, as has been shown in previous work,^{3,4} the solvent confined inside porous materials or inside the network of polymeric gels behaves differently from the solvent remaining outside. In particular, the temperature of crystallization observed for the confined solvent is lower than that of the free solvent remaining on the surface of the material. This freezing point depression depends on the radius of the pore or the size of the mesh of the network in which the crystallization takes place. That is, more precisely, the basis of the thermoporosimetry technique^{5–7} which allows a good determination of the pore or mesh size distributions in the porous materials and the polymeric gel as well. The objective of this work is, consequently, to demonstrate that, after a precise calibration thanks to inorganic matrixes with well defined textural properties, the thermoporosimetry can be successfully applied both to polymeric samples for the determination of their degree of swelling and to inorganic materials for the measurement of the total pore volume.

2. Experimental Section

2.1. Materials. The nanoporous gel-derived silica monoliths (2.5 mm × 5.6 mm diameter cylinders) were prepared by the acid-catalyzed hydrolysis and condensation of an alkoxysilane precursor, following procedures described elsewhere.⁸

Careful control of the aging procedure performed at 900 °C allowed the production of matrixes with tailored textural properties. In this study, five different samples corresponding to different aging procedures were used. The textural properties (specific surface area (SSA), total pore volume (Vp), and pore size distribution (PSD)) were determined by N₂ sorption on a Quantachrome AS6 Autosorb apparatus. Five samples with different pore size were used, and their textural data are displayed in Table 1.

All of the solvents (*n*-heptane, cyclohexane, chloroform and methanol) which were used to swell the polymeric gels, to soak

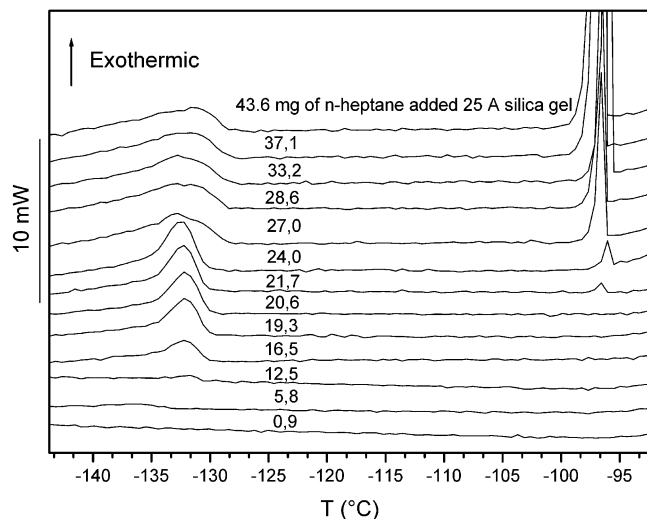
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TABLE 1: Textural Data of the Porous Gel-Derived Silica Samples and Their Corresponding Deviations

sample	SSA (m ² /g)	σ (m ² /g)	V_p (cm ³ /g)	σ (cm ³ /g)	D_p (Å)	R_p (Å)	σ (Å)	Max PSD (Å)
25 Å	537	12.8	0.333	0.001	24.8	12.4	0.5	17.5
50 Å	532	9.5	0.696	0.028	52.3	26.15	3	24
75 Å	472.7	1.5	0.922	0.082	78	39	6.7	34.2
200 Å	166.2	3.2	0.991	0.071	238.3	119.15	12.4	87
270 Å	183.1	1	1.327	0.072	289.8	144.9	14.1	142.5

**Figure 1.** DSC thermal curves of the crystallization of *n*-heptane in the 25 Å silica gel sample.

the silica gel samples, and to purify the elastomers were of HPLC grade. The terpolymer ethylene propylene diene monomer (EPDM) used was based on the 5-ethylidene-2-norbornene as diene monomer. Its molar contents, determined by ¹H NMR at 400 MHz, were 60.0/37.3/2.7 mol % of ethylene/propylene/diene, respectively.

Polycyclo-octene which was used has an 80% *cis* configuration. Both polymers were purified to remove residual oxidized products and stabilizing additives. This was carried out by precipitating the sample into methanol from a chloroform solution.

A first set of polymeric films (thickness $\sim 100 \mu\text{m}$) was prepared by molding the EPDM in an electric heating laboratory press hold at 145 °C and 19 MPa for 1 min. They were then photooxidized. Photooxidation was performed by exposing film samples in a polychromatic setup based on the conventional accelerating device. This instrument, already described elsewhere,⁹ is equipped with a medium-pressure mercury lamp filtered with a borosilicate envelope (MA 400) in order to cutoff wavelengths below 300 nm, reproducing, in this way, the spectrum of sun light. Samples were irradiated at 35 °C for periods ranging between 2 and 20 h (EPDM1, 20 h; EPDM2, 12 h; EPDM3, 9 h; and EPDM4, 2 h). This group of samples is then soaked in *n*-heptan.

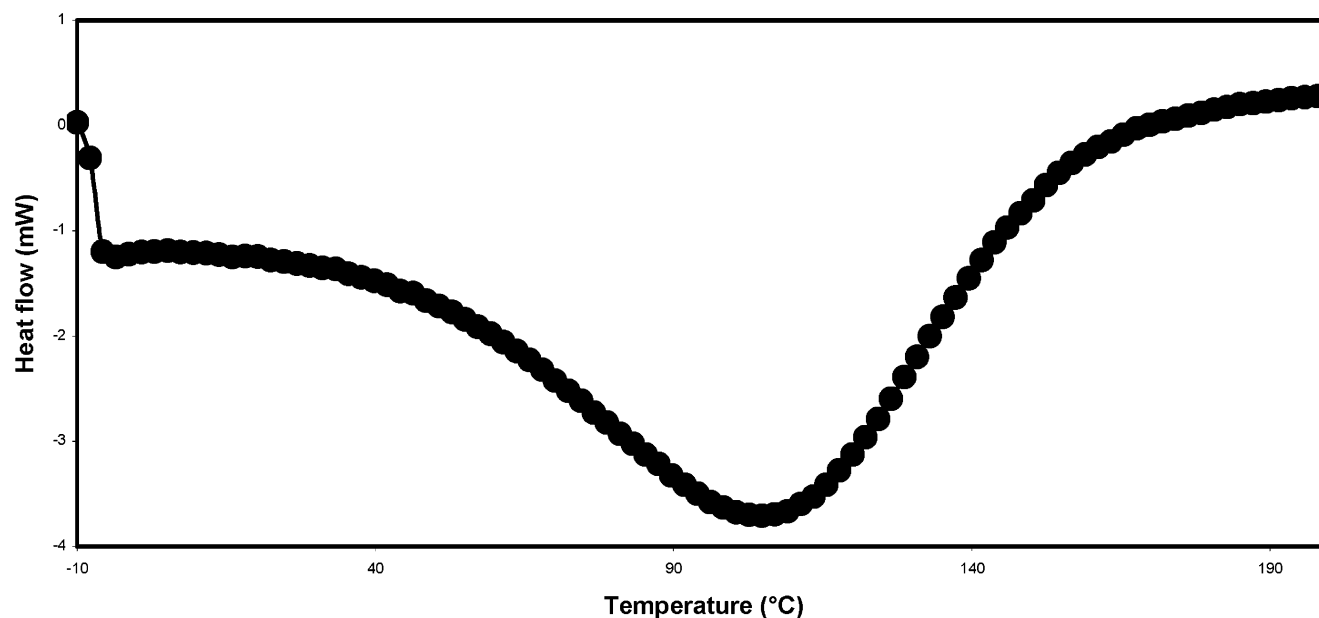
Two polycyclo-octene samples were prepared by chemical cross-linking using dicumyl peroxide (DCP). The DCP was introduced (5% w/w) in the matrix by dissolving the peroxide together with polycyclo-octene into chloroform and coprecipitating this solution into methanol. Once the solvent was evaporated, the sample was molded in an electric heating laboratory press hold at 145 °C and 19 MPa for 25 and 35 min, respectively, to get two different cross-linking levels (polycyclo-octene1 and polycyclo-octene2). These two samples were swollen in cyclohexane.

After being cross-linked, by photo-oxidation or by chemical way, elastomeric samples were characterized by measuring their degree of swelling (*G*) which is defined as the ratio of the mass of swollen polymer to the one of the dry polymer

$$G = \frac{m_{\text{swollen}}}{m_{\text{solvent}}} = 1 + \frac{m_{\text{solvent}}}{m_{\text{dry}}}$$

where *G* is the degree of swelling, m_{swollen} is the mass of the swollen sample, m_{dry} is the mass of the dry sample, and m_{solvent} is the mass of the solvent trapped inside the gel at the swelling equilibrium.

2.2. Techniques. The amount of solvent confined inside the divided medium is assessed by differential scanning calorimetry (DSC). We used a Mettler DSC 30 apparatus calibrated (both for temperature and enthalpy) with metallic standards (In, Pb, and Zn). Silica gel samples were introduced in an aluminum

**Figure 2.** DSC thermal curve of the heating of the silica gel sample with 5.8 mg of *n*-heptane.

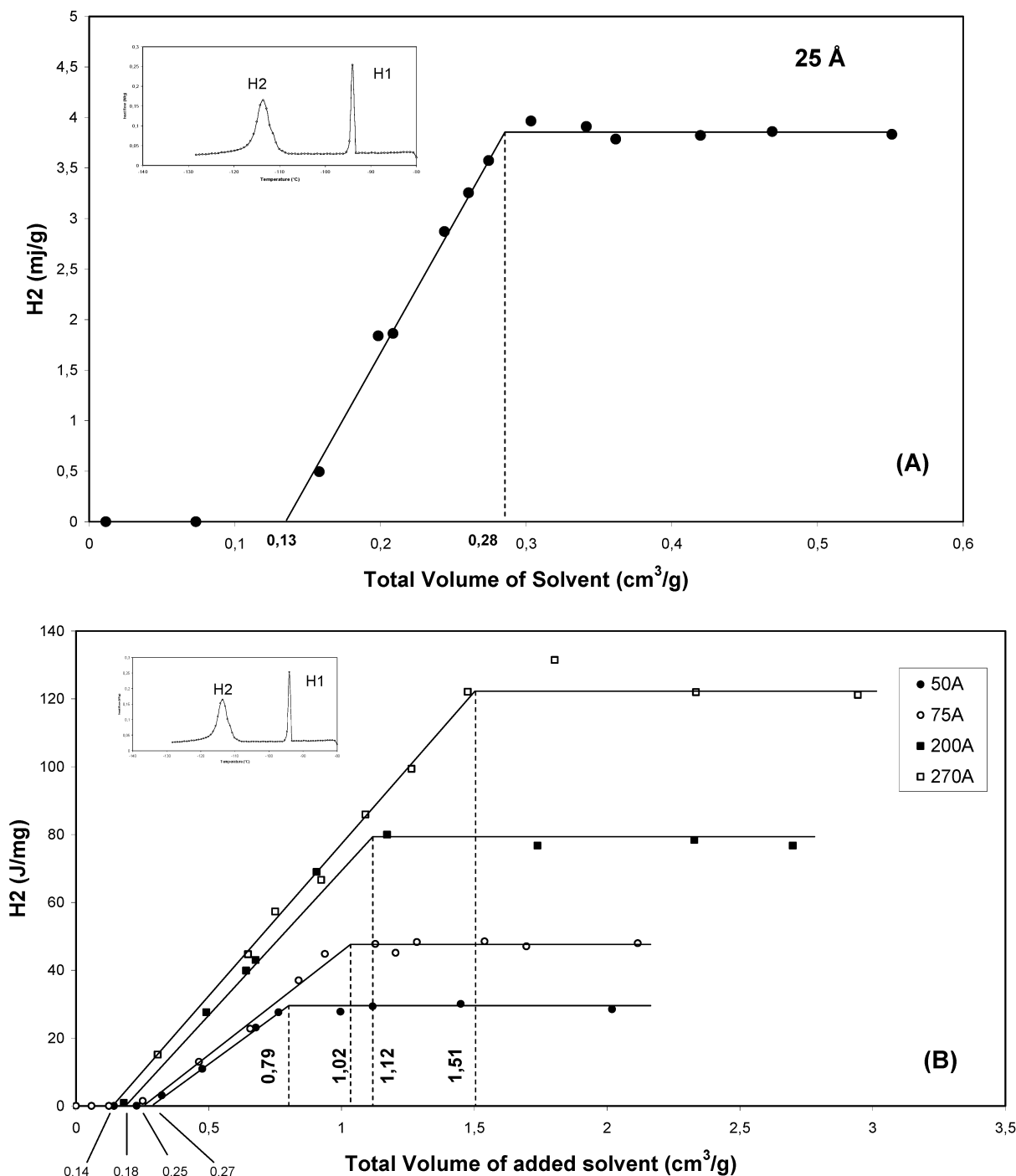


Figure 3. Heat of crystallization of the confined solvent (H2 peak) versus the total volume of solvent added to the silica gel sample for 25 Å sample (A) and 50, 75, 200, and 270 Å (B). The break points give the porous volumes and the intercepts of these curves with X axis give the volumes of the adsorbed layers.

DSC pan of 140 μL . A very little hole (10 μm) was drilled in the cover of the DSC pan in order to add *n*-heptane dose by dose using a microsyringe. The DSC pan is then submitted, for each solvent addition, to a decreasing temperature program from -90 to -150 $^{\circ}\text{C}$ with a 0.7 $^{\circ}\text{C}/\text{min}$ cooling rate. Polymeric samples, previously swollen in the appropriate solvents (*n*-heptane for EPDM and cyclohexane for polycyclo-octene) for 48 h, were introduced in a similar DSC pan which was hermetically sealed. To maintain the polymeric gel in a swelling equilibrium state, the solvent was introduced in excess before sealing the DSC pan. For each DSC experiment, the masses of dry samples and the total amount of solvent were determined by weighing.

3. Results and Discussion

3.1. Porous Volume of Silica Samples. Figure 1 shows the DSC thermal curves recorded from the cooling of the 25 Å silica gel sample soaked with *n*-heptane. The first two curves (from the bottom) are completely flat. No crystallization signals are detected even if a certain amount of *n*-heptane was added inside the DSC pan. Moreover, to confirm that the solvent is really present, we heated the DSC pan, corresponding to the second thermal curve of Figure 1 (with 5.8 mg of *n*-heptane), and we recorded the thermal signal from -10 to $+200$ $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}/\text{min}$. A large endothermal peak resulted (Figure 2) corresponding to the evaporation of *n*-heptane and thus confirming its presence. The first amount of *n*-heptane introduced in the porous sample

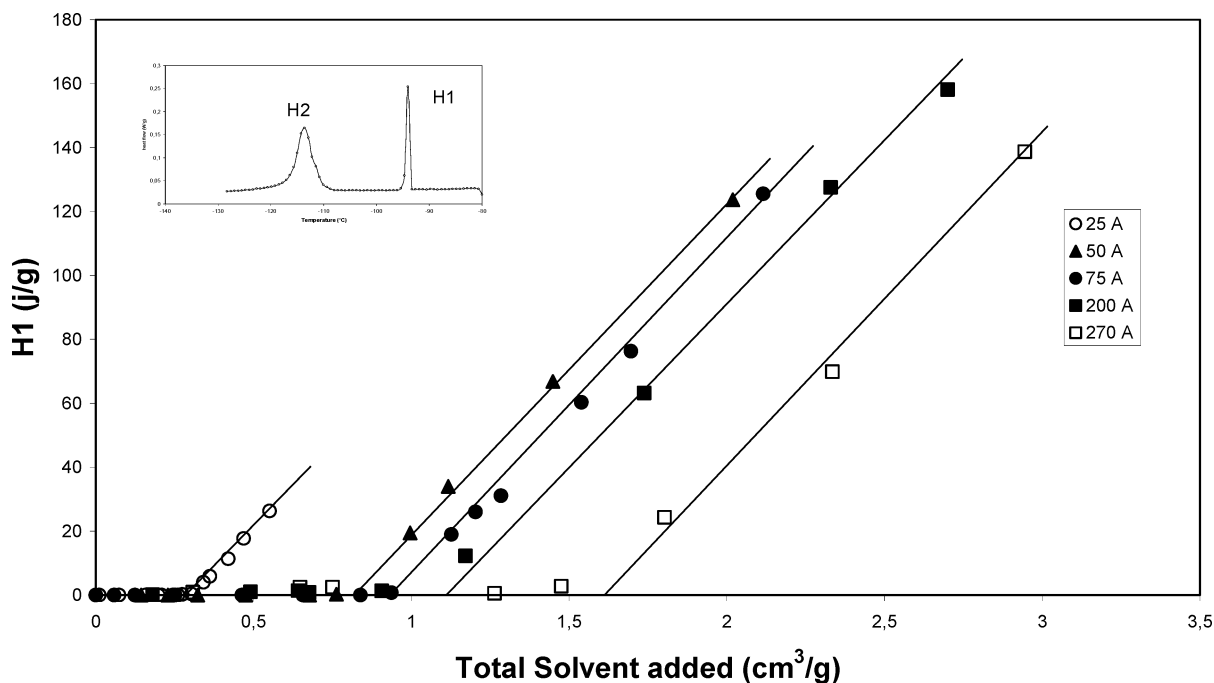


Figure 4. Heat of crystallization of the free solvent (H1 peak) remaining outside the pores versus the total volume of solvent added. The intercepts of these curves with the X axis give the porous volumes.

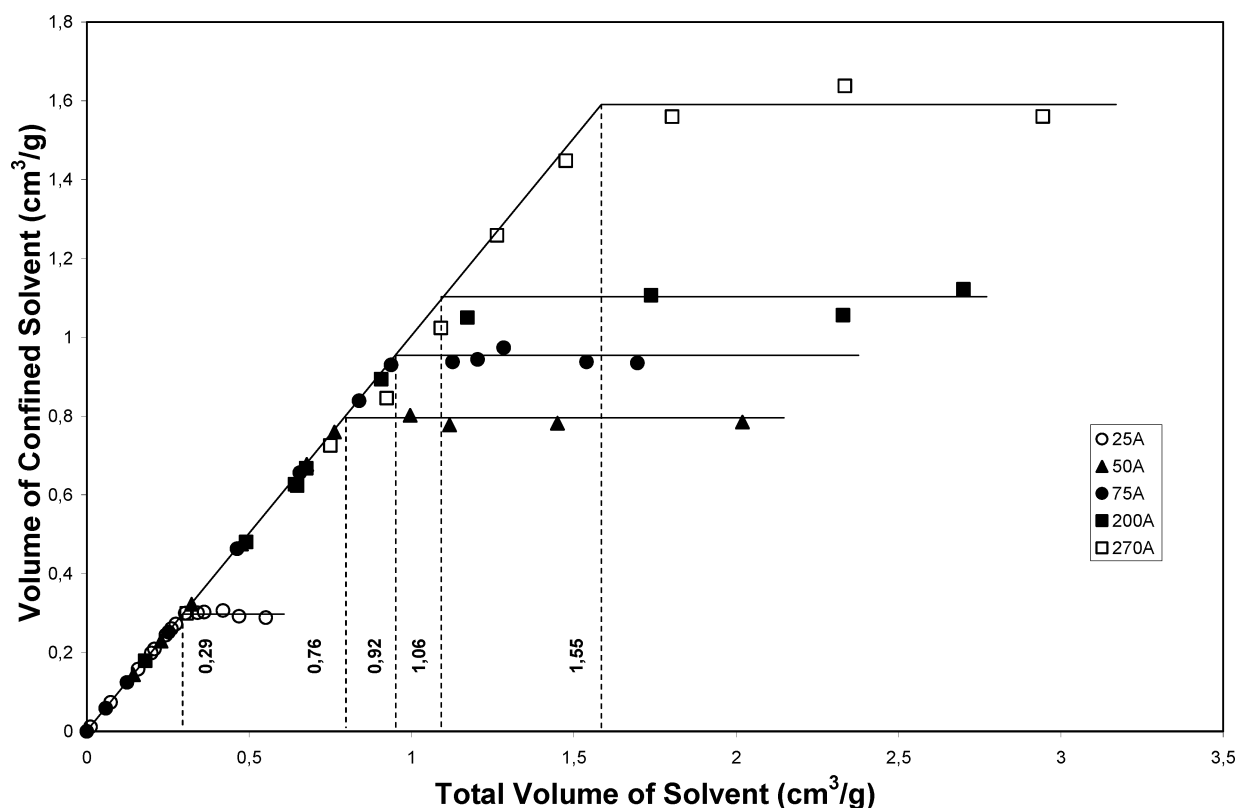


Figure 5. Volume of the confined solvent versus the total volume of solvent added to the silica gel sample. The break points give the porous volume.

does not crystallize. It probably remains adsorbed as a thin layer on the walls of the pores.

This layer of solvent adsorbed has already been pointed out by other authors.^{5,10} From the third curve (Figure 1), a signal starts to be observable, confirming that the liquid has covered all of the surface of the porous material and began to fill its pores. After the sixth thermal recording, a second peak starts to grow, and at the same time the first one stops increasing. The second peak is attributable to free solvent remaining outside

the porous material. Its detection reveals that pores are filled and that there is an excess of solvent. Thus, two stages can be observed during these experiments: the first one is when all of the walls of pores are coated, and the second one is when pores are filled. The porous volume corresponds to the end of the first stage. To determine this volume precisely, three representations were performed as is shown in Figures 3–5.

As stated before, two peaks are observed in the DSC curve corresponding to crystallization of *n*-heptane when it is in excess.

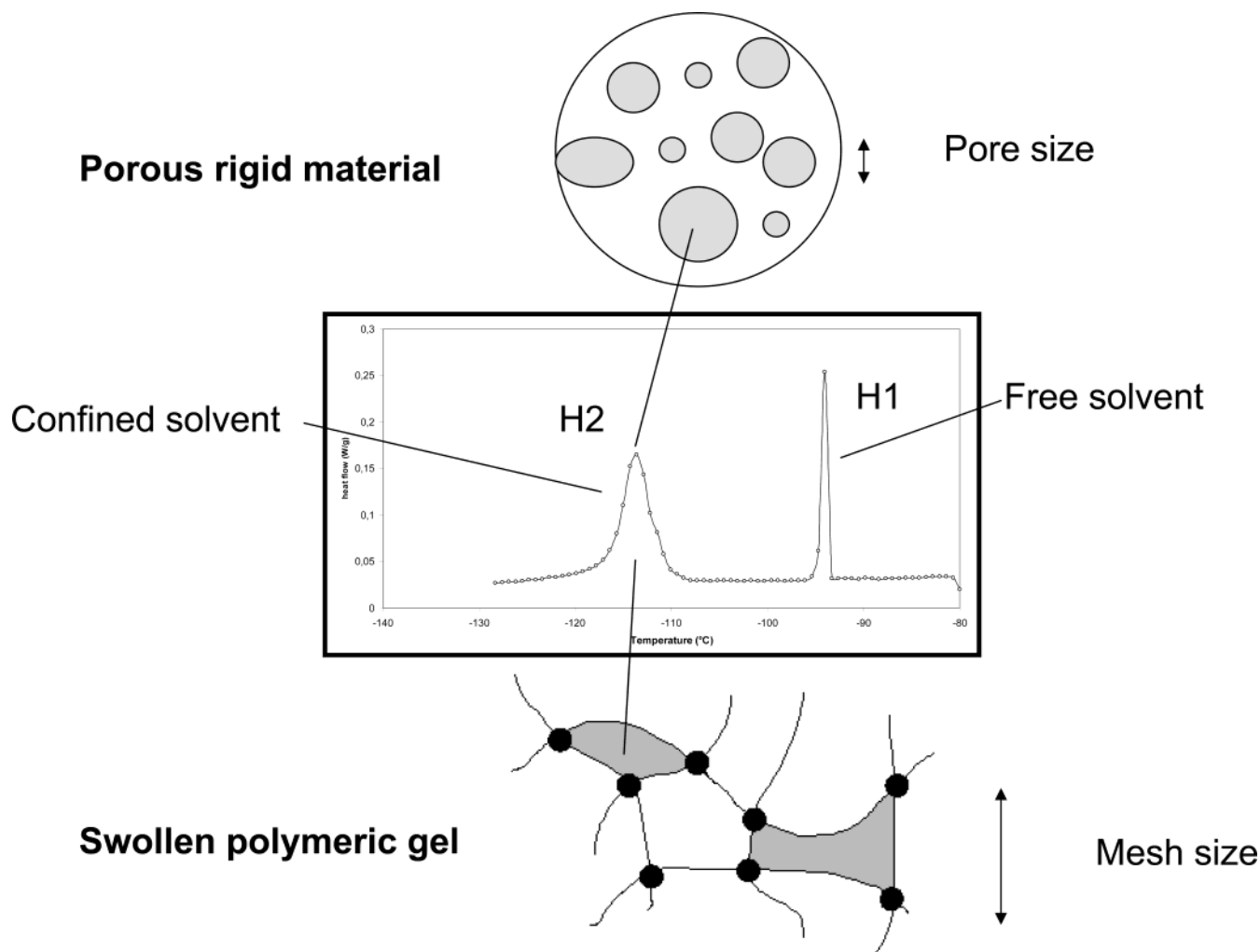


Figure 6. *n*-Heptane crystallization in a divided media

The first peak (labeled H1 on the figures), corresponding to the excess solvent, is situated around $-96\text{ }^{\circ}\text{C}$ and well shifted to low temperature because of the supercooling phenomenon. The second one (H2) is due to the confined solvent and depends on the size of the pore where the crystallization occurs: the smaller the pore the lower the temperature of H2.

Figure 3a displays the plot of H2 (J/g of dry sample) versus the total amount of solvent (cm^3/g of dry sample) which was introduced in the DSC pan containing the $25\text{ }\text{\AA}$ silica sample. The first observation that can be pointed out is that the linear section does not intercept the origin. The point where this section intercepts the abscissa axis (V_1) represents the amount of solvent remaining under thin adsorbed layer form. Knowing the specific surface area of these samples, previously determined by BET technique and listed in Table 1, it is possible to calculate the thickness e of this layer as follows:

$$e = \frac{V_1}{SSA}$$

where e is the thickness of the adsorbed layer, V_1 is the volume of the adsorbed solvent, and SSA is the specific surface area of silica gel sample.

Figure 3b shows the results obtained for the other samples. The second remarkable point is the break points of those curves. The abscissas of these points give the values of the porous volumes (V_p). Indeed, once this volume is reached, the values

of H2 remain constant thus revealing that all of the pores were completely filled.

A second representation is shown in Figure 4 where H1 (heat released by the crystallization of the excess of solvent by gram of dry sample expressed in J/g) is plotted versus the total quantity of solvent introduced inside the DSC pan. The first flat parts of these curves correspond to the filling of the pores of the material. Once the pores are completely filled, H1 starts to increase and the abscissa of this particular one gives the total porous volume values. Figure 5 is devoted to a third representation showing the plots of the confined solvent volume (cm^3/g of dry sample) versus the total volume of solvent which was added in the DSC pan. The volume of the confined solvent was calculated from the knowledge of the total volume of the solvent on one side and the volume of the solvent in excess on the other side. The volume of the solvent in excess was determined from the H1 peak, knowing the specific heat of crystallization of the *n*-heptane (146.53 J/g , derived from the slopes of the linear segments of curves in Figure 4). At the beginning, the solvent fills the pores, and once they are completely filled, the volume of confined solvent remains constant. Consequently, the abscissas of the break points in Figure 5 correspond to the porous volumes.

In Table 2, we compare the porous volumes calculated from the three representations with those derived from gas sorption technique (BJH). The agreement is fairly good. In the same table, we reported values of thickness of the adsorbed solvent

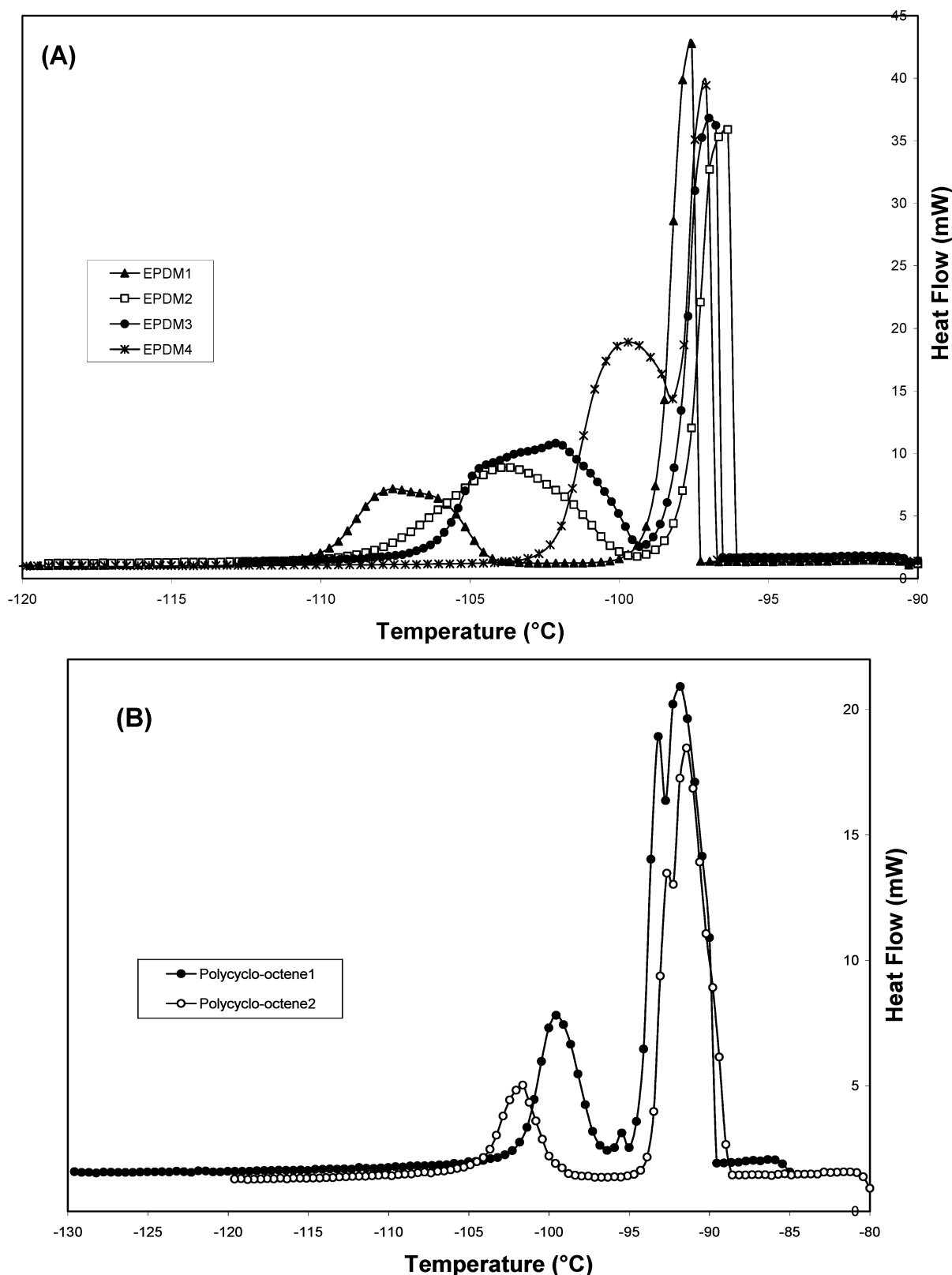


Figure 7. DSC thermal curves of thermal transitions of swelling solvents. (A) Crystallization of *n*-heptan in photooxidized swollen EPDM samples with various degree of swelling, *G*, of 3.25, 4.25, 5.01, and 11.5 for EPDM1, EPDM2, EPDM3, and EPDM4, respectively. (B) Solid–solid cyclohexane transition in swollen chemically cross linked polycyclo-octene sample with two degrees of swelling, *G*, of 5.48 and 4.31 for polycyclo-octene1 and polycyclo-octene2, respectively.

layer for each silica sample. These values range between 2.4 and 10.8 Å which agrees quite well with the value obtained for benzene.⁵

To demonstrate the efficiency of this method, we carried out a large number of measurements. However, it is not always

necessary to conduct all of these experiments if the aim is only the determination of the porous volume. Indeed, it is enough to record the DSC curve of a sample which was soaked in a light excess of solvent. Knowing the mass of the dry sample, the total volume of the solvent, and the heat released by the

TABLE 2: Porous Volume Values (V_p) Derived from Figures 3–5 Respectively V_p (DSC)3, V_p (DSC)4, and V_p (DSC)5 Compared to the Values Calculated by BJH Adsorption Gas Method V_p (BJH)

sample	SSA (m ² /g)	V_l (cm ³ /g)	ϵ (Å)	V_p (BJH) (cm ³ /g)	V_p (DSC)4 (cm ³ /g)	V_p (DSC)5 (cm ³ /g)	V_p (DSC)6 (cm ³ /g)
25 Å	537	0.13	2.42	0.333	0.28	0.31	0.29
50 Å	532	0.27	5.07	0.696	0.79	0.78	0.76
75 Å	472.7	0.25	5.31	0.922	1.02	0.96	0.92
200 Å	166.2	0.18	10.8	0.991	1.12	1.06	1.06
270 Å	183.1	0.14	7.62	1.327	1.51	1.52	1.55

crystallization of the free solvent (H1), it is easy to reach the porous volume (V_p). That is the principle of the application of this method to determine the degree of swelling of elastomers.

3.2. Swelling Degree of Elastomers. Once cross-linked, an elastomer is no longer soluble in the solvent in which it was before cross-linking. However, the solvent is still able to swell the elastomer. The cross-linked elastomer swollen by the solvent gives a gel. The solvent inside the gel is “compartmentalized” and prevented from moving freely. This reduction in degrees of freedom of the solvent enables us to compare the swollen polymeric gel with a divided medium and the solvent behaves as if it was confined in the pores of a rigid material. To simplify, we assume that the swollen gel is built from adjacent cells in which the solvent has a reduced mobility and which will be called “mesh” recalling the idea of a tri-dimensional network. The more the polymer is cross-linked, the smaller the size of the mesh. Figure 6 shows the correspondence between the pore notion in the rigid material and the mesh notion in the polymeric swollen gel.

To demonstrate the efficiency of this technique, we carried out experiments with both cyclohexane and *n*-heptane. The *n*-heptane was used to swell the photooxidized EPDM samples and cyclohexane the chemically cross-linked ones. Figure 7a shows the DSC curve of the crystallization of *n*-heptane swelling EPDM samples (with an excess of heptane). As was expected, two peaks are observed: the first one corresponds to excess solvent remaining outside the sample and the second one is attributable to the *n*-heptane confined inside the polymeric network of the gel. Knowing the specific heat of crystallization of *n*-heptane (146.53 J/g), it is possible to calculate the amount of the excess solvent from the area under the first peak and, by subtracting it from the total mass of the solvent, to determine the quantity of the confined solvent.

As far as cyclohexane is concerned, we chose to use the solid-to-solid-phase transition undergone by this solvent instead of its crystallization. In fact, the cyclohexane solid-to-solid transition has been pointed out and studied by several authors for example by using Raman spectroscopy,¹¹ thermal analyses,¹² or neutron scattering.¹³ It is admitted that this transition derives from the evolution from a plastic crystal state (phase I) to a rigid crystal state (phase II). Phase I is disordered and cubic, whereas phase II is ordered and monoclinic. Under atmospheric pressure, this transition occurs at -87°C and releases 81 J/g, whereas the melting of cyclohexane involves only 30 J/g.

Figure 7b shows the DSC curve of the solid-to-solid transition of cyclohexane swelling polycyclo-octene samples (with an excess of cyclohexane).

TABLE 3: Comparison between the Degrees of Swelling Calculated from DSC Measurements, G_{dsc} , and the Degree of Swelling Derived from the Gravimetric Method, G_{grav}

	EPDM1	EPDM2	EPDM3	EPDM4	polycyclo- octen1	polycyclo- octen2
G_{grav}	3.25	4.25	5.01	11.5	5.48	4.31
G_{dsc}	3.14	4.11	4.95	9.78	5.34	4.21

Similarly to the crystallization of *n*-heptane, two peaks are observed: the first peak is due to the free solvent and the second is attributable to the confined cyclohexane and depends on the degree of cross-linking. Calculating the amount of confined solvents (cyclohexane or *n*-heptane) from those DSC thermal recording, we determined degrees of swelling of all elastomeric samples. In Table 3, we compare degrees of swelling derived from the gravimetric method (G_{grav}) with those calculated from DSC measurements (G_{DSC}). A good agreement is found especially for the highly cross-linked elastomers. It can be noticed that G_{grav} values are systematically higher than G_{DSC} values. This is probably due to the difficulty in removing the excess of the solvent from the gel before weighing it during the gravimetric procedure.

4. Conclusion

DSC measurements of the heat of thermal transitions (liquid to solid or solid-to-solid transitions) undergone by a confined solvent in a divide medium seem to be a reliable tool to obtain relevant textural data related to the materials. Porous volumes of rigid divided media and degrees of swelling of elastomeric gels were accurately determined in this way and successfully compared with the same data derived from independent techniques (BJH gas sorption for the porous volume and gravimetry for the degree of swelling). In addition to the porous volume or the degree of swelling, thermoporosimetry can be used to calculate the pore size distribution (PSD) in the rigid material or the mesh size distribution (MSD) in the polymeric swollen gel at the same time.

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