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Jyotsana Lal, Sunil Sinha, Loïc Auvray. Structure of Polymer Chains Confined in Vycor. Journal de Physique II, 1997, 7 (11), pp.1597-1615. 10.1051/jp2:1997205 . jpa-00248538

HAL Id: jpa-00248538

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Submitted on 4 Feb 2008

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Structure of Polymer Chains Confined in Vycor

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(Received 11 August 1995, revised 21 July 1997, accepted 28 July 1997)

PACS.61.12.Ex – Neutron scattering techniques (including small-angle scattering)

PACS.61.25.Hq – Macromolecular and polymer solutions; polymer melts; swelling

PACS.82.70.-y – Disperse systems

Abstract. — We observe by Small Angle Neutron Scattering the structure of polystyrene chains in semi-dilute solutions confined in a model porous medium, Vycor. The size of the free chains in solution is always larger than the pore diameter, 70 Å. The use of a suitable mixture of hydrogenated and deuterated solvents and polymers enables us to measure directly the form factor of one single chain among the others. The penetration of the chains in the porous medium is almost complete for the concentration ($\Phi = 20\%$) and the range of molecular weight ($35\,000 < M_w < 800\,000$) used. The radius of gyration of the confined chains is always smaller than the radius of gyration of the free chains in the equivalent bulk solution. Our measurements are in agreement with the theoretical predictions established by Daoud and de Gennes for chains confined in a cylindrical pore when the chains are entangled and laterally squeezed but remain ideal at large scale along the cylinder axis because of the screening of the excluded volume interactions (so-called regime of “semi-dilute cigars”). The values of the partition coefficient of the chains between the porous medium and the free solution and the asymptotic behavior of the structure factors indicate that polystyrene adsorbs onto the bare surface of Vycor. We show that silanizing Vycor suppresses this adsorption.

Résumé. — Nous observons par diffusion de neutrons aux petits angles la structure de chaînes de polystyrène en solution semi-diluée confinées dans un milieu poreux modèle, le Vycor. La taille des chaînes en solution à l'état libre est toujours supérieure au diamètre des pores, 70 Å. L'utilisation d'un mélange adéquat de solvants et de polymères hydrogénés et deutérés nous permet de mesurer directement le facteur de forme d'une seule chaîne au milieu des autres. La pénétration des chaînes dans le milieu poreux est presque totale pour la concentration ($\Phi = 20\%$) et la gamme de poids moléculaire ($35\,000 < M_w < 800\,000$) utilisées. Le rayon de gyration des chaînes confinées est toujours inférieur au rayon de gyration des chaînes libres dans la solution équivalente. Nos mesures sont en accord avec les prédictions théoriques établies par Daoud et de Gennes pour des chaînes confinées dans un pore cylindrique quand les chaînes sont enchevêtrées et comprimées transversalement mais restent idéales à grande échelle dans la direction du cylindre à cause de l'écrantage du volume exclus (régime dit “de cigares semi-dilués”). Les valeurs des coefficients de partage des chaînes entre le milieu poreux et la solution libre ainsi que le comportement asymptotique des facteurs de structure montrent que le polystyrène s'adsorbe sur la surface nue du Vycor. Nous montrons que la silanisation du Vycor supprime cette adsorption.

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1. Introduction

The structure and dynamics of polymer chains confined in porous materials are relevant to a broad class of practical applications such as filtration, gel permeation chromatography and enhanced oil recovery. Size exclusion techniques traditionally deal with dilute polymer solutions, but as proposed recently [1], they can be extended to concentrated solutions.

Depending on the physical situation and on the nature of the porous medium, the effect on the chains is usually calculated theoretically or by simulation techniques in terms of the statistical mechanics of chains in well-defined model geometries [2] or in random potentials [3]. The case of confinement of polymers by deformable fluid interfaces, liquid droplets [4] or surfactant membranes [5] has also begun to be considered. All these theoretical studies reveal again the well-known analogy between polymer systems and other strongly fluctuating systems as binary mixtures or liquid helium close to their critical point [6]. Depending on the approach they demonstrate either the effects of confinement on the fluctuations, correlations and dynamics of the systems or deal with the effects of localization of the chains induced by a random quenched disorder.

Experimentally, the partitioning and diffusion of polymer chains has been observed in model porous membranes and controlled pore glasses [7]. In dilute solutions the diffusion is highly hindered when the chain size becomes larger than the pore diameter. However, the penetration of the chains into the pores is large as soon as the concentration of the bulk solution is large, in qualitative agreement with the somewhat paradoxical but essential theoretical prediction that the chains should enter the pores when the correlation length of the semi-dilute bulk solution becomes smaller than the pore size. Polymers confined in gels [8], possibly a particular realization of a random potential, and polymers trapped inside droplet microemulsions [9], a case of a deformable confining interface, as well as polymers in lamellar phases, have been studied recently using Small Angle Neutron Scattering (SANS) but to our knowledge there has been no detailed study of the static molecular conformations of polymer chains in confined geometries with well-defined solid boundaries. Initially, one faces the problem both of getting the long polymer chains into a suitable microporous material and of observing them once they are there. We have tried to overcome some of these difficulties.

The choice of a suitable porous medium is crucial but limited in practice. If one wishes to get a high porosity with the smallest possible pores, to avoid organic or inorganic polymer gels which have no pores with well-defined boundaries and surfactant systems which may raise particular problems related to their deformability, one is led to a class of "controlled pore glasses", used as classical chromatographic media, whose most popular representative is the famous Vycor. Vycor presents several advantages: it can be obtained as bulk material; the pore structure is well-studied, well-defined and rather regular on local scales and disordered on large scales (greater than 300 Å), according to the numerous studies performed by different techniques [10–12], although there is a small controversial uncertainty about the roughness of the pore surfaces [13]. Finally, the average diameter of the pores, 70 Å, may be small enough to lead to significant confinement effects with typical polymer chains.

Dilute polymer chains of reasonable molecular weights do not penetrate the pores as such and so we have focussed the first study on semi-dilute solutions, where the concentration is chosen so that the correlation length of the solution is smaller than the pore diameter. Our polymer is polystyrene, which may not be the best choice because of the glassy character of this polymer, which hinders the study of very concentrated solutions at ambient temperature. However, an advantage of polystyrene is that its interaction with silica in toluene, the solvent we use, is weak so that we may possibly neglect adsorption phenomena in our initial analysis. In most of our experiments we will thus use bare Vycor without special surface treatment,

except in one case where the results between bare Vycor and silanized Vycor are compared. Polystyrene can also be obtained easily in deuterated form, which facilitates the observation of its structure by SANS.

In fact the observation of the structure of the polymer chains confined in Vycor is a complicated problem because in the general case the scattering signal may be dominated not by the polymer in its solvent, but by the porous medium itself. This problem can be solved by matching the scattering length density of the Vycor and of the solvent using an appropriate mixture of hydrogenated and deuterated toluene. In order to simplify the study further, we have also chosen to use a suitable mixture of physically identical hydrogenated and deuterated polymer chains such that the scattering intensity becomes proportional only to the form factor of one chain among the others. We will thus ignore the correlations between different chains. This is known as the method of zero average contrast [14,15].

We present in the first section the theory of the scattering by confined chains, we then describe in the second section the systems studied and the experimental conditions. In the last section we present and discuss the results obtained as a function of the molecular weight of the chains in comparison with the different theoretical predictions, which we recall in the course of the discussion.

2. Scattering by Confined Polymer Chains

Let us consider a solution of hydrogenated (H) and deuterated (D) polymer chains in a solvent (S) confined in a porous medium (P). If as usual the assumption of global incompressibility is used then the scattering intensity can be expressed in term of 6 partial structure factors $S_{ij}(q)$ ($i, j = H, D, P$) defined as the Fourier transform of the constituents volume fraction correlation function:

$$S_{ij}(q) = \int d^3\mathbf{r} \langle \delta\Phi_i(0)\delta\Phi_j(\mathbf{r}) \rangle e^{i\mathbf{q}\cdot\mathbf{r}} \quad (1)$$

$\Phi_i(\mathbf{r})$ is the local volume fraction of constituent i and $\delta\Phi_i(\mathbf{r})$ the local deviation from the average value in the sample volume V .

In particular, $S_{PP}(q)$ is the structure factor of the porous medium which can be measured on the bare sample without polymer. The terms S_{PH} and S_{PD} describe the correlations between the porous medium and the polymer chains (H or D). They contain in principle information on the pore geometry (the chains have to stay in the pore volume) and also on the interaction between the chains and the pore surfaces. It could in particular reveal adsorption of the chains [16]. The other three structure factors S_{HH} , S_{DD} and S_{HD} are related to the chain structure and their correlations. S_{HD} depends only on the interchain correlations, while S_{HH} and S_{DD} contain also a contribution of the intra-chain form factors. It should be emphasized that both the intra- and interchain correlations indirectly depend on the pore geometry.

Although this is a complicated task, it would be interesting in the future to measure each of the five polymer structure factors by suitable contrast variation experiments. Here, however we restrict ourself to a simpler situation where the scattering length densities of the solvent and of the porous medium are matched. This eliminates the direct contribution of the porous medium to the scattering and we are left only with the contributions of the three polymer structure factors S_{HH} , S_{DD} and S_{HD} . The total scattering intensity $I(q)$ per unit sample volume (in cm^{-1}) is then written as [15]

$$I(q) = (n_D - n_0)^2 S_{DD} + (n_H - n_0)^2 S_{HH} + 2(n_D - n_0)(n_H - n_0) S_{HD} \quad (2)$$

n_D , n_H and n_0 are respectively the scattering length density of the deuterated and hydrogenated chains and of the solvent (in cm^{-2}).

Let us further assume the case that the H and D chains are physically identical (with the same index of polymerization N) and that the interactions between all the monomers, H or D are the same (this may not be the case in the melt state but is certainly a good approximation in semi-dilute solutions [17]). Each of the partial structure factors can be decomposed into an intra-chain and interchain contribution. Let x be the proportion of deuterated chains, v the molecular volume of one H or D monomer and Φ the total average effective volume fraction of polymer in the whole sample (including the volume of the solid part of the porous medium). The chain form factor $P(q)$ and the interchain structure factor $Q(q)$ are defined as:

$$P(q) = 1/N^2 \sum_{i1=1 \text{ to } N} \sum_{j1=1 \text{ to } N} \langle \exp(i\mathbf{q} \cdot \mathbf{r}_{i1j1}) \rangle$$

$$Q(q) = 1/N^2 \sum_{i1=1 \text{ to } N} \sum_{j2=1 \text{ to } N} \langle \exp(i\mathbf{q} \cdot \mathbf{r}_{i1j2}) \rangle.$$

Here $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The sum runs in the first expression over monomers belonging to the same chain and over monomers belonging to different chains in the second expression. With our assumptions, $P(q)$ and $Q(q)$ are independent of the chain labelling and $P(q)$ is normalized to 1 at vanishing scattering vector. Then the partial structure factors are expressed as:

$$S_{DD} = xv\Phi NP(q) + Vx^2\Phi^2Q(q)$$

$$S_{HH} = (1-x)v\Phi NP(q) + V(1-x)^2\Phi^2Q(q)$$

$$S_{HD} = Vx(1-x)\Phi^2Q(q).$$

This yields the following result

$$I(q) = (n_D - n_H)^2 x(1-x)v\Phi NP(q) + (xn_D + (1-x)n_H - n_0)^2 [v\Phi NP(q) + V\Phi^2Q(q)]. \quad (3)$$

The average contrast between the polymer and the solvent is $xn_D + (1-x)n_H - n_0$. If one can adjust x such that it vanishes

$$xn_D + (1-x)n_H - n_0 = 0 \quad (4)$$

the scattering intensity has a very simple expression:

$$I(q) = (n_D - n_H)^2 x(1-x)v\Phi NP(q). \quad (5)$$

This yields directly the form factor of the polymer molecules confined in the porous medium even at high concentration of polymer. This is the main interest of this method, which for the moment has only been used to study bulk polymer solutions [14, 15]. It offers the advantage that it requires only one sample.

3. Samples and Experiments

3.1. POROUS MATERIAL. — Vycor was used (Corning Vycor Brand 7930) [10–12] for confining the polymer solutions. As is well-known, Vycor is made by a process of spinodal decomposition leading to a SiO_2 rich phase and a B_2O_3 rich phase, of which the latter is leached out leaving behind an almost pure SiO_2 skeleton with an interconnected structure. The porosity is typically 28% by volume and the characteristic internal diameter of the pores is 70 Å. There is a large uncertainty on the specific area of this system. Its nominal value is stated to be 200 m²/g while gas adsorption isotherm measurements yield 108 m²/g [10–12]. Still smaller values,

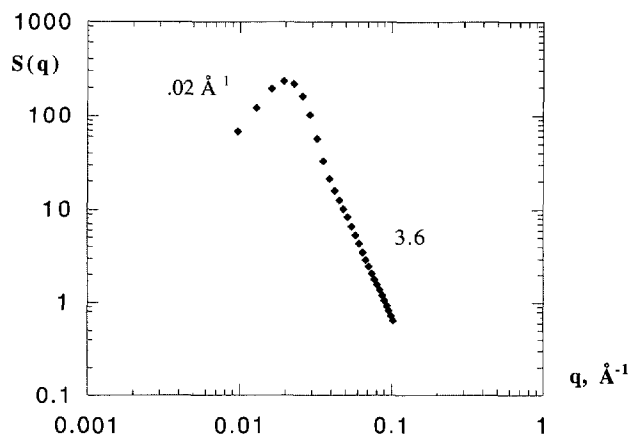


Fig. 1. — Small angle scattering intensity of the bare porous Vycor glass. A strong correlation peak is observed for $q \sim 0.02 \text{ \AA}^{-1}$, the asymptotic behavior is characterized by a power law dependence of the form $q^{-3.7 \pm 0.1}$.

around $80 \text{ m}^2/\text{g}$, are obtained by direct energy transfer method and analysis of the electron microscopy pictures [10–12]. This discrepancy in the values of specific area could be due to surface roughness which varies from sample to sample and also results from the fact that different techniques of measurement probe different length scales. This is in agreement with several sets of scattering data [10–12]. The scattering curve from bare Vycor measured by Small Angle Neutron Scattering (SANS) is shown in Figure 1.

The main scattering feature of this porous solid is the occurrence of a strong correlation peak at 0.02 \AA^{-1} corresponding to a length of 300 \AA . The asymptotic behavior is characterized by a power law dependence of the form $q^{-3.7 \pm 0.1}$ in agreement with the observations of several authors [10–12]. This power law could be interpreted in terms of self-affine roughness, but is not fully understood and is still controversial [10–13].

Vycor was cut into very fine pieces of 1 mm in thickness and 1.4 cm in diameter with help of a rotating diamond saw. The pieces were finely sanded to fit exactly inside the neutron scattering cell. Vycor is easily contaminated, and so several cleaning procedures were tried. The following one was finally adopted. First Vycor was rinsed just by distilled water in a soxhlet extractor. It was then washed in 30% hydrogen peroxide solution and again washed by distilled water in a soxhlet. Afterwards it was gently dried under vacuum at room temperature. The Vycor was then slowly heated to $540 \text{ }^\circ\text{C}$ in order to burn off any hydrocarbon impurities from the glass pores. After this cleaning, the Vycor pieces were immersed for various periods of time in the polymer solutions to be measured.

In one case, we have derivatized the silanol groups on Vycor by reacting them with a 10% solution of trimethylchlorosilane in toluene. This method yields a more hydrophobic surface less prone to adsorption of polymers.

3.2. MATCHING BETWEEN SOLVENT AND VYCOR. — The nominal scattering length density of Vycor based on composition (96% SiO_2 , 3% B_2O_3 and $< 1\%$ Al_2O_3) density of Vycor (1.45 g/cm^3) and porosity (28%) is $3.2 \times 10^{10} \text{ cm}^{-2}$. Since Vycor may be not quite homogeneous and have traces of other oxides, the real scattering length density may be slightly different. It was determined by contrast variation experiments using mixtures of hydrogenated and

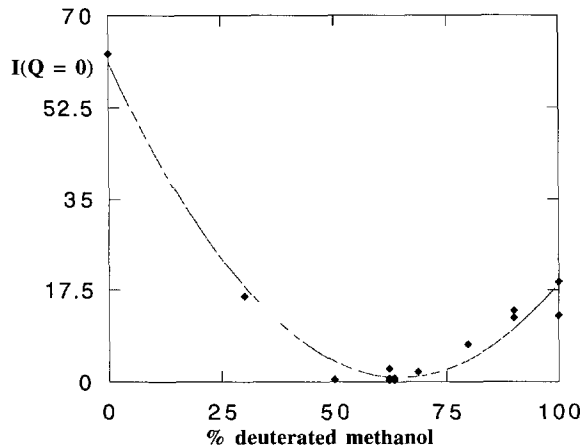


Fig. 2. — Contrast matching experiment on bare Vycor. Extrapolated value of the scattering intensity $I(q)$ at $q \rightarrow 0$ as function of % deuterated methanol (CD_3OD). The minimum value of the parabola is the matching point which is 63.3% of CD_3OD .

deuterated methanol, and looking for the minimal value of the scattering intensity extrapolated at vanishing scattering vector. Methanol was chosen because it can be easily evaporated. This enabled us to use the same Vycor piece during the experiment. In Figure 2 the intensity at vanishing angle $I(q \rightarrow 0)$ is plotted as a function of the percentage of deuterated methanol in the mixture. The minimum value of the best fitting parabola is the matching point realized for 63.3% of CD_3OD . This corresponds to a scattering length density of $3.55 \times 10^{10} \text{ cm}^{-2}$ close to the nominal value for pure silica with a density of 2.2 g/cm^3 .

This value determines thus the isotopic composition of the solvent that was used to prepare the polymer solutions. Two solvents were used successively. The study was started with perdeuterated dichloromethane which in practice perfectly matches Vycor. This solvent presents the advantage of minimizing the incoherent background in the scattering experiments. However, dichloromethane is very volatile and the neutron scattering cells were not sealed tightly enough to prevent drying of the Vycor after a few hours. Finally, the solvent was changed to toluene with 55% of deuterated molecules. It was observed that the data were insensitive to this change of solvent.

3.3. POLYSTYRENE SOLUTIONS SATISFYING THE ZERO AVERAGE CONTRAST CONDITION.

— The second condition that was satisfied in order to observe the form factor of the polymer chains inside Vycor is the condition of average contrast matching between the chains and the solvent expressed by equation (4). The value of the scattering length density of deuterated polystyrene (PSD), $n_{\text{D-pol}} = 6.54 \times 10^{10} \text{ cm}^{-2}$, and the one of hydrogenated polystyrene (PSH), $n_{\text{H-pol}} = 1.43 \times 10^{10} \text{ cm}^{-2}$, determine the relative proportion of deuterated chains in the mixture which has to be $x = 41\%$. Fortunately, this is close to the value $x = 0.5$ which maximizes the scattering intensity.

3.4. CHOICE OF POLYMER CONCENTRATION. — In order to choose the polymer concentration such that the chains can enter the pores we have used the scaling picture of semi-dilute solution in terms of a closely packed system of “blobs”. The size of a blob is proportional to the correlation length of the solution ξ_{bulk} which can be precisely measured from scattering

Table I. — *Characterization of the polystyrene chains.*

M_w PSD	M_w/M_n	M_w PSH	M_w/W_n	$R(\Phi) \sim aN^{1/2}\Phi^{-1/8}$ Å	c^* g/cm ³	$\xi = 0.43(c/c^*)R_F$ Å
32700	1.06	33500	1.03	60.8	0.056	10.2
75000	1.02	717000	1.04	92.1	0.029	10.2
137000	1.06	120000	1.05	124.5	0.018	10.2
351000	1.03	336000	1.03	199.4	0.008	10.2
795000	1.07	781000	1.02	299.8	0.004	10.2

experiments. One can also precisely define a blob radius ξ_{blob} such that ξ_{blob} becomes equal to the radius of gyration of a dilute chain at the overlap concentration c^* , then experimentally $\xi_{\text{bulk}} = 0.35 \xi_{\text{blob}}$. The empirical relation between ξ_{blob} and the polymer volume fraction bulk is for polystyrene $\phi_{\text{bulk}} = 19.8(\xi_{\text{blob}})^{-1.3}$ with ξ_{blob} in Å. We then chose ϕ_{bulk} such that ξ_{blob} was at most equal to the average pore radius 35 Å, this yielded $\phi_{\text{bulk}} = 0.2$. For such a concentration, the correlation length ξ_{bulk} is about 10 Å.

3.5. SAMPLES. — Five solutions of a mixture of monodisperse hydrogenated and deuterated polystyrene with increasing molecular weight were prepared, the polymer and the solvent satisfying both their respective contrast matching conditions described above. The mass of the H and D chains in a given sample (respectively, $M_w^H = 33500, 71700, 120000, 336000, 781000$ and $M_w^D = 32700, 75000, 137000, 351000, 795000$) were chosen to be as close as possible. The list and characterizations of the samples are given in Table I. The radius of gyration of the deuterated chains in bulk semi-dilute toluene solutions at a volume fraction $\Phi = 0.2$, can be calculated from known experimental results, the values being 61 Å, 92 Å, 124 Å, 199 Å and 300 Å respectively. In each case, it is always larger than the pore radius.

The samples of confined polymers were prepared by immersing a dry piece of cleaned bare Vycor in each of the above solutions of H and D polystyrene chains for various periods of time, *viz.* 3 days, 23 days and 65 days. We observed that the solutions were slowly sucked into the Vycor. The samples, which were initially rather white and opaque become translucent.

The same procedure was used to prepare two test samples with the silanized Vycor, one was immersed in a polystyrene solution made with the 120 K, 137 K pair of H and D chains at a volume fraction of 20%, the other in a 781 K-795 K solution at a smaller volume fraction of 10%.

3.6. SCATTERING EXPERIMENTS. — The scattering experiments were performed in Saclay on the PACE spectrometer. The measurements were done in several different configurations: a first series in the q range 2.89×10^{-3} to 0.1 \AA^{-1} (wavelength $\lambda = 6.47 \text{ \AA}$, sample-detector distance $d = 3.0 \text{ m}$ and $\lambda = 14 \text{ \AA}$, $d = 4.67 \text{ m}$) and a second series in the q range 3×10^{-3} to 0.3 \AA^{-1} ($\lambda = 5.12 \text{ \AA}$, $d = 1.0 \text{ m}$ and $\lambda = 12.15 \text{ \AA}$, $d = 4.5 \text{ m}$). Water (which scatters isotropically) was used to normalize the intensities on a absolute scale. In each case the small angle scattering from the bare Vycor sample in its contrast matching solvent, the bulk solutions of mixed H and D chains and the Vycor samples containing the polymer solutions at zero average contrast, respectively were measured. The data of these last samples were treated by subtracting the raw intensity of the bare matched Vycor from the raw intensity of the samples in order to eliminate very precisely the incoherent scattering from the solvent and the residual signal of the nominally matched Vycor which can never be completely extinguished.

4. Results and Discussion

4.1. PENETRATION OF POLYMER INTO THE PORES. — The first immediate, but non trivial result of our experiments is that the polymer chains enter the pores of Vycor (diameter $D = 70 \text{ \AA}$) whatever their molecular weight at the concentration of 20%, that was used. This was first evident qualitatively from the macroscopic observation of the samples: the Vycor pieces become much more chalk white in colour and more opaque after drying of the samples than they were without having been in contact with a polymer solution. The penetration of polymers is also of course revealed directly and quantitatively by the scattering experiment.

In Figure 3a the results of a first scattering experiment are presented where the signal (bottom curve) of a bare Vycor piece matched in deuterated dichloromethane (CD_2Cl_2) is compared with the signal (top curve) of a sample imbibed with a solution of deuterated chains *only* ($M_w = 351 \text{ K}$) in the same solvent. Although the Vycor is not perfectly matched due to a cleaning problem at this stage of the experiment, the difference between the two signals is large.

On the spectrum of the sample containing only deuterated polymer the characteristic peak of non-matched Vycor (*cf.* Fig. 1) which is absent in the matched bare Vycor is again observed. Thus it can be concluded qualitatively that indeed the deuterated chains penetrate into the pores and that with this contrast, the main effect of confined polymer chains on the scattering intensity is to reveal the pore structure at large scales, *i.e.* at low scattering vectors, by breaking the contrast matching with the solvent. This demonstrates also the utility of the zero average contrast method which eliminates the trivial effects of the structure of the porous medium on the scattering intensity.

Indeed more information can be obtained by observing the samples satisfying this zero average contrast condition. As a first easy example, we consider the case, shown in Figure 3b, of the sample with the smallest molecular weight ($M_w^D = 32.7 \text{ K}$) in deuterated dichloromethane. The bare Vycor (also in deuterated dichloromethane) is perfectly matched (bottom spectrum) and yields a much smaller signal than the zero average contrast sample (middle spectrum). It is observed that the scattering intensity is now a smoothly decreasing function of q as is the scattering intensity of the bulk corresponding solution (top curve). Both of them as expected look very much like the form factor of a chain. The comparison between these two spectra shows that the ratio of the intensities at large scattering vector of the confined chains and of the bulk solution is about 25%. As this ratio should be proportional to the ratio of polymer volume fraction in the two samples it can be concluded that there is 4 times less polymer in the Vycor samples than in the bulk solution. As the porosity of Vycor is about 28%, we conclude that the penetration of the polymer solution into the Vycor pores is almost complete and that the partition coefficient of the chains between the Vycor and the solution of immersion is practically one.

Similar observations have been made on the other samples prepared from 55% deuterated toluene solutions. The comparison between the spectra of the bulk and confined polymer solutions are shown respectively in Figures 4a, b, c, d and e for the different samples (molecular weights 32.7 K, 75 K, 137 K, 351 K and 795 K). In Figures 4a, b, c and d the data are taken after being imbibed for 23 days, when even the chains of 351 K have thoroughly penetrated the Vycor. In Figure 4e, corresponding to the largest chains $M_w = 795 \text{ K}$, the Vycor stayed immersed in the bulk solution for 2.5 months. In each case the chains of polymer definitely enter the Vycor. The intensities at large scattering vectors show that the concentration of the chains in the Vycor sample is always about 25% of the bulk concentration which corresponds well with the 28% porosity of Vycor. Within the uncertainty of the intensity measurements and

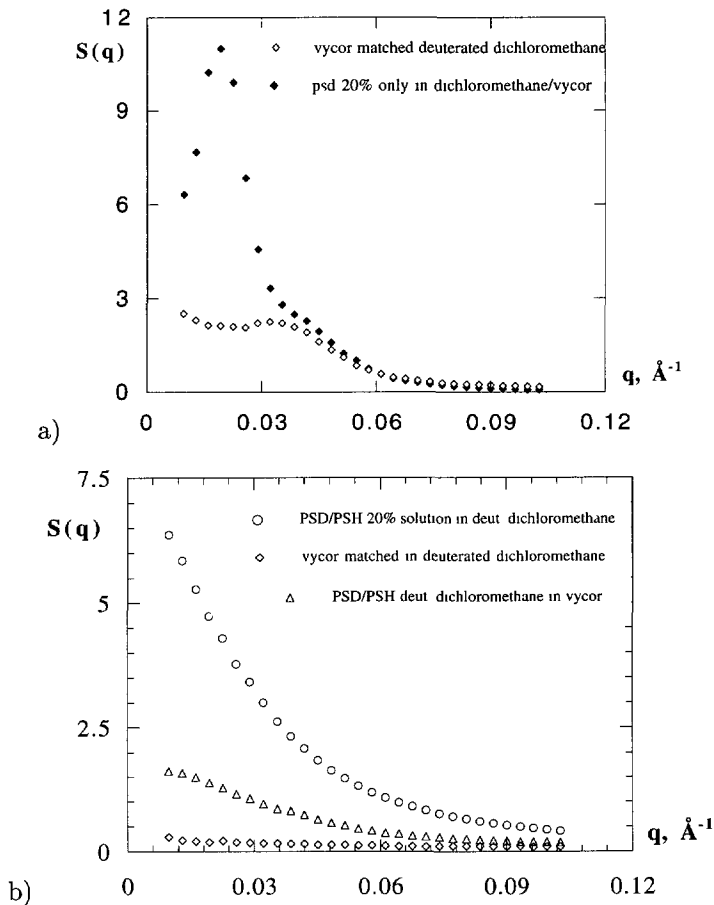


Fig. 3. — a) Raw scattering intensity $S(q)$ versus q for deuterated chains of 351 K PSD inside Vycor matched in deuterated dichloromethane (top) compared with the scattering intensity of the corresponding matched Vycor (bottom). b) Raw scattering data $S(q)$ versus q for a mixture of H and D chains of 32.7 K satisfying the zero average contrast condition inside Vycor matched in deuterated dichloromethane (middle spectrum) compared with the scattering of the bare matched Vycor (bottom spectrum) and the one of the corresponding bulk polymer solutions (top spectrum).

normalization, the concentration of polymer inside Vycor is independent of the chain molecular weight at the used volume fraction of 20%.

Different results have been obtained with the silanized pieces of Vycor observed after 2.5 months of imbibition. For the 137 K chains ($\Phi = 0.2$) less polymer enters inside Vycor and the intensity measurements (Figure 4c) indicate that the overall concentration in the Vycor sample is 15% of the bulk concentration. Taking into account the porosity, this means a partition coefficient of 0.5. For the more dilute 795 K chains ($\Phi = 0.1$), the effect is even more drastic. Some scattering signal is observed at very small q but no measurable intensity at large q (after subtraction of the empty matched Vycor signal), so that the amount of chains entering the pores is not measurable.

Thus we have obtained evidence that, for high bulk concentration of the polymer solution and unsilanized Vycor, penetration in the pores occurs when the bulk correlation length ξ_{bulk} is smaller than the average size of pore. It must be noticed that this phenomenon is just not

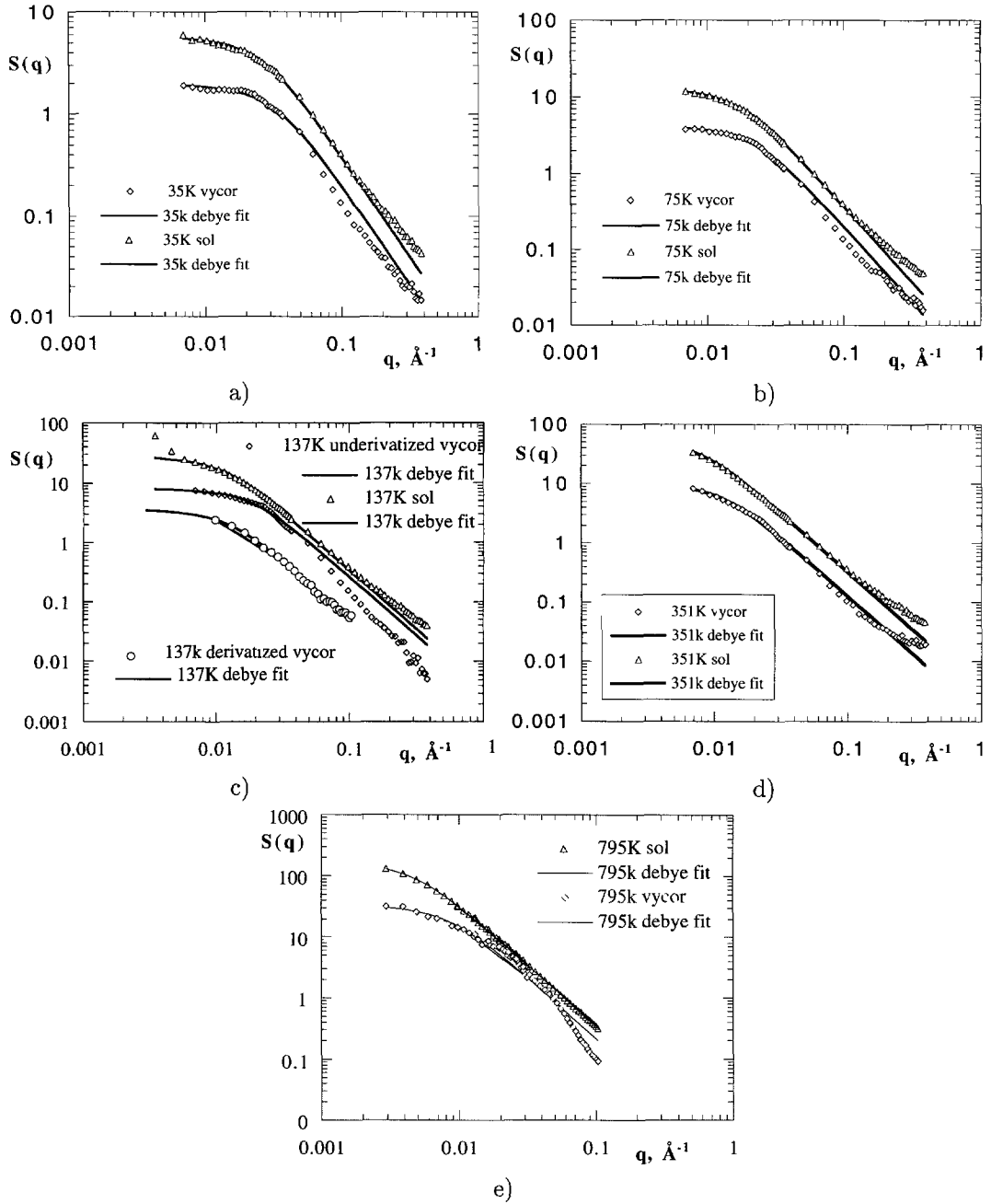


Fig. 4. — Normalized scattering intensities using average matched H and D chains inside Vycor and in the bulk (symbols) and the corresponding Debye fits (full lines) for the molecular weights of (a) 32.7 K, (b) 75 K, (c) 137 K, (d) 351 K and (e) 795 K polystyrene chains in 55% deuterated toluene.

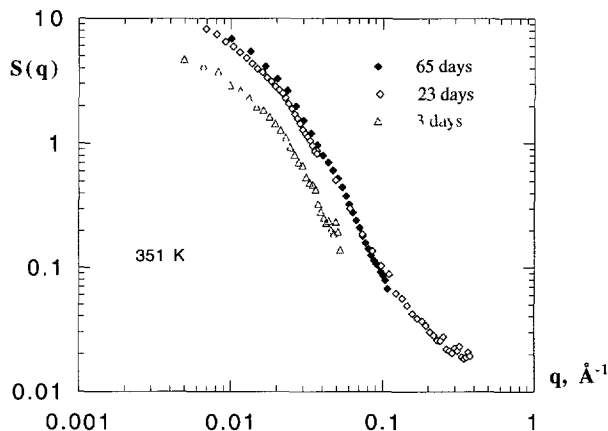


Fig. 5. — Time evolution of the scattering signal for average matched H and D chains of molecular weight 351 K in 55% deuterated toluene inside Vycor.

governed by the static length ξ_{bulk} but there is also a kinetic aspect governed by the reptation time τ_{R} of the chains in the bulk. Using the measured reptation time [18] from the relation $\tau_{\text{R}} = \eta/G$ where η is the viscosity and G the elastic modulus a rough estimate of the time to penetrate the pores over a distance of 1 mm, which neglect suction phenomena related to wetting, is respectively, 0.028, 0.2, 1.5, 20 and 37 days for the molecular weights of 32.7 K, 75 K, 137 K, 351 K and 795 K polystyrene chains. This agrees qualitatively with our experimental data which shows that the largest molecular weights polystyrene chains 351 K enter well the pores only after 23 days (Fig. 5).

The difference of behaviour between the bare and silanized Vycor calls for more experiments; however already some conclusions can be drawn. At first the observations on silanized Vycor can easily be explained if one admits that the silanized Vycor surfaces strongly repels the polymer chains. One expects then a depletion zone of the polymer close to the pore surfaces. If the chains nevertheless enter freely into the pores because the bulk solution is concentrated enough, the thickness of this depletion zone is of order ξ_{bulk} , the correlation length of the bulk solution [19]. The chains are thus effectively contained locally in cylinders of diameter $D - 2\xi_{\text{bulk}}$. The volume accessible to the chains is reduced by a factor $[(D - 2\xi_{\text{bulk}})/D]^2$ which is in this simplified picture the partition coefficient of the chains. For $\Phi = 0.2$, $\xi_{\text{bulk}} \approx 10 \text{ \AA}$, the partition coefficient α can then be estimated to be $(50/70)^2$, about 0.5, which is our measured value. For $\Phi = 10\%$, ξ_{bulk} is equal approximately to 20 \AA , the same calculation would yield $\alpha = 0.18$. This is clearly an overestimation since $D - 2\xi_{\text{bulk}}$ becomes itself of the same order of magnitude as ξ_{bulk} . In this intermediate regime of concentration, it is quite plausible that the pores are almost impenetrable to the chains, as observed.

This analysis now implies that the surface of the bare Vycor does not repel the polymer chains as strongly as the surface of the silanized Vycor or even attracts them since the partition coefficient is much higher in the first case than in the second. A possible adsorption of polystyrene on bare Silica, particularly from concentrated solution, is of course not unexpected. This point has been particularly investigated in former experiments performed to study the building of polystyrene layers grafted on porous Silica [19]. This adsorption depends on the solvent, the type of Silica, the polymer concentration, molecular weight and isotopic composition. We will take into account its possible occurrence in the analysis of the scattering spectra.

Table II. — *Experimental results.*

M_w PSD	Measured R_g in bulk Å	Measured R_g in Vycor Å	Cross-section of cigars D_{eff} Å	$(R_g^2, \text{vycor})^{1/2} =$ $(R_g^2 \text{bulk}/3 + D^2/8)^{1/2}$ Å
32 700	54.5	43.5	—	—
75 000	83.8	63.9	75.8	54.3
137 000	126.6	77.4	102.6	77.2
351 000	184.7	127.0	109.2	109.5
795 000	311.8	174.6	105.2	181.7

4.2. THE FORM FACTOR OF THE CHAINS. — We now proceed to the analysis of the form factor of the free and confined chains as provided by the zero average contrast method. It is simple and useful for the sake of comparison with the confined case to start with the free chains in bulk solutions. The structure of one single chain among the others in semi-dilute solutions is well-known [19]. The chains are ideal at large scales, larger than ξ_{bulk} , and are swollen at small scales exhibiting locally the features of chains with excluded volume as in dilute solutions. The form factor is then given by the well-known Debye scattering law [19] in the range $q\xi_{\text{bulk}} < 1$

$$P(q) = (2/x^2)(x - 1 + e^{-x}) \quad (6)$$

with $x = q^2 R_g^2$ (R_g is the radius of gyration of the chains) and decreases as the power law $q^{-1.67}$ at larger scattering vectors.

This is indeed what is observed for the free chains in bulk solution. The fits to the Debye formula are shown in Figure 4. The R_g 's values drawn from the fits are written in the Table II, they increase as the square root of the molecular weight of the chains in agreement with the relation $R_g(\phi) \sim M^{1/2} \phi^{-1/8}$, which is well-established theoretically and experimentally [20] (here, ϕ is the volume fraction of polymer in solution).

For chains inside Vycor, we also find it useful to try to fit the data to the Debye scattering law. At low q , this is an efficient way of determining the radius of gyration of the chains, as efficient and justified as the Guinier or Lorentzian laws, and at large q , this is a way to reveal the differences with the case of the free chains. Indeed the fits are good only at very low q in a much smaller range of scattering vector ($qR_g < 1$ but not $q\xi_{\text{bulk}} < 1$) than for the corresponding free chains.

The first observation is that the values of the radii of gyration of the confined chains are *smaller* than the bulk values. They are written in Table II and plotted in Figure 6 together with the bulk values.

The second observation is that there is a marked deviation from the classical asymptotic behavior for ideal chains $P(q) \sim q^{-2}$ in the regime of scattering vectors corresponding to distances $R_g \gg q^{-1} \gg \xi_{\text{bulk}}$. The intensities decrease more rapidly than $1/q^2$. Power laws greater than 2 are observed by plotting the scattering intensities in logarithmic coordinates. These slopes apparently vary with the molecular weight of polystyrene chains.

4.3. COMPARISON WITH THEORETICAL PREDICTIONS. — At present no general theory describes the behaviour of polymer solutions in structures such as Vycor, which are regular at small scales, with a well-defined local geometry, and random at large scales. We try here to separate these different aspects. We first confront our data to the predictions of the simplest

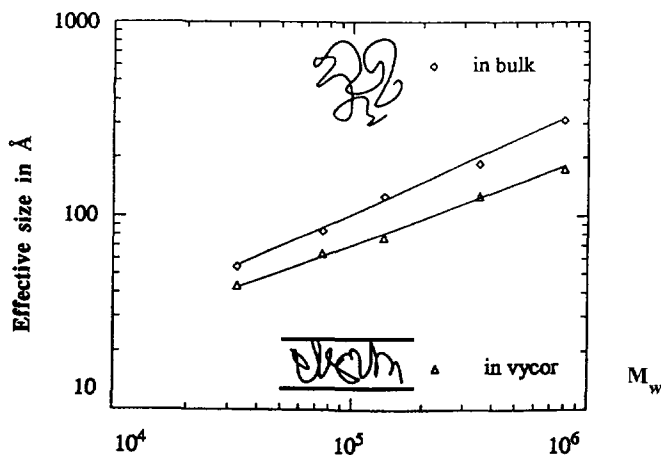


Fig. 6. — The effective size of polymer chains in bulk solution and in Vycor defined by the measured radius of gyration as a function of molecular weight.

theories of polymer confinement in a straight cylindrical pore, taking into account possible adsorption effects; we then discuss the relevance of the random field approach and describe finally how the randomness and tortuosity of the pore structure might concern our results.

4.3.1. Polymer Confinement in a Cylindrical Pore. — We owe to Casassa [2] the earliest work on the confinement of polymer chains. He calculated the conformation of dilute ideal Gaussian chains confined in simple model geometries (plates, cylinders, spheres) as a probability density satisfying the diffusion equation with suitable boundary conditions at the walls. A more complete description of these situations incorporating excluded volume and concentration effects was developed later by Daoud and de Gennes [2] using the scaling theory of polymer solutions. Their initial treatment of the chains confined in cylindrical pores was recognized to be incorrect in the regime of large concentration and strong confinement, and was subsequently rectified by Brochard and de Gennes [2].

Briefly one can say that four main effects govern the behaviour of chains confined in a small cylindrical non adsorbing pore: the confinement of the chains by the cylinder walls squeezes the chains laterally, the intrachain excluded volume effect swells the chains and stretches them along the cylinder axis, the entropic elasticity of the chains limits the swelling and stretching, the interchain excluded volume effect screens the intrachain effect but may lead to chain segregation. The strength of these different effects depends on the polymer concentration and on the degree of confinement, and their competition leads to different regimes that can be expressed in terms of reduced variables $x = R_F/D$ and $y = R_F/\xi$ (D = pore diameter, $R_F = N^{3/5}a$ is the Flory radius of the excluded volume chain in dilute free solution and ξ is the bulk correlation length of the semi-dilute solution).

- At low concentration ($y < x$) and strong confinement (regime of dilute stretched cigars) the chains are dilute (separated) and stretched by intrachain excluded volume effects.
- As the concentration increases, the cigars enter into contact but remain segregated by interchain excluded volume effect. However the stretching of the chains decreases because of the interchains interactions (regime of stretched segregated cigars).

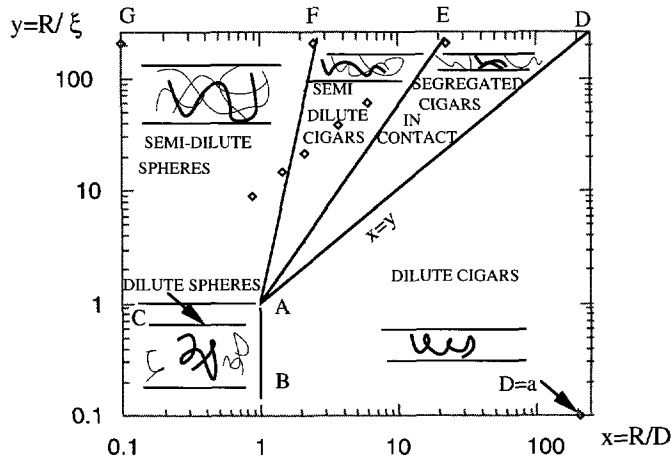


Fig. 7. — Phase diagram for polymer solutions confined in a capillary as a function of the reduced variables $y = R_F/\xi$ (R_F , Flory radius of the dilute chains) and $x = R_F/D$ (as y increases, ξ decreases and the concentration of chains increases; as x increases, D decreases).

- If the confinement is very strong the cigars remain segregated and stretched as the concentration still increases until the melt state is reached.
- On the other hand if the confinement is only moderate, the cigars become entangled (semi-dilute cigars) and the chains become ideal at large scale, particularly along the cylinder axis. This means that the chains are of course squeezed perpendicularly to the cylinder axis) but *not stretched* with respect to their equivalent bulk conformation (regime of squeezed ideal semi dilute cigars).

The phase diagram showing the different regimes is shown in Figure 7. These different regimes are delimited by cross-over lines that we describe briefly. The cross-over between the regime of semi-dilute non confined polymer coils and the regime of semi-dilute cigars is given by the condition that D be of the order of the radius of gyration of the chains in the bulk semi dilute solutions $R_g = N^{1/2}a\phi^{-1/8}$

$$D \approx R_g = N^{1/2}a\phi^{-1/8}.$$

This cross-over is given by the line AF in Figure 7, whose equation in the reduced variables x and y is

$$y = x^6. \quad (7)$$

When the monomer concentration c in the pore is larger than the concentration $c_1^* = N/D^2R_{||}$, ($R_{||}$ is the length of the cigar) dilute cigars begin to touch each other and one has to take into account interchain excluded volume effects. If these effects are strong enough (large chains, high concentration, strong confinement), the chains remain segregated and touching at their ends, as occurs in the limiting case ($D = a$) of an extremely confined melt (Brochard and de Gennes [2]). The condition for this is $y > x$ ($D > \xi$), $y > 1$ and $D < (N/g)^{1/4}\xi$. (g is the number of monomers of a given chain inside a correlation domain (blob) of size ξ .) In the segregated regime, $\xi < D < (N/g)^{1/4}\xi$, the chains are stretched, $R_{||} = (N/g)\xi^3/D^2 = Na^3/D^2(ca^3)^{-1}$. In terms of reduced units the cross-over between the two regimes of semi-dilute entangled cigars

and stretched segregated cigars is given by the line AE

$$y = x^{12/7} \quad (8)$$

We have plotted in Figure 7 the points corresponding to the five samples studied in this article at the fixed volume fraction of 20% assuming that the Vycor pores can be represented by cylinders of 70 Å diameter. The three largest molecular weight chains fall in the regime of semi-dilute ideal cigars where the chains are interpenetrating, confined, squeezed but not stretched. The two smallest molecular weight chains are close to the cross-over line between non confined and confined semi-dilute solution. In any case, the prediction of the theory in our case is that the chains are perhaps squeezed but *not stretched* along the axis of the pores.

Let us assume that this picture of cylindrical ideal squeezed cigars is true and that the monomers of one chain are uniformly distributed in the cross section of the cylinder. The radius of gyration of a cigar can then be expressed as:

$$R_{g \text{ Vycor}}^2 = \frac{D^2}{8} + R_{gz}^2$$

where R_{gz} is the radius of gyration along the axis of the pore while $D^2/8$ is the contribution of the cigar cross section. If the cigar is not stretched there is a simple relation between R_{gz} and the radius of gyration of the chain in the bulk solution, namely $R_{gz}^2 = R_{g \text{ bulk}}^2/3$, imposed by the isotropy of the chain in the bulk solution. Assuming $D = 70$ Å and taking the measured values of $R_{g \text{ bulk}}$, we can calculate $R_{g \text{ Vycor}}$ from the above expression and compare it with the experimental values. As shown in Table II, the agreement is very good for the different molecular weights. The hypothesis of squeezed ideal cigars thus accounts well for the variation of the measured radius of gyration.

If the cigar picture is true, it must describe not only the radius of gyration but also the scattering intensity in the intermediate regime $D < q^{-1} < R_g$ where the scattering depends only of the overall rodlike shape of the chain. Let assume that the average shape of one chain is a cylinder of length $R_{||}$ and diameter D and that on average, the monomers of this chain are distributed radially with a given concentration profile $c(\rho)$, (ρ is the radial coordinate) normalized such that $2\pi R_{||} \int \rho d\rho c(\rho) = N$. In the intermediate regime $qR_{||} > 1$ that we consider, the average form factor of the chain is then given by the following expression (normalized according to the definition of Sect.2):

$$N^2 q P(q) = \pi R_{||} \alpha(q)^2 \quad (9)$$

where $\alpha(q)$ is the average scattering amplitude of the cigar cross section:

$$\alpha(q) = 2\pi \int \rho d\rho J_0(q\rho) c(\rho)$$

$J_0(q\rho)$ being the Bessel function of zero order.

In the range $qD < 1$, we may apply the 2-dimensional Guinier approximation and write $N^2 q P(q) = \pi R_{||} \alpha(0)^2 \exp(-q^2 R_C^2/2)$ or $qR_{||} P(q) = \pi \exp(-q^2 R_C^2/2)$, R_C being the 2-dimensional radius of gyration of the cigar cross-section. For a homogeneous cylinder of diameter D_{eff} , R_C is given by $R_C^2 = D_{\text{eff}}^2/8$ and the preceding equation becomes

$$qR_{||} P(q) = \pi \exp(-q^2 D_{\text{eff}}^2/16). \quad (10)$$

The slope from the plot of $\ln q S(q)$ versus q , should yield D_{eff} the effective cross-section of the cigars. The value of D_{eff} deduced from such a plot for the larger molecular weight chains where D_{eff} can be reasonably measured (*cf.* Fig. 8) are shown in Table II. The values of D_{eff} (in the range 75-100 Å) measured from such an analysis are slightly larger than the nominal diameter of pores in Vycor but still of the same order of magnitude. This confirms the cigar picture.

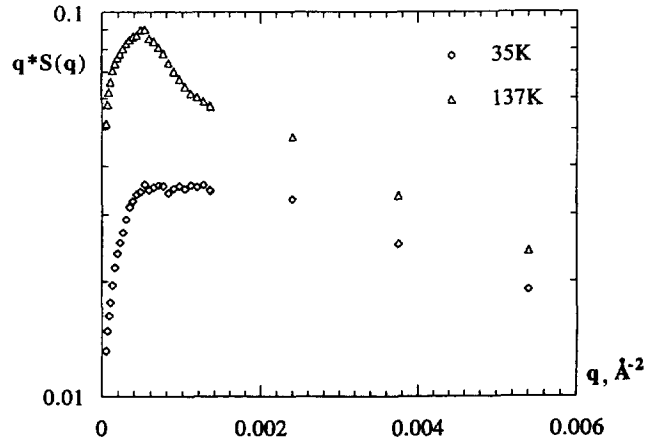


Fig. 8. — Test of the cigare picture. $qS(q)$ versus q^2 for the chains of molecular mass 35 K and 137 K. D_{eff} is deduced from the initial slope of the exponential decay of the curves.

4.3.2. *Possible Effects of Adsorption.* — At large scattering vector, the description of the form factor of a confined chain in term of a global shape is no longer valid and one has to take into account precisely the distribution and the correlations of the monomers of a chain inside the pores.

The scattering intensity then results quite generally from the contribution of the average radial concentration profile of the monomers of one chain inside the pores introduced above in equation (9) plus a contribution from the internal correlations between the monomers in the chain, often expressed in term of blobs. If there is adsorption the concentration of monomers $c(\rho)$ is not vanishing at the pore surface and one can expect that the scattering intensity in the asymptotic limit can be written as

$$I(q) = A/q^4 + B/q^{1.7}. \quad (11)$$

The first term is analogous to Porod's law and the second term is simply the classical expression of the scattering by a locally free polymer chain in the asymptotic limit. The coefficient A is proportional to the square of the monomer concentration of one chain at the pore surface [16], $c_S = \Phi_S/v$, and B is proportional to the total average concentration of polymer. The asymptotic behaviour of the average form factor of one chain at large scattering vector ($qD > 1$) in the cigar picture can be calculated from equation (9) assuming that the concentration profile is not too thin and singular, one obtains:

$$N^2 P(q) = 2\pi(\pi DR_{||})c_S^2 q^{-4}.$$

The expression (3) of the scattering intensity then implies the following explicit formula for the coefficient A :

$$A = (n_D - n_H)^2 x(1-x) \Phi 2\pi(\pi DR_{||}) \Phi_S^2 / Nv. \quad (12)$$

Equation (11) fits rather well our experimental data in Vycor at large scattering vector. The typical value of B is 0.002 for polymer inside Vycor and 0.008 in the bulk solutions from the fits. This value of B is indeed proportional to the total concentration of polymer as already noticed in Section 4.1. The typical measured value of A is $2.0 \times 10^{-6} \text{ \AA}^{-4} \text{ cm}^{-1}$. Considering the case of the 75 K chains ($N = 750$), assuming $R_{||} \approx 100 \text{ \AA}$ (a value of the order of the measured

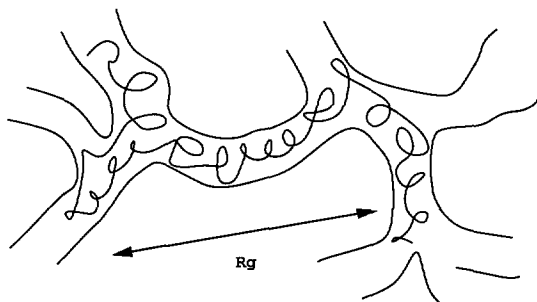


Fig. 9. — A large polymer spanning many pores and thus revealing the pore correlations.

radius of gyration), knowing the molar volume of styrene, 98 cm^3 , remembering $x = 0.41$ and $\Phi = 0.2 \times 0.28 = 0.056$, we deduce from expression (12) an estimation of the polymer volume fraction right at the Vycor surface, $\Phi_S = 0.22$.

The fact that this surface volume fraction is non vanishing implies that the monomers are adsorbed on the surface, but it is striking that the measured value is of the same order of magnitude as the average volume fraction of polymer in the pore, 20%. It thus appears that the Vycor surface behaves in the present case as a “neutral” surface: the attractive interaction between the polystyrene and the silica appears sufficient strong to destroy the depletion layer that one would expect for a sterically repulsive surface but not strong enough to build an adsorbed layer with a positive surface excess as the one observed for instance with PDMS [16]. In this case, the concentration is uniform everywhere in the pores and one expects that the partition coefficient with the bulk is 1 as we have indeed observed.

Our interpretation in terms of adsorption is confirmed by the observation that the surface treatment of Vycor has also an effect on the asymptotic behaviour of the chain form factors. The apparent slope at large scattering vector of the polymer form factor in logarithmic coordinates diminishes from 2.5 in case of the underivatized Vycor to 1.9 for the chains confined in the derivatized Vycor (Fig. 4c). At the same time the effective size of the chains in derivatized Vycor is 118 \AA close to the value in the untreated Vycor.

4.3.3. Interpretation in Terms of Random Fields. — Since we observe that the radii of gyration of the confined chains are smaller than their bulk values and that the chain form factors decrease more rapidly at large scattering vector than in the bulk, we might conclude that the confined chains are denser than the free chains at an equivalent concentration with, let us say, a larger fractal dimension, which would explain both these observations. We might attribute this compaction or deswelling of the chains to the effect of a random field imposed by Vycor and this would be indeed what the theory predicts qualitatively [3]. We want to stress however that this interpretation is probably not justified in our case because the chains we use are still too small to feel the effect of the disorder of Vycor which occurs at scales larger than the one defined by the correlation peak at $q = 0.02 \text{ \AA}^{-1}$, *i.e.* $150\text{-}300 \text{ \AA}$. In our case, the chains are found to be smaller than in the bulk simply because of the lateral confinement by the pores and because we are not in a regime where the chains are stretched along the pores by the excluded volume interactions.

4.3.4. Effect of the Pore Geometry at Large Scale. — There is however an interesting question about what happens when a very large chain spans many intersecting pores of Vycor as shown in Figure 9. Since the chains are *in* the pores, the two point monomer-monomer correlation function vanishes if one of these two points is outside the pores and inside the glass.

This means that this correlation function can be written formally as the product of a geometrical term, which is the pore correlation function, with a polymeric term, which has at large scale a real space cut-off of order of the polymer size R_g . The form factor of one chain can thus be written as the convolution product of the structure factor of Vycor, $S_{\text{Vycor}}(q)$, (the Fourier transform of the pores correlation function) by a polymeric structure factor whose typical width in reciprocal space is $1/R_g$. At small scattering vector in the Guinier range ($qR_g < 1$), we can write approximately

$$P(q) \sim S_{\text{Vycor}}(q)\exp(-q^2 R_g^2/3).$$

This implies that on large scales, the Vycor pore correlations, *i.e.* the Vycor peak, may reappear even at contrast matching in the form factor of a long confined chain. In fact, if we look at the data for the largest molecular weight chains, it seems that the Vycor peak has indeed slightly reappeared at $q \sim 0.02 \text{ \AA}^{-1}$ in slightly broadened form (*e.g.* Figs. 4c, d, e corresponding to molecular weights of 137 K, 351 K and 795 K, respectively). It thus would be interesting to explore this regime more.

5. Conclusions

We have presented the first direct observation of the structure of polymer chains confined in a porous medium. We have obtained both qualitative and quantitative results. From a qualitative point of view, we have shown that semi-dilute polymer chains enter the pores of Vycor when their concentration is larger than 20% and that one can observe the structure of a single chain by Small Angle Neutron Scattering using the condition of zero average contrast inside Vycor. Polystyrene chains are adsorbed on the bare surface of Vycor, but the effects of this adsorption are small for two reasons: the strength of the adsorption is weak (the measured polymer volume fraction at the surface does not exceed the bulk volume fraction, 20%), the possible long range effect of the adsorption are screened because we deal with semi-dilute solutions. Thus the concentration profile of the monomers in the pores is essentially constant. The polymer adsorption can be removed by silanizing the Vycor surface, this lowers in particular the partition coefficient of the chains with the bulk. In the regime of concentration and molecular weight that we have studied, the measured radii of gyration of the chains are smaller inside Vycor than in the bulk. Our data are well-interpreted by the model of Daoud and de Gennes, assuming that the chains are confined in locally straight cylindrical pores as ideal semi-dilute cigars: the chains are interpenetrating, squeezed by the confinement but not stretched with respect to their bulk conformations. One of the aims of future experiments should be to explore the numerous regimes that this confinement situation can present. Particularly interesting is the regime of very strong confinement possibly obtained at large concentration and molecular weights where the chains can be at the same time elongated by the confinement and segregated because of interchain excluded volume effects or possible immiscibility effects, and also where the large scale disordered structure of Vycor might enter into play.

Acknowledgments

We thank G. Jannink, M. Daoud and J.M. Drake for discussions, F. Boué for gift of some polymer samples. Part of this work was initiated during the stay of one of us (J.L.) at Exxon Research and Engineering Company, Annandale, N.J., U.S.A.

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