Neutron Scattering Study of Chain Conformations in the Energetically Neutral Pores of Vycor Glass

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ABSTRACT: Small-angle neutron scattering is used to study the conformation of polymer chains of various lengths, $N \sim 1200-7000$, in good solvent confined to the *energetically neutral* pores of a model Vycor glass with a mean pore diameter of $D = 70$ Å. This study utilized an external polymer concentration, c_{free}, well into the overlapped or semidilute regime. Analysis of the experimental data using the standard bulk analysis procedure yields the surprising result that the chain dimensions in the pore are the same as in the unconfined solution. Since simulation results for comparable physical situations, which suggest that chains expand when they are strongly confined, are not in agreement with this interpretation, we conclude that our analysis misses some aspect of the experimental situations. To reconcile this discrepancy between theory and experimental results, we utilize the facts that the chains are strongly confined in one direction by the pore walls and that the pores are themselves random walks rather than straight cylindrical objects. A reanalysis of the experimental data on this basis then shows that chain dimensions in the pores are swollen relative to an unconfined chain, in a manner that is in agreement with the recent simulations of van Giessen and Szleifer. While these results provide the first quantitative tests of these simulation results, we nevertheless conclude that the random nature of the pore geometry in Vycor makes the conclusions drawn very subject to the particular models employed in the analysis of experimental data.

I. Introduction

When a polymer solution is placed in contact with a porous medium with pore dimensions comparable to the chain size, it is expected that fractionation based on molecular weight will occur. Thus, longer chains, which lose more entropy on confinement, will be preferentially excluded from the pores. This idea underpins commercially important separation schemes, such as gel permeation chromatography, where fractionation is based on molecular size. The theoretical understanding of these size-based separations was first proposed by Casassa,[1] who derived the conformational entropy loss on confinement for polymer chains. This argument is only valid for polymer concentrations less than the overlap concentration, i.e., for $c < c^*$, where chains can be considered as effectively isolated. On the basis of these ideas, it has been shown that the partition coefficient between a free solution and a porous medium with a pore size of D decreases exponentially with chain length for $R_{\mathrm{f0}} > D$, where R_{f0} is the Flory radius of a single chain in good solvent. Cannell and Rondolez found, in agreement with these ideas, that significant infiltration of the polymer into the pore did not occur as long as $c < c^*$.[2] Since the quantity of material that actually fractionates into the pores is small, operating below c^* is not useful for preparatory fractionation schemes.

Teraoka and co-workers[3,4] utilized ideas of Daoud and de Gennes[5,6] and suggested that fractionation schemes be conducted in semidilute solution. Polymer chains will then infiltrate the pores as long as the external concentration is large enough to satisfy the inequality, $\xi_{\mathrm{blob}} < D < R_{\mathrm{f0}}$, where ξ_{blob} is the blob size in semidilute solution.[7] In these cases, the osmotic pressure of the solution drives the chains into the pores, with the longer chains being preferentially excluded from the pores since they lose more entropy on confinement. The ratio of polymer concentration in the pores, c_{i}, to the free solution, c_{e}

$$K \equiv \frac{c_{\mathrm{i}}}{c_{\mathrm{e}}} \tag{1}$$

can be as large as 0.1−1, allowing this methodology to be employed for fractionating large quantities of polymer.

While the amount of polymer chains infiltrating into a porous medium is understood quantitatively at this time, little is known about chain size and conformation in highly confined environments. This knowledge is important in interpreting the transport properties of chains in restricted environments[8,9] and also to assess whether theories of partitioning, which assume that chains maintain their random walk statistics in the pore, are accurate or whether they work simply due to cancellation of errors. The earliest ideas in this context were proposed by de Gennes,[7] who considered isolated chains (dilute solutions) and suggested that the role of confinement on chain conformation was also dictated by the same parameter relevant to partitioning,

$$\frac{D}{R_{\mathrm{f0}}}$$

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For all the cases we shall consider experimentally this parameter is always much less than unity, suggesting that confinement effects should be strong. In these cases simulations[10−12] and theory[7] suggest that the chains should be strongly swollen on confinement. Note that these results have been derived for dilute solutions and that for higher concentrations in the pore the chains begin to shrink, as anticipated recently by Teraoka and co-workers.[13]

These findings should be contrasted to recent theories for chains in quenched random media for small volume fraction of defects.[14−16] In particular, we point to the recent work of Gilra et al.,[14] whose simulations show that the dimensions of free chains immersed in a cross-linked network hardly changed as the cross-link density is increased (even in the case where the distance between cross-links is much smaller than the length of the chains). These simulation results have been verified by these same workers,[17] by measuring chain dimensions in cross-linked networks. However, these recent experiments and simulations are in disagreement with past experiments for chain in networks.[18] The previous work of Liu et al.[18] were for chains embedded in networks formed by the polymerization around linear chains, which were probably driven beyond equilibrium conditions by the polymerization reaction. In this context, we note that the confinement provided by a cross-linked network is much softer than that provided by a porous medium with hard walls, and hence this might provide the basis for any observed differences.

We now consider past work on enumerating chain conformations in Vycor, which is a porous medium, with 28% porosity, created by the spinodal decomposition of borosilicate glass, followed by the etching of the boron oxide phase. This gives rise to an interconnected pore structure, with a mean pore diameter of $D \sim 70$ Å.[19] The conformation of confined polymer chains in semidilute solution in a good solvent was first examined by Lal et al.[20] These workers report that measured *average* chain sizes in Vycor are *smaller* than in unconfined solution, with this effect becoming more pronounced with increasing polymer length. As noted above, this result appears to contradict the results of computer simulations of chains in confined spaces, which suggest that chain dimensions should increase sharply with increased confinement. However, two factors need to be considered. First, the simulations are for isolated chains, while the experiments were conducted for solutions which were well into the semidilute regime at least in the bulk solution. Second, the Vycor pore surfaces studied by Lal et al.[20] were untreated, and consequently, they should be strongly adsorbing for polystyrene.[20] As a result, the chain dimensions reported in ref 20, which are probably affected by both confinement *and adsorption* and also by solution concentration, cannot be used to critically examine the scaling predictions and simulation results for isolated chain dimensions in porous media where only confinement effects apply. To best mimic the simulations, we have considered situations where the pore walls were treated with chlorotrimethylsilane, to minimize the adsorption of polystyrene. Following Lal,[20] we utilized contrast matched [CM] mixtures of isotopic polystyrenes [PSH/PSD] with molecular weights up to 700 000 g/mol ($N \sim 6700$) in a CM mixture of protonated and deuterated toluene. We also utilized a symmetrical disordered diblock copolymer of PSH−PSD in CM toluene solution. In all cases we find that the chains are isolated in the pores but that the sizes of the chains, as deduced by the same analysis techniques applied to the bulk, are apparently unaffected by confinement. Since these conclusions are in disagreement with simulation results, we reanalyze the data accounting for the tortuosity of the Vycor pores. The resulting chain dimensions are then in near quantitative agreement with the theoretical predictions and computer simulations for chain dimensions in porous media, which imply strong swelling on confinement. Nevertheless, we stress that our results are strongly influenced by the analysis techniques used in the treatment of experimental data.

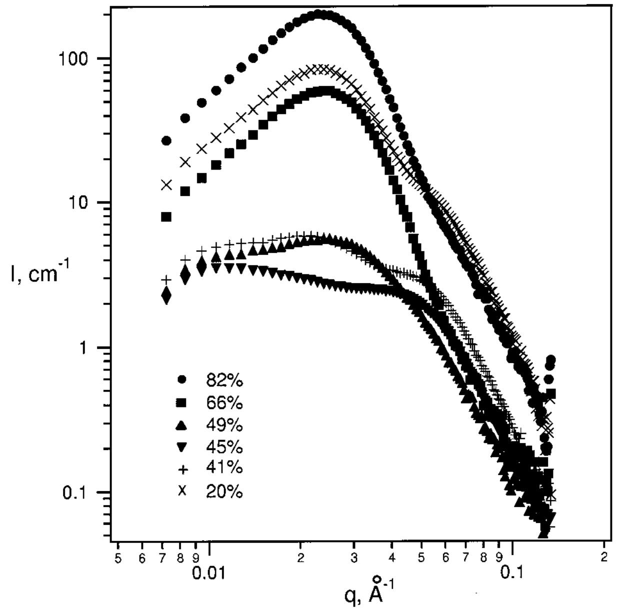

Figure 1. Neutron scattering intensity plotted as a function of q for Vycor contacted with isotopic mixtures of cyclohexane. The numbers in the figure refer to the hydrogenated cyclohexane content in the contacting mixture. This procedure is utilized to locate the contrast matching point.

II. Experimental Details

Preparation of Vycor Disks. Vycor disks (7930, Corning) with a diameter of 2.5 cm and thickness of 0.12 cm were baked overnight in an oven at 500 °C and then cleaned with hot nitric acid (~80 °C) for 3 days.[21] The pore walls were chemically modified to be less absorbing to the polymer by exposing them to a mixture of chlorotrimethylsilane and toluene (1:4) at 70 °C for 2 days.[22] The disks were then refluxed in methanol for 2−3 days, to remove any excess silane in the pores, and finally dried at 90 °C under flowing nitrogen.

Details of the SANS Experiments. SANS experiments were performed using the 30 m SANS instruments at the NG3 and NG7 beamlines at the National Institute of Standards and Technology Center for Neutron Research (NCNR). The experimental q was in the range 0.004-0.3 Å^{-1}, and each measurement was taken at room temperature (22−24 °C). ($q = 4\pi/\lambda \sin \theta/2$, where λ is the neutron wavelength and θ is the scattering angle.) The raw experimental data were corrected for the empty cell scattering and the detector background using standard means.

Contrast variation SANS experiments were performed using mixtures of protonated and perdeuterated cyclohexane with different compositions. Figure 1 shows that, away from the contrast match condition, a peak occurs at $q = 0.025$ Å^{-1}. This peak, which has previously been identified with the pore structure of Vycor,[20] can be minimized when a cyclohexane solution with 44.5 wt % h-C_6H_{12} is used. On this basis we estimate that Vycor has a neutron scattering length density,

Table 1. Sample Specifications and Results

sample	dPS M_w ($\times10^{-3}$) (M_w/M_n)[a]	hPS M_w ($\times10^{-3}$) (M_w/M_n)[a]	R_g (Å) free[b]	c_{free}[c]	R_g (Å) pore[d]	c_{pore}[e]	K[e]	c^*_{free} (calc)[f]	R_{g0} (Å) (bulk) (calc)	ζ (calc)[g]	$R_{g0,pore}$ (Å) (pore) (calc)[h]
120K blend	117.9 (1.06)	120.2 (1.04)	115	0.154	108	0.033	0.22	0.021	132	0.143	141
260K blend	272.5 (1.04)	257.9 (1.04)	166	0.156	154	0.037	0.24	0.011	211	0.213	204
500K blend	507.0 (1.05)	490.0 (1.05)	225	0.151	213	0.012	0.08	0.006	285	0.295	284
700K blend	730.8 (1.08)	717.6 (1.12)	288	0.141	303	0.015	0.11	0.004	406	0.300	405
500K diblock	233.0 (1.12)	265.0 (−)	292	0.05	292						
137K blend[20]	137.0 (1.06)	120.0 (1.05)	125	0.20	121	0.086	0.43				

[a] Columns 2 and 3 correspond to the molecular weights of the two polymers in each blend or the molecular weight of the diblock copolymer. The numbers in parentheses are the polydispersities of the samples. All results are those reported to us by the manufacturer. [b] Column 4 corresponds to chain dimensions in the external solution. These results were obtained by a Debye function fit to the SANS data from the blends. For the diblock, the RPA model was employed. [c] Column 5, c_{free}, is the polymer density in the external solution in units of g of polymer/cm^3. [d] Column 6, R_g(pore), are the results obtained for chain size from a Debye function fit to the SANS data from the pore data from the blends. For the diblock, the RPA model was employed. [e] Columns 7 and 8. c_{pore} is the polymer concentration [g of polymer/cm^3] in the pores. Result derived from the SANS data. $K \equiv c_{pore}/c_{free}$. [f] Column 9. Overlap concentration in the free solution. We utilized the isolated chain dimension, R_{g0}, which was used as an input to theory and optimized by forcing the theory to fit the experimental K data. The equation utilized was $c^* = (NM_{mono})/({}^4/_3\pi R_{g0}{}^3)$, where M_{mono} is the monomer molecular weight. [g] Column 11. The monomer concentration inside the coil, ζ, is calculated following the equation: $\zeta = (NM_{mono})/(\pi(D/2)^2L)$, where D is the mean diameter of the Vycor pores and L is the length of the polymer, which is modeled as a cylinder. This result assumes that the Vycor pores are straight cylinders. [h] Column 12. The $R_{g0,pore}$ numbers were calculated using eq 6 and assuming that the Vycor pores are long cylinders.

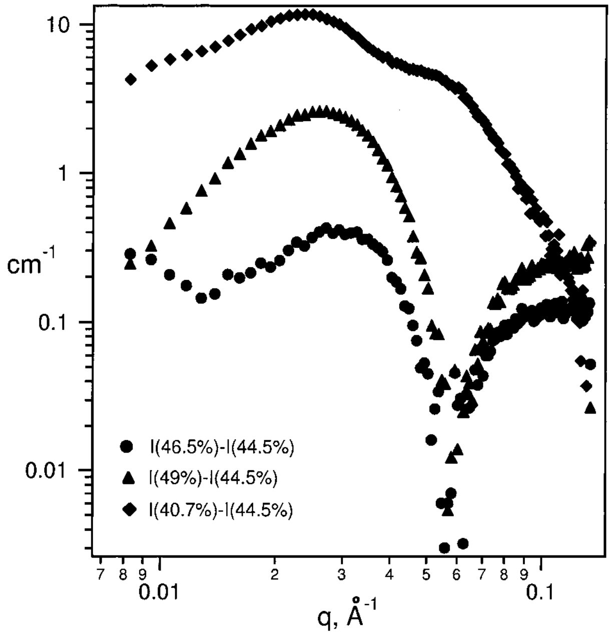

Figure 2. Illustration of the sensitivity of the contrast matching procedure. We have taken the contrast matched cyclohexane solution, comprised of 44.5% of protonated cyclohexane, as the baseline and subtracted it from various other compositions of isotopic cyclohexane mixtures. Notice the appearance of strong scattering features even for slightly off-contrast solutions. These features are absent in all our polymer data, suggesting that we have matched the zero average contrast condition to better than 2%.

$\rho_g = 3.57 \times 10^{-6}$ Å^{-2}. These results should be contrasted to literature estimates of the scattering length density of Vycor, namely $(3.35 \pm 0.13) \times 10^{-6}$,[23] 3.43×10^{-6},[21] and 3.55×10^{-6} Å^{-2}.[20] While the literature values of this quantity vary by about 8%, and it has even been argued that perfect contrast matching at all q values is impossible,[23] we are interested primarily in obtaining reliable data in the low q range ($q < 0.03$ Å^{-1}) where we shall fit our data to known models for polymer chain conformation. Under these conditions we find practically no remnant of the Vycor scattering in our experiments (see below). To subtract the effects of the imperfect matching of the Vycor, and also to remove any incoherent scattering from the protons in the sample, we follow the established procedure of Lal and subtract the scattering intensity of the Vycor filled with the contrast matched toluene from the sample scattering.

We want to stress the sensitivity of the contrast matching scheme and how breaking this condition will be manifested unequivocally in the scattering patterns observed. To make these points, in Figure 2, we have taken the difference in scattering patterns between a noncontrast matched mixture of isotopic cyclohexanes and the contrast matched sample. This figure conclusively shows that even small deviations from the contrast matched point yield scattering curves with well-defined maxima and minima. We shall use this figure in the rest of our analysis, and in particular, we shall use the absence of such peaks and valleys as conclusive proof of having satisfied the contrast matched condition in our scattering experiments.

Sample Preparation. Mixtures of normal and deuterated polystyrenes with a composition at the Vycor match point (44.5% PSD) or a H/D polystyrene block copolymer (also with a composition close to the Vycor contrast match point) were dissolved in H/D contrast matched toluene mixtures. Note that the composition of the copolymer ($\phi_{PSD} \sim 0.47$) is somewhat different from the match point ($\phi_{PSD} \sim 0.445$). However, we do not see any real departure from the contrast match condition, since the copolymer concentrations in the pore are small (1−5%, see below). The characteristics of the various samples studied are listed in Table 1. Solution concentrations, which were always larger than c^*, were 15 wt % for the blends and 5 wt % for the copolymer. The polymer solutions can be infiltrated into the pores by diffusion or capillary action. The former situation, which is effected by first dipping a Vycor sample in pure toluene and then replacing the pure toluene with the polymer solution, is driven by the osmotic pressure difference between the exterior solution and the pure solvent in the pores. This process can result in molecular weight fractionation of the polymer.[24] For typical polymers, with chain diffusion coefficient in solution of $D \sim 10^{-6}$ cm^2/s and diffusion lengths of 0.1 cm, this process can take several days.[8,9] The latter process of polymer infiltration, by capillary action, is performed by dipping a piece of dry Vycor directly into the polymer solution. This second approach was used in our experiments since previous work by McKenna and co-workers[25] on controlled pore glass powder has shown that it results in no molecular weight fractionation. Further, the polymer concentration inside the glass powder and the external solution were found to be the same. To minimize any molecular weight fractionation, which would be expected at equilibrium, we soaked a dry Vycor piece into the solution and minimized the soaking time to less than 15 min.

Although the use of capillary action to fill the pores, combined with a relatively short soaking time of the Vycor disks in the polymer solution limits molecular weight fractionation, the polymer concentration inside the Vycor pores was found to be significantly smaller than in the external solution, i.e., $K < 1$. This finding is not in contradiction with the earlier results of McKenna and co-workers but rather

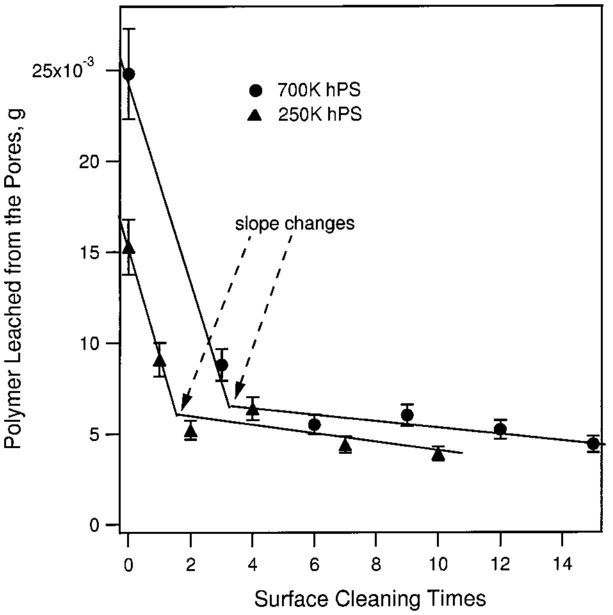

Figure 3. Quantity of polymer recovered after successive washes of the substrate with toluene. The Vycor was contacted with the solvent for no more than 30 s each time.

reflects the differences in mass transport resistance in the two experiments. To reiterate, the McKenna experiments were conducted on powders, while ours utilized monolithic samples. It is easy to appreciate that the monolithic samples were much more mass transport limited, thus resulting in partition coefficients being much less than unity. After initially imbibing the polymer solutions into the pores, we allow the samples to "equilibrate" in the absence of external polymer solution for periods up to 2 months. This procedure allows the chains to assume their preferred conformations. However, no fractionation on the basis of molecular weight occurs since no external solution is present to facilitate this process.

We have verified that polymer does enter the pores by performing two different experiments. First, we utilized a contrast matched toluene solution to infiltrate the Vycor. In this case the Vycor peak disappears. However, when we use a deuterated polystyrene in a CM toluene solution, we see the presence of the Vycor scattering peak. This is consistent with the notion that the contrast matched condition is broken by the presence of deuterated polymer chains in the pores. In a second, macroscopic experiment, we placed a polymer solution on one side of a Vycor disk, while the other side was exposed to air. After a few days solution diffuses through the Vycor and emerges on the air side. Evaporation of the solution which emerges confirms the presence of the polymer in the Vycor pores.

While polymer does penetrate the pores in all cases, the polymer concentration in the pores is significantly smaller than in the free solution. In addition, a polymer rich solution wetting layer is always found on the surface of the Vycor after the sample is removed from the solution. Proper removal of this surface layer of polymer solution is critical, since it can contribute significantly to the scattering intensity. Because of the high viscosity of this polymer-rich adsorbed layer, several iterations of rinsing the surface with pure solvent (contact time < 30 s) followed by wiping the surface of the Vycor were needed to remove the residual polymer on the exterior surface. Figure 3 illustrates that at least two iterations of surface cleaning are required to remove the polymer adsorbed on the Vycor surface for the 250 000 molecular weight blend, while four iterations are necessary for the highest molecular weight blend. Beyond this point, the amount of polymer recovered by subsequent surface washing is nearly constant, which we presume to be the leaching of polymer adsorbed into the Vycor pores.

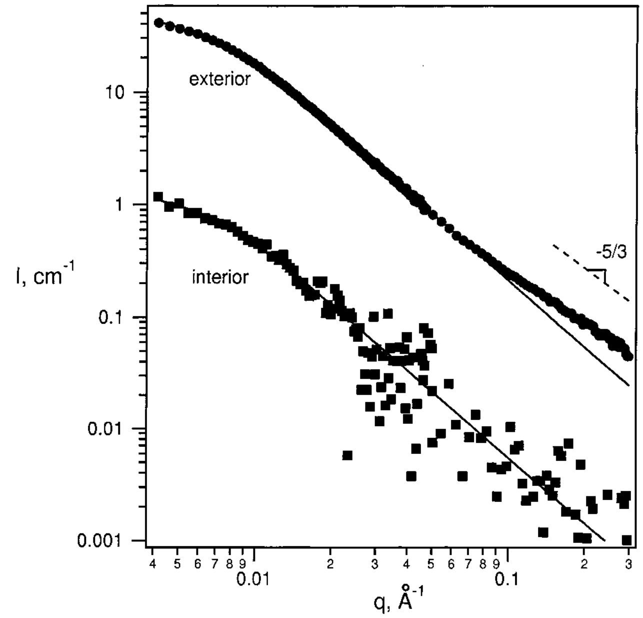

Figure 4. Scattering intensity as a function of q for a PSH–PSD blend in toluene. The upper curve is for a bulk solution of 15 wt % polymer, while the lower curve is for the same solution in Vycor. Lines are fits to a Debye function as detailed in the text.[20]

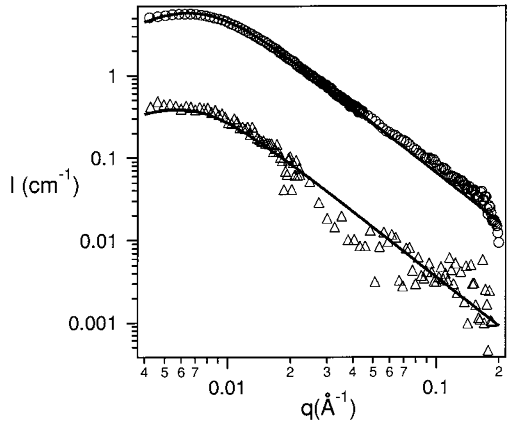

Figure 5. Scattering intensity as a function of q for a PSH–PSD copolymer in toluene. The upper curve is for a bulk solution of 5 wt % polymer, while the lower curve is for the same solution in Vycor. Lines are fits to the Leibler theory.[20]

III. Results

The scattering of the nonconfined polymer mixtures and block copolymer solutions are shown in Figures 4 and 5, respectively. The blend shows behavior consistent with that expected from a contrast matched semidilute solution of polymer in a good solvent. At low to intermediate q values the data can be fit with a standard Debye function,[26]

$$P(x) = \frac{2}{x^2}[e^{-x} - 1 + x] \tag{2}$$

where $x = q^2R_g^2$, and R_g is the radius of gyration of the chains. At higher q values there is deviation from the Debye function scaling, which is appropriate for chains in good solvent. The diblock copolymer solution displays a peak at $q = 0.006$ Å^{-1}, corresponding to the size of the polymer. The scattering from the block copolymer solution is fit to the random phase approximation (RPA) calculation for this system.[26]

We now consider the scattering of the solutions of contrast matched toluene with nearly contrast matched polymers [either the blend or the disordered copolymer] imbibed in Vycor. The absence of the Vycor peak in the measured scattering after solution adsorption confirms that the contrast matched condition is not broken when the polymer solution enters the pores (see Figures 4 and 5). We therefore deduce that there is no isotopic preference for adsorption into the pores, or at the pore walls, within the uncertainties of our experiments. In the case of the diblock, the chain conformation in the Vycor pores is practically unaltered on confinement since the peak position and peak shape are the same in the Vycor and in the nonconfined solution (see Figure 5). Similar results are found for the blends, and the scattering data from the unconfined solution and data from the bulk can be superposed simply by vertically shifting one set of data. From the scattering information we can deduce two pieces of information: the size of the chains in the Vycor and the concentration of polymers in the pores. The chain size is deduced by fitting the data to either the Debye function for the blends or the RPA theory to the diblock. The partition coefficient, K, is deduced by taking a ratio of the intensity at zero wavevector of the confined to the unconfined solutions. Table 1 presents the radii of gyration numbers obtained from fitting the scattering data from the blends and the copolymer. To establish the reliability of our results, we present the chain dimensions and polymer concentration in Vycor pores for the one case reported in ref 20, where the pore walls are treated to be nonadsorbing to the polymer. Note that the solution concentration employed by Lal et al.[20] was slightly higher than ours, i.e., 20 wt % compared to our values of 15 wt %. Several things are immediately obvious by examining these data sets. The R_g values obtained in all cases are essentially equal to their unperturbed solution values, within the uncertainties in the experiments. The data from the bulk and the pores can be fit to the power law, $R_g \sim N^\nu$, where $\nu = 0.50 \pm 0.02$ for the free solution and 0.55 ± 0.08 for the confined solution. Within experimental uncertainties, both numbers are equivalent to the $\nu = 0.50$ scaling exponent expected for a semidilute polymer solution in good solvent. The confined exponent is also consistent with $\nu = 0.588$ expected for a dilute polymer solution in good solvent. Second, the results for chain dimensions are unaffected by the free solution polymer concentration. This result is deduced from the fact that all of our solutions comprised of the polymer blends were at a concentration of 15 wt % and the Lal et al.[20] blend was at a concentration of 20 wt %, while our copolymer result was at a concentration of 5 wt %.

We also deduce the K values, the partitioning based on polymer concentration between pore and free solution. As noted above, there is no fractionation based on molecular weight, and we find that, as expected intuitively, the partition coefficient decreases with increasing chain length of the polymers in question. This result reflects the fact that the entropic penalty for confinement increases with the chain length of the polymer, scaling with the ratio $D/R_{f0} \propto D/R_{g0}$, where R_{g0} is the radius of gyration of an isolated chain in good solvent (see Appendix I). However, in all cases we find that polymer did enter the Vycor pores in substantial amounts, and K values as large as 0.11 were found for the largest molecular weight considered. These findings are consistent with ideas presented in the literature, which suggest that significant chain penetration into the pores would occur as long as the blob size is much smaller than the pore diameter (70 Å). For isolated chains (i.e., dilute solutions) we would find essentially no polymer in the pores, since $\xi_{\text{blob}} \sim R_{f0} > D$ for the molecular weights we consider. For semidilute solutions, however, $\xi_{\text{blob}} \sim \phi^{-3/4} < D$, and significant polymer concentration is found in the pores. For the external concentrations we employ, following Lal et al.,[20] we estimate $\xi_{\text{blob}} = 43$ Å, which is smaller than the pore diameter. Thus, chains are forced into the pores due to the high osomotic pressure in the external solution.

A formalism proposed by Teraoka was used to obtain a quantitative understanding of these results.[24] This model has previously been shown to quantitatively capture the K values obtained by contacting a free solution with pores.[24] The consequences of these ideas on chain conformation have, however, remained unexplored. Here a thumbnail sketch of our implementation of this theory is provided, and the interested reader is referred to the original papers and to the Appendix for more details. The theory accounts for the two major effects on the chemical potentials of the polymer chains. These are (a) the osmotic pressure differences, driven by concentration differences, between the pore and exterior, and (b) the confinement entropy contributions to the chemical potential of the polymer chains. The single chain theory of Casassa[1] was utilized to account for the entropy loss of the polymer chains on confinement. Use of this theory in this context implies that the following two assumptions are obeyed:

(i) Chain conformations in the pores can be modeled by random walks. It is unknown whether random walk statistics are applicable to a confined polymer chain in good solvent.

(ii) The theory of Casassa applies only to isolated chains. While the concentration in the free solution is always much larger than the free solution overlap concentration, the chains in the pores are at low enough concentration that we will approximate them as nonoverlapping. If this fact is verified, it would give considerable confidence for the applicability of Casassa's theory in this context.

The calculations were performed by guessing the unperturbed radius of gyration in the free solution, R_{g0}. This yielded the overlap concentration in the bulk,

$$c^* = \frac{NM_{\text{mono}}}{\frac{4}{3}\pi R_{g0}^{\ 3}} \tag{3}$$

which was the major input into the calculation. For the chains in the pores, we assumed that the coils were isolated, and hence the dilute solution limit of the chemical potential needed to be employed. The R_{g0} numbers were then adjusted so as to match the theoretical estimates of partition coefficients to the experimental value. We chose this route since the K values are very sensitive to the R_{g0} values. Table 1 shows that c^* numbers estimated in this fashion are very close to the published results of Lal et al.,[20] giving us considerable confidence in this protocol. Further, our computed values of R_{g0} match independent light scattering measurements to within 10 Å in all cases except for the highest molecular weight considered, where the deviation was 35 Å.[27] Note that the light scattering experiments were conducted at 30 °C, while our experiments were conducted in the 22−24 °C range, which might account for these small discrepancies. Our results suggest that the protocol of Teraoka quantitatively reproduces the partitioning of polymer chains between the free solution and the pores.[24]

Chain Conformations Deduced by Assuming that Vycor Pores Are Straight Cylinders. We now interpret the size of the chains in the framework of a model where Vycor pores are modeled as straight cylinders. To utilize this information and predict the size of the polymers in the pores, we recognize that the pores are randomly oriented in Vycor. Thus, the SANS experiment provides an angularly averaged dimension of a coil. The radius of gyration of a cylinder of length L and diameter D, the pore diameter, is given by the expression

$$R_g^{\,2} = \frac{L^2}{12} + \frac{D^2}{8} \tag{4}$$

We can then define ζ, the monomer concentration inside the coil,

$$\zeta \sim \frac{NM_{\mathrm{mono}}}{\pi(D/2)^2 L} \tag{5}$$

where N is the chain length and M_{mono} is the monomer molecular weight. Using a $D = 70$ Å, and the computed values of R_g in the pores, we can calculate L and hence ζ (see Table 1). Since $c_{\mathrm{pore}} < \zeta$, it implies that c^* values in the pores are equal to ζ (see Table 1), and hence we deduce that although coils are strongly overlapped in the free solution, they are effectively isolated in the pores.

We now note that the radius of a sphere and its radius of gyration are related by the equation $R^2 = 5R_g^{\,2}/3$. Given the fact that $L = 2R$, and the chain assumes its unperturbed dimensions along the pore axis, it follows that $L^2 = 20R^2_{\mathrm{g0,pore}}/3$, where $R_{\mathrm{g0,pore}}$ is the size along the pore axis of the isolated coils. Thus, eq 4 is rewritten as

$$R_g^{\,2} = \frac{5R^2_{\mathrm{g0,pore}}}{9} + \frac{D^2}{8} \tag{6}$$

This approach of calculating the chain radius of gyration in the porous geomtery must be contrasted with the earlier approach of Lal et al.,[20] who had used eq 4 and assumed that $L = 2R_g$(free). The radii of gyration, $R_{\mathrm{g0,pore}}$, estimated following eq 6 are listed in the last column Table 1. It is immediately clear that the $R_{\mathrm{g0,pore}}$ values estimated in this fashion are apparently equal to our estimates of the dimensions of isolated coils in the free solution (also listed in Table 1). On this basis, it would therefore be tempting to conclude that the molecular dimensions parallel to the pore axis are not expanded in spite of the very strong confinement, as implied by the quantity D/R_{f0}, which is much smaller than unity. In the bulk solution, the relevant quantity is the ratio D/ξ_{blob}, which is larger than unity, ensuring that chains do penetrate into the pores. If D/ξ_{blob} continued to be the operative variable in the pores, then it might be reasonable to conclude that penetration effects on chain conformation would be small. However, the decrease of concentration in the pores relative to the bulk concentration, coupled with the unusually high overlap concentration in the pores immediately, suggests that the correct operating variable is indeed D/R_{f0}, which suggests strong confinement effects should be manifested in chain dimensions. In fact, computer simulations on isolated chains in one and two-dimensional confinement show conclusively that chains are strongly perturbed and that the $R_{\mathrm{g0,pore}} \sim N$; that is, the coils are strongly extended on confinement.

Thus, the simple conclusion that $R_{\mathrm{g0,pore}} \sim R_{\mathrm{g0}}$ is not a self-consistent result for confined chain dimensions in our experiments. To reconcile this apparent disagreement between theory and this interpretation of experiments, we suggest two alternatives. First, Vycor has relatively large interconnects between the pores, and it is possible that the chains are located in these areas. While appealing, we do not ascribe to this viewpoint since we would expect to see a signature in the scattering patterns corresponding to the mean distance between these interconnects (∼200 Å), which is not observed in our experiments. A second possibility is that the Vycor pores are not long cylinders. Rather, one may expect that the pore axis is a random walk with a step length similar to the pore diameter. The analysis of experimental on the basis of this assumption is presented next.

Analysis of Data Assuming That the Pores Are Random Walks. The underlying assumption here is that the pores are not long cylinders, but rather are random walks of step length ∼70 Å. (We chose to treat the pores as random walks rather than the more realistic description as self-avoiding walks since the data have been fit to a Debye function, which is more descriptive of a random walk.) Thus, the R_g values obtained from the experiments are used to analyze the “number of steps”, N_p, of a walk of step size D (∼70 Å):

$$R_g^{\,2} = \frac{N_p D^2}{6}$$

We then recognize that the polymer chain adopts a conformation where its diameter is D and its lateral “contour” length is

$$L = N_p D = \frac{6R_g^{\,2}}{D} \tag{7}$$

By this process we have “straightened” out the effect of the pore tortuosity and can now finally estimate a radius of gyration of the chains, which has been deconvoluted from the Vycor geomtery. We now employ eq 4, with the L value estimated following eq 7, to compute the R_g of the chains in the confined environments and compare it to the extrapolations of simulation results to this range of chain lengths and confinement (see Figure 6). It is immediately clear that, in spite of the approximations in data analysis, the results of our experiments qualitatively match the simulations over much of the range considered. There are clear deviations between the simulations and the experiments, but we conclude that there is a persuasive case for chains being strongly expanded in the pores.

A few salient features are in order here. First, we find that the chain dimensions parallel to the straightened pore axis follow the scaling law, $L \sim N^{1.1}$, which is consistent with past simulations. However, note that this result arises simply because we have assigned the contour length along the pore as being equal to the size of the chain in this direction. The overlap concentra-

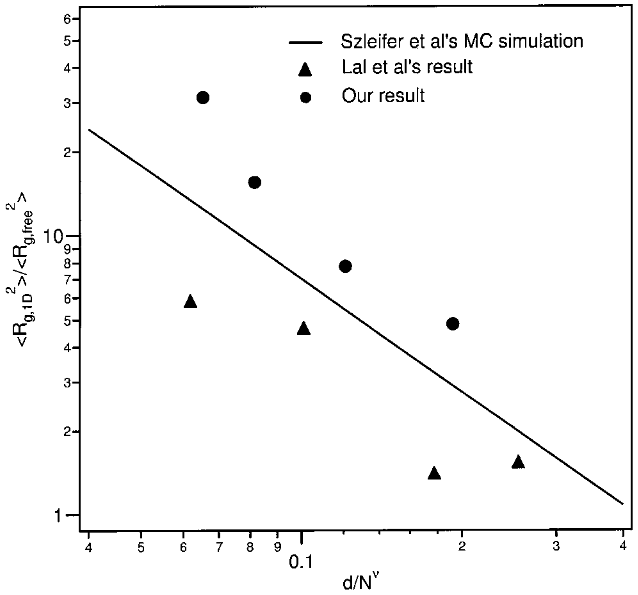

Figure 6. Comparison of the experimentally determined coil size expansion on confinement vs simulation results of van Giessen and Szleifer[12] plotted as a function of d/N^{ν}, where $d = D/\sigma$, where σ is the Kuhn length of the chains and N is the degree of polymerization.

tions, ζ, based on eq 5 are ~0.05 ± 0.01 independent of molecular weight. Thus, the polymer concentrations in the pores are small enough in all cases considered that chains are effectively isolated in these confined environments.

IV. Discussion

Critical Comparison of Our Results to Previous Work of Lal et al.[20] While our results are the first concrete evidence of the fact that chain conformations are strongly swollen on confinement, these results are apparently in disagreement with the previous findings of Lal et al.[20] These workers had found that the radius of gyration, as deduced by a Debye function analysis of the data, is decreased on confinement. We have reanalyzed the Lal data using the protocal presented above, where the pores are modeled as random walks with step size equal to the pore diameter. These data are also plotted in Figure 6. This analysis shows that chains will be swollen in all cases except for the lowest molecular weight, 32 000, where the Flory radius is expected to be ~66 Å. In this case the D/R_{f0} value is comparable to unity, and no confinement effects are expected. The analysis presented above should therefore not be employed in this case, and in fact, it produces a wrong conclusion that chains are contracted on confinement. For all other molecular weights we do find chain expansion, but to a much lower extent than that expected by theory.

Lal et al.[20] had found $K \sim 1$ in all cases, except the one situation where the walls were treated to be nonadsorbing to the polymer. In contrast, our results suggest $K \ll 1$. Considering these facts, we emphasize the important role of the pore walls in the two sets of experiments. The pore walls in the experiments of Lal were not functionalized so as to be nonadsorbing to the polymer, while our case correspond to "passivated" walls. Thus, the pore polymer concentrations are higher in the Lal experiments. In fact, we expect the pore concentration in these cases to be much higher than the overlap concentration, a conclusion which can qualitatively rationalize a decrease in chain swelling (Figure 6). Further, in the one set of experiments of Lal where the walls were functionalized we found that the chain dimensions virtually identical to our estimates. Thus, we conclude that the nature of the pore surface can critically affect the K values for polymer solutions, and hence chain conformations, when they are contacted with highly confined environments.

High Overlap Concentrations in the Pores. The overlap concentration in these porous hosts can be derived by using the L values derived in the case where the pores are modeled are random walks:

$$c^* \sim \frac{Nb^3}{\pi(D/2)^2 L} \tag{8}$$

Since $L \sim N$, the overlap concentration in the pores is high (0.05 ± 0.01) and is predicted to *be independent* of molecular weight. These findings should have interesting consequences on the transport properties of chains in these porous hosts. Our results appear to suggest that chain dynamics will be unaffected by concentration over a broad range, i.e., for $c \leq c^* \sim \zeta$, but that collective effects should take over for higher concentrations. To our knowledge no one has systematically tested these ideas, although there is plenty of macroscopic diffusion coefficient data for polymers in porous hosts.

Connections of These Results to Those in Other Environments. A final point to note is the consequence of these ideas on the conformation of polymer chains in thin films, and hence on the intercalation of polymers into the galleries of clay sheets, which is relevant to the creation of polymer-inorganic composites. If one extends the ideas presented above to a polymer chain intercalated into the gallery, we can derive that no confinement effects should be felt on chain dimensions as long as $D > \xi$, where ξ for a melt of chains is comparable to the monomer size (the screening length). This result directly implies that chain conformations parallel to the sheets will not be affected unless the sheet separation is smaller than the persistence lengths of the chains in question. These results are consistent with our earlier results for melt conformations in thin films,[28] which found for $D/R_g \geq 0.5$ that the R_g values were unaffected by confinement into thin films. However, the results of Stamm et al.[29] and Brulet et al.,[30] which found significant changes in R_g, cannot be rationalized by these findings. Instead, these latter findings might be affected by adsorption of the chains to the boundaries (especially the substrate interface).

V. Conclusions

Our results clearly demonstrate that chain conformations are strongly affected on confinement as long as the ratio of the confining dimension to the appropriate correlation length is much smaller than unity. Concurrent with this result is the fact that the overlap concentration in these confined geometries are high, relative to the unconfined solution. Since K values are typically smaller than 1 when a polymer system is placed in a confined environment, chains that are strongly overlapped in the unconfined state can be isolated in the confined geometry. These results are expected to strongly impact the dynamic behavior of these confined polymers, an aspect that has not been studied in detail to date. A final aspect we stress here is the importance of the analysis procedure utilized in the treatment of experimental data. Our results and conclusions are strongly affected by the particular protocols employed in the analysis, and hence we caution against the use of materials with random pore geometries such as Vycor. Rather, the use of well-defined pore geometries will help to address these issues in an unequivocal manner.

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Appendix

The partition coefficient can be obtained from the chemical potential equilibrium between exterior and interior polymer solutions. The chemical potential of a polymer solution can be expressed in terms of the reduced osmotic pressure (Π), polymer concentration (c), and confinement effect. Ohta and Oono derived Π as a function of c from renormalization group theory.[31] This yields

$$\Pi = 1 + \frac{1}{2}x \exp\left[\frac{1}{4}\left(\frac{1}{x} + \left[1 - \frac{1}{x^2}\right]\ln(1+x)\right)\right] \qquad (9)$$

where $x = 3.49c/c^*$. Using this result, Teraoka equated the interior and exterior chemical potentials of the polymer chains.[24]

$$\ln c_\mathrm{i} + I\left(\frac{c_\mathrm{i}}{c^*}\right) - \frac{\Delta S}{k_\mathrm{B}} = \ln c_\mathrm{e} + I\left(\frac{c_\mathrm{e}}{c^*}\right) \qquad (10)$$

where $I(a) = \Pi(a) - 1 + \int_0^a [(\Pi(a') - 1)/a']\,\mathrm{d}a'$, k_B is Boltzmann's constant, and the subscripts i and e denote respectively the inside and outside polymer concentrations. For all the cases considered here the inside concentration of polymer is always less than the calculated overlap concentration inside the pores. Hence, the I term inside the pore is equal to 0, and only the ideal entropy contribution to the chemical potential exists in this environment. ΔS is the entropy loss associated with confining a single Gaussian chains, as derived by Casassa for cylindrical pores,[1]

$$\Delta S = \ln\left(4\sum_{m=1}^{\infty}\frac{1}{{\beta_m}^2}\exp\left[-{\beta_m}^2\left(\frac{2R_\mathrm{g}}{D}\right)^2\right]\right) \qquad (11)$$

where β_m are the roots of the zero-order Bessel function of the first kind.

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