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Adsorption of Poly(methyl methacrylate) on Concave Al_2O_3 Surfaces in Nanoporous Membranes

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Abstract

The objective of this study was to determine the influence of polymer molecular weight and surface curvature on the adsorption of polymers onto concave surfaces. Poly(methyl methacrylate) (PMMA) of various molecular weights was adsorbed onto porous aluminum oxide membranes having various pore sizes, ranging from 32 to 220 nm. The surface coverage, expressed as repeat units per unit surface area, was observed to vary linearly with molecular weight for molecular weights below ~120 000 g/mol. The coverage was independent of molecular weight above this critical molar mass, as was previously reported for the adsorption of PMMA on convex surfaces. Furthermore, the coverage varied linearly with pore size. A theoretical model was developed to describe curvature-dependent adsorption by considering the density gradient that exists between the surface and the edge of the adsorption layer. According to this model, the density gradient of the adsorbed polymer segments scales inversely with particle size, while the total coverage scales linearly with particle size, in good agreement with experiment. These results show that the details of the adsorption of polymers onto concave surfaces with cylindrical geometries can be used to calculate molecular weight (below a critical molecular weight) if pore size is known. Conversely, pore size can also be determined with similar adsorption experiments. Most significantly, for polymers above a critical molecular weight, the precise molecular weight need not be known in order to determine pore size. Moreover, the adsorption developed and validated in this work can be used to predict coverage also onto surfaces with different geometries.

1. Introduction

Polymer adsorption onto surfaces of all geometries is relevant to many fields and applications. One example is the coating of particles with a very thin polymeric layer to provide strength to ceramic parts before firing (i.e., to serve as a binder in ceramic processing). The nature of the adsorbed polymer layer (its density and conformation, for example) influences particle packing density and, therefore, the strength of the final product.¹ Furthermore, it has been shown that polymer adsorption influences the size of nanoscale inorganic particles that nucleate from molecular precursors.^{2–7} Adsorption to concave surfaces, the topic of this article, is applicable

to chromatography. The most obvious example is in the field of adsorption chromatography, wherein the strength of adsorption between molecules and a porous (concave) solid causes molecules to elute at different rates from the stationary phase.⁸ Also, although adsorption is undesirable in typical size exclusion chromatography,^{9,10} a similar experiment, in which polymers of known molecular weights are eluted through a porous analyte, can determine the structure of the porous stationary phase. This technique is particularly relevant when studying swollen gels, which are difficult to analyze by traditional porosimetry.¹¹ Furthermore, it will be shown in this paper that polymer adsorption onto concave surfaces can measure the molecular weight or the conformation of the adsorbing chains.

In previous communications, we have developed a model, supported by experimental data, that accurately describes the chemisorption of poly(methyl methacrylate) (PMMA) onto alumina particles of various sizes. This model is based on two competing processes: (1) the energetically favorable bonding that occurs between the polymer and the surface and (2) the mutual repulsion of chain segments that reside in the proximity of the metallic surface. We have shown that the latter process, which is essentially entropy-driven, varies with surface curvature. For small magnitudes of the curvature (i.e., for large particles), this term is practically identical to that observed for flat surfaces. For medium-sized particles, those having approximately the same size as the radius of gyration of the polymer, this confinement energy changes, resulting in an inverse scaling of the adsorption coverage with the curvature. At very small particle sizes, having dimensions that are much less than the radius of gyration of the polymer, the number of chains bound to the surface is identical regardless of molecular weight because the polymer chains extend outwardly, again due to the change in the entropic term.^{12–14}

In this paper we study, both experimentally and theoretically, the adsorption of polymers onto concave (as opposed to convex) surfaces, in order to shed new light upon the nature of curvature-dependent adsorption. Experimentally, we analyze the chemisorption of PMMA onto various concave aluminum oxide media in order to determine the effects of both polymer molecular weight and curvature on the adsorption process. The Al_2O_3 –PMMA system was chosen because of its well-understood mechanism of adsorption. This mechanism is characterized by the de-esterification of the side group, followed by the interaction of the resultant conjugate base with a positively charged aluminum atom on the surface in the presence of a minimal amount of water, as shown in Scheme 1.^{15–19} Polymer chains that are unbound to the surface can be rinsed away, allowing for the analysis of only those chains in which at least one repeat unit is in intimate contact with the surface. The Al_2O_3 concave surfaces consist of porous sheets with different pore sizes, as shown in Figure 1a–c. While the effective cavities in which the adsorption takes place in this case are cylinders, the concavity of the system is two-dimensional, and hence the theoretical application of our previously developed model is altered accordingly.¹² Therefore, the goal of the work is to relate experimental measurements of polymer coverage onto these cylindrical surfaces to the previously developed theory.

2. Experimental Section

2.1. Materials

Anodized aluminum oxide disks (Anodisc) having a diameter of 13 mm were purchased from Whatman (a unit of GE Healthcare). The membranes featured open cylindrical pores of narrow size distribution and differed in pore size. The pore diameters as reported by the manufacturer were 20, 100, and 200 nm. Independent SEM analysis has determined the mean diameter of these films to be 32, 100, and 220 nm. These disks were determined to be amorphous by X-ray diffraction, and their specific surface areas were calculated by analysis of the scanning electron micrographs shown in Figure 1. SEM imaging of the uncoated disks was accomplished by mounting them to a conductive stage with conductive powder and analyzing them under a Zeiss SEM Ultra60 at 5 kV with an in-lens secondary electron detector. It is important to note

that the convex (disk circumference) and flat (disk faces) surface areas are negligible because they account for less than 0.3% of the entire surface area on the disk. Therefore, at least 99.7% of all the surface area on the disk resides in cylindrical pores and is concave. The table in Figure 1 shows significant geometric properties of the disks examined in this experiment.

Poly(methyl methacrylate), PMMA, polymers were purchased from various vendors (Sigma Aldrich Chemical Co., Fisher Scientific, Polysciences, Inc., and Scientific Polymer Products), and their molecular weights are 15 000, 75 000, 120 000, 350 000, and 996 000 g/mol. Polydispersity indices were generally ~ 1.5 .

Solutions having concentrations of 15% and 1% (w/v) PMMA were prepared by adding appropriate masses of dry polymer to volumetric flasks, filling to the to-contain line with chlorobenzene (99.5%, Acros), and allowing at least 2 days for complete dissolution.

2.2. Experimental Procedure

Adsorption of PMMA to the surfaces was achieved by the following process: Each disk was exposed to 3 mL of polymer solution after the alumina disk and the glass sample vial were rinsed twice with clean solvent. The vials were placed in a laboratory oven at 343 K, sealed after their temperature equilibrated, and tilted so that both faces of the disk would be accessible to the polymer solution. Each trial was repeated in triplicate, and the durations of the experiments were 1, 3, or 7 days.

Before data acquisition, PMMA-rich disks were rinsed in order to remove unbound polymer. Each disk was cooled, removed from its vial, and rinsed at least five times with at least 5 mL of pure solvent in a Soxhlet extraction apparatus. The disk was removed and examined visually upon drying. If the disk dried unevenly or showed shiny spots on its surface, it was rinsed again in the apparatus in order to remove all unbound polymer. Disks with dirt or other contaminants were discarded.

After ensuring that all disks were viable and free of unbound polymer, their decomposition profiles were measured in a TA Instruments Q50 thermogravimetric analyzer (TGA). Each disk was heated at 20 K/min from room temperature to 720 K in oxygen. The decomposition profile of the very thin adsorbed PMMA layer matched well with the decomposition profile of bulk PMMA. A typical decomposition plot is shown in Figure 2. Polymer adsorption was determined by the mass loss between 373 and 720 K. A control experiment conducted in this temperature range showed that the mass of the substrate remained constant.

3. Results and Discussion

3.1. Experimental Results and Analysis

It was determined that a duration of 3 days was necessary to achieve saturation in all of these systems and that the kinetics of adsorption were indicative of equilibrium (as opposed to steady-state conditions), which implies complete, exhaustive coverage over all surfaces, thereby justifying the calculations of coverage. As can be seen by plotting the duration of experiment vs coverage for two different molecular weights and three different pore sizes, shown in Figure 3, saturation appears complete by 3 days for all systems analyzed. Furthermore, equilibrium conditions - and not steady-state conditions - were determined to occur because saturation was reached faster in the lower molecular weight system and on the same time scale for both large and small pore sizes and molecular weights. It was assumed that the only way to prevent equilibrium conditions from occurring is what we call clogging, in which the local concentration of polymer chains inside a pore is so great that subsequent chains cannot penetrate this mass in order to access the interior, uncovered surfaces. Such clogging, if it were to occur, would indicate that calculations of coverage were artificially low. However, because

of the observed saturation kinetics, shown in Figure 3, clogging did not occur. If clogging would have occurred, we would have expected that saturation would be reached faster in systems with smaller pores and in systems with higher polymer molecular weights, much for the same reasons that a smaller drain would be clogged more easily than a larger drain and that long hair would clog a drain more easily than short hair. Also, if plugging were to occur, lower molecular weights would feature less plugging and would have more mass adsorbed to the surface; however, the opposite trend was observed, presumably due to the higher mobility of the smaller chains.²⁰ The data show that plugging does not occur, thereby indicating the equilibrium state of the system at saturation.

The achievement of equilibrium is a critical assumption in this work, and we have confirmed it by additional methods other than the saturation argument outlined above. After 3 days of exposure of 32 nm pore size disks to 350 000 g/mol PMMA, the disks were cleaned as usual and subjected to 10 min of ultrasound treatment in pure solvent, followed by reinsertion of new polymer solution. If plugging were to occur, we would have expected to see more mass adsorbed onto the disks after this treatment. No such increase was observed.

In addition, a separate experiment was designed to determine the role of diffusion on the adsorption process. In this experiment, both oven-dry and wet-with-solvent 32, 100, and 220 nm disks were exposed to PMMA solutions having a PMMA molecular weight of 120 000 g/mol. If plugging were to occur, we would have expected the wet-with-solvent disks to adsorb less mass than the oven-dry disks because, in the latter case, the concentration of polymer inside the pore is instantaneously identical at all locations (because of fluid flow), as opposed to the former case, in which uniform concentration across the pore length is gradually achieved by the diffusion of polymer through solvent. No such differences were observed as the measurements were statistically identical. Furthermore, a logical argument using previously collected data supports the equilibrium argument. If plugging were to occur, we would have expected almost all of the surface area of the pores to be inaccessible to the polymer. In such a case, assuming the coverage to be on the same order of magnitude as adsorption to flat surfaces,¹² the mass adsorbed would be so small as to be practically immeasurable, given the precision of the TGA balance. All of these arguments, in addition to the saturation argument described in the previous paragraph, indicate that equilibrium is reached.

In our previous work,¹² we have shown that the coverage of the polymer on convex surfaces was dependent only on the curvature and independent of the polymer molecular weight. However, in the concave case, a plot of coverage vs polymer molecular weight, shown in Figure 4, clearly demonstrates the existence of two distinct adsorption regimes: a molecular-weight-dependent regime and a regime in which adsorption is independent of molecular weight. At 120 000 g/mol and below, the adsorption per unit surface area appears to vary linearly with polymer molecular weight. This linear dependence can be seen more easily in Figure 5.

The slopes of these lines at low values of molecular weight (<120 000 g/mol), i.e., the linear variation in coverage with polymer molecular weight, will be referred to in this paper as the specific molar coverage. As shown in Figure 6, the specific molar coverage increases with the increase in pore size. An explanation of this phenomenon may be rationalized in the following manner: Above a critical polymer length regime, the adsorption layer would have a width L and a constant coverage, regardless of the length of the polymer chains, even if shorter chains will have a smaller number of contact points per chain with the surface, as shown in Figure 7a.²¹ When the polymer chain length decreases such that it has the precise length to form a brush with length L , the adsorption will exhibit one contact point per polymer chain, as shown in Figure 7b. For even shorter polymer chains, the single anchoring point per chain with the alumina surface still remains valid, forcing the formation of an adsorption layer with a width that is less than L , as shown in Figure 7c. In this polymer length regime, the coverage will

decrease and will be proportional to the length of the chains, i.e., to the mass of the polymers. It is important to note that the dependence of adsorption on polymer molar mass is not identical for every system,^{20,22} and care must be taken to avoid overgeneralization of system-specific results. Although the dependence of the specific molar coverage on pore size appears to be linear, we are hesitant to assert a definite relationship. Clearly, additional data points are required in order to assess the nature and universality of this dependence.

A similar relationship can be seen when examining the effect of polymer concentration on coverage, as shown in Figure 8. In this case, the dependence of the adsorption on pore size seems to be linear (as expected from the previously developed model¹²), and the slope changes with polymer concentration. Polymer chains are more likely to leave the solution for the surface in the more concentrated system. During adsorption, dissolved PMMA is in equilibrium with PMMA that has precipitated onto the surface, and hence, an increase in dissolved PMMA concentration will result in more PMMA adsorbed onto the aluminum oxide surface.²³

The experimental evidence of the relationships among the specific molar coverage, the pore size, and the polymer concentration in solution indicates that the adsorption of PMMA onto anodized aluminum oxide media can be used as a direct measurement of either molecular weight or pore size if the other is known. For example, PMMA molecular weight (below 120 000 g/mol) can be measured by adsorbing it to commercially available anodized aluminum oxide disks of known pore size. Likewise, pore size of anodized aluminum oxide can be measured by using it as a substrate for the adsorption of PMMA of known molecular weight. In fact, for large polymers, the molecular weight must not be known accurately in order to determine pore size due to the independence of the adsorption on polymer size in this molar mass regime. The importance of a new way of measuring molecular weight is obvious, but the significance of measuring pore size requires some explanation. These membranes were fabricated by the anodization of aluminum, a process that is known to yield open, cylindrical pores. Depending on the anodization conditions (e.g., acid strength, voltage, and temperature), pore size varies and is often too small to measure with a conventional light microscope.²⁴ Therefore, after fabrication of such anodized aluminum oxide media, pore size could be measured directly by a simple adsorption experiment, rendering traditional pore size measurement tools, such as electron microscopy, porosimetry, and gas adsorption unnecessary (especially if such methods were prohibitive or unavailable).

3.2. Theoretical Analysis and Adsorption Model

The experimental results reported in this article show a remarkable resemblance to the experimental results that we obtained for the adsorption of PMMA on spherical alumina particles. More specifically, on both concave and convex surfaces, it was demonstrated that the coverage per unit surface area is proportional to the radius of the spherical particles and independent of the molecular weight of the polymer. Both types of adsorption experiments, i.e., on the convex alumina surfaces and on the concave alumina described in this work, have been performed in systems with the following characteristics: (a) semidilute polymer solutions, (b) small adsorption energy per repeat unit, (c) low coverage of the surface with directly adsorbed (anchored) repeat units, and (d) the radius of curvature of the adsorbent surface was larger than the two typical lengths of the problem, i.e., the polymer radius of gyration and the typical width of the adsorbed layer. This was pertinent to all systems with the exception of those having very small radii (~5 nm in diameter), which were not duplicated for the concave case.

This similarity indicates that both cases of adsorption, i.e., on concave and convex surfaces, exhibit a universal behavior that describes the adsorption on any curved surface. Existing theory for the adsorption on polymers on spherical particles that is based on scaling arguments²⁵ predicts that for the same experimental setup the coverage should be independent of the size

of the adsorbing particle. This result stands in complete opposition to our experimental results, which show a linear dependence of the coverage on the radius of curvature. In our previous study we have explained the discrepancies between the theory and the experimental results by adding an additional force term that was proportional to the monomer density gradient. The outcome of this force was a repulsion of the adsorbed polymer chains away from the surface. We have shown that for spherical particles the density gradient in the adsorption layer is proportional to $1/R$, where R is the radius of the adsorbing particles. This term imparted a positive addition to the free energy of the adsorption layer, which was increasing linearly with the curvature, resulting in the contraction of the adsorption layer.

Here we are applying the same construction to develop a density gradient term for the case of the adsorption of polymer chains on the inside surface of a cylinder. For the clarity of the explanation we are using a model^{25,26} that approximates the loop distribution in the adsorption layer with a brush of disconnected tails, as shown in Figure 9. The adsorbed layer can be assumed to behave as a brush of disconnected tails. Using this assumption, the connecting segments of the loops can be isolated and assumed negligible, resulting in an idealized brush.

Figure 10 shows the structure of the adsorbed layer in a cross section of the cylinder. An approximation that we made was that the number of tails in each cylindrical annulus of the adsorption layer was constant and noted by N_R . In actuality, although some of the tails will invariably be shorter than others,²⁷ this fact will not change the curvature dependence of the gradient term significantly. Each tail was now represented by a sequence of blobs (segments of the freely coiled chain encased in a sphere), such that the blobs become smaller as a function of their increased distance from the inner surface of the cylinder. The radius of the largest blob at a distance R from the center of the cylinder is b_R , and the radius of a given blob along the tail at a distance r from the center of the cylinder is b_r . The radius of the blob at distance r from the center of the cylinder is given by $b_r = a_0 N_r^{1/\nu}$, where a_0 is the dimension of a segment of PMMA, N_r is the number of segments constituting the portion of the polymer tail contained in a blob, and ν is the Flory coefficient (e.g., $1/2$ for a theta solvent and $3/5$ for a good solvent). In our development, we will always assume that $1/2 < \nu < 1$; i.e., we are operating in the good solvent regime. The number of segments in a blob of radius b_r at a distance r from the center of the cylinder is therefore $N_r = (b_r/a_0)^{1/\nu}$, and the total number of segments that could reside in a blob is given by $\hat{N}_r = (2\pi b_r^2/2\pi a_0^2) = (b_r/a_0)^2$. Since the radii of the blobs scale as $b_r = b_R(r/R)$ and $b_R = (1/2N_R)$, the fraction of 2D sites in an annulus of distance r from the center of cylinder that are occupied by polymer segments is given by

$$\phi(r) = \frac{N_r}{\hat{N}_r} = \left[\frac{(b_r/a_0)^{1/\nu}}{(b_r/a_0)^2} \right] = \left(\frac{b_R r}{a_0 R} \right)^{(1/\nu)-2} = \left(\frac{1}{2a_0 N_R R} \right)^{(1/\nu)-2} r^{(1/\nu)-2}$$

The fraction of 2D sites occupied by polymer segments, $\phi(r)$, may be approximated to represent the density of polymer segments in a given annulus of the cylinder. Note that because of the geometry of the cylinder, it is sufficient to just consider the planar density: The spatial density is simply the planar density divided by the height of the cylinder.

For simplicity, the expression $(1/2a_0 N_R)^{(1/\nu)-2}$ will be replaced by a constant denoted as Z_R . The volume fraction (i.e., density) gradient of 2D sites in a given annulus that are occupied by polymer segments is given by

$$\phi'(r) = \frac{d\phi(r)}{dr} = Z_R \left(\frac{1}{R} \right)^{(1/\nu)-2} [(1/\nu) - 2] r^{(1/\nu)-3}$$

The energy per unit of surface associated with the adsorption of the polymer chains onto the inner surface of the pore (cylinder) is responsible for this density gradient $\phi'(r)$. As the curvature of the pore increases, the density of the polymer segments in the adsorption layer increases, and hence, $\phi'(r)$ increases. For a flat surface, the density of segments in the adsorption layer L is constant, i.e., $\phi'(r) = 0$. The same adsorption energy will have the effect to minimize the density gradient in the adsorption layer of a curved adsorbent surface.¹² Therefore, the magnitude of the density gradient $\phi'(r)$ scales with the curvature $1/R$ (provided $|\phi'(r)| \neq 0$).

The total density per unit area can be obtained by integrating the density gradient over the whole adsorption layer L . Since we assume that $L \ll R$, we can compute the following:

$$\Gamma_R = \frac{R}{L} \int_{R-L}^R \phi'(r) r dr = \frac{Z_R}{L} \left(\frac{1}{R} \right)^{(1/v)-3} \left(\frac{(1/v)-2}{(1/v)-1} \right) \left[R^{(1/v)-1} - (R-L)^{(1/v)-1} \right] \approx Z_R R (2 - 1/v)$$

The term Γ_R is, by definition, the number of adsorbed repeating units per unit surface area, i.e., the total coverage. For a good solvent, we have that $v = 3/5$, and hence the total coverage becomes

$$\Gamma = \Gamma_R = \frac{1}{3} Z_R R = \frac{1}{3} \left(\frac{1}{2a_0 N_R} \right)^{(1/v)-2} R$$

Therefore, the theoretical prediction of the linear dependence of the coverage on R matches well, at least qualitatively, with the observed relationship between coverage and pore size (see Figure 8, for example).

4. Conclusions

In this work we have analyzed the adsorption behavior of polymers onto concave surfaces by exploring the equilibrium adsorption of PMMA onto alumina membranes with varying pore sizes. On the basis of the experimental results for this cylindrical geometry, we developed a mathematical model by considering the polymer density gradient onto the adsorbent surface, i.e., at the inner wall of each cylindrical pore in the membrane. The density gradient of the polymer chains adsorbed on the interior of each such cylinder increased as the distance between the wall and the center of the cylinder decreased; i.e., it was directly proportional to curvature. As a result, the total coverage of the polymer varied linearly with pore size. It is noteworthy that the planar monomer densities (the coverage Γ) scale with R , for both the convex and the concave cases. This scaling emerges from the fact that the adsorption of polymer chains on surfaces that are not flat is inherently influenced by geometric constraints.

On a flat surface, the monomer concentration is approximately constant in the adsorption layer of thickness L and decreases until it becomes equal to the bulk concentration. The adsorption energy per unit of surface is responsible for this concentration gradient. While this is straightforward for the planar geometry, in the curved geometry, there is an additional component to the density gradient that is inversely proportional to the difference between the area of the curved surface and that of the sphere in which the bulk adsorbed concentration is achieved. On a convex surface, this difference is $A_{A+L} - A_R = dA_R/dr \approx R$, when L is sufficiently small. Hence, the same adsorption energy can sustain a smaller concentration gradient along L in the convex case and a higher concentration gradient along L in the concave case.

In addition to its dependence on pore size, the total coverage was also dependent on polymer molecular weight for low molecular weights but independent of molecular weight for high

molecular weights, the latter case being similar to adsorption on convex surfaces. The practical implication of these results is that simple adsorption experiments may be used to measure directly both pore size and molecular weight.

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Figure 1.

Characterization of the alumina membranes used in this study: (a–c) Scanning electron (SEM) images and pore size distributions (insets) of 32 nm (a), 100 nm (b), and 220 nm (c) pores (nominal manufacturer values). The bottom right of the figure shows a detailed table of pore geometry and surface area, indicating that the available surface originates almost entirely from the concave portions of the alumina membrane. The bottom left of the figure shows an idealized illustration of the porous alumina membranes used (not to scale).

Figure 2.

Typical thermogravimetric (TGA) analysis profile of a sample of PMMA having a molecular weight of 120 000 g/mol adsorbed on an alumina membrane having pores with 100 nm in diameter. The normalized mass of polymer adsorbed on the membrane may be directly extracted from the thermal degradation plots and used to calculate the polymer coverage.

Figure 3.

Plots of polymer coverage (in units of segments nm⁻²) as a function of time: (a) adsorption on 220 nm pores, (b) adsorption on 32 nm pores. These adsorption plots indicate that the systems reach equilibrium after 3 days. If equilibrium were not reached, it would have been expected that polymers with higher molecular weights would have saturated the surface sites faster than polymers with lower molecular weight, and smaller pores would have been covered faster than larger pores. Neither occurrence is observed.

Figure 4. Plot of coverage as a function of polymer molecular weight for each pore size. The plot shows a molecular-weight-dependent regime and a molecular-weight-independent regime.

Figure 5. Plot of the coverage (in units of segments nm⁻²) as a function of polymer molecular weight, showing that the coverage varies linearly for low values of molecular weight (<120 000 g/mol) but is independent of molecular weight at higher values of molecular weight.

Figure 6.

Plot of the specific molar coverage, i.e., coverage that was normalized by the molecular weight of the (in units of segments mol g⁻¹ cm⁻²) as a function of membrane pore diameter.

Figure 7.

Schematic description of the relationship between the thickness of the adsorbed polymer layer and the polymer molecular weight. (a) At high molecular weights the adsorbed polymer forms loops, trains, and tails on the surface. (b) As polymer molecular weight decreases, the contribution of loops decreases to the limit at which the polymer chains are anchored through only one segment and the other segments constitute the polymer tails. The thickness of the adsorbed polymer layers are equal to L because both molecular weights are greater than or equal to a critical molecular weight (in this case $\sim 120\,000$ g/mol). As a result, coverage in this regime is independent of polymer molecular weight (the flat lines in Figure 4). (c) The polymer molecular weight in this case is lower than the critical value, and hence, despite the fact that the polymer chains are anchored through only one segment (as in (b)), the thickness of the adsorbed layer is less than L (the sloped lines in Figure 4).

Figure 8.

Plot of polymer coverage (in units of segments nm⁻²) as a function of pore size for two different polymer concentrations, 1% and 15% (w/v). The similarity of the two plots indicates that polymer concentration plays only a minor role on the extent of adsorption. Polymer chains are more likely to leave the more concentrated solution for the adsorbent. The molecular weight of the polymer for both systems was 120 000 g/mol.

Figure 9.

Schematic representation of the adsorbed polymer layer approximated as a brush of disconnected tails. (a) The adsorbed polymer chains form loops, trains, and tails on the surface. (b) According to the model by Aubouy et al.,^{25,26} the connecting segments of the loops are removed. (c) The result is an idealized brush.

Figure 10.

Schematic description of the structure of the adsorbed layer in a cross section of the cylinder. R is the diameter of the cylinder, L is the thickness of the adsorbed polymer layer, b_R is the radius of the largest blob directly residing on the surface (at approximately distance R from the center of the cylinder, given that $b_R \ll R$), and b_r is the radius of the blob residing at a distance r from the center of the cylinder.

Scheme 1. Description of the Chemical Process Responsible for the Adsorption of PMMA onto Alumina^a

^a The bonds between the COO^- groups on the PMMA and the Al^{3+} sites on the surface are formed by two subsequent reactions: (1) conversion of Al_2O_3 to $\text{AlO}(\text{OH})$ on the surface of the adsorbent in the presence of H_2O and (2) de-esterification of the methacrylate group in the presence of the surface OH groups to form the carboxylate group.