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Swelling process investigation of polymer layer deposited on siliceous materials using SAXS method

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Abstract

The paper examines the advantages of the SAXS method in the investigation of the swelling degree of the polymer layer formed on rigid porous materials. Among others, the SAXS allows for the estimation of the value of interfacial surface as well as the value of the volume fraction of the material, which is related to scattering objects. The swelling process leads to change in the radius of pores and, in consequence, change in the volume fraction of solid phase. The paper presents the theory which allows for calculating the influence of this change in increment of polymer thickness on SAXS data as well as the experimental results of the SAXS study of the porous materials composed of controlled porosity glass with formed polysaccharide–polyimine surface layers differing in cross-linking degree. The presented results reveal the usefulness of the SAXS method in investigating the swelling degree of polymer layers formed on the surface of rigid porous materials. This is because obtained values from the SAXS data are in agreement with the knowledge of the physicochemical properties of polymers. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many efforts have been undertaken to modify the physicochemical character of siliceous surface, to increase its chemical resistance in alkaline solution as well as to block strong interacting adsorptive centres, particularly silanol groups. As it has been shown in [1–5] one method of doing this is the formation of a polymer layer on the surface of these materials. Polysaccharide, a polyimine copolymer can function as such a layer [6,7]. The formation of polysaccharide–polyimine layer on the surface of silica–gel or controlled porosity glass (CPG) results in the materials which exhibit high mechanical resistance and can be used in affinity chromatography columns or in biotechnological processes with alkaline buffer media.

The process of swelling is one of the characteristic features of polymers. The degree of the polymer material swelling can be extremely high, even a few times larger than the initial dimensions, and depends on many parameters such as a polymer type, cross-linking degree, solvent type, amount of solvent, and temperature. Swelling of the polymer layer deposited in the pores of the siliceous support material effects the change in the dimension of the main pores. As a result, swelling can vary and, in consequence, so can the pore diameter changes. Therefore, at this point the problem is how to estimate the real pore diameter in materials with surface polymer layer under conditions in which they are used.

Inverse size exclusion chromatography (iSEC) is a very convenient method making it possible to calculate the pore volume, the pore diameter, and the pore size distribution function of porous materials in conditions in which they are used. Assuming the absence of any secondary phenomena disturbing the pure size exclusion effect, the values and functions mentioned are calculated on the basis of the penetrability of the porous material by polymer molecules of a defined size. This method is particularly useful in the study of the physicochemical properties of swelling polymer porous materials. To obtain reliable results by iSEC, it is necessary to employ well-characterised polymer standards. The application of iSEC in characterising the porous structure in water solution, however, seems to be problematic as no such standard soluble in water exists [6].

As it appears from [6,8,9], the SAXS method seems to be extremely useful in the analysis of porous structure of siliceous materials with a surface polysaccharide–polyimine layer. This method allows not only for the measurement of the main parameters of the porous structure but also for the demonstration of the presence and the dimension of a

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very thin transition polymer layer, which can exist at the polymer/air interface border in this composite material [6,9].

The experiment carried out recently [10] has shown the usefulness of the SAXS method in the investigation of water evaporation process from the siliceous materials covered with a polysaccharide–polyimine layer. In others words, it is the investigation of the porous structure changes of materials in which, due to the swelling process, the dimension of the surface polymer layer varies and results in the changes of the diameter of main pores.

It should be observed that so far SAXS has been used in measuring particle sizes after swelling for latex particles coated with a shell of gelnetwork [11].

X-ray scattering at a small angle occurs when the examined system contains heterogeneity differing in the electron density from its surroundings. Practically, the diameter of the heterogeneity should remain within the range of 8–1000 Å.

In the case of porous materials, pores play the role of such heterogeneities. Pores can contain different mediums (gas or liquid). Among others, the SAXS allows for the estimation of the value of interfacial surface as well as of the volume fraction of the material, which is related to scattering objects (in the case of porous material — the volume fraction of material corresponding with pores). As it has been established, the swelling process of the polymer layer contained in the pores leads to the change in both the interface surface value and the pore volume not occupied by the polymer.

The present paper shows the possibility of applying the SAXS in the investigation of the swelling degree of the polymer layer formed on rigid porous materials.

2. Theory

The SAXS intensity by the investigated material $I(q)$ is the function of the angle of scattering (2θ) and the wavelength (λ) of the applied radiation. For porous structures this relation can be illustrated with the following formula [12].

$$I(q) = V\varphi_1\varphi_2(\Delta\rho)^2 \int_0^\infty 4\pi r^2 \gamma_0(r) \frac{\sin qr}{qr} \mathrm{d}r \qquad (1)$$

where $q = 4\pi\sin\theta/\lambda$; V the volume of the system in which X-rays are scattered by electrons; φ_1, φ_2 the volume fractions of the solid phase and pores, respectively; $\gamma_0(r)$ the correlation function; $\Delta\rho$ the average electron density difference between two phases, from which the investigated material is composed (in our case between the solid phase constituting the skeleton of the porous material and the medium which fills the pores).

Expansion and transformation of the above equation allows, among others, for calculating the interface surface value.

Two collimating systems for SAXS measurements are used: a point one (desmeared data) or a slit one (smeared data). There exist mathematical procedures, which can be used for recalculation of smeared type data into desmeared

ones, but there are also many equations allowing for calculation of some values directly from smeared type SAXS data. The surface area from smeared type SAXS data can be estimated using the following equation.

$$\frac{S}{V} = 4\varphi_1\varphi_2 \frac{\lim_{q\to\infty} I(q)q^3}{\int_0^\infty I(q)q\,\mathrm{d}q} \qquad (2)$$

where φ_1 is the volume fraction of phase 1 and φ_2 the volume fraction of phase 2 $(\varphi_2 = 1 - \varphi_1)$.

In the case of CPG, silica is one of these phases whereas the other one is air contained in the pores. In the case of CPG with a surface polymer layer, the air in the pores always plays the role of the phase of the lower density while the solid phase is composed of silica and a polymer layer.

When the latter material is placed in water, a two-phase system still exists, but the air is replaced with water. Assuming that the presence of water does not cause the polymer swelling, the ratio

$$W = \frac{\lim_{q\to\infty} I(q)q^3}{\int_0^\infty I(q)q\,\mathrm{d}q} \qquad (3)$$

should remain the same for dry and wet materials. The investigation of the water evaporation process from the CPG coated with polysaccharide–polyimine layers revealed the change in W value [10]. Therefore, it can be concluded that during the water evaporation process the polymer layer changes its dimensions and that the SAXS method can be helpful in calculating the changes in the polymer layer thickness.

Let us assume that pores have a cylindrical shape of infinite length ("bunch capillaries" model). The swelling process leads to change in the radius of the cylinder and, in consequence, to the change of φ_1 and φ_2 values as well as of the cylinder's interior surface area. The surface area after swelling of the surface polymer layer (S_N) can be calculated from

$$S_N = S_T \frac{R - \Delta}{R} \qquad (4)$$

while the volume fraction of pore phase from

$$\varphi_{N_p} = \varphi_p \left[\frac{R^2 - 2R\Delta + \Delta^2}{R^2} \right] \qquad (5)$$

where S_T is the surface area before the swelling of the surface polymer layer, R the pore radius before the polymer swelling, Δ the change of the pore radius resulting from the swelling of the surface polymer layer, φ_p the volume fraction of pore phase before the swelling of the surface polymer layer.

At this point, it should be stressed that assumed cylindrical pore shape of infinite length as well as a monodispersity of pore structure should be treated as a simplification. Consideration of other models (for example, a sphere or a conical shape of pores as well as polydispersity) is also possible. Of course, this does not change further procedures described

in the paper below but will only complicate the Eqs. (4) and (5). Hence, the proposed calculations in the paper can be treated as only some of possible cases. The model of bunch capillaries seems to be reasonable in the case of controlled porous glasses (materials used for experiments).

The calculation of S_N and φ_{N_p} allows for the calculation of the W value. The determination of S_N versus $(R - \Delta)$ and φ_{N_p} versus $(R - \Delta)$ and, in consequence, of W versus $(R - \Delta)$ functions makes it possible to compare the calculated W values with those estimated experimentally and to calculate Δ, i.e. the change in the polymer thickness resulting from the surface polymer layer swelling after the immersion of the material in liquid.

In the course of the above calculation one has to remember that the intensity of the SAXS depends on the difference between the electron density of a scattering object and its surroundings. In the case of dry porous materials (silica–gel, controlled porosity glasses, etc.), the electron density difference between a silica skeleton and air in pores is significant. In such a situation there are no problems in defining the interface area for such materials. The formation of the polymer layer on the surface of the above-mentioned materials somewhat complicates the distribution of the electron density in the material because the electron density of a polymer can be different from that of a support material. However, when air occupies the pores of the material coated with polymer (i.e. dry material), the ultimate difference between electron densities for a support and a polymer in comparison to the electron density difference between a polymer and air (in the pores) is insignificant. Such a material, in relation to the

electron density, can be then treated as a double-phase system, while the interface surface area calculated from SAXS data can be treated as a surface area of polymer. The situation changes radically when air in the pores is replaced with liquid, a medium of a higher electron density.

In such a case the electron density difference between a support material and a polymer can be comparable to the electron density difference between a polymer and a liquid in pores. In extreme cases, when a swelling polymer layer fills the pores completely, the electron density difference will be present only at the support — polymer border. In consequence, the interface surface area calculated from SAXS data will be equal to the surface area of the pure support material. The W value will paradoxically show the lack of polymer swelling. All the above-mentioned remarks should be taken into account while considering the applicability of the SAXS method in the investigation of the swelling degree of a polymer layer formed on the surface of hard solid support material.

Fig. 1 presents a theoretically calculated change in the W ratio resulting from the swelling process of a surface polymer layer deposited on the surface of two different rigid porous materials.

The calculations were performed for imaginary materials, which after a surface layer formation in dry state are characterised by varying parameters (Fig. 1).

As it appears from the demonstrated relationships, the decrease in pore diameter resulting from the polymer layer swelling process leads to the W_x/W_d (where W_x means W value for investigated sample whereas W_d for dry sample)
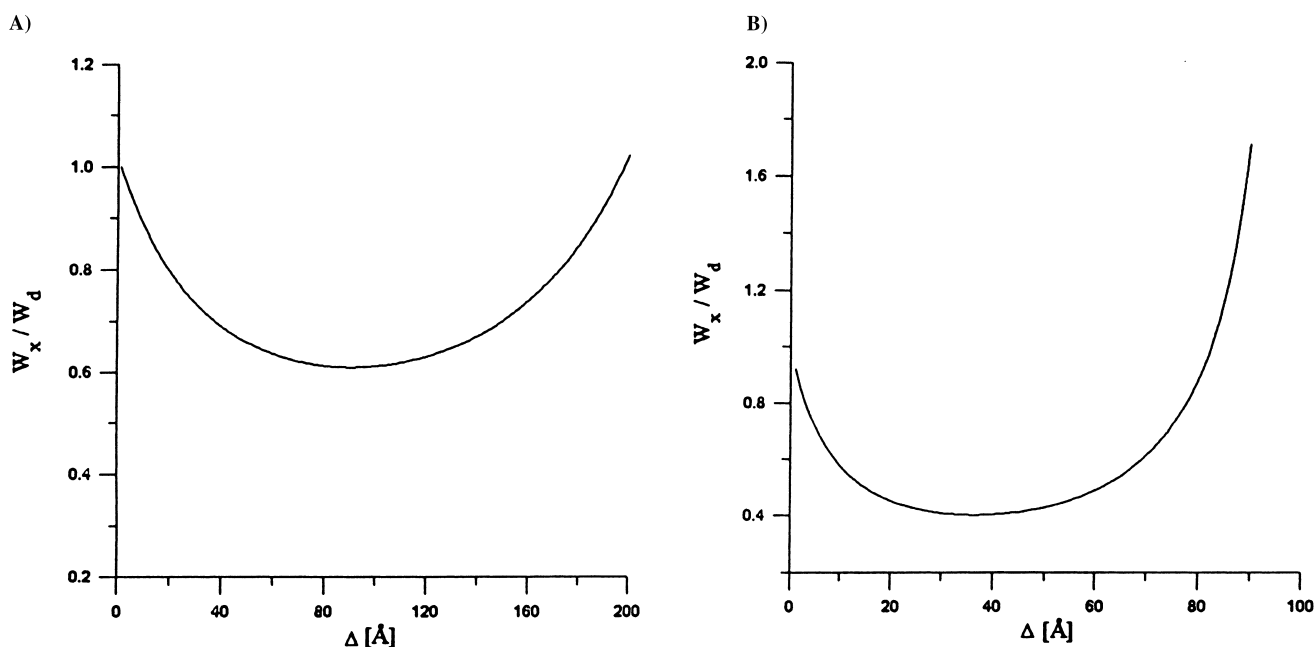

Fig. 1. The theoretical plots of W_x/W_d vs. Δ (increment of polymer thickness) for two imaginary materials. Curve A: thickness of the polymer layer in dry state 20 Å, volume fraction of solid phase (support + polymer layer) 0.27, radius of pore in dry state 300 Å. Curve B: thickness of the polymer layer in dry state 20 Å, volume fraction of solid phase (support + polymer layer) 0.17, radius of pore in dry state 100 Å.

function run in which two compartments can be distinguished, one manifesting a decrease in W_x/W_d versus Δ and the other an increase in this function.

Hence, the W_x/W_d ratio obtained from SAXS data can correspond to one of two compartments of the polymer layer thickness increment. In consequence, circumspection is required while interpreting the SAXS results. SAXS measurement for samples differing to a small degree in the amount of medium causing a swelling process seems to be the right way to find a proper compartment of W_x/W_d versus Δ. A small increment in the polymer layer thickness occurs when an increase in the content of the medium (which is responsible for the surface polymer layer swelling) leads to a decrease in W_x/W_d. The swelling degree is very high when an increase in the medium content causes an increase in W_x/W_d function.

To verify the presented theory in practice, the SAXS investigations were carried out using porous materials composed of controlled porosity glass with formed polysaccharide–polyimine surface layers differing in cross-linking degree. The samples of each material contained different amounts of water to cause a different swelling degree of the surface polymer layer.

3. Experimental

3.1. Materials

Materials composed of CPG with polysaccharide–polyimine layer were investigated. The surface layer in the materials was formed using mixture of dextran and tri-ethylenetetramine of different composition according to the procedure described elsewhere [7,8,10]. Table 1 lists some physicochemical properties of investigated materials (in dry state).

All types of initial materials (A, B, C) were placed in water so that the pores were completely filled with water. Subsequently, the samples were dried in the room temperature, applying various time periods. Samples indicated as A_{IV}, B_{IV} and C_{IV} were dried at 60°C in the vacuum conditions. The amount of water was estimated by weighing materials at subsequent stages of the water evaporation process.

3.2. Small-angle X-ray scattering (SAXS) measurements

SAXS measurements were performed on a slit-collimated Kratky camera using a Cu anode tube as the radiation source.

The geometry of the SAXS camera and other conditions of the SAXS experiments allowed for treating the obtained scattering curves as slit-smeared data for a beam of the infinite length. The background scattering curves (for the empty cuvette) were each time subtracted from the scattering curve for an investigated sample. As a result of the measurements, the curve (intensity scattering ($I(q)$) versus module of scattering vector (q)) for the sample was obtained. All scattering intensity curves were recalculated considering the differences in the sample transmission. No smoothing procedure to SAXS curves was employed.

4. Results and discussion

In order to find out if the SAXS method can be used in the study of the polymer swelling process in sorbents with a surface polymer layer, the W values were calculated from the SAXS data obtained for materials (Table 1) at different stages of their drying process after previous wetting with water. The first column of the Table 2 contains codes of the drying stages whereas the amounts of water at a given drying stage of the material A or B or C are listed in the second column of Table 2. The latter values are expressed as a percent of pore volume occupied by water and are calculated in relation to the pore volume of a given dry material.

As results from the data presented earlier, the investigated materials demonstrate the presence of the transition layer at the polymer/air interface border, which is why they do not fulfil the classical Porod law. For this reason, $\lim_{q\to\infty} I(q)q^3$ was calculated using the Eq. (3b) from [8]. According to this paper, the application of the mentioned equation gives reasonable values of specific surface area. Therefore, the estimation of $\lim_{q\to\infty} I(q)q^3$ using the above-mentioned equation seems to be fully reasonable.

The third column of Table 2 presents the relative W_x/W_d values obtained from SAXS data for the materials at different stages of their drying process (where W_x means W value for an investigated sample and W_d for a dry sample).

Using the data for dry materials (Table 1), the theoretical runs of the W_x/W_d versus Δ functions for these materials were calculated and shown in Figs. 2–4. The shapes of these curves are similar but their runs differ from one another as they are calculated for materials A or B or C differing in their physicochemical properties (Table 1). The fourth column of Table 2 lists the values of the increment of the surface polymer layer thickness resulting from the swelling process

Table 1
Physicochemical properties of investigated materials (in dry state)

Sample	Copolymer amount in (wt.%)	Density of solid phase (g cm^{-3})	Bulk density (g cm^{-3})	φ_p	φ_s	Thickness of copolymer layer (Å)
A	11.9	1.97	0.52	0.73	0.27	23
B	12.4	1.96	0.46	0.76	0.24	24
C	5.3	2.09	0.563	0.77	0.23	10

Table 2
Amount of water and values determined by SAXS method

Sample	Amount of water (%)	W_x/W_d	Increment of polymer thickness (Å)	Total thickness of polymer layer (Å)	Increment of polymer thickness (%)
A_I	83	0.765	24	47	104
A_{II}	41	0.794	20	43	87
A_{III}	17	0.810	18	41	78
A_{IV}	5.5	0.891	9.5	32.5	41
B_I	89	0.705	28	52	116
B_{II}	33	0.764	20	44	83
B_{III}	15	0.818	14	38	58
B_{IV}	7.5	0.891	8	32	33
C_I	92	0.714	25	35	250
C_{II}	59.5	0.782	17	27	170
C_{III}	59	0.787	16.5	26.5	165
C_{IV}	11	0.916	6	17	55

at a given amount of water. These values were estimated comparing relative W_x/W_d values from SAXS data (third column of Table 2) and a proper curve from Figs. 2–4.

As an increase in the water content in the sample causes a decrease in the W_x/W_d ratio, the values shown in the fourth column of the Table 2 were calculated considering the first compartment of the W_x/W_d versus Δ functions.

The values of the total thickness of a surface polymer layer at a given amount of water (the thickness increment plus the thickness of the polymer layer in the dry material) and the percent of the thickness of the polymer layer in comparison to the dry material are contained in the last two columns of Table 2.

As it appears from the presented data, the SAXS method reveals changes in the structure of the investigated materials resulting from change in the water content in the pores of materials.

Considering the values from Table 2 two general rules can be formulated:

- an increase in the polymer layer thickness or the thickness increment coincides with an increase in the water content in pores;
- greater polymer layer thickness changes in the case of material C whereas the lower ones in the case of material A.

Both findings are in agreement with the knowledge about polymers (Section 1).

The first results from the dependence between a polymer swelling degree and the amount of solvent in the polymer. The second is connected with the polymer cross-linking degree. The increasing amount of TETA in the TETA–dextran mixture at the constant amount of cross-linking agent (EGD-2) results in polymers of decreasing cross-linking
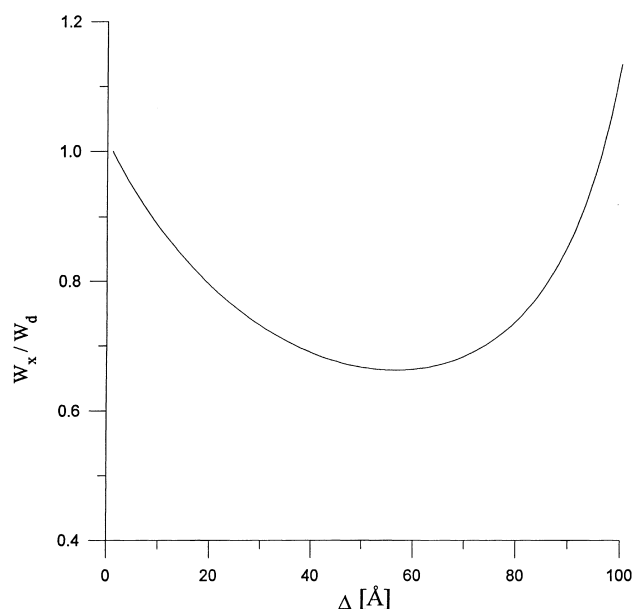

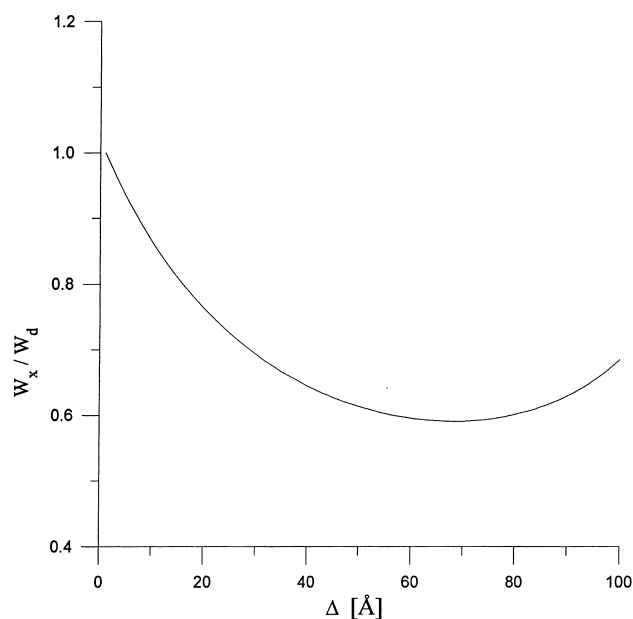Fig. 2. The theoretical plot of W_x/W_d vs. Δ for material A.

Fig. 3. The theoretical plot of W_x/W_d vs. Δ for material B.
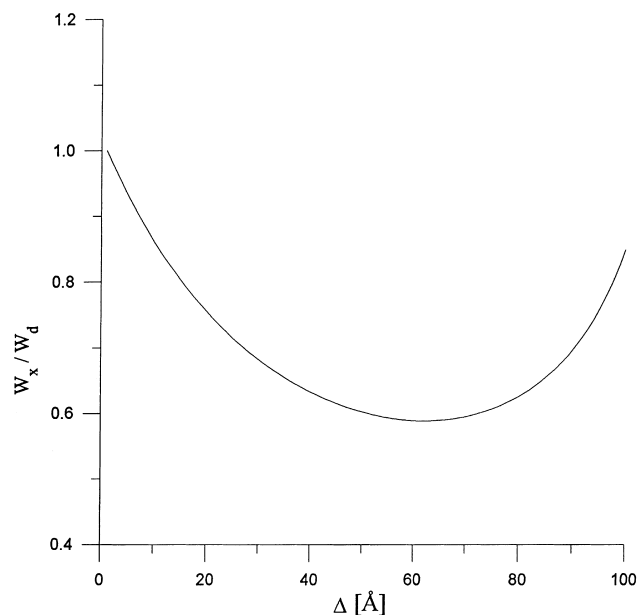
Fig. 4. The theoretical plot of W_x/W_d vs. Δ for material C.

degree. Therefore, the observed differences in SAXS data for the investigated materials are consistent with the knowledge about polymers.

Presented results reveal the potential of the SAXS method in investigating the swelling degree of polymer layers formed on the surface of rigid porous materials. The conclusions obtained from SAXS data are in agreement with the knowledge related to the physicochemical properties of polymers, they demonstrate that the proposed method is practical. At this point, the question appears concerning the reliability of calculated values. The described way of the estimation of the swelling degree of polymer layer seems to be particularly precise for low values of swelling degree, when pores are partly filled with gas phase (with

air). The run of W_x/W_d versus Δ function confirms that. As it appears from Figs. 1–4 there are considerable changes in W_x/W_d values at small changes in Δ values in the first compartment of the W_x/W_d versus Δ functions. The presence of air in pores partly filled with liquid ensures the great difference of electron density of phases (swollen polymer/air), which causes an increase in the SAXS intensity and, in consequence, the precision of the SAXS curve. It can be assumed that for such systems, the electron density difference between a rigid support and a polymer layer is small (in relation to the difference between polymer and air) and can be disregarded in the above considerations.

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