

# Fractal Analysis of the Distribution of High-Viscosity Fluids in Porous Supports

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The distribution of a highly viscous fluid in porous media has been investigated by the example of polymer-coated supports for liquid chromatography. A system of practical interest in protein separation, namely polybutadiene on porous silica LiChrospher Si 300, has been explored. The values of the surface fractal dimensions for the parental support and the samples with varying polymer loading have been obtained from low-temperature nitrogen adsorption isotherms using the thermodynamic method. The increase of polymer content does not have a significant impact on the surface properties. The fractal dimensions for polymer-coated samples do not differ essentially from the value of 2.22, inherent for the parental support, over the scale range of about 10–150 Å. The effect of defractalization, which is characteristic for wetting films, has not been observed. On the basis of the fractal analysis, we concluded that the polymer is predominantly sited in inclusions or ganglia and the pore volume is filled at random with bulk polymer. The proposed ganglia model for the polymer distribution in porous supports describes sufficiently the observed changes in the pore structure caused by the polymer loading. It is consistent with independent solid-state NMR measurements and can be used for the interpretation of chromatographic data. The thermodynamic method of the fractal analysis based on adsorption and/or capillary experimental data is recommended for the investigation of high-viscosity liquids or other host phase distributions in different porous systems.

## 1. Introduction

Porous materials which are partially saturated with high-viscosity fluids are applied in various fields of modern technology and, therefore, are the traditional objects for scientific research. Among them there are oil reservoirs,<sup>1</sup> supported liquid-phase catalysts,<sup>2</sup> polymer-impregnated porous solids.<sup>3</sup> The distribution of the liquid within the porous matrix is important for the technological properties of these materials. In this paper, with the example of polymer-coated supports, we demonstrate the effectiveness of fractal analysis on the study of host phase distributions in porous media. The explored system, polybutadiene on porous silica (LiChrospher Si 300), is used in reversed-phase liquid chromatography (RPC) of proteins and polypeptides.<sup>4</sup> We used low-temperature nitrogen adsorption isotherms at 77 K as the initial experimental data for the calculation of the surface fractal dimensions of parental and polymer-coated silica by means of the thermodynamic method, proposed recently for the data treatment in adsorption and capillary measurements.<sup>5,6</sup>

## 2. Theory. The Surface Fractal Dimension and the Thermodynamic Method of Fractal Analysis

**2.1. Surface Fractal Dimension.** About 1 decade ago, the surface fractal dimension was introduced as a new structure characteristic of porous materials as a complement to the conventional characteristics such as porosity, specific surface area, and pore size distribution. After the works of Mandelbrot,<sup>7</sup> where the initial notions and possible applications of fractals had been formulated for the first time, several experimental techniques and corresponding theories have been proposed for the determination of surface fractal dimension.<sup>8,9</sup> The data of adsorption, electron microscopy, small angle scattering, direct energy transfer, and other experiments point toward the fractal properties of a

number of porous materials, e.g. rocks, coals, natural minerals, carbon blacks, evaporated films, active carbons, aerogels, porous glasses, and silica gels. For a recent review see ref 10. On the other hand, it is well-known that the distribution of a host phase, e.g. impregnated liquid or precipitated solid, in pores is mainly disordered even when the porous structure is more or less regular.<sup>1,9,11,12</sup> Therefore, the application of fractal analysis for studies of host phase distributions in porous media seems to be a reasonable approach. At the same time, one has to keep in mind that not all disordered systems are fractals and all fractal models have strong limitations and can only be applied over certain scale ranges.

The notions of fractals and fractal dimension are closely related to the problem of measuring the metric parameters of disordered and hierarchical systems. For such systems the result of measurement depends significantly on the size of a gauge or a yardstick. A rough surface is a characteristic example. By using a gauge of size  $a$ , it is possible to probe those of the surface indentations and pores whose size is larger than  $a$ . Therefore, the decrease of the gauge size leads to the increase of the measured surface area. When the relationship between the measured surface area  $S$  and the gauge size  $a$  fits a power law<sup>7,8</sup>

$$S(a) \propto a^{2-d_{fs}} \quad (1)$$

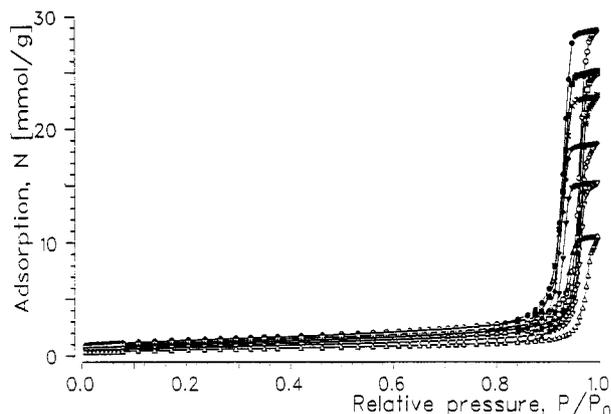
over the range of scales,  $a_{\min} < a < a_{\max}$ , then this surface can be regarded as a fractal surface. The exponent  $d_{fs}$  denotes the surface fractal dimension over this particular scale range. The relationship 1 is one of the possible definitions of the surface fractal dimension,  $d_{fs}$ , which can be used for its experimental determination.

For solids with intermediate porosity, the surface fractal dimension,  $d_{fs}$ , varies between 2 and 3 and characterizes the level of surface roughness:  $d_{fs} = 2$  for a smooth surface and the larger values reflect the existence of hierarchical structure of the surface indentations and pores. Therefore, the surface fractal dimension is helpful for the comparative study of porous materials, e.g. for the investigation of changes of the initial structure caused by a particular treatment or modification. The increase of the surface fractal dimension,  $d_{fs}$ , should highlight the increase of roughness

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**Figure 1.** Low-temperature nitrogen adsorption isotherms on the samples of polybutadiene-coated LiChrospher Si 300: parental silica (O, adsorption; ●, desorption), PBD 5 (□, adsorption; ■, desorption), PBD 10 (\*, adsorption; ×, desorption), PBD 20 (◇, adsorption; ◆, desorption), PBD 30 (▽, adsorption; ▼, desorption), and PBD 40 (△, adsorption; ▲, desorption).

of the surface whereas the decrease of  $d_{fs}$  should highlight the smoothing of the surface indentations or, in other words, the defractalization of the initial surface.<sup>13,14</sup>

**2.2. Thermodynamic Method of Fractal Analysis.** In this paper we investigated the host phase distribution in porous media by means of a thermodynamic method, which has been developed recently for the fractal analysis of porous solids.<sup>5,6</sup> The thermodynamic method employs experimental data obtained from equilibrium capillary measurements, namely capillary condensation, intrusion of a nonwetting fluid, imbibition of a wetting fluid, and drainage. The choice of the experimental technique depends on the scale range of inherent irregularities for a given sample. Since we regarded here the distribution of a high-viscosity fluid in so-called mesoporous materials with pores in the range of 10–1000 Å, the use of capillary condensation from a gas phase is reasonable.<sup>15</sup> In this case, we derived initial experimental information from adsorption isotherms, which are usually represented as the amount of adsorbate (adsorption),  $N$  as a function of the equilibrium relative pressure of adsorptive in the gas phase,  $P/P_0$ ; see Figure 1.

The thermodynamic method employs the following equation valid for a capillary condensation on a fractal surface characterized by the fractal dimension  $d_{fs}$  over the scale range  $a_{\min} < a_c < a_{\max}$ :<sup>5</sup>

$$S_{lg}(P/P_0) \propto [a_c(P/P_0)]^{2-d_{fs}} \quad (2)$$

or in a logarithmic form

$$\log[S_{lg}(P/P_0)] = \text{const} - (d_{fs} - 2) \log[a_c(P/P_0)] \quad (3)$$

Here,  $S_{lg}(P/P_0)$  is the area of the condensed liquid–gas interface at a given value of relative pressure calculated by integrating the adsorption isotherm from the current value,  $N(P/P_0)$ , to the maximal value,  $N_{\max}$ , available as  $P/P_0 \rightarrow 1$  with respect to the Kiselev equation:

$$S(P/P_0) = (RT/\sigma) \int_{N(P/P_0)}^{N_{\max}} \ln(P_0/P) dN \quad (4)$$

where  $\sigma$  is the surface tension of the liquid adsorbate,  $R$  is the universal gas constant, and  $t$  is the temperature.  $a_c(P/P_0)$  is the mean radius of the curvature of this interface calculated by the Kelvin equation:

$$a_c(P/P_0) = 2\sigma v_m / RT \ln(P_0/P) \quad (5)$$

where  $v_m$  is the molar volume of the liquid adsorbate.

In fact, eq 2 represents the basic relationship 1 for the area of a fractal surface. Within the framework of the thermodynamic method, the interface area  $S_{lg}(P/P_0)$  is regarded as the area of the solid surface measured by a gauge of size equal to  $a_c(P/P_0)$ .

In order to obtain the value of the surface fractal dimension,  $d_{fs}$ , it is necessary to plot the dependence  $S_{lg}(P/P_0)$  against  $a_c(P/P_0)$  in double logarithmic coordinates. In response to eq 3, the boundaries of the linear part of this plot are regarded as the boundaries of the scale range of the surface fractality and the slope gives the value of  $d_{fs}$ . For details concerning the thermodynamic method see refs 5 and 6.

**2.3. Advantage of Low-Temperature Nitrogen Adsorption at 77 K for Fractal Analysis.** It is possible to use the adsorption isotherms of any available adsorbate, which is weakly bonded (physisorbed) to the sample surface, as a probe gas for the determination of the surface fractal dimension by means of the thermodynamic method. However, there are several reasons to employ low-temperature nitrogen adsorption at 77 K.

It is well-known that nitrogen adsorption is not too sensitive to the nature of a solid surface. The adsorbate–adsorbent interactions as well as the chemical and geometrical surface heterogeneity on the molecular level affect the nitrogen adsorption only in the early stages and are reduced during the monolayer filling.<sup>15</sup> Therefore, the inclusions and/or films of the host phase should not essentially affect the nitrogen adsorption. The profile of nitrogen adsorption isotherms is mainly caused by geometrical peculiarities of the pore structure. In addition, low-temperature adsorption isotherms of nitrogen at 77 K on numerous surfaces of different origin obey a single empirical law when the physical adsorption is not accompanied with the capillary condensation, i.e. in the case of a smooth nonporous solid.<sup>15,16</sup> When this takes place, the isotherm measured on a porous solid in the region of polymolecular adsorption up to the beginning of capillary condensation is proportional to the so-called “standard” isotherm or  $t$ -curve of de Boer, which corresponds to a nonporous smooth surface of reference material:

$$N(P/P_0) = N_{mi} + S_{me} N_{st}(P/P_0) \quad (6)$$

where  $N(P/P_0)$ , in mmol/g, is the adsorption on a given sample;  $N_{st}(P/P_0)$ , in mmol/m<sup>2</sup>, is the adsorption on a smooth surface of unit area, at the same relative pressure,  $P/P_0$ ;  $N_{mi}$ , in mmol/g, is the adsorption in micropores and a factor of proportionality; and  $S_{me}$ , in m<sup>2</sup>/g, is the specific surface area of mesopores. For mesoporous materials without any appreciable amount of micropores, the value of  $S_{me}$  does not differ significantly from the BET surface area.

Recently,<sup>17</sup> a simple method has been proposed to use nitrogen adsorption isotherms for the discrimination of surface irregularities, particularly fractal-type irregularities. The idea is as follows. The existence of surface irregularities of the size more than the molecular diameter of nitrogen ( $\sim 4$  Å) should lead to a deviation from the linear relationship, eq 6, in the region of polymolecular adsorption. On the other hand, if the adsorption isotherm on an explored surface obeys eq 6 over a particular range of relative pressures, then it can be concluded that in the corresponding range of scales the given surface is similar to a smooth surface and therefore not fractal. In the region where the experimental nitrogen isotherm does not fit the empirical law, eq 6, it is possible to investigate fractal properties using, e.g. the thermodynamic method. When this occurs, the upper limit of validity of eq 6 is the lower limit of the possible fractality. The comparative method is a helpful complement to the thermodynamic method for the investigation of mesoporous materials.

The thermodynamic method, based on low-temperature nitrogen adsorption, can be readily realized in practice. Nitrogen adsorption at 77 K is the procedure recommended by IUPAC and national institutions.<sup>15</sup> Low-temperature nitrogen adsorption isotherms are available in a number of surface science laboratories by using automated instruments. Moreover, most researchers dealing with porous materials employ nitrogen adsorption for calculations of standard structure parameters, namely porosity, BET specific surface area, pore size distribution. Therefore, they

can carry out the fractal analysis in addition by employing the same experimental data.

To measure the nitrogen adsorption isotherms the sample previously degassed in high vacuum at elevated temperature is cooled down with liquid nitrogen. Subsequently, starting from vacuum the gas pressure is increased stepwise or continuously and the adsorption is recorded as a function of the pressure (see Figure 1). Isotherms may be measured either volumetrically or gravimetrically. During the analysis of samples impregnated with the high-viscosity fluids, this procedure provides a fast solidification of the nonvolatile liquids without any appreciable changes in its distribution.

These factors make nitrogen adsorption one of the most indicative methods of fractal analysis available for the comparison of different samples, especially the samples with a host phase. It is worth noting that low-temperature adsorption isotherms of nitrogen and also of argon have successfully been used for the analysis of liquid distribution in mesoporous solids in several papers published earlier.<sup>14,18-25</sup>

### 3. Experimental Section

We have explored six samples of parental and polymer-coated silica with varying content of polymer.

**3.1. Preparation and Analysis of Samples.** Parental silica, LiChrospher Si 300 with a mean particle diameter of 10  $\mu\text{m}$ , was obtained from E. Merck (Darmstadt, FRG). Coating agent, polybutadiene, was supplied by Aldrich Chemie (Steinheim, FRG).

The coating procedure was carried out as described in ref 26. Defined amounts of the prepolymer, oligobutadiene, MW = 4500 (Aldrich), were added into a dispersion of 15 g of LiChrospher Si 300 in *n*-pentane, according to the desired loading. After solvent evaporation the PBD was immobilized in a chamfered flask at 440 K for 4 h, while the mixture was rotated at 30 rpm in a dry argon atmosphere. The loaded silicas were suspended in dioxan/toluene (1:1, v/v) and subjected to ultrasonic treatment. The suspension was filtered through a porous PTFE membrane of 0.2- $\mu\text{m}$  porosity (Catridge system; Sartorius, Goettingen, FRG), by applying a pressure of 0.4-0.5 MPa. The product was washed with tetrahydrofuran, methanol, and diethyl ether consecutively in order to remove the oligomers of polybutadiene.

The denotations PBD 5-PBD 40 describe the initial mass proportion between polybutadiene and silica in the prepolymer-silica suspension (5-40 g of PBD/g of  $\text{SiO}_2$ , respectively). The real polybutadiene content in the prepared samples was determined from elemental analysis. Elemental analyses of parental and coated samples were obtained from a model 240 B Elemental Analyzer (Perkin-Elmer, Uberlingen, FRG). Duplicate analysis for carbon and hydrogen were performed. The reproducibility of the measurements was within 2% (absolute standard deviation).

The chromatographic experiments were performed with a LC unit consisting of an Autochrom 300 benchtop gradient controller system/terminal, two Model A2200 LC pumps (Bischoff, Leonberg, FRG), and a Rheodyne 7410 injector. A Shimadzu SPD-6VA UV detector and a Shimadzu C-R3A integrator were also used. The PBD-silicas were suspended in 1,4-dioxane/toluene/cyclohexanol (1:1:1, v/v/v) and packed by the downward-flow method into steel columns (34  $\times$  4.6 mm i.d.) (Bischoff, Leonberg, FRG) at a packing pressure of 250 bar, using methanol as a packing solvent. For the polypeptide separation, we used a 20-min gradient from water, 0.05% TFA, 0.1 M NaCl (A) to acetonitrile/water (65:35, v/v), 0.05% TFA, 0.1 M NaCl (B).

**3.2. Adsorption Isotherms.** Low-temperature (77 K) nitrogen adsorption isotherms on the samples of parental and polymer-coated silica have been obtained using the automated sorptometer ASAP 2000 (Micromeritics, Neuss, FRG).<sup>27</sup> The isotherms are plotted in Figure 1 by using traditional coordinates: adsorption,  $N$ , mmol/g of sample, versus relative pressure,  $P/P_0$ .

**TABLE I: Structure Characteristics of the Samples of Polybutadiene-Coated LiChrospher Si 300**

parameter <sup>a</sup>	Si 300	PBD 5	PBD 10	PBD 20	PBD 30	PBD 40
$C_{EA}$	0	0.045	0.089	0.135	0.158	0.232
$V_{\Sigma}$ , cm <sup>3</sup> /g	1.00	0.87	0.80	0.65	0.53	0.37
$S_{BET}$ , m <sup>2</sup> /g	111	99	88	75	63	46
$r_{hyd}$ , Å	179	177	181	173	167	159

<sup>a</sup>  $C_{EA}$  = the weight concentration of PBD in the sample obtained from elemental analysis;  $V_{\Sigma}$  = the pore volume;  $S_{BET}$  = the specific (BET) surface area;  $r_{hyd}$  = the mean hydraulic radius.

Table I shows the main characteristics of the samples employed in this study, derived from elemental analysis and nitrogen adsorption data. The values of pore structure parameters have been calculated from the isotherms by means of conventional procedures: the total pore volume,  $V_{\Sigma}$ , is from the maximal adsorption;  $N_{max}$  is available as  $(P/P_0) \rightarrow 1$  in response to the Gurvitch rule,  $V_{\Sigma} = v_m N_{max}$ , the specific surface area,  $S_{BET}$ , is from the BET equation; the mean hydraulic pore radius,  $r_{hyd}$ , is from the ratio  $r_{hyd} = 2V_{\Sigma}/S_{BET}$ .<sup>15</sup>

### 4. Results and Discussion

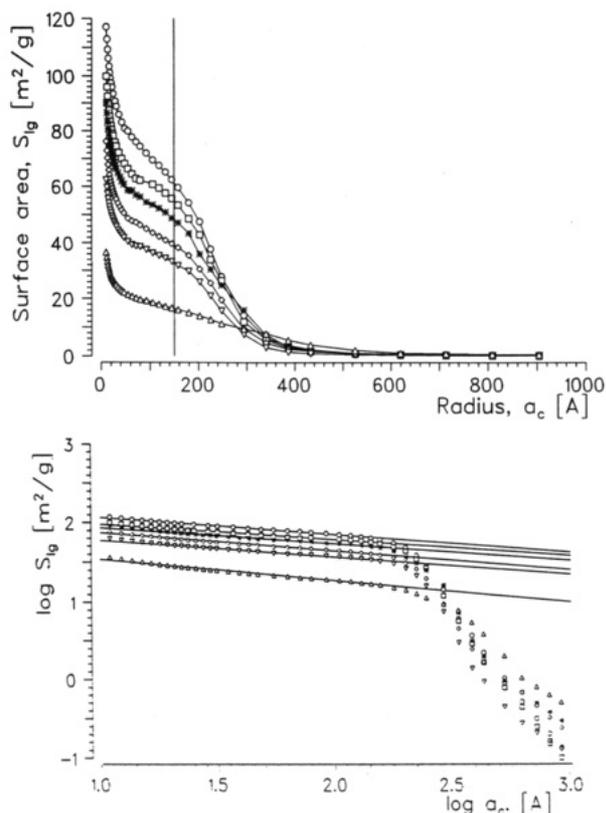
From the structure characteristics listed in Table I, one can make the qualitative conclusion that, as a result of the coating procedure, most of the polymer does not cover the external surface of the silica particles with a uniform film but occupies the pores. The increase in polymer loading leads to the proportional decrease of the total pore volume and the specific surface area. But, at the same time, with regard to the usual deviations of adsorption measurements, the value of the mean hydraulic radius in parental silica and coated samples are quite similar independent to the polymer loading. These data cannot be explained by means of the traditional film model of polymer distribution on the internal surface of porous particles. The film distribution should lead to a progressing decrease of the mean hydraulic radius with increasing polymer loading.

**4.1. Fractal Analysis of Nitrogen Adsorption Isotherms.** The isotherms plotted in Figure 1 are typical for mesoporous silica gels. The adsorption and the desorption branches form a well-defined hysteresis loop of type H1 by the IUPAC classification.<sup>15</sup> Such a hysteresis loop indicates a relatively narrow mesopore size distribution in the sample. The reversible part of the isotherm below the hysteresis corresponds to the mono- and polymolecular adsorption on the surface of mesopores and to reversible capillary condensation in the surface indentations.

In order to assess the surface fractal properties of the samples under consideration, we have used the thermodynamic method, eqs 3-5. In Figure 2A are presented the dependencies of the interface surface area  $S_{ig}$  calculated from the adsorption branches of the isotherm, eq 4, versus the mean radius of meniscus curvature  $a_c$  calculated from eq 5. The power law, eq 2, takes place to the left of the vertical line corresponded to 150 Å. The plots are limited at the left by the value of  $a_c = 11$  Å (we took this size as a possible lower limit of the surface fractality). It is worth noting that the limit values of the interface area  $S_{ig}$ , which are related to the mean radius of curvature  $a_c = 11$  Å, are in satisfactory agreement with the values of the BET surface area. These values are listed in Table II.

In Figure 2B the plots based on the adsorption branches of the isotherms are drawn using the standard by employing standard coordinates of the thermodynamic method,  $\log S_{ig} - \log a_c$  (eq 3). The region of fractality corresponds to the linear part of the  $\log S_{ig} - \log a_c$  plot. All plots show the fractal properties over the scale range from 10-15 Å to ~150 Å, where the plots can be regarded as linear.

We emphasize that for all samples the lower limit of fractality  $a_{min}$ , is about 10-15 Å, which can be supported by the comparative method of discrimination of surface fractality.<sup>17</sup> The adsorption



**Figure 2.** Fractal analysis of the samples of polybutadiene-coated LiChrospher Si 300. (A) The results of calculations, based on the adsorption branch of the isotherm, of the surface area,  $S_g$  (eq 4), of condensed nitrogen as a function of the current mean radius of curvature,  $a_c$  (eq 5), for parental (O) and polymer-coated samples [PBD 5 ( $\square$ ), PBD 10 ( $\ast$ ), PBD 20 ( $\diamond$ ), PBD 30 ( $\nabla$ ), and PBD 40 ( $\Delta$ )]. The vertical line corresponds to the upper limit of surface fractality of 150 Å. (B) The plots drawn with the standard coordinates of the thermodynamic method,  $\log S_g$  versus  $\log a_c$ . The straight lines correspond to the linear regression in the scale range 15–150 Å. The surface fractal dimensions obtained from their slopes are listed in Table II.

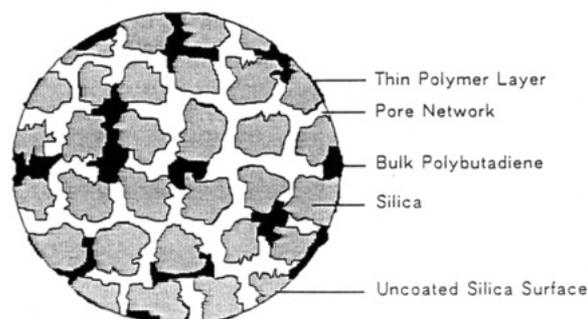
**TABLE II: Results of Fractal Analysis of the Samples of Polybutadiene-Coated LiChrospher Si 300**

parameter <sup>a</sup>	Si 300	PBD 5	PBD 10	PBD 20	PBD 30	PBD 40
$d_{fs}$	2.22	2.21	2.22	2.23	2.22	2.28
$S_{g,n}$ , $\text{m}^2/\text{g}$	117	100	90	76	62	37
$S_{mc}$ , $\text{m}^2/\text{g}$	107	101	91	78	63	48

<sup>a</sup>  $d_{fs}$  = the surface fractal dimension;  $S_{eg}$  = the surface area of condensed nitrogen related to the mean radius of curvature;  $a_c = 11 \text{ Å}$ ;  $S_{mc}$  = the mesopore surface area calculated by means of the comparative method.

isotherms,  $N(P/P_0)$  isotherms for all explored samples, are linear functions of the standard isotherm  $N_{st}(P/P_0)$  up to the relative pressure  $P/P_0 \approx 0.45$ – $0.5$  only and the departures from the linear equation 6 are observed long before the beginning of capillary hysteresis, which occurs at  $P/P_0 > 0.85$ . The relative pressure  $P/P_0 \approx 0.45$ – $0.5$  corresponds to capillary condensation in pores of size 10–15 Å, in conformity with the Kelvin equation, eq 5. In response to eq 6, this value is the upper limit of similarity of the adsorption process on the explored samples and on a smooth surface. Such behavior suggests the existence of surface roughness on the scale of more than 10–15 Å. The fractal type of this roughness is highlighted by the results of the thermodynamic method. The values of the mesopore surface calculated from eq 6 are listed in Table II. They are in satisfactory agreement with the BET specific surface area as well as with the interface area  $S_{ig}$  related to the lower limit of surface fractality.

The upper limit of fractality,  $a_{max} \approx 150 \text{ Å}$ , is comparable with the mean hydraulic radius,  $r_{hyd}$ . We would expect this type of fractality in such mesoporous materials as LiChrospher Si 300,



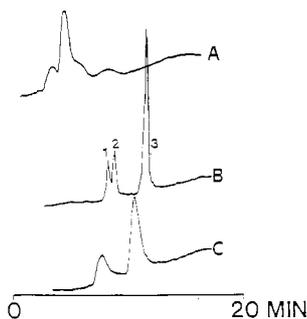
**Figure 3.** The ganglia model for the polymer distribution in the pore structure.

which consist of primary particles with diameters of up to several hundred ångström. In such a structure the pores between the primary particles are linked together and constitute a network available for the adsorbing species. Here the fractality reflects the roughness of the primary particles of  $\text{SiO}_2$  but not the pore network geometry. This is characteristic for a porous structure, where the pore network is constituted by channels with a relatively narrow distribution of hydraulic radii but, at the same time, with rough walls. In this case, it is obvious that the mean hydraulic radius, i.e. characteristic pore radius, is the upper limit of the possible fractality.

The values of the surface fractal dimensions,  $d_{fs}$ , are listed in Table II. These values for polymer-coated samples are hardly changed compared to those of the parental support. The difference between  $d_{fs} = 2.28$  for the sample with the highest polymer loading (PBD 40) and  $d_{fs} = 2.22$  inherent for the parental support and other samples is insignificant. Hence the effect of defractalization, which is characteristic for wetting films, is not observed up to at least a loading of 0.3 g of PBD/g of  $\text{SiO}_2$ .

**4.2. Ganglia Model of Polymer Distribution.** We can conclude that the polymer loading does not essentially affect the roughness of the primary  $\text{SiO}_2$  particles. We cannot exclude that at least a thin polymer film, which does not smooth the surface indentations larger than 10–15 Å, is covering at least partly the primary particles of LiChrospher Si 300. We suppose that most of the polymer forms separate volume inclusions or, using petroleum terminology, ganglia which fill a certain amount of the pores between the particles and may partly block others. Hence, the polymer inclusions turn out to be distributed randomly in the pore network (see Figure 3). The increase of the polymer content does only lead to a progressive bulk filling of the pores, which influences the available pore volume, the specific surface area, the effective diffusion coefficients of adsorbing species, and so on, but not the properties of the unfilled pores. The properties of the unfilled pores of the loaded support seem to be similar to those of the parental support.

The ganglia model of polymer distribution explains a number of different observations with the PBD/LiChrospher Si 300 system published in our previous paper.<sup>27</sup> First, the characteristic changes in the pore structure caused by polymer loading are explained, namely the proportional reductions of the pore volume and the specific surface area with the increase of polymer loading and, at the same time, the similarity of the pore size distribution functions in the loaded samples, which hardly change in comparison to the parental support. In addition, the NMR spectra, which showed an increasing coverage of silanols for higher loadings, tested that the silica surface of the polymer loaded silica remains partly uncovered in the pores. Furthermore, the chromatographic behavior of PBD-coated LiChrospher Si 300 during separation of polypeptides (ribonuclease A, insulin chain B and lysozyme) and chrysene showed the optimum in polymer loading at  $\sim 10\%$  PBD. This material (PBD 10) delivers the best resolution of the protein peaks and also the mostly satisfactory peak shape for the hydrophobic analyte. The typical chromatograms are presented in Figure 4.



**Figure 4.** Chromatograms of ribonuclease A (1), insulin chain B (2), and lysozyme (3) on parental (A) and polymer-loaded (B, 10% PBD; C, 40% PBD) silica; conditions described in the Experimental Section.

We can explain the optimal polymer content with the ganglia model of PBD distribution. The parental support cannot be employed in reversed-phase chromatography (RPC) and it is necessary to cover the silica surface with a certain amount of polymer in order to receive sufficient chromatographic retention and selectivity. However, the increase of polymer content leads to a decrease of permeability of the pore network because the polymer inclusions break down the pore connectivity. The diffusion limitations cause the peak broadening for higher polymer loadings. This is a typical percolation effect well-known in different porous systems containing a host phase.<sup>1,11</sup> The ganglia model makes it possible to calculate the dependency of effective diffusion coefficients of adsorbing species on the polymer content and, therefore, to predict the broadening of chromatographic peaks.

## 5. Conclusions

The distribution of a high-viscosity fluid in porous media has been investigated with the example of polybutadiene-coated porous silica (LiChrospher Si 300), which is a system of practical interest in protein separation.

The values of the surface fractal dimensions for the parental support and the samples with varying polymer loading have been obtained from low-temperature nitrogen adsorption isotherms using the thermodynamic method. We have found that an increase in polymer content does not significantly affect the surface properties. The fractal dimensions for the polymer-coated samples do not differ essentially from the value of 2.22 inherent for the parental support over the scale range of about 10–150 Å. This type of fractality is characteristic for the roughness of the primary SiO<sub>2</sub> particles, which are forming the porous structure of the given porous silica. The effect of defractalization, which is characteristic for wetting films, has not been observed.

On the basis of fractal analysis, we concluded that the polymer is predominantly distributed in inclusions or ganglia, which fill the pore volume in random. The proposed ganglia model for the polymer distribution in porous supports describes well the observed changes in the pore structure caused by the loaded polymer. The ganglia model is consistent with independent solid-state NMR measurements and can be used for the interpretation of the chromatographic data.

The ganglia model appears to be a general model reflecting the overall picture of high-viscosity liquid distribution in porous media. A similar model has been proposed earlier to mimic the distribution of an active component in supported liquid-phase catalysts,<sup>11,28</sup>

but only as a working hypothesis in order to describe the macrokinetics of catalytic reactions. In this way here we have convincing experimental evidence and the results of fractal analysis based on low-temperature nitrogen adsorption data which support this type of polymer distribution in mesoporous silica.

We recommend the thermodynamic method of fractal analysis based on adsorption and/or capillary experimental data for the investigation of high-viscosity liquids or other host phase distributions in different porous systems. It is worth noting that this method can be applied to the experimental study of the interaction of polymer chains with solid surfaces of fractal and also non-fractal structure. This problem is discussed in a number of papers.<sup>29–35</sup> For the purpose of investigation of the fractal structure of an adsorbed polymer layer, the combination of nitrogen adsorption and thermoporometry<sup>36</sup> seems to be helpful.

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