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Abstract

Pore-size distributions have been measured for N-isopropylacrylamide (NIPA) hydrogels at 25 and 32 °C with swelling capacities 11.3 and 6.0 g swollen gel per g dry gel. The mixed-solute-exclusion method (introduced by Kuga) was used to obtain the experimental solute-exclusion curve which represents the amount of imbibed liquid inside the gel inaccessible for a solute of radius r. The pore-size distributions were obtained by using Casassa's Brownian-motion model and numerically solving the Fredholm integral equation. The pore-size distributions of temperature-sensitive NIPA hydrogels are strongly dependent on temperature which determines swelling capacity. With increasing swelling capacity (from 6.0 to 11.3), the pore-size distribution shifts to higher mode values (27.3 to 50.6 Å) and to higher variance ($1.07 \cdot 10^3$ to $3.58 \cdot 10^3$ Å^2).

Introduction

Gels are cross-linked polymer networks that can imbibe large quantities of liquid. When the liquid is water, the cross-linked polymer is a hydrogel. Hydrogels have received increased attention in recent years because of their large number of potential biomedical and biochemical applications.[1-3]

N-isopropylacrylamide (NIPA) hydrogels are of particular interest because they are temperature-sensitive; they undergo large volume changes at about 33 °C,[4] which is approximately the lower critical solution temperature (LCST) of the linear polymer dissolved in water.[5] LCST behavior in aqueous polymer solutions is due to order-disorder transitions in systems of molecules capable of forming hydrogen bonds with water.[6]

As reported earlier[7-10], pore-size distributions have been measured for cationic polyacrylamide and cationic 2-hydroxyethyl methacrylate hydrogels by an indirect method based on the mixed-solute-exclusion (MSE) method introduced by Kuga.[11,12]

In this work we adopt a major assumption identical to that in our previous work[9]: size effects alone are responsible for the partitioning of solutes. Therefore, our experiments were performed with one solute series: poly-(ethylene glycol)/poly-(ethylene oxide). The measurements were made with hydrogels prepared by aqueous free-radical reaction of N-isopropylacrylamide with the cross-linking agent N,N'-methylenbis(acrylamide).

Following well-established convention, the composition of the uncharged NIPA-hydrogel is characterized by two concentration parameters which determine the properties of the gel:

$$\%T = \frac{\text{mass of all monomers (g)}}{\text{volume of water (ml)}} \times 100$$

%T (total monomer concentration) is an index for the concentration of physical entanglements of polymer strands. A higher %T implies a more rigid and dense gel.

$$\%C = \frac{\text{moles of crosslinking agent in feed solution}}{\text{total moles of monomer in feed solution}} \times 100$$

%C (crosslinking ratio) gives the concentration of chemical crosslinks of polymer strands. Raising %C increases the number of bonded connections that bridge polymer chains. Raising %C implies a more rigid and mechanically stabilized gel.

In this work we discuss the results of pore-size-distribution measurements of 15 %T, 1.0 %C N-isopropylacrylamide hydrogels at two temperatures (25 and 32 °C) corresponding to two swelling capacities (11.3 and 6.0 g swollen gel / g dry gel).

Theoretical Section

It is difficult to determine the porous structure of a swollen material because of its fragility. Hydrogels may consist of more than 90 percent water and less than 10 percent polymer network. The porous structure exists only in contact with an aqueous solution; when dehydrated, the network collapses into a compact mass. Therefore, the method used to obtain the pore-size distribution of hydrogels is based on the mixed-solute-exclusion (MSE) method[11,12] modified by Kremer.[7] The MSE method studies the distribution of a series of probe solutes between the gel phase and the surrounding solution phase. The decrease of each solute concentration relative to its initial stock-solution concentration is used for calculating the gel's pore-size distribution. To obtain concentration changes for all probe solutes, the solutes in the solutions must be separated by size-exclusion chromatography (SEC) prior to concentration measurements.

Measurements yield the non-accessible mass, $m''_{non\text{-}acc}(MW)$, which is the non-accessible fraction of liquid imbibed by the hydrogel for solutes of molecular weight, MW. The non-accessible mass is a function of the initial total mass of gel samples, m'_{GS}; the cross-linked polymer network, m_{PN}; the mass of the solvent, m_S; and the dilution ratio, $\frac{w''(MW)}{w'(MW)}$, which is the ratio of the equilibrium concentration of the probe solute of molecular weight MW, w'(MW) to that of the stock concentration, w"(MW):

$$m''_{non\text{-}acc}(MW) = m'_{GS} - m_{PN} + [1 - \frac{w'(MW)}{w''(MW)}] m_S \qquad (1)$$

The dilution ratio $\frac{w''(MW)}{w'(MW)}$ is determined by SEC. The remaining quantities are measured by weighing.

To convert molecular weight MW into a solute radius, the hydrodynamic volume has widely been accepted as a general size parameter in SEC.[13] The experimentally determined relationships between molecular weight MW and hydrodynamic radius r of solutes in water are given by[13]:

$$\text{PEG} \quad r(\text{Å}) = 0.255\ MW^{0.517} \tag{2}$$

$$\text{PEO} \quad r(\text{Å}) = 0.166\ MW^{0.573} \tag{3}$$

Using Eqs. (2) and (3), $m''_{non\text{-}acc}(MW)$ can be converted into $m''_{non\text{-}acc}(r)$, which is interpreted as the cumulative pore-size distribution of the gel sample.[11] The integral distribution coefficient K(r) is a function of solute radius r; it is calculated from the experimentally-measured non-accessible amount of imbibed liquid:

$$K(r) = \frac{m_{non\text{-}acc,\infty} - m_{non\text{-}acc}(r)}{m_{non\text{-}acc,\infty}} \tag{4}$$

Eq. (1) represents the solute-exclusion curve, which provides information about the quantity of non-accessible water within the gel as a function of probe-solute radius. Earlier, this relationship was regarded as the cumulative pore volume of the gel. However, identification of the solute-exclusion curve with the pore-size distribution is incorrect because it would imply that all the liquid existing in pores greater than the molecular size of a solute is accessible for the solute. But the center of gravity of a solute molecule cannot migrate everywhere within the accessible pores with equal probability as long as the solute has a finite volume.[12] In our work, this hindered diffusion effect, known as the wall effect[14], is taken into account. The wall effect requires information about partitioning of solutes between the outer-solution phase and the gel phase as a function of pore size and solute size; this information is expressed by the differential distribution coefficient K(R,r) where R is the pore radius. In this work, we used the

relation between the differential distribution coefficient K(R,r) and the ratio r/R derived by Casassa.[15] Casassa used the model of Brownian motion for linear and branched polymers to calculate distributions between a bulk solution and small pores of simple geometries. Expressions for differential distribution coefficients K(R,r) can be found for simple geometries in the heat-transfer literature. For example, the solution for a slab (i.e. the void between two parallel planes separated by a distance 2R) is[15]:

$$K(R,r) = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\left(\frac{(2n+1)\pi}{2}\frac{r}{R}\right)^2} \qquad (5)$$

Although this model does not directly correspond to the real structure of hydrogels, Eq. (5) was chosen to consider the wall effect in this work because it shows good agreement with experimentally determined distribution coefficients for porous glasses with a narrow pore-size distribution[7] where experimental and calculated values for K(r) are almost identical. To obtain the differential pore-size distribution f(R) from the experimental data obtained here, we must solve the equation:

$$K(r) = \int_0^{R_\infty} K(R,r)\, f(R)\, dR \qquad (6)$$

The left-hand side of Eq. (6) represents the measured overall (integral) distribution coefficient K(r) as a function of solute radius r. The right-hand side consists of the differential distribution coefficient K(R,r) as a function of solute radius r and pore radius R (Eq. (5)) and the desired pore-size distribution f(R). Eq. (6) is the well-known inhomogeneous Fredholm equation of the first kind which we solve numerically. For that purpose we use the com-puter program CONTIN developed by Provencher.[16,17] Details are given elsewhere.[7-9]

Experimental Section

Measurements were made for the pore-size distributions of temperature-sensitive N-isopropylacrylamide hydrogels at two temperatures which correspond to two swelling capacities. A modification of the MSE method[11] was applied. Sodium azide (NaN_3) was used as an antibacterial agent to prevent the destruction of solutes by bacteria and to inhibit decomposition of the hydrogels.[7] Due to the limited separation power of the size-exclusion column, several solutions had to be prepared, each containing not more than three kinds of probe solutes. A sodium chloride solution was used as mobile phase in the HPLC measurements to prevent overlapping of a peak caused by impurities of the sodium azide in the solutions with the solute peaks.

Materials

N-isopropylacrylamide (NIPA), N,N'-methylenebis(acrylamide) (BIS, electrophoresis grade), Ammonium persulfate (APS, Reagent ACS) and NaN_3 (99%) were purchased from Eastman Kodak, Rochester, NY. Sodium metabisulfite (SM) was purchased from Fisher Scientific, Fair Lawn, NJ. The probe solutes poly-(ethylene glycol) and poly-(ethylene oxide) (PEO/PEG) were purchased from Polymer Products Inc., Ontario, NY; Ethylene Glycol (Reagent ACS) was obtained from Polysciences Inc., Warrington, PA; properties of the probe solutes are summarized in Table 1. NaCl (99.999%) was purchased from Aldrich Chemical Co., Milwaukee, WIS. All materials were used without further purification. Water for synthesis and for swelling measurements was distilled and filtered through a Barnstead Nanopure II System (Barnstead/Thermolyne, Dubuque, IW).

Gel Synthesis

The gels were synthesized using the method described by Beltran et al..[18] The gels were prepared by free-radical solution copolymerization of 7.4 g NIPA and 0.1 g BIS as

crosslinker per 48 ml Nanopure water. To start the polymerization, 1 ml solution A and 1 ml solution B were added as initiator to 48 ml of solution. Solution A contained 0.1 g APS in 20 ml H_2O. Solution B contained 0.1 g SM in 20 ml H_2O. Chemicals and Nanopure water were mixed in an icebath in appropriate amounts and degassed for 15 minutes. The resulting solution was then poured into ice-cold gel molds (two parallel glass plates with Teflon frames and a volume of 1.6x80x80 mm). After an incubation period of 24 hours in a refrigerator at about 5 °C, the gels were removed from the molds, sliced into disks (approximately 7 mm in diameter) and soaked in a 0.001 M NaN_3 solution. The gels were stored at about 5 °C and rinsed several times with water to remove impurities and unreacted chemicals trapped in the network. The synthesized NIPA gels had the composition 15 %T and 1.0 %C.

Pore-size-distribution measurements

Stock solutions were prepared by dissolving two or three nearly monodisperse probe solutes for the PEO/PEG series (ranging in molecular weight from 62 to 500,000) into 0.001 M NaN_3 solution. The stock solutions and the appropriate amounts of gel were equilibrated at 25 or 32 °C. The split into five different solutions was necessary because of the limited separation power of the size-exclusion column. Table 2 gives concentrations of the solutions.

For each combination of gel and stock solution, two beakers were used to estimate the experimental error. For each beaker, about 2 g of swollen gel and an amount of stock solution of about 1.5 times the weight of the swollen gel were weighed into the beaker; all mass measurements used a Mettler HK 160 balance with uncertainty ± 0.0001 g (Mettler, Giessen, Germany). For each beaker, this amount of solution was chosen to obtain a maximum decrease of the concentration of the small probe solutes to guarantee a significant signal/noise ratio in the chromatogram. The filled beakers were sealed with

Parafilm M (American National Can, Greenwich, CT) and stored in water baths at 25±0.5 or 32±0.2 °C (heat and control unit No 730, Cole Palmer Instruments Co., Chicago, IL) until equilibrium.

To monitor diffusion of the solutes into the gels until equilibrium, two additional beakers were prepared to contact the gel at 32 °C with the largest probe solute (PEO with molecular weight of 600,000). Every other day the surrounding solution was used to measure the concentration as a function of time necessary to determine the partitioning equilibrium of the probe solutes.

After equilibrium was reached (about 2 1/2 weeks), the gels were separated from the equilibrated solutions and thoroughly washed several times with Nanopure water to remove essentially all probe solutes and salt. The gels were weighed, subsequently dried and reweighed to determine the mass of the polymer network and hence the swelling capacity. The equilibrated solutions were first filtered (Millipore filter GS, pore size 0.22 μm, Millipore Corp., Bedford, MA) to remove gel particles which would affect the chromatographic measurements. After filtering, the solutions and the corresponding stock solutions were alternately chromatographed three times. A Bio-Gel SEC 40 XL Column (Bio-Rad Lab., Hercules, CA) was used to separate the probe solutes. Solute concentrations were measured with a UV detector using a HP Series II 1090 Liquid Chromatograph (Hewlett Packard, Pleasanton, CA). Because of interactions of the sodium azide in the samples with the Silica-gel matrix of the size-exclusion column, an additional peak occurred which overlapped with solute peaks of low retention time. Therefore a sodium-chloride solution (M NaCl = 0.002) was used as a second mobile phase in addition to water as mobile phase to shift this additional peak to higher retention times and to prevent overlapping with the solute peaks. Because impurities in sodium

chloride interfere with resolution of the peaks, it was necessary to use very high-purity (99.999%) sodium chloride. All HPLC measurements were performed in triplicate.

Results and Discussion

Figures 1 and 2 show the size-exclusion curves for the NIPA hydrogels investigated here. The lower limit, the non-accessible mass of zero, was confirmed experimentally. However, some of the data points lie in the slightly negative range, due to the limited accuracy of the measurements, especially for small probe solutes. The standard deviations for the non-accessible mass are about 4.4 % for the gel at 25 °C with a swelling capacity 11.3±0.2 (Figure 1) and about 10.7 % for the gel at 32 °C with a swelling capacity 6.0±0.5 (Figure 2). Despite experimental scatter, the lower limit of the non-accessible mass for the hydrogels of swelling capacity 6.0 (Figure 2) is independent of solute radius below about 2 Å. For higher swelling capacity, these lower-limit solute radii rise to about 4 Å (swelling capacity 11.3, Figure 1). Here molecules with radii below 4 Å are able to migrate into the entire hydrogel-pore structure.

The upper limit of the size-exclusion curve, representing the swelling capacity, can be determined experimentally by two different methods. The dashed lines of Figures 1 and 2 show the gravimetrically determined swelling capacities of the hydrogels in equilibrium with the probe solutes; the data points represent the results of the GPC measurements. Generally, with increasing swelling capacity, the data scatter rises due to increasing gel fragility. The swelling capacities of both measurements (max. deviations 6.2 %) agree within the experimental uncertainties for GPC measurements (generally within 4 %) and for weighing (max. 3 %). For the gels with swelling capacity 6.0, solutes of radii greater than about 60 Å are excluded (Figure 2). However, the gels at lower temperature and

higher swelling capacity are accessible to large probe molecules, up to about 100 Å (Figure 1). The solid lines are curves calculated by computer program CONTIN; these lines give the smoothest non-negative pore-size distributions. Tables 3 and 4 present the pertinent experimental data.

Figure 3 shows the calculated pore-size distribution for the NIPA hydrogels. Table 5 gives statistical results: mode, mean and variance; the mode is the pore radius with the highest probability while the mean radius is the first moment and the variance is the second moment of the pore-size distribution. The pore-size distribution is strongly affected by the swelling capacity which depends on temperature. The mode increases from 27.3 to 50.6 Å with a rise in swelling capacity in spite of decreasing temperature. Increasing swelling capacity leads to a looser network and therefore a broader distribution as indicated by higher variances, increasing from $1.07 \cdot 10^3$ to $3.58 \cdot 10^3$ Å^2.

The results agree well with earlier investigations of size-exclusion properties.[19] The results confirm that for hydrogels, the swelling capacity is a very important variable in determining the hydrogel's size-exclusion properties.

Acknowledgments

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Figure 1

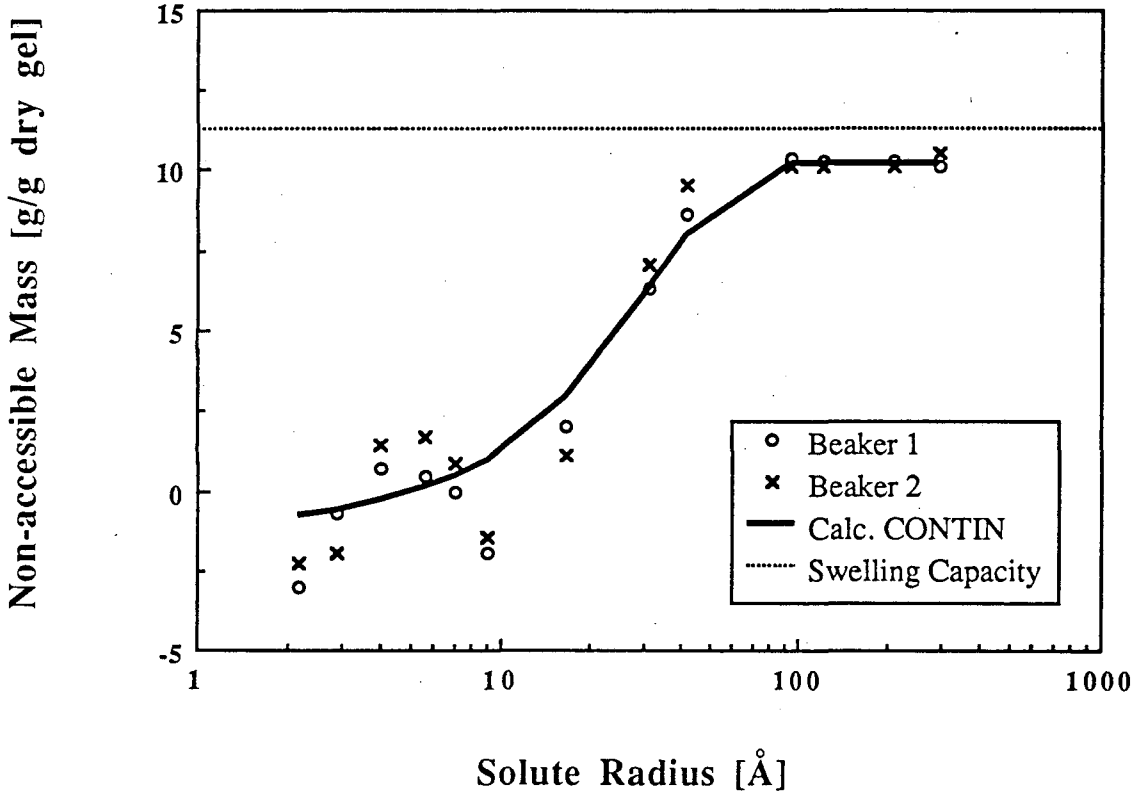

Non-accessible Mass [g/g dry gel]
15
10
5
0
-5
1
10
100
1000
Solute Radius [Å]
Beaker 1
Beaker 2
Calc. CONTIN
Swelling Capacity

Figure 2

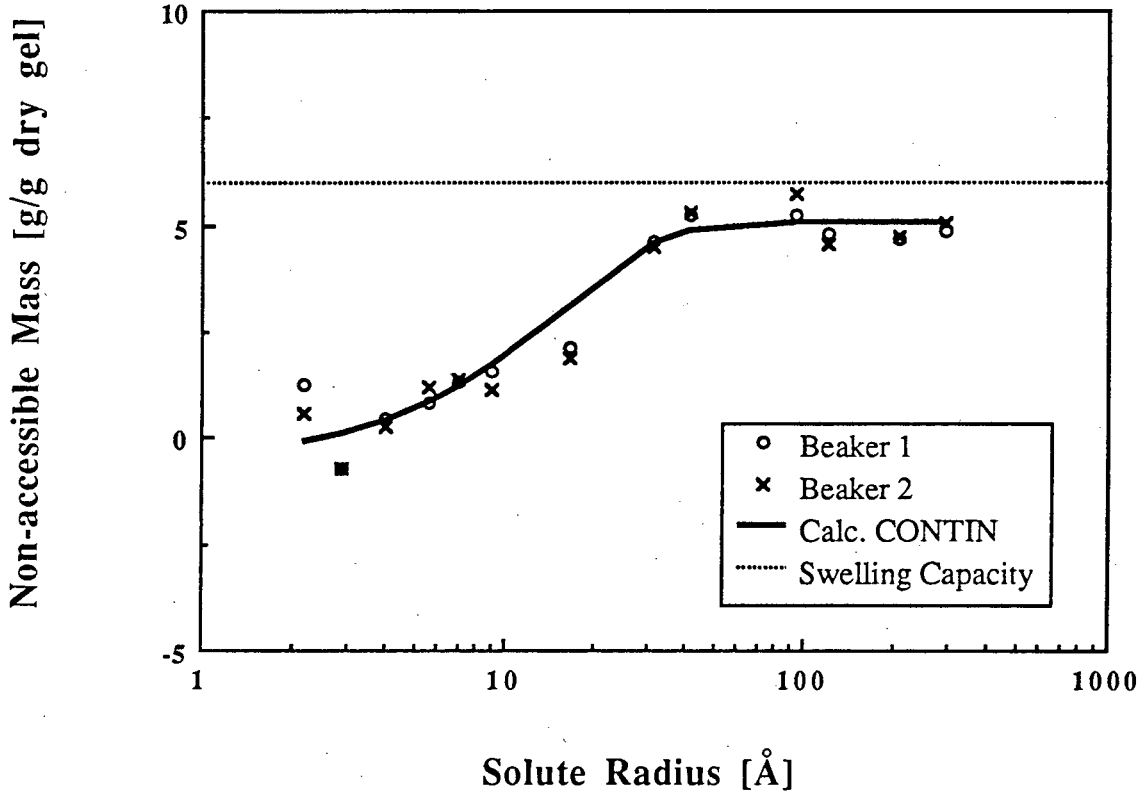
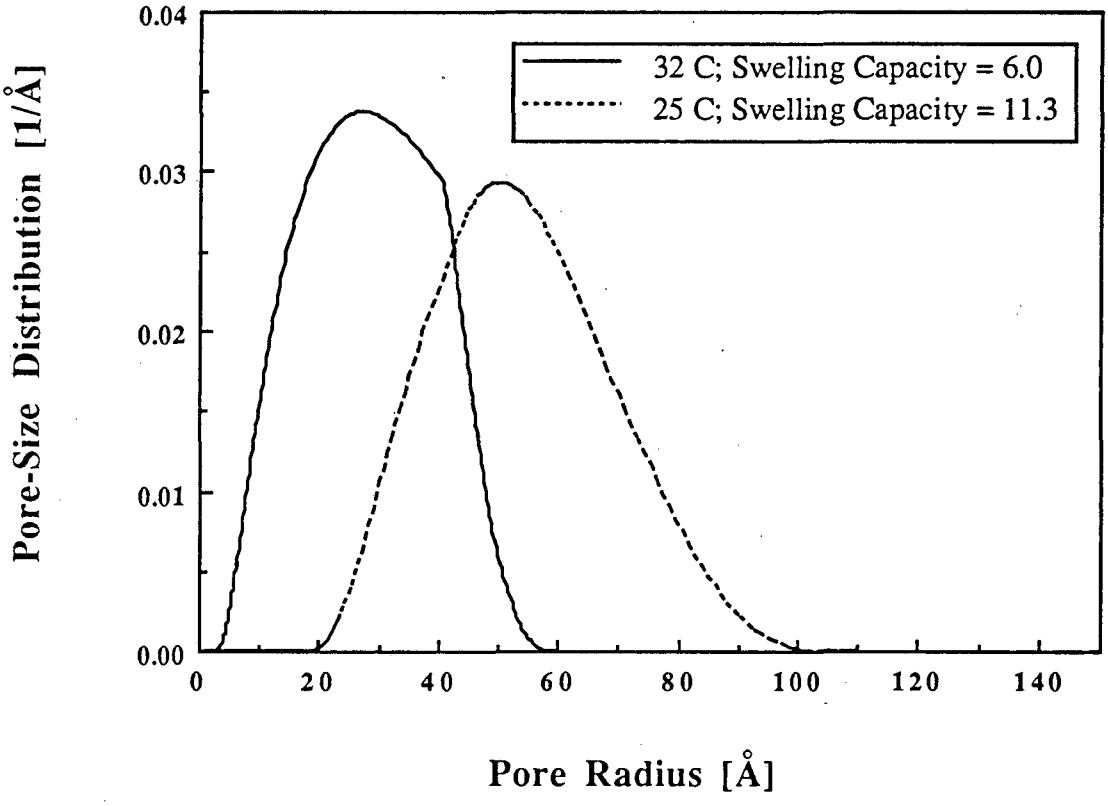

Non-accessible Mass [g/g dry gel]
10
5
0
-5
1
10
100
1000
Solute Radius [Å]
Beaker 1
Beaker 2
Calc. CONTIN
Swelling Capacity

Figure 3


0.04
0.03
0.02
0.01
0.00
0
20
40
60
80
100
120
140
32 C; Swelling Capacity = 6.0
25 C; Swelling Capacity = 11.3
Pore-Size Distribution [1/Å]
Pore Radius [Å]

List of Tables

Table 1: Probe solutes, molecular weight Mp (corresponding to the peak volume, GPC) and hydrodynamic radius r [Å]

Probe Solute	Molecular Weight Mp	r [Å]
EG	62	2.15
PEG 100	109	2.88
PEG 200	210	4.05
PEG 450	400	5.65
PEG 600	600	6.96
PEG 1,000	970	8.93
PEG 3,500	3,140	16.39
PEG 11,000	10,900	31.18
PEG 20,000	19,000	41.56
PEO 61,000	64,703	94.79
PEO 105,000	97,400	119.8
PEO 266,000	249,900	205.6
PEO 500,000	468,300	294.7

Table 2: Stock solutions PEO/PEG series

Solution	Molecule	Weight %
S1	EG	5.6
	PEG 1,000	1.1
	PEO 105,000	0.7
S2	PEG 100	1.2
	PEG 3,500	1.2
	PEO 266,000	0.8
S3	PEG 200	1.2
	Peg 11,000	1.2
	Peo 500, 000	0.8
S4	PEG 450	1.2
	PEG 20,000	1.2
S5	PEG 600	1.2
	PEO 61,000	0.8

Table 3: Measurements (beaker 1 and 2) and calculations (with computer program CONTIN) of the non-accessible mass [g/g dry gel] for the NIPA hydrogel 15 %T 1.0 %C at 25 °C and swelling capacity 11.3 g swollen gel per g dry gel.

r [Å]	Non-accessible Mass [g/g]		
	beaker 1	beaker 2	calculated
2.15	-3.02	-2.31	-0.82
2.88	-0.73	-1.92	-0.62
4.05	0.72	1.45	-0.33
5.65	0.43	1.66	0.09
6.96	-0.07	0.85	0.44
8.93	-1.93	-1.48	0.95
16.93	2.04	1.16	2.91
31.18	6.34	7.10	6.34
41.56	8.68	9.53	8.00
94.79	10.35	10.12	10.18
119.8	10.26	10.10	10.23
205.6	10.30	10.15	10.23
294.7	10.09	10.50	10.23

Table 4: Measurements (beaker 1 and 2) and calculations (with computer program CONTIN) of the non-accessible mass [g/g dry gel] for the NIPA hydrogel 15 %T 1.0 %C at 32 °C and swelling capacity 6.0 g swollen gel per g dry gel.

r [Å]	Non-accessible Mass [g/g]		
	beaker 1	beaker 2	calculated
2.15	1.27	0.55	-0.11
2.88	-0.73	-0.75	0.09
4.05	0.44	0.27	0.42
5.65	0.82	1.22	0.85
6.96	1.34	1.41	1.19
8.93	1.59	1.12	1.68
16.93	2.13	1.90	2.64
31.18	4.59	4.50	4.56
41.56	5.23	5.27	4.87
94.79	5.21	5.72	5.02
119.8	4.82	4.55	5.02
205.6	4.67	4.73	5.02
294.7	4.88	5.07	5.02

Table 5: Modes, means and variances of the calculated pore-size distributions. Results of solving the Fredholm equation (Eq. (6)) with computer program CONTIN.

Hydrogel	Temperature [°C]	Swelling Capacity [g sw. gel / g dry gel]	Pore Radius		
			Mode [Å]	Mean [Å]	Variance [Å^2]
15 %T 1.0 %C	25.0	11.3	50.6	54.2	$3.58 \cdot 10^3$
15 %T 1.0 %C	32.0	6.0	27.3	28.5	$1.07 \cdot 10^3$

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