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Pore-Size Distributions of Cationic 2-Hydroxyethyl Methacrylate (HEMA) Hydrogels

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Pore-Size Distributions of Cationic 2-Hydroxyethyl Methacrylate (HEMA) Hydrogels

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Abstract

Pore-size distributions have been measured for cationic 2-hydroxyethyl methacrylate (HEMA) hydrogels varying in cross-linker / monomer ratio and initial concentration of cationic comonomer MAPTAC, at swelling capacities ranging from 12 to 24 g swollen gel / g dry gel. Swelling capacities were measured at about 6 ^{o}C in pure water and in aqueous sodium-azide solutions ranging in concentration from $5 \cdot 10^{-4}$ to $2 \cdot 10^{-1}$ M. The mixed-solute-exclusion method (introduced by Kuga) was used to obtain the experimental solute-exclusion curve, representing the amount of imbibed liquid inside the gel inaccessible to 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 shift to higher mode values (57.8 to 60.9 Å) with decreasing initial cross-linker concentration at the same swelling capacity of about 12. Raising swelling capacities from 11.1 to 23.9 significantly increases the variance from $5.66 \cdot 10^{3}$ to $2.67 \cdot 10^{4}$ $Å^2$. Changes in the concentration of the cationic comonomer MAPTAC do not significantly influence the pore-size distributions.

Introduction

Hydrogels are cross-linked polymeric systems that, as a result of their high hydrophilicity, can imbibe large quantities of water or aqueous solutions. The three-dimensional network is able to retain the liquids forming a swollen gel phase and the liquid prevents the polymer network from collapsing into a compact mass.[1,2] Swelling properties of polyelectrolyte gels depend strongly on gel composition, temperature, electric fields and the concentration of electrolyte solutes in the surrounding solution.

Hydrogels are used as thickening agents in foods, absorbents in disposable diapers, filters for water purification, packings in chromatography and contact lenses or other pharmaceutical products .[3,4] HEMA-based hydrogels are of particular interest, because they can easily be polymerized, they are biocompatible and have an increasing number of applications in biomedical technology.[1,5]

For a better understanding of gel properties, it is useful to establish relations between gel microstructure, gel composition and swelling capacity. Such relations can lead to more efficient design of new gels to achieve specific applications.

As reported earlier[6-8], pore-size distributions have been measured for cationic polyacrylamide hydrogels by an indirect method based on the mixed-solute-exclusion (MSE) method introduced by Kuga.[9,10]

Using the MSE method, stock solutions of probe solutes at known concentration (which cover a substantial range of molecular sizes) are brought into contact with the hydrogel. Due to the difference between solute size and pore size, some of the solutes can migrate into the gel, while others cannot. For a fixed solute size, the difference in solute

concentration between the initial stock solution and the equilibrated solution surrounding the gel is measured by gel-permeation chromatography (GPC). The decrease in solute concentration is used to calculate the gel's pore-size distribution.

In previous work[6] we assumed that size effects alone are responsible for the partitioning of solutes, because solutes were used that do not have specific interactions with the charged polymer matrix. Following the same assumptions here, our experiments were performed with one solute series: poly-(ethylene glycol)/poly-(ethylene oxide). The measurements were made with hydrogels polymerized from 2-hydroxyethyl methacrylate, the cationic comonomer MAPTAC and ethylene dimethacrylate as cross-linker, as discussed later.

Following well-established convention, the composition of the hydrogel is characterized by three 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.

$$\%M = \frac{\text{moles of MAPTAC in feed solution}}{\text{total moles of monomer in feed solution}} \times 100$$

%M (charged-comonomer ratio) is an index for the net charge of the hydrogel. That charge is defined by the initial concentration of the cationic comonomer MAPTAC. Gels with higher MAPTAC-concentrations show higher swelling capacities in salt-free water.

This work discusses the results of pore-size-distribution measurements of cationic 2-hydroxyethyl methacrylate hydrogels of three different compositions (%C ranging from 0.2 to 0.8 and %M from 7 to 10) at varying swelling capacities (12 to 24 g swollen gel / g dry gel). The hydrogels were prepared by aqueous free-radical reaction of 2-hydroxyethyl methacrylate (HEMA), copolymerized with the cationic [(Methacrylamido)propyl]tri-methylammonium chloride (MAPTAC). The crosslinking agent ethylene dimethacrylate (EDMA) was added to obtain a network structure.

Swelling capacities were measured in pure water and in salt-containing aqueous solutions which varied from $5 \cdot 10^{-4}$ to $2 \cdot 10^{-1}$ M NaN_3. Sodium azide (NaN_3) also served as an antibacterial agent.[7]

Determination of Pore-Size Distributions

The method used to obtain the pore-size distribution of hydrogels is based on the mixed-solute-exclusion (MSE) method[9,10] modified by Kremer.[8] 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 mixture must be separated by size-exclusion chromatography (SEC) prior to concentration measurements.

Measurements yield the non-accessible mass, $m''_{non\text{-}acc}(MW)$, the non-accessible fraction of liquid imbibed by the hydrogel for solutes of molecular weight, MW, which 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.[11] The experimentally determined relationships between molecular weight MW and hydrodynamic radius r of solutes in water are given in the following equations[11]:

PEG $r(Å) = 0.255\ MW^{0.517}$ (2)

PEO $r(Å) = 0.166\ MW^{0.573}$ (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.[9]

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:

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

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.[10] In our work, this hindered diffusion effect, known as the wall effect[12], 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, which 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.[13] 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[13]:

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

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[8] 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:

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

The left-hand side of Eq. (6) represents the measured overall 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 computer program CONTIN developed by Provencher.[14,15] Details are given elsewhere.[6-8]

Experimental Methods

Measurements were made for the pore-size distributions of three cationic 2-hydroxyethyl methacrylate hydrogels of different compositions at each of two swelling capacities. A modification of the MSE method[9] was applied. Sodium azide (NaN_3) was used to vary the ionic strength which affects the swelling capacities of the hydrogels. Sodium azide also served as an antibacterial agent preventing the destruction of solutes and gels by bacteria.[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

2-Hydroxyethyl methacrylate (HEMA, 98%) and Ammonium persulfate (APS, Reagent ACS) were purchased from Eastman Kodak, Rochester, NY. [(Methacrylamido)propyl]-trimethylammonium chloride (MAPTAC, in 50% aqueous solution) was obtained from Aldrich Chemical Co. Inc., Milwaukee, WIS; Ethylene dimethacrylate (EDMA) was purchased from Fisher Scientific, Fair Lawn, NJ. The probe solutes PEO/PEG were purchased from Polymer Products Inc., Ontario, NY; Ethylene Glycol (Reagent ACS) was obtained from Polysciences Inc., Warrington, PA; the properties are summarized in Table 1. NaN_3 (99%) was purchased from Eastman Kodak, Rochester, NY; 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 Hooper et al..[16] The gels were prepared by free-radical solution copolymerization of HEMA and MAPTAC, using EDMA as the crosslinker and 0.125 g APS per 50 ml solution as initiator. Chemicals and Nanopure water were mixed in appropriate amounts and degassed for 15 minutes. The resulting solution was then poured into 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 water bath at 50 °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 6 °C and rinsed several times to remove impurities and unreacted chemicals trapped in the network. Three HEMA-based hydrogels were synthesized and used for the pore-size distribution investigations:

65 %T 0.2 %C 10 %M

65 %T 0.2 %C 7 %M

65 %T 0.8 %C 10 %M

Swelling Measurements

Before pore-size distribution studies, it was necessary to measure the swelling capacities of the gels at different ionic strengths. Therefore, the hydrogels were placed in Nanopure water and in seven NaN_3 solutions (0.0005, 0.001, 0.005, 0.01, 0.05, 0.1 and 0.2 M) where they were allowed to swell to equilibrium at room temperature. The solutions were changed at least three times to extract undesired solutes or salt molecules from the gels. For each kind of gel and solution, beakers with five gels and about 25 ml solution were prepared. To prevent evaporative losses, which could appreciably increase the ionic strength of the solution, the beakers containing gels and solution were sealed with Parafilm M (American National Can, Greenwich, CT). Equilibrium was reached after

approximately two weeks; approach to equilibrium was monitored by mass measurements of the swollen hydrogels (using a Mettler HK 160 balance with uncertainty ± 0.0001 g, Mettler, Giessen, Germany). Once equilibrium was attained, the swelling ratios in water and in the NaN_3 solutions were determined for each hydrogel. Equilibrated gel disks were weighed, dried at room temperature for one week and re-weighed. The swelling ratio is defined as the mass ratio of swollen hydrogel to dry hydrogel at room temperature. All swelling studies were performed in duplicate.

Pore-size distribution measurements

Stock solutions were prepared by dissolving two or three monodisperse probe solutes for the PEO/PEG series (ranging in molecular weight from 62 to 450,000) into the sodium-azide solutions obtained from the swelling measurements. The division into four 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 solution, duplicate experiments were performed. About 6 g of swollen gels (ten, twelve, fourteen and twenty gels, respectively) and an amount of stock solution of about 1.4 times the weight of the swollen gels were weighed into the beakers. 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 and stored in a water bath at 25±0.5 °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 most dense gel (65 %T 0.8 %C 1.0 %M, at the swelling capacity of 12 g swollen gel / g dry gel) with the largest probe solute (PEO with

molecular weight of 1,000,000). The surrounding solution was used each second day to measure the concentration as a function of time necessary to determine the partitioning equilibrium of the probe solutes.

After equilibrium was reached, 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 subsequently dried and weighed 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. The solute concentrations were measured via 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 Nanopure water as mobile phase to shift this additional peak to higher retention times and to prevent overlapping with the solute peaks. All HPLC measurements were performed in triplicate.

Results and Discussion

Figure 1 shows the swelling capacities of the HEMA hydrogels. The swelling capacities were measured in pure water and in NaN_3 solutions ranging from 0.0005 to 0.1 M with uncertainties generally less than 1 %. The swelling capacity rises with decreasing crosslink density (%C) because networks with larger mesh widths have larger swelling capacities[17] and because the cross-linking agent EDMA is more hydrophobic than HEMA.[18] The results are in good agreement with those reported in other investigations.[18,19,20] Increasing charge density (%M) raises the swelling capacity enormously, especially at low salt concentration in the surrounding solution, because the counterions that neutralize the fixed-charge groups on the hydrogel network give rise to an osmotic force that causes the hydrogel to swell.[21] At lower ionic strength, the concentration of bound charges within the gel exceeds the concentration of salt in the solution and a large ion-swelling pressure causes the gel to expand. However, as the external salt concentration rises, the difference between internal and external ion concentration decreases and the gel deswells.

Figures 2 to 4 show the size-exclusion curves for all hydrogels investigated here. The lower limit (all water in the gel is accessible to the probe solutes) 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 smaller probe solutes. The standard deviations for the non-accessible mass range from about 1.7 % for the gel 65%T 0.8%C 10%M at a swelling capacity of 12.7 (Figure 2) to about 14 % for the gel 65%T 0.8%C 10%M with a swelling capacity of 15.1 (Figure 2). Despite the deviations of the measurements, the lower limit of the non-accessible mass for the hydrogels of swelling capacities about 12 (Figures 2 to 4) is independent of solute radius below about 3 Å. For higher swelling capacities, these lower-limit solute radii rise to about 6 Å (gel 65%T

0.2%C 10%M, swelling capacity of 23.9, Figure 4). Here molecules with radii below 6 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 2 to 4 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 agree well (max. deviations 1.5 %). The experimental uncertainties for GPC measurements and for weighing are generally less than 3 %. For the gels with swelling capacities of about 12, solutes of radii greater than about 100 Å are excluded. However, the gels with higher swelling capacity are accessible to larger probe molecules, up to about 250 Å for a swelling capacity of 23.9 (Figure 4). The solid lines are the curves calculated by the computer program CONTIN which gives the smoothest non-negative pore-size distribution.

Figures 5 and 6 show the calculated pore-size distribution for all hydrogels. Table 3 gives statistical results: mode, mean and variance (the mode represents pore radii with the highest probability, the mean radius is the first moment and the variance is the second moment of the pore-size distribution). With decreasing crosslinker concentration for the gels with swelling capacities of about 12 (Figure 5), the mode increases from 57.8 to 59.0 and 60.9 Å. Decreasing %C produces a looser network and therefore a broader distribution as indicated by higher variances (increasing from $4.29 \cdot 10^3$ to $5.66 \cdot 10^3$ and $6.81 \cdot 10^3$ Å^2). The influence of the swelling capacity on the pore-size distribution is most significant as shown in Figure 6. Increasing swelling capacity leads to a broader pore-size distribution. This increase is very significant for the HEMA hydrogel 65%T 0.2%C

10%M where increase of the swelling capacity from 11.1 to 23.9 gives a much broader pore-size distribution with the variance rising from $5.66 \cdot 10^3$ to $2.67 \cdot 10^4$ Å^2 (Figure 7).

The results agree well with earlier investigations of Walther et al.[6] and Kremer et al.[7] The results show that the total monomer concentration at gel formation[22] together with the swelling capacity are the most important variables in determining the hydrogel's size-exclusion properties.

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Figure 1: Swelling capacities of HEMA hydrogels as a function of ionic strength of the surrounding solution.

Figure 2: Size-exclusion curve for the HEMA hydrogel 65%T 0.8%C 10%M at swelling capacities [g swollen gel / g dry gel] of 12.7 and 15.1. Relation between the non-accessible mass of imbibed liquid and the solute radius. Experimental data (o, Δ = beaker 1; x,+ = beaker 2) and calculations using computer program CONTIN (▬, ••••) to solve the Fredholm equation.

Figure 3: Size-exclusion curve for the HEMA hydrogel 65%T 0.2%C 7%M at swelling capacities [g swollen gel / g dry gel] of 11.8 and 18.6. Relation between the non-accessible mass of imbibed liquid and the solute radius. Experimental data (o, Δ = beaker 1; x,+ = beaker 2) and calculations using computer program CONTIN (▬, ••••) to solve the Fredholm equation.

Figure 4: Size-exclusion curve for the HEMA hydrogel 65%T 0.2%C 10%M at swelling capacities [g swollen gel / g dry gel] of 11.1 and 23.9. Relation between the non-accessible mass of imbibed liquid and the solute radius. Experimental data (o, Δ = beaker 1; x,+ = beaker 2) and calculations using computer program CONTIN (▬, ••••) to solve the Fredholm equation.

Figure 5: Pore-size distributions of HEMA hydrogels at a swelling capacity of about 12 as a function of pore radius. Results of solving the Fredholm equation (Eq. 6) with computer program CONTIN.

Figure 6: Pore-size distributions of HEMA hydrogels at swelling capacities from 15.1 to 23.9 as a function of pore radius. Results of solving the Fredholm equation (Eq. 6) with computer program CONTIN.

Figure 10: Pore-size distributions of the HEMA hydrogel 65%T 0.2%C 10%M at swelling capacities of 11.1 to 23.9 as a function of pore radius. Results of solving the Fredholm equation (Eq. 6) with computer program CONTIN.

Figure 1

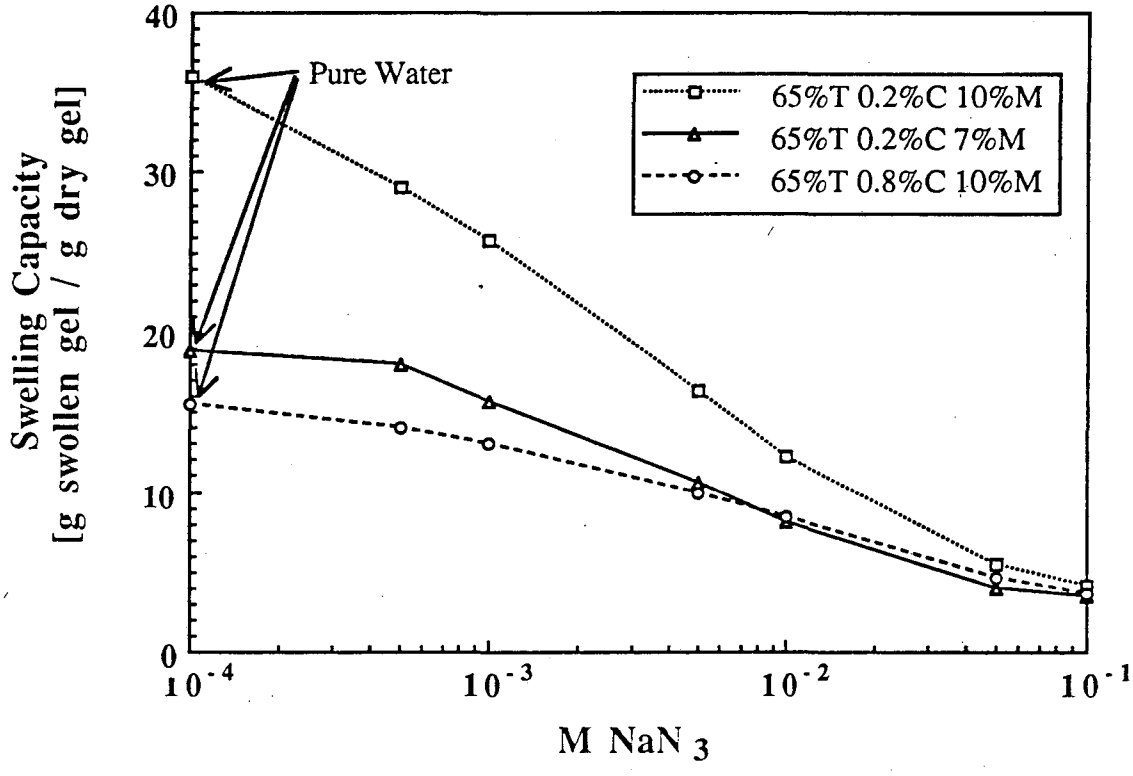
Swelling Capacity
[g swollen gel / g dry gel]
40
30
20
10
0
Pure Water
65%T 0.2%C 10%M
65%T 0.2%C 7%M
65%T 0.8%C 10%M
10-4
10-3
10-2
10-1
M NaN 3

Figure 2

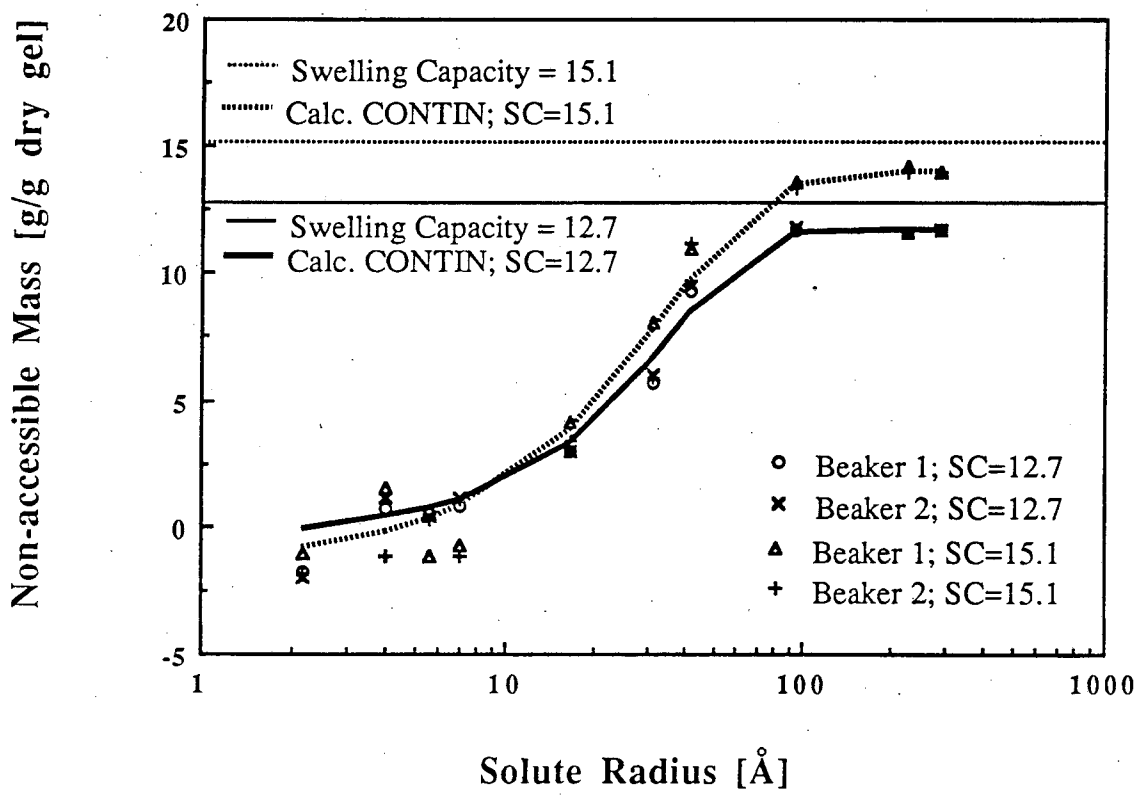
Swelling Capacity = 15.1
Calc. CONTIN; SC=15.1
Swelling Capacity = 12.7
Calc. CONTIN; SC=12.7
Beaker 1; SC=12.7
Beaker 2; SC=12.7
Beaker 1; SC=15.1
Beaker 2; SC=15.1
Non-accessible Mass [g/g dry gel]
Solute Radius [Å]
20
15
10
5
0
-5
1
10
100
1000

Figure 3

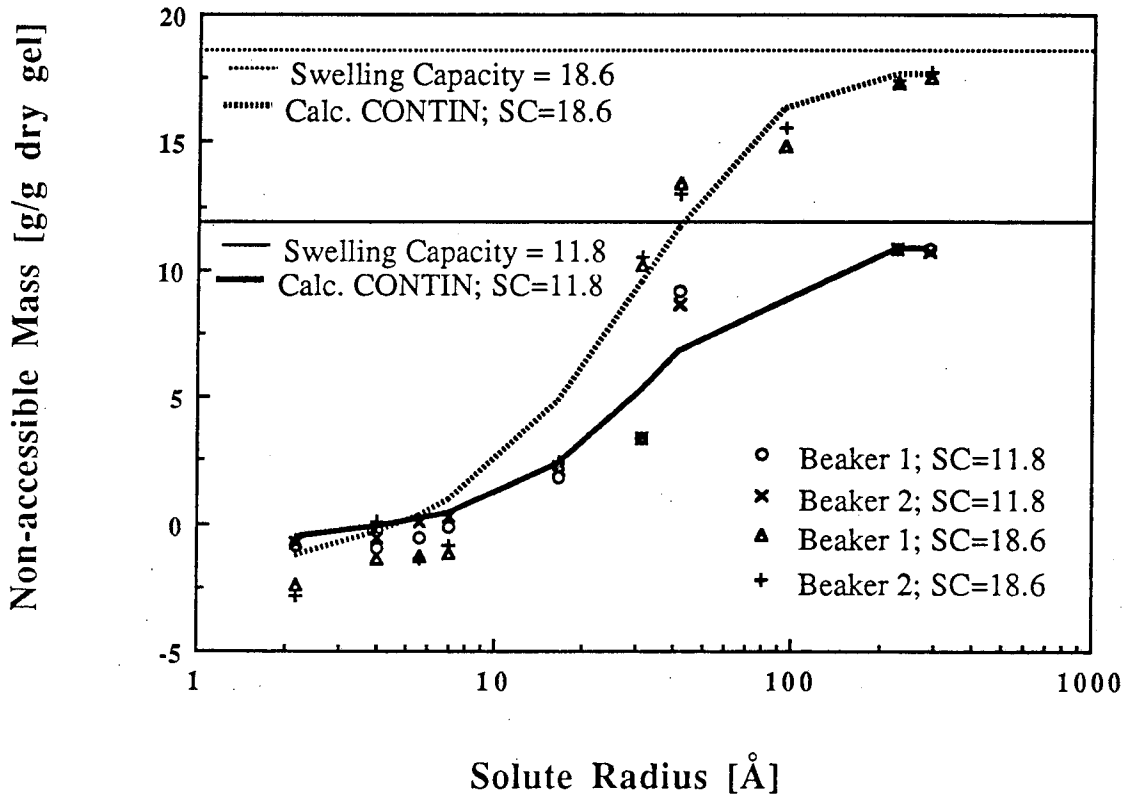
Swelling Capacity = 18.6
Calc. CONTIN; SC=18.6
Swelling Capacity = 11.8
Calc. CONTIN; SC=11.8
Beaker 1; SC=11.8
Beaker 2; SC=11.8
Beaker 1; SC=18.6
Beaker 2; SC=18.6
Non-accessible Mass [g/g dry gel]
Solute Radius [Å]
20
15
10
5
0
-5
1
10
100
1000

Figure 4

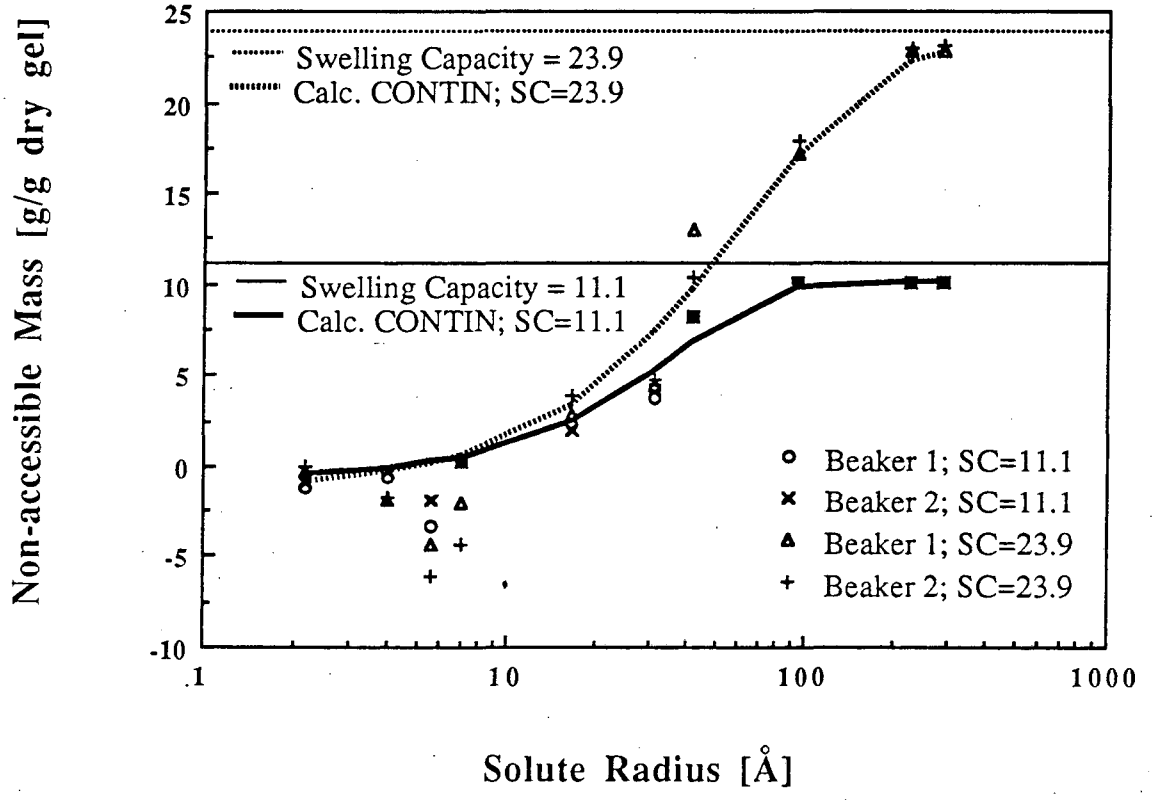
Swelling Capacity = 23.9
Calc. CONTIN; SC=23.9
Swelling Capacity = 11.1
Calc. CONTIN; SC=11.1
Beaker 1; SC=11.1
Beaker 2; SC=11.1
Beaker 1; SC=23.9
Beaker 2; SC=23.9
Non-accessible Mass [g/g dry gel]
Solute Radius [Å]
25
20
15
10
5
0
-5
-10
.1
10
100
1000

Figure 5

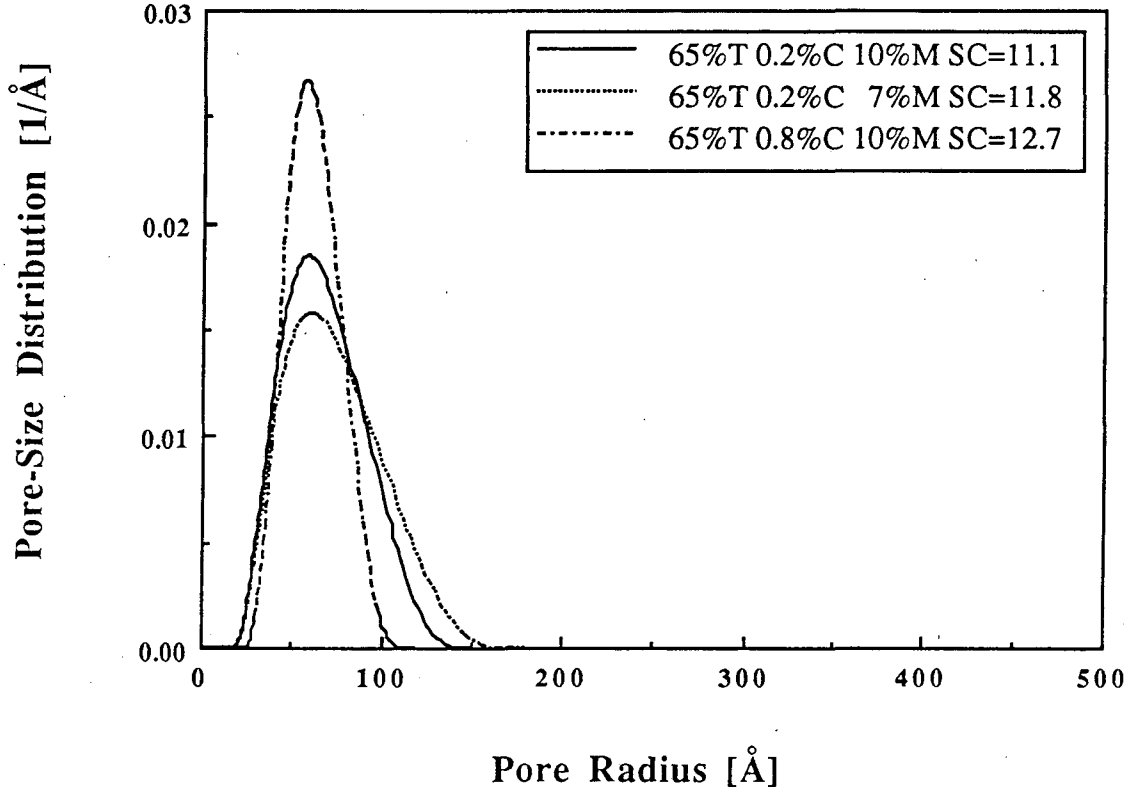
0.03
0.02
0.01
0.00
0
100
200
300
400
500
Pore-Size Distribution [1/Å]
Pore Radius [Å]
65%T 0.2%C 10%M SC=11.1
65%T 0.2%C 7%M SC=11.8
65%T 0.8%C 10%M SC=12.7

Figure 6

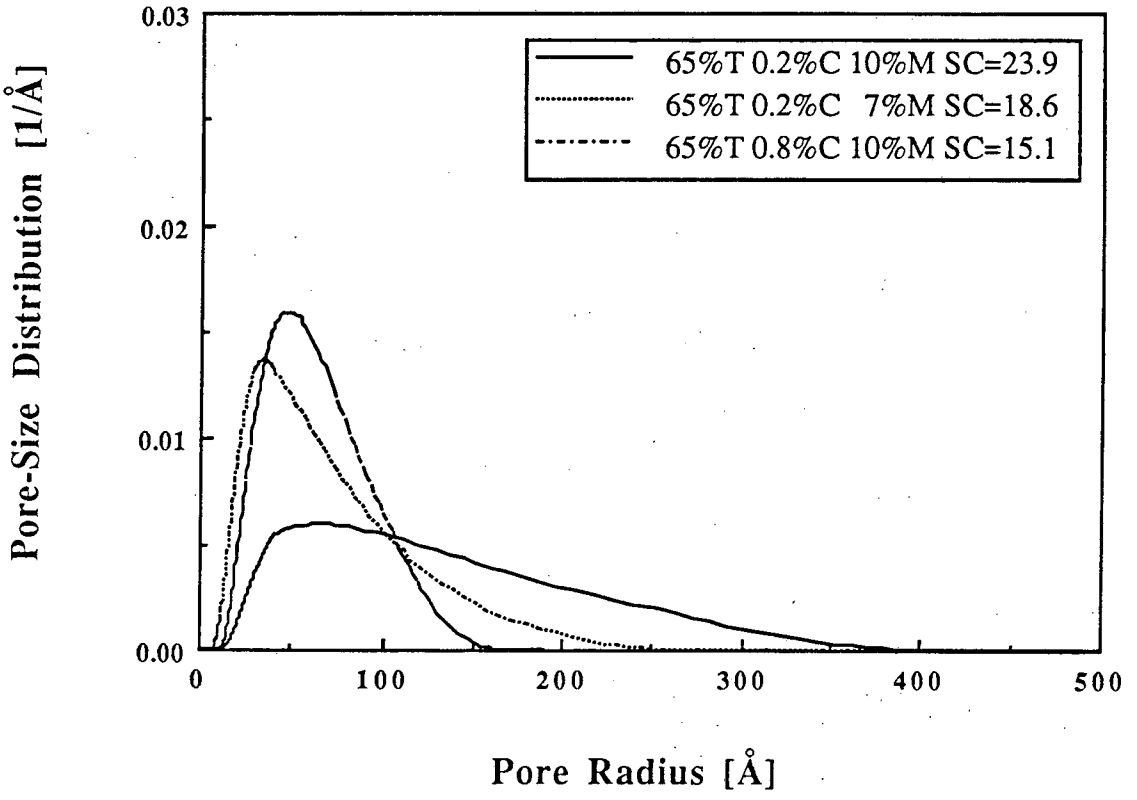
0.03
0.02
0.01
0.00
0
100
200
300
400
500
Pore-Size Distribution [1/Å]
Pore Radius [Å]
65%T 0.2%C 10%M SC=23.9
65%T 0.2%C 7%M SC=18.6
65%T 0.8%C 10%M SC=15.1

Figure 7

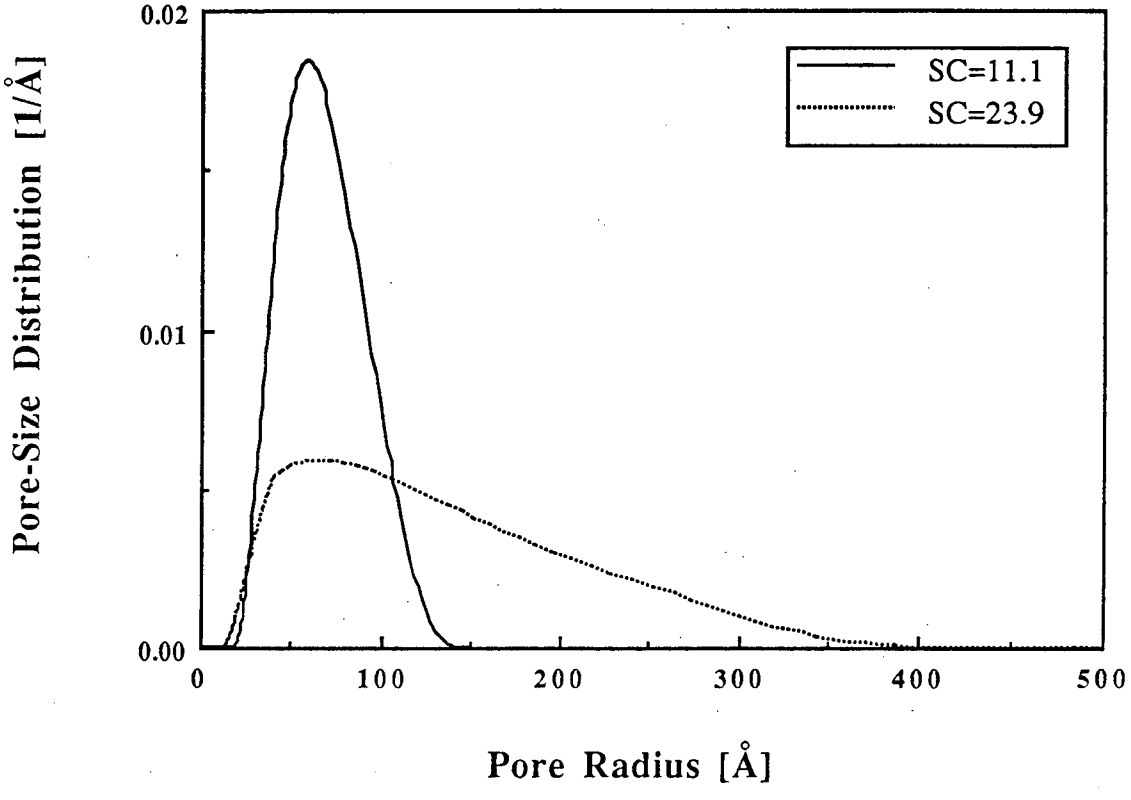
0.02
0.01
0.00
0
100
200
300
400
500
SC=11.1
SC=23.9
Pore-Size Distribution [1/Å]
Pore Radius [Å]

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

Probe Solute	Molecular Weight Mp	r [Å]
EG	62	2.15
PEG 200	210	4.05
PEG 450	400	5.65
PEG 600	600	6.96
PEG 3,000	3,140	16.39
PEG 10,000	10,900	31.18
PEG 20,000	19,000	41.56
PEO 60,000	64,703	94.79
PEO 200,000	293,400	225.4
PEO 500,000	447,300	287.01

Table 2: Stocksolutions PEO/PEG series

Solution	M NaN_3	Molecule	Weight %	Solution	M NaN_3	Molecule	Weight %
P11	0.0002	200,000	0.34	P31	0.0002	20,000	0.8
		3,000	0.8			450	0.8
		EG	4				
P12	0.0005	200,000	0.34	P32	0.0005	20,000	0.8
		3,000	0.8			450	0.8
		EG	4				
P13	0.0015	200,000	0.34	P33	0.0015	20,000	0.8
		3,000	0.8			450	0.8
		EG	4				
P14	0.0018	200,000	0.34	P34	0.0018	20,000	0.8
		3,000	0.8			450	0.8
		EG	4				
P15	0.0032	200,000	0.34	P35	0.0032	20,000	0.8
		3,000	0.8			450	0.8
		EG	4				
P16	0.0106	200,000	0.34	P36	0.0106	20,000	0.8
		3,000	0.8			450	0.8
		Eg	4				
P21	0.0002	500,000	0.34	P41	0.0002	60,000	0.45
		10,000	0.8			600	0.8
		200	0.8				
P22	0.0005	500,000	0.34	P42	0.0005	60,000	0.45
		10,000	0.8			600	0.8
		200	0.8				
P23	0.0015	500,000	0.34	P43	0.0015	60,000	0.45
		10,000	0.8			600	0.8
		200	0.8				
P24	0.0018	500,000	0.34	P44	0.0018	60,000	0.45
		10,000	0.8			600	0.8
		200	0.8				
P25	0.0032	500,000	0.34	P45	0.0032	60,000	0.45
		10,000	0.8			600	0.8
		200	0.8				
P26	0.0106	500,000	0.34	P46	0.0106	60,000	0.45
		10,000	0.8			600	0.8
		200	0.8				

Table 3: Modes, means and variances of the calculated pore-size distributions. Results of solving the Fredholm equation (Eq. (6)) with computer program CONTIN.

Gel	Swelling Capacity [g sw. gel / g dry gel]	Pore Radius		
		Mode [Å]	Mean [Å]	Variance [$Å^2$]
65%T 0.8%C 10%M	12.7	57.8	62.2	$4.29 \cdot 10^3$
65%T 0.8%C 10%M	15.1	48.1	65.5	$5.61 \cdot 10^3$
65%T 0.2%C 7%M	11.8	60.9	74.3	$6.81 \cdot 10^3$
65%T 0.2%C 7%M	18.6	34.9	74.3	$8.47 \cdot 10^3$
65%T 0.2%C 10%M	11.1	59.0	68.4	$5.66 \cdot 10^3$
65%T 0.2%C 10%M	23.9	64.6	137.6	$2.67 \cdot 10^4$

Supplementary material for:

Pore-Size Distributions of Cationic 2-Hydroxyethyl Methacrylate (HEMA) Hydrogels

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Department of Chemical Engineering, University of California, Berkeley and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

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Table 1: Swelling capacity measurements of HEMA hydrogels as a function of sodium azide (NaN_3) concentration.

Table 2: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.8%C 10%M at the swelling capacity of 12.7 [g swollen gel / g dry gel].

Table 3: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.8%C 10%M at the swelling capacity of 15.1 [g swollen gel / g dry gel].

Table 4: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.2%C 7%M at the swelling capacity of 11.8 [g swollen gel / g dry gel].

Table 5: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.2%C 7%M at the swelling capacity of 18.6 [g swollen gel / g dry gel].

Table 6: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.2%C 10%M at the swelling capacity of 11.1 [g swollen gel / g dry gel].

Table 7: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.2%C 10%M at the swelling capacity of 23.9 [g swollen gel / g dry gel].

Table 1: Swelling capacity measurements of HEMA hydrogels as a function of sodium azide (NaN_3) concentration.

	Swelling Capacities HEMA-based hydrogels							
Gel	65 %T 1.0 %C 10 %M							
Salt conc. [M]	0.0005	0.001	0.005	0.01	0.05	0.1	0.2	water
stdev/av*100 in %	0.9459	0.9955	0.7678	0.7322	0.6758	0.8419	0.7785	0.8758
swell. capacity	13.285	12.57	10.115	8.5684	4.9124	3.8946	3.2942	14.579
Gel	65 %T 0.2 %C 5 %M							
Salt conc. [M]	0.0005	0.001	0.005	0.01	0.05	0.1	0.2	water
stdev/av*100 in %	0.7546	0.4684	0.5854	0.5726	0.5988	0.6384	0.6495	0.5199
swell. capacity	7.9693	7.2041	5.7095	4.6106	2.8492	2.5318	2.4401	10.046
Gel	65 %T 0.2 %C 10 %M							
Salt conc. [M]	0.0005	0.001	0.005	0.01	0.05	0.1	0.2	water
stdev/av*100 in %	0.8607	0.7024	0.5843	0.7353	0.6186	0.4837	0.5802	0.7627
swell. capacity	29.065	25.772	16.327	12.151	5.4316	4.0787	3.4206	36.019
Gel	65 %T 0.2 %C 7 %M							
Salt conc. [M]	0.0005	0.001	0.005	0.01	0.05	0.1	0.2	water
stdev/av*100 in %	0.5762	0.7568	0.6532	0.7228	0.7302	9.91	0.4085	0.5827
swell. capacity	17.987	15.749	10.473	8.1063	3.9397	3.4941	2.9792	18.846
Gel	65 %T 0.8 %C 10 %M							
Salt conc. [M]	0.0005	0.001	0.005	0.01	0.05	0.1	0.2	water
stdev/av*100 in %	0.6286	0.7836	0.6196	0.5815	0.5392	0.601	0.2155	0.6332
swell. capacity	14.017	13.009	10.005	8.371	4.6483	3.6778	3.3368	15.491

Table 2: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.8%C 10%M at the swelling capacity of 12.7 [g swollen gel / g dry gel].

r[Å]	Non-accessible Mass [g/g]		calc. contin
	beaker 1	beaker 2	
2.15	-1.83E+00	-1.97E+00	-8.18E-02
4.05	6.91E-01	1.15E+00	3.62E-01
5.65	4.77E-01	4.12E-01	7.48E-01
6.96	8.29E-01	1.09E+00	1.05E+00
16.39	3.01E+00	3.03E+00	3.28E+00
31.18	5.70E+00	5.98E+00	6.63E+00
41.56	9.35E+00	9.47E+00	8.50E+00
94.79	1.17E+01	1.18E+01	1.16E+01
225.4	1.16E+01	1.16E+01	1.17E+01
287.01	1.17E+01	1.17E+01	1.17E+01

Table 3: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.8%C 10%M at the swelling capacity of 15.1 [g swollen gel / g dry gel].

r[Å]	Non-accessible Mass [g/g]		calc. contin
	beaker 1	beaker 2	
2.15	-1.04E+00	-1.87E+00	-8.10E-01
4.05	1.57E+00	-1.12E+00	-1.82E-01
5.65	-1.12E+00	2.94E-01	3.35E-01
6.96	-7.55E-01	-1.14E+00	7.69E-01
16.39	4.17E+00	3.43E+00	3.80E+00
31.18	8.04E+00	5.88E+00	7.77E+00
41.56	1.10E+01	1.12E+01	9.74E+00
94.79	1.35E+01	1.34E+01	1.35E+01
225.4	1.41E+01	1.40E+01	1.40E+01
287.01	1.40E+01	1.39E+01	1.40E+01

Table 4: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.2%C 7%M at the swelling capacity of 11.8 [g swollen gel / g dry gel].

r[Å]	Non-accessible Mass [g/g]		calc. contin
	beaker 1	beaker 2	
2.15	-8.87E-01	-7.51E-01	-5.73E-01
4.05	-9.38E-01	-5.50E-01	-1.84E-01
5.65	-5.79E-01	9.30E-02	1.41E-01
6.96	-1.76E-01	3.12E-01	4.11E-01
16.39	1.80E+00	2.11E+00	2.36E+00
31.18	3.36E+00	3.37E+00	5.20E+00
41.56	9.17E+00	8.63E+00	6.81E+00
94.79			
225.4	1.08E+01	1.08E+01	1.08E+01
287.01	1.08E+01	1.07E+01	1.08E+01

Table 5: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.2%C 7%M at the swelling capacity of 18.6 [g swollen gel / g dry gel].

r[Å]	Non-accessible Mass [g/g]		calc. contin
	beaker 1	beaker 2	
2.15	-2.45E+00	-2.79E+00	-1.24E+00
4.05	-1.41E+00	1.10E-01	-3.88E-01
5.65	-1.23E+00	-1.37E+00	3.18E-01
6.96	-1.21E+00	-9.08E-01	8.83E-01
16.39	2.34E+00	2.47E+00	4.82E+00
31.18	1.02E+01	1.05E+01	9.45E+00
41.56	1.34E+01	1.30E+01	1.16E+01
94.79	1.49E+01	1.55E+01	1.63E+01
225.4	1.74E+01	1.74E+01	1.76E+01
287.01	1.76E+01	1.78E+01	1.77E+01

Table 6: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.2%C 10%M at the swelling capacity of 11.1 [g swollen gel / g dry gel].

r[Å]	Non-accessible Mass [g/g]		calc. contin
	beaker 1	beaker 2	
2.15	-1.19E+00	-9.14E-01	-5.16E-01
4.05	-5.80E-01	-3.12E-01	-1.32E-01
5.65	-3.33E+00	-1.84E+00	2.03E-01
6.96	2.32E-01	2.79E-01	4.66E-01
16.39	2.34E+00	1.98E+00	2.40E+00
31.18	3.74E+00	4.24E+00	5.21E+00
41.56	8.20E+00	8.17E+00	6.78E+00
94.79	1.01E+01	1.01E+01	9.84E+00
225.4	1.01E+01	1.01E+01	1.01E+01
287.01	1.01E+01	1.01E+01	1.01E+01

Table 7: Measurements (beaker 1 and beaker 2) and calculations (with the computer program CONTIN) of the non-accessible mass [g/g dry gel] for the HEMA hydrogel 65%T 0.2%C 10%M at the swelling capacity of 23.9 [g swollen gel / g dry gel].

r[Å]	Non-accessible Mass [g/g]		calc. contin
	beaker 1	beaker 2	
2.15	-3.76E-01	1.89E-02	-8.71E-01
4.05	-1.92E+00	-1.81E+00	-2.98E-01
5.65	-4.39E+00	-6.11E+00	1.83E-01
6.96	-2.05E+00	-4.41E+00	5.73E-01
16.39	2.85E+00	3.82E+00	3.35E+00
31.18	4.40E+00	4.73E+00	7.31E+00
41.56	1.30E+01	1.03E+01	9.65E+00
94.79	1.72E+01	1.80E+01	1.71E+01
225.4	2.28E+01	2.30E+01	2.22E+01
287.01	2.28E+01	2.31E+01	2.27E+01

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