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**Pore-Size Distributions of Cationic Polyacrylamide Hydrogels of
Different Compositions Maintained at the Same Swelling Capacity**

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Abstract

Pore-size distributions have been measured for cationic acrylamide-based hydrogels of different compositions maintained at the same swelling capacity (27.8 ± 0.7 g swollen gel / g dry gel) by varying the ionic strength of the surrounding solution. Swelling equilibria were measured at about 6 °C in pure water and aqueous sodium azide solutions ranging in concentration from 10^{-3} to 10^{-1} M. 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 to a solute of radius r . The pore-size distribution was obtained by using Casassa's Brownian-motion model and numerically solving the Fredholm integral equation. The modes of the pore radii range from 20.4 to 47.1 Å for acrylamide-based hydrogels containing varying amounts of cationic comonomer (1.5 and 4.0 %M), cross-linker (0.3 and 1.0 %C) and initial concentration of total monomer (15 and 35 %T).

Introduction

Hydrogels can be defined as three-dimensional networks of polymers which have the ability to swell to several hundred times the dry network mass when in contact with water or aqueous solutions. Gel properties depend strongly on the degree of cross-linking, the chemical composition of the polymer chains and the interactions of network and surrounding liquid. The liquid prevents the polymer network from collapsing into a compact mass and the network prevents the liquid from flowing away (1).

Gels provide important intermediates and end products in the manufacture of commercial polymers such as rubbers or glues. Gels are also used as absorbents in disposable diapers, filters for water purification, packings in chromatography and as contact lenses or pharmaceutical products (2, 3, 4).

Despite considerable progress in gel technology over the past twenty years (3, 5), fundamental understanding of gel properties is far from complete. Toward increased understanding, we require information about how gel micro-structure is related to gel composition. Such information is useful for efficient design of new gels to achieve specific applications.

Although particular pores do not exist in gels and although the real gel structure is determined by local differences in the network density, an apparent pore-size distribution can be regarded as an index of the pore structure. The main concern of previous work, e.g. Warren et al. (6), has been with commercially available and highly cross-linked gels. Only very few systematic data are available on the influence of gel composition on pore structure.

Determining the pore structure of a swollen gel is a difficult task because that structure is highly sensitive to the strong interactions between the gel matrix and the surrounding solution. Common methods such as mercury porosimetry or nitrogen adsorption (7) are not suitable for measuring gel micro-structure because hydrogels are swollen in an aqueous solution and therefore the pores are not accessible to mercury or nitrogen. The results presented here were measured by an indirect method based on the mixed-solute-exclusion (MSE) method introduced by Kuga (8, 9).

Using the MSE method, stock solutions of probe solutes at known concentration (which cover a substantial range of molecular weight) 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. The difference in solute concentration between the stock solution and the equilibrated solution surrounding the gels is measured by gel-permeation chromatography (GPC). The decrease in solute concentration relative to the initial stock-solute concentration is used for calculating the gel's pore-size distribution.

To maximize the size-exclusion effect relative to the molecular attraction/repulsion effect, experiments were performed with solutes that do not have specific interactions with the charged polymer matrix. To investigate the influence of different probe solutes, two solute series, a poly-(ethylene glycol)/poly-(ethylene oxide) series and a Dextran/oligo-saccharides series, were used in separate experiments. Our measurements were made with polyelectrolyte gels polymerized from acrylamide, the cationic comonomer MAPTAC and BIS as cross-linker, as discussed later. Polyacrylamide hydrogels

are of particular interest both as a model system and due to applications as media for separation processes.

The composition of the hydrogel is determined by three concentration parameters:

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

%T 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 gives the concentration of chemical cross-links of polymer strands. Raising %C increases the number of 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 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.

It is the objective of this investigation to determine the pore-size distribution of cationic polyacrylamide hydrogels of different compositions (varying %T, %C and %M) at the same swelling capacity (27.8 ± 0.7 g swollen gel / g dry gel), by varying the ionic strength of the surrounding solution. Four different

polyelectrolyte hydrogels were prepared by aqueous free-radical reaction of acrylamide (AAm) copolymerized with the cationic [(Methacrylamido)propyl]-trimethylammonium chloride (MAPTAC). The cross-linking agent N,N'-methylene(bisacrylamide) (BIS) was added to obtain a network structure (10). The compositions synthesized were:

15 %T, 0.3 %C, 4.0 %M

35 %T, 0.3 %C, 4.0 %M

15 %T, 1.0 %C, 4.0 %M

15 %T, 0.3 %C, 1.5 %M

The swelling capacities were measured in pure water and at different ionic strengths of the surrounding solution, which varied from 10^{-3} to 10^{-1} M NaN_3 . Sodium azide (NaN_3) also served as an antibacterial agent preventing the destruction of solutes and gels by bacteria (11).

Theoretical Basis for the Determination of an Effective Pore-Size Distribution

The method used to obtain the pore-size distribution of hydrogels is based on the mixed-solute-exclusion (MSE) method (8) modified by Kremer (11). The MSE method studies the distribution of a series of probe solutes between the gel and the surrounding solution. 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 prior to concentration measurements. The method is summarized below. Further details are given elsewhere (11, 12).

The initial total mass of the gel samples (m'_{GS}) in the swollen state is composed of the cross-linked polymer network (m_{PN}), the imbibed liquid ($m'_{L,imb}$) and the excess liquid ($m_{L,exc}$) which adheres to the surface of the gel but does not contribute to the imbibed liquid:

$$m'_{GS} = m_{PN} + m'_{L,imb} + m_{L,exc} \quad (1)$$

Contacting the stock solution with the gel samples results in an initial uneven distribution of pore solutes in the entire system. Due to the porous structure of the gel, the equilibrium concentration of the solutes in the gel phase is smaller than that in the surrounding solution. This difference provides a driving force for the imbibed liquid to dilute the solution to achieve osmotic equilibrium. Therefore swelling of the gel in equilibrium with the probe solution gives:

$$m''_{GS} = m_{PN} + m''_{L,imb} \quad (2)$$

The amount of liquid imbibed by the hydrogel can be divided into an accessible ($m''_{acc}(MW)$) and a non-accessible fraction ($m''_{non-acc}(MW)$) to solutes of molecular weight MW:

$$m''_{L,imb} = m''_{acc}(MW) + m''_{non-acc}(MW) \quad (3)$$

The difference between the initial imbibed liquid ($m'_{L,imb}$) and the imbibed liquid in equilibrium ($m''_{L,imb}$) with the solute solution represents the expelled liquid:

$$m_{exp} = m'_{L,imb} - m''_{L,imb} \quad (4)$$

At the beginning of the experiment, the weight fraction of a probe solute of molecular weight MW ($m_p(MW)$) changes because the excess liquid ($m_{L,exc}$), the expelled liquid (m_{exp}) and the accessible part of the imbibed liquid ($m''_{acc}(MW)$) contribute to a dilution of the surrounding solution. The initial weight fraction $w'(MW)$ is given by:

$$w'(MW) = \frac{m_p(MW)}{m_s + \sum m_p(MW)} \sim \frac{m_p(MW)}{m_s} \quad (5)$$

where m_s is the mass of solvent. When the gel is added to the solution, the weight fraction $w''(MW)$ becomes:

$$w''(MW) = \frac{m_p(MW)}{m_s + m''_{acc}(MW) + m_{exp} + m_{L,exc} + \sum m_p(MW)} \quad (6)$$

The dilution ratio is the equilibrium concentration divided by the stock concentration, which can be expressed simply by ignoring the mass of the probe solutes in the solution ($\sum m_p(MW) \sim 0$):

$$\frac{w''(MW)}{w'(MW)} = \frac{m_S}{m_S + m''_{acc}(MW) + m_{exp} + m_{L,exc}} \quad (7)$$

Combination of Eq. (7) with Eqs. (1) - (4) yields the non-accessible mass:

$$m''_{non-acc}(MW) = m'_{GS} - m_{PN} + \left[1 - \frac{w'(MW)}{w''(MW)}\right] m_S \quad (8)$$

The dilution ratio $\frac{w''(MW)}{w'(MW)}$ is determined by gel chromatography. 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 size-exclusion chromatography (SEC) (7). The experimentally determined relationships between molecular weight MW and hydrodynamic radius r_H of the solutes in water are given in the following equations (7):

$$\text{Dextran} \quad r_H(\text{\AA}) = 0.271 MW^{0.498} \quad (9)$$

$$\text{PEG} \quad r_H(\text{\AA}) = 0.255 MW^{0.517} \quad (10)$$

$$\text{PEO} \quad r_H(\text{\AA}) = 0.166 MW^{0.573} \quad (11)$$

Using Eqs. (9) - (11), $m''_{non-acc}(MW)$ can be converted into $m''_{non-acc}(r_H)$, which is interpreted as the cumulative pore-size distribution of the gel sample (8).

We define the distribution coefficient $K(r)$ as the ratio of the accessible volume (V_{acc}) of imbibed liquid for a solute of radius r to the total volume of imbibed liquid and using the assumption earlier mentioned:

$$K(r) = \frac{V_{acc}(r)}{V_{total}} \sim \frac{m_{acc}(r)}{m_{total}} \quad (12)$$

The accessible mass ($m_{acc}(r)$) and the total mass of imbibed liquid (m_{total}) are defined by:

$$m_{acc}(r) = m_{total} - m_{non-acc}(r) \quad (13)$$

$$m_{total} = \lim_{r \rightarrow \infty} m_{non-acc}(r) = m_{non-acc,\infty} \quad (14)$$

Combination of Eqs. (12) - (14) yields:

$$K(r) = \frac{m_{non-acc,\infty} - m_{non-acc}(r)}{m_{non-acc,\infty}} \quad (15)$$

$K(r)$ is the integral distribution coefficient which is calculated from the experimentally-measured non-accessible amount of imbibed liquid by Eq. (8).

Eq. (8) 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. This relationship may be 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 throughout within the accessible pores with equal probability as long as the solute has a finite volume (9). This hindered diffusion effect, known as the wall effect (13), is considered in this work. 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. The expression for the differential distribution coefficient $K(R,r)$ used in this work was derived by Casassa et al. (14-16). Casassa et al. used the model of Brownian motion for linear and branched polymers to calculate their 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 (14):

$$K(R,r) = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\left(\frac{(2n+1)\pi}{2} \frac{r}{R}\right)^2} \quad (16)$$

Although this model does not directly correspond to the real structure of hydrogels, Eq. (16) with $r = r_H$ (the hydrodynamic radius) 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 (11) where $K_{\text{exper}}(r)$ and $K(r)$ are almost identical.

The differential pore-size distribution, denoted by $f(R)$, is defined so that $f(R) dR$ represents the fraction of the total pore volume containing pores with radii between R and $R+dR$.

To obtain the differential pore-size distribution from the experimental data obtained here, we must solve for $f(R)$ using the equation:

$$K(r) = \int_0^{R_m} K(R,r) f(R) dR \quad (17)$$

The left-hand side of Eq. (17) represents the measured overall distribution coefficient $K(r)$ as a function of molecular radius r . The right-hand side consists of the differential distribution coefficient $K(R,r)$ as a function of r and R and the desired pore-size distribution $f(R)$. The differential distribution coefficient $K(R,r)$ is provided by the Casassa model (cf. Eq. (16)).

Eq. (17) is the well known inhomogeneous Fredholm equation of the first kind, which is generally solved numerically. For that purpose we use the computer program CONTIN developed and maintained by Provencher (17, 18). For details see Kremer et al. (11, 12).

Experimental Section

Measurements were made for the pore-size distributions of four cationic polyacrylamide hydrogels of different compositions maintained at the same swelling capacity by varying the ionic strength of the surrounding solution. A modification of the mixed-solute-exclusion method (8) was used. Sodium azide (NaN_3) was used to vary the ionic strength and also served as an antibacterial agent preventing the destruction of solutes and gels by bacteria (12). Due to the limited resolving power of the chromatographic equipment (the size-exclusion column had only limited separation power for the probe solutes used (11)), several solutions, each containing not more than three probe solutes, had to be prepared. To assure that size effects alone are responsible for the observed results, two solute series, a poly-(ethylene glycole)/(poly-(ethylene oxide) (PEO/PEG) series and a Dextran/oligosaccharides series were used in separate experiments.

Materials

Acrylamide (AAM) and N,N'-methylenebis(acrylamide) (BIS), both electrophoresis grade, 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; Ammonium persulfate (APS) was purchased from Eastman Kodak, Rochester, NY. The properties of the probe solutes (PEO/PEGs and Dextrans) are summarized in Table 1. 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) before use.

Gel Synthesis

The gels were synthesized using the method described by Baker et al. (10, 19). The gels were prepared by free-radical solution copolymerization of AAm and MAPTAC, using BIS as the cross-linker and 0.025 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 NaN₃ solution. The gels were stored at about 6 °C and rinsed several times. Four acrylamide-based hydrogels were synthesized and used for the pore-size distribution investigations; characterization parameters for these gels are given at the end of the Introduction.

Swelling Measurements

Before pore-size distribution studies, it was necessary to measure the swelling capacities of the gels at varying ionic strengths of the surrounding solution. Therefore, the four different polyelectrolyte hydrogels were put into Nanopure water and five different NaN₃-solutions (0.001 , 0.005 , 0.01 , 0.05 and 0.1 M) and allowed to swell to equilibrium at room temperature. For each kind of gel and solution, beakers with 10 gels and 50 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). The solutions were changed at least three times. Equilibrium was reached after approximately one week; approach to

equilibrium was monitored by mass measurements (using a Mettler HK 160 balance with uncertainty ± 0.0001 g, Mettler, Giessen, Germany) of the swollen hydrogels. Once equilibrium was attained, the swelling ratios in water and the sodium-azide solutions were determined for each hydrogel. Equilibrated gel disks were weighed, dried at room temperature 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 triplicate.

Pore-size distribution measurements

Stock solutions were prepared by dissolving two or three probe solutes for the Dextran series and the PEO/PEG series, respectively, into the sodium-azide solutions obtained from the swelling measurements. The split into eight different solutions was necessary because of the limited resolving power of the chromatographic equipment. The concentrations of the solutions are given in Tables 2 and 3.

For each combination of gel and solution, two beakers were used to determine the experimental error and to minimize the number of beakers. About 6 g of swollen gels (twenty and ten gels, respectively) and an amount of stock solution 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, four additional beakers were prepared to contact the most dense gel (35 %T 0.3 %C 4.0 %M) with the largest probe solutes of each series (PEO 4,000,000 and Dextran 2,000,000). 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 solution, thoroughly washed several times with Nanopure water to remove essentially all probe solutes and salt and subsequently dried and weighed to determine the mass of the polymer network and hence the swelling capacity. The equilibrated solutions were first filtered (filter paper No 40, Whatman, Maidstone, England) to remove gel particles which would affect the chromatographic measurements. After filtering, the solutions and the corresponding stock solutions were alternately chromatographed at least three times. For details of the equipment see Kremer et al. (11). This procedure of alternate measurements of stock solutions and equilibrated solutions was necessary to obtain accurate chromatographic results, because slight changes in the GPC equipment (state of column, state of mobile phase, temperature) greatly affect the results.

Results and Discussion

Figure 1 shows the swelling capacities of the polyacrylamide-based hydrogels. The uncertainties of measured swelling capacities were generally less than 4.5 %. The swelling capacity rises with decreasing cross-link density (%C) and initial total monomer concentration (%T). On the other hand, increasing charge density (%M) has stronger influence; it raises the swelling capacities enormously, especially at low salt concentration in the surrounding solution. 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 gels deswell.

Figures 2 to 5 show the size-exclusion curves for all hydrogels investigated here. The lower limit, the non-accessible volume of zero, could be confirmed by the gels 15 %T 0.3 %C 4.0 %M (Figure 2) and 15 %T 0.3 %C 1.5 %M (Figure 3). However, some of the data points lie in the negative range, due to the limited accuracy of the measurements, especially for smaller probe solutes. Despite the deviations of the measurements, the lower limit of the non-accessible volume for these two gels is independent of solute radius below about 5 Å, molecules with radii smaller than 5 Å are able to migrate into the entire hydrogel pore structure.

However, the gels with higher initial total monomer concentration (35 %T 0.3 %C 4.0 %M, Figure 4) and higher cross-linker concentration (15 %T 1.0 %C 4.0 %M, Figure 5) have pores which are non-accessible even to the smallest probe solutes used, i.e. the network of these gels is very dense, giving pores with very small radii.

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 5 represent the swelling capacities of the hydrogels in equilibrium with the probe solutes; the data points represent the results of the GPC measurements. The deviations of both methods (max. 8.4%) agree within the experimental uncertainties (GPC measurements about 5 % and weighing about 3 %). For the gels with lower total monomer concentration (15 %T) and lower cross-linker concentration (0.3 %C), solutes of radii greater than about 200 Å are totally excluded. However, the gels with 1 %C and 35 %T are accessible to larger molecules, up to about 250 Å and 350 Å, respectively.

In general, the deviations of the measurements using the PEO/PEG series are smaller than those using the Dextran series. But there is no significant difference in the results using either of the probe-solute series. Hence, as expected, size effects alone are responsible for the observed partitioning.

Figure 6 shows the calculated pore-size distributions for all hydrogels. Table 4 gives statistical results such as 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). The gels with lower initial total monomer and cross-linker concentration (15 %T and 0.3 %C) show only little deviations; the mode varies from 47.1 to 43.6 Å and the variance from $7.91 \cdot 10^3$ to $7.41 \cdot 10^3$ Å². There is no influence of the initial concentration of cationic comonomer MAPTAC on the pore-size distribution. On the other hand, there is a strong influence of %T and %C on the pore size. With higher concentration of cross-linker and total monomer, the mode values shrink from 47.1 to 35.7 and 20.4 Å, respectively. The variance rises from $7.91 \cdot 10^3$ to $1.14 \cdot 10^4$

and $1.62 \cdot 10^4 \text{ \AA}^2$. These results indicate that the gels with higher %T and higher %C have a more uneven network with some local very dense network and very small pore radii but also with a broader pore-size distribution as shown by the large variances. Such micro structural inhomogeneities in polyacrylamide gels were also found by Cohen et al. (20). They assumed that these inhomogeneities arise from stationary density variations due to regions of higher polymer concentration as a result of clustering of the cross-linking agent BIS.

The observed influence of initial concentration of total monomer and cross-linker on the pore-size distribution is in good agreement with the results of Vashegani-Faharani et al. (21), who investigated the swelling and size-exclusion behavior of acrylamide and N-isopropylacrylamide hydrogels. They also found that the total monomer concentration at gel formation is the most important variable in determining the gel's size-exclusion properties. New gels can be more efficiently designed with pores closer to the desired pore-size distribution by varying design parameters %T and %C.

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Nomenclature

AAm	acrylamide	
APS	ammonium persulfate	
BIS	N,N'-methylenebis(acrylamide)	
CS	swelling capacity	[g/g]
f(R)	differential pore-size distribution	[Å ⁻¹]
g(R)	cumulative pore-size distribution	[-]
GPC	gel-permeation chromatography	
K(r)	integral distribution coefficient	[-]
K(R,r)	differential distribution coefficient	[-]
m	mass	[g]
M	molarity	[mol/l]
MAPTAC	[(methacrylamido)propyl]trimethylammonium chloride	
MW	molecular weight	[g/mol]
n	variable	
NaN ₃	sodium azide	
PEG	poly-(ethylene glycol)	
PEO	poly-(ethylene oxide)	
r	solute radius	[Å]
R	pore radius	[Å]
SEC	size-exclusion chromatography	
V	volume	[Å ³]
%C	per cent of cross-linker	[mol/mol]
%M	per cent of MAPTAC	[mol/mol]
%T	per cent of total monomer	[g/ml]

Subscripts

acc	accessible
exp	expelled
exper	experimental
GS	gel in swollen state
H	hydrodynamic
L _{exc}	excess liquid
L _{imb}	imbibed liquid
max	maximum
non-acc	non-accessible
P	probe solute
PN	polymer network
S	solvent
total	total

Superscripts

'	initial
"	in equilibrium

References

1. T. Tanaka, *Sci. Am.*, 244, 124 (1981).
2. T. Tanaka, *Encyclopedia of Polymer Science and Engineering*, Vol. 7, 2nd Edition, ed. by H. F. Mark, N. M. Bikales, C. G. Overberger G. Menges and J. L. Kroschwitz, John Wiley & Sons, New York, NY, 1986, pp. 514-531.
3. D. DeRossi, K. Kajiwarra, Y. Osada and A. Yamanchi (editors), *Polymer Gels, Fundamentals and Biomedical Applications*, Plenum Press, New York, NY, 1991.
4. S. W. Kim, Y. H. Bae, and T. Okano, *Pharmac. Res.*, 9, 283 (1992).
5. J. P. Montheard, M. Chatzopoulos and D. Chappard, *J. Macromol. Sci. - Rev. Macromol. Chem. Phys.*, C32, 1, 1 (1992).
6. F. V. Warren and B. A. Bidlingmeyer, *Anal. Chem.*, 56, 950 (1984).
7. L. Hagel, *Aqueous-Size-Exclusion Chromatography*, *Journal of Chromatography Library - Volume 40*, ed. by P.L. Duplin, Elsevier, Amsterdam, 1988, Chapt. 5, pp. 119-155.
8. S. Kuga, *J. Chromatogr.*, 206, 449 (1981).

9. S. Kuga, Aqueous-Size-Exclusion Chromatography, Journal of Chromatography Library - Volume 40, ed. by P.L. Dublin, Elsevier, Amsterdam, 1988, Chapt. 6, pp. 157-170.
10. J. P. Baker, Polyacrylamide Copolymer Gels: Synthesis, Swelling, Microstructure, M. S. Thesis, University of California, Berkeley, CA, 1989.
11. M. Kremer and J. M. Prausnitz, LBL-Report No. 32845, Lawrence Berkeley Laboratory, Berkeley, CA, 1992.
12. M. Kremer, E. Pothmann, T. Rössler, J. P. Baker, A. Yee, H. W. Blanch and J. M. Prausnitz, LBL-Report No. 34534, Lawrence Berkeley Laboratory, Berkeley, CA, 1993..
13. M. Kubin and S. Vozka, J. Polym. Sci., Polym. Symp., 68, 209 (1980).
14. E. F. Casassa, Polym. Letters, 5, 773 (1967).
15. E. F. Casassa and Y. Tagami, Macromolecules, 2, 14 (1969).
16. E. F. Casassa, Sep. Sci., 6, 305 (1971).
17. S. W. Provencher, Makromol. Chem., 180, 201 (1979).
18. S. W. Provencher, Technical Report EMBL-DA07 CONTIN (Version 2) User's Manual (March 1984).

19. H. H. Hooper, J. P. Baker, H. W. Blanch and J. M. Prausnitz, *Macromolecules* 23, 1096 (1990).
20. Y. Cohen, O. Ramen, I.J. Kopelman and S. Mizrahi, *J. Polym. Sc.*, 30, 1055 (1992)
21. E. Vasheghani-Farahani, D. G. Cooper, J. H. Vera and M. E. Weber, *Chem. Eng. Sci.*, 47, 31 (1992).

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Table 1: Probe solutes, molecular weight, hydrodynamic radius and supplier

Probe Solute	Molecular Weight Weight (GPC) Mw	Molecular Weight Number (GPC) Mn	Molecular Weight Peak (GPC) Mp	Mw/Mn	r_H Å	Supplier
PEO 4,000,000	-	-	-	-	1,007.1	Aldrich
PEO 1,000,000	832,700	876,400	881,500	1.06	423.4	Sc. Polymer
PEO 500,000	444,900	432,300	447,300	1.03	287	Sc. Polymer
PEO 200,000	305,400	285,600	293,000	1.08	225.4	Sc. Polymer
PEO 60,000	62,600	61,400	64,400	1.02	94.5	Sc. Polymer
PEG 20,000	19,700	14,700	19,000	1.34	41.6	Sc. Polymer
PEG 10,000	10,900	9,200	10,900	1.19	31.2	Sc. Polymer
PEG 3,000	3,700	2,890	3,140	1.06	16.4	Sc. Polymer
PEG 600	629	574	625	1.1	7.1	Sc. Polymer
PEG 450	420	370	400	1.14	5.6	Sc. Polymer
PEG 200	229	206	210	1.11	4	Sc. Polymer
DEX 2,000,000	-	-	-	-	372.3	Sigma
DEX 670,000	667,800	332,800	-	2.01	181.3	Fluka
DEX 150,000	147,600	100,300	-	1.47	92.3	Fluka
DEX 80,000	80,900	55,500	-	1.47	68.6	Fluka
DEX 50,000	48,600	35,600	-	1.36	54.1	Fluka
DEX 12,000	11,600	8,110	-	1.43	26.2	Fluka
Raffinose	-	-	-	1	6	Fischer
Sucrose	-	-	-	1	5	Fischer
Glucose	-	-	-	1	3.6	Aldrich

Table 2: Stocksolutions Dextran series

Solution	M NaN ₃	Solute	Weight %	Solution	M NaN ₃	Solute	Weight %
D11	0.0245	150,000	0.2	D31	0.0245	80,000	0.2
		12,000	0.1			Sucrose	0.07
		Raffinose	0.06				
D12	0.0078	150,000	0.17	D32	0.0078	80,000	0.2
		12,000	0.1			Sucrose	0.07
		Raffinose	0.06				
D13	0.005	150,000	0.12	D33	0.005	80,000	0.2
		12,000	0.1			Sucrose	0.07
		Raffinose	0.06				
D14	0.0023	150,000	0.12	D34	0.0023	80,000	0.2
		12,000	0.1			Sucrose	0.07
		Raffinose	0.06				
D21	0.0245	670,000	0.2	D41	0.0245	2,000,000	0.2
		50,000	0.15				
		Glucose	0.06				
D22	0.0078	670,000	0.2	D42	0.0078	2,000,000	0.2
		50,000	0.15				
		Glucose	0.06				
D23	0.005	670,000	0.18	D43	0.005	2,000,000	0.2
		50,000	0.15				
		Glucose	0.06				
D24	0.0023	670,000	0.13	D44	0.0023	2,000,000	0.2
		50,000	0.15				
		Glucose	0.06				

Table 3: Stocksolutions PEO/PEG series

Solution	M NaN ₃	Solute	Weight %	Solution	M NaN ₃	Solute	Weight %
P11	0.0245	200,000	0.19	P31	0.0245	1,000,000	0.25
		3,000	0.4			20,000	0.6
P12	0.0078	200,000	0.25	P32	0.0078	1,000,000	0.25
		3,000	0.4			20,000	0.6
P13	0.005	200,000	0.25	P33	0.005	1,000,000	0.25
		3,000	0.4			20,000	0.6
P14	0.0023	200,000	0.25	P34	0.0023	1,000,000	0.25
		3,000	0.4			20,000	0.6
P21	0.0245	500,000	0.19	P41	0.0245	4,000,000	0.2
		10,000	0.5			60,000	0.25
P22	0.0078	500,000	0.25	P42	0.0078	4,000,000	0.2
		10,000	0.5			60,000	0.25
P23	0.005	500,000	0.25	P43	0.005	4,000,000	0.2
		10,000	0.5			60,000	0.25
P24	0.0023	500,000	0.25	P44	0.0023	4,000,000	0.2
		10,000	0.5			60,000	0.25
		200	0.8			600	0.7

Table 4: Modes, means and variances of the calculated pore-size distributions. Results of solving the Fredholm equation (Eq. (17)) with the computer program CONTIN.

Gel	Pore Radius		
	Mode [Å]	Mean [Å]	Variance [Å ²]
15%T 0.3%C 1.5%M	47.1	74.6	7.91*10 ³
35%T 0.3%C 4.0%M	20.4	94.9	1.62*10 ⁴
15%T 1.0%C 4.0%M	35.7	86.0	1.14*10 ⁴
15%T 0.3%C 4.0%M	43.6	71.9	7.41*10 ³

Supplementary material for:

Pore-Size Distributions of Cationic Polyacrylamide Hydrogels of Different Compositions Maintained at the Same Swelling Capacity

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

Gel	NaN_3 conc.	Swell Capacity			Error	
		average	min	max	std	std/av(%)
35/0.3/4.0	pure water	44.8	43.6	45.9	1.01	2.26
	0.001 M	37.7	37.3	38.3	0.36	0.95
	0.005 M	24.2	22.9	25.2	0.9	3.74
	0.010 M	19.8	19.3	20.5	0.43	2.18
	0.050 M	11.7	11.5	11.9	0.15	1.25
	0.100 M	10.3	10.1	10.4	0.11	1.03
15/1.0/4.0	pure water	54.7	53.5	55.8	1.22	2.23
	0.001 M	44.7	43.2	47.3	2.01	4.49
	0.005 M	30.4	28.8	31.5	1.2	3.96
	0.010 M	24.4	24.2	24.6	0.14	0.59
	0.050 M	13.4	13.3	13.7	0.19	1.43
	0.100 M	11.4	11.3	11.4	0.07	0.59
15/0.3/4.0	pure water	219.5	218.5	221	1.12	0.51
	0.001 M	123.6	122.3	124.7	1.03	0.83
	0.005 M	61.5	60.7	62.6	0.78	1.27
	0.010 M	42.6	42.4	42.8	0.19	0.44
	0.050 M	21.5	21.3	22.1	0.27	1.24
	0.100 M	17	16.8	17.1	0.15	0.87
15/0.3/1.5	pure water	111.5	109.7	113.6	2.03	1.82
	0.001 M	65.6	61.6	68.1	3.06	4.66
	0.005 M	36	34.7	40.6	2.26	6.28
	0.010 M	27.1	22	30.8	3.16	11.66
	0.050 M	17.2	17.1	17.3	0.09	0.5
	0.100 M	15.1	15	15.1	0.04	0.25

Table 2: Measurements (for the probe solute series PEO/PEG and Dextran) and calculations (CONTIN) of the non-accessible mass [g/g dry gel] for the polyacrylamide hydrogel 15 %T 0.3 %C 4.0 %T.

r[Å]	Non-accessible Mass [g/g]		Calc. CONTIN
	PEO/PEG	Dextran	
4.05E+00	-1.39E+00		-6.70E-01
5.65E+00	-8.36E-01		4.47E-01
7.11E+00	1.04E+00		1.46E+00
1.64E+01	8.28E+00		7.43E+00
3.12E+01	1.58E+01		1.47E+01
4.16E+01	1.91E+01		1.83E+01
9.45E+01			
2.25E+02	2.71E+01		2.79E+01
2.87E+02	2.74E+01		2.79E+01
4.23E+02	2.72E+01		2.79E+01
1.01E+03	2.77E+01		2.79E+01
3.60E+00		3.39E-01	-9.77E-01
4.95E+00		-3.35E-01	-2.79E-02
6.01E+00		4.34E-01	7.03E-01
2.62E+01		7.64E+00	1.25E+01
5.41E+01		2.25E+01	2.14E+01
6.86E+01		2.49E+01	2.38E+01
9.23E+01		2.65E+01	2.60E+01
1.81E+02		2.74E+01	2.78E+01
3.72E+02		2.85E+01	2.79E+01

Table 3: Measurements (for the probe solute series PEO/PEG and Dextran) and calculations (CONTIN) of the non-accessible mass [g/g dry gel] for the polyacrylamide hydrogel 15 %T 0.3 %C 1.5 %T.

r[Å]	Non-accessible Mass [g/g]		Calc. CONTIN
	PEO/PEG	Dextran	
4.05E+00	-3.20E+00		-7.12E-01
5.65E+00	1.42E+00		3.76E-01
7.11E+00	-6.06E-01		1.36E+00
1.64E+01	9.78E+00		7.21E+00
3.12E+01	1.31E+01		1.45E+01
4.16E+01	1.95E+01		1.81E+01
9.45E+01			
2.25E+02	2.73E+01		2.85E+01
2.87E+02	2.75E+01		2.85E+01
4.23E+02	2.74E+01		2.85E+01
1.01E+03	2.66E+01		2.85E+01
3.60E+00		1.75E+00	-1.02E+00
4.95E+00		-4.49E+00	-8.54E-02
6.01E+00		-5.01E+00	6.21E-01
2.62E+01		7.15E+00	1.23E+01
5.41E+01		2.23E+01	2.14E+01
6.86E+01		2.45E+01	2.39E+01
9.23E+01		2.79E+01	2.63E+01
1.81E+02		2.96E+01	2.84E+01
3.72E+02		2.74E+01	2.85E+01

Table 4: Measurements (for the probe solute series PEO/PEG and Dextran) and calculations (CONTIN) of the non-accessible mass [g/g dry gel] for the polyacrylamide hydrogel 35 %T 0.3 %C 4.0 %T.

r[Å]	Non-accessible Mass [g/g]		Calc. CONTIN
	PEO/PEG	Dextran	
4.05E+00	2.93E+00		2.40E+00
5.65E+00	3.31E+00		3.67E+00
7.11E+00	4.13E+00		4.77E+00
1.64E+01	1.09E+01		1.03E+01
3.12E+01	1.86E+01		1.60E+01
4.16E+01	2.20E+01		1.88E+01
9.45E+01			
2.25E+02	2.92E+01		3.04E+01
2.87E+02	3.01E+01		3.07E+01
4.23E+02	3.10E+01		3.08E+01
1.01E+03	3.06E+01		3.08E+01
3.60E+00		1.50E+00	2.04E+00
4.95E+00		8.23E+00	3.14E+00
6.01E+00		6.09E+00	3.96E+00
2.62E+01		1.04E+01	1.43E+01
5.41E+01		2.11E+01	2.14E+01
6.86E+01		2.53E+01	2.36E+01
9.23E+01		2.80E+01	2.61E+01
1.81E+02		2.86E+01	2.99E+01
3.72E+02		3.08E+01	3.08E+01

Table 5: Measurements (for the probe solute series PEO/PEG and Dextran) and calculations (CONTIN) of the non-accessible mass [g/g dry gel] for the polyacrylamide hydrogel 15 %T 1.0 %C 4.0 %T.

r[Å]	Non-accessible Mass [g/g]		Calc. CONTIN
	PEO/PEG	Dextran	
4.05E+00	5.12E+00		3.68E+00
5.65E+00	1.76E+00		4.70E+00
7.11E+00	3.12E+00		5.60E+00
1.64E+01	7.20E+00		1.05E+01
3.12E+01	1.87E+01		1.61E+01
4.16E+01	2.21E+01		1.90E+01
9.45E+01			
2.25E+02	2.89E+01		2.91E+01
2.87E+02	2.92E+01		2.92E+01
4.23E+02			
1.01E+03	2.93E+01		2.92E+01
3.60E+00		5.11E+00	3.38E+00
4.95E+00		7.83E+00	4.26E+00
6.01E+00		1.05E+01	4.92E+00
2.62E+01		1.01E+01	1.45E+01
5.41E+01		2.10E+01	2.15E+01
6.86E+01		2.61E+01	2.37E+01
9.23E+01		2.92E+01	2.60E+01
1.81E+02		2.90E+01	2.89E+01
3.72E+02		2.90E+01	2.92E+01

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