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Summary

Cationic HEMA-based hydrogels were synthesized by copolymerizing HEMA with [(methacrylamido)propyl]trimethylammonium chloride (MAPTAC). Swelling equilibria were measured in pure water and in aqueous sodium chloride solutions. Hydrogel swelling is an increasing function of the MAPTAC content. A Flory-type swelling model using a concentration-dependent Flory $\chi$ parameter semi-quantitatively describes poly(HEMA co-MAPTAC) hydrogel swelling in aqueous sodium chloride.

Experimental Section

Materials. 2-Hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) were purchased from Polysciences. [(Methacrylamido)propyl]trimethylammonium chloride (MAPTAC) (50% solution in water) was purchased from Aldrich. Ammonium persulfate (APS) (certified ACS grade) was purchased from Fisher. All reagents were used as received. Water was distilled, then filtered and deionized with a Barnstead Nanopure II unit.

Synthesis. Clear, homogeneous HEMA-based hydrogels with cationic character were synthesized by the free-radical copolymerization of HEMA, MAPTAC and the crosslinking monomer EGDMA. APS was used to initiate polymerization; an initiator concentration of 1 mg/ml was used in the synthesis. Water served as the diluent in the synthesis.

A series of hydrogels was prepared such that the mole percent crosslinker on a diluent-free basis (%C) and the total initial monomer concentration (w/v) (%T) in the reaction mixture were fixed at 1.0 and 65, respectively. The mole percent MAPTAC in the reaction mixture on a diluent-free basis (%MAPTAC) was varied from zero to 6. The reaction mixture was poured into 10 x 75 mm Pyrex test tubes. The test tubes were immersed in a water bath at 50°C for 24 hours. The hydrogels were liberated from the test tubes, sliced
into 3 mm-thick disks, then soaked in an excess of water to extract the soluble fraction and initiator residues.

**Swelling.** Equilibrium-swelling measurements were conducted in water and in aqueous NaCl solutions. We report the swelling ratio, which is the mass ratio of swollen hydrogel to dry hydrogel (Tables 1 and 2).

**Swelling Theory**

Measured swelling equilibria are compared with predictions from a Flory-type swelling model. The Flory-type swelling model used for this work contains terms for polymer/solvent mixing (Flory-Huggins theory), network elasticity (phantom theory) and ion/solvent mixing (ideal Donnan equilibria). The swelling model is discussed in detail elsewhere (Baker, 1993; Baker et al., 1993a,b).

**Results and Discussion**

Figure 1 shows swelling equilibria in pure water for the %MAPTAC-varying poly(HEMA co-MAPTAC) hydrogels. Swelling increases with rising %MAPTAC. The fixed-cationic charges on the network are accompanied by osmotically-active counterions. Since the water contains no added ions, the unequal distribution of mobile ions between the hydrogel and the water provides for a net osmotic pressure which causes water to enter the hydrogel.

The nominal values of the hydrogel-preparation parameters (65 %T, 1.0 %C, 0 - 6 %MAPTAC) and the measured swelling ratios in water were inserted into the Flory-type swelling model; Flory χ parameters were fit to the data. Table 1 provides the results of the fits. As expected, the χ parameter decreases with rising %MAPTAC indicating that the network polymer is rendered more hydrophilic as its charge density increases. A best-fit exponential function was derived for χ as a function of swelling ratio for use in calculations.
described below. For the uncharged hydrogel, we calculated a value of 0.82 for \( \chi \); other workers have obtained similar values (Peppas and Moynihan, 1987).

Figure 2 shows swelling equilibria in aqueous sodium chloride for the \( \% \text{MAPTAC} \)-varying hydrogels. Hydrogel swelling declines with rising NaCl concentration. The added NaCl renders more equal the distribution of osmotically-active mobile ions between hydrogel and external solution. This levelling of the distribution of mobile ions removes the main driving force for swelling; thus swelling declines. Also shown in Figure 2 are predictions from the Flory-type swelling model including the concentration-dependent Flory \( \chi \) parameter. Fair agreement between theory and experiment is obtained.

Acknowledgments
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References


Figure 1. Swelling ratios (g swollen gel/g dry gel) in water for poly(HEMA co-MAPTAC) hydrogels prepared with varying %MAPTAC. The hydrogels were 65 %T and 1.0 %C.
Figure 2. Comparison of measured and predicted swelling equilibria in aqueous NaCl for \%MAPTAC-varying poly(HEMA co-MAPTAC) hydrogels.
Tables

**Table 1.** Swelling ratios in pure water for poly(HEMA co-MAPTAC) hydrogels. Also listed are Flory $\chi$ parameters fitted to the swelling data.

<table>
<thead>
<tr>
<th>%MAPTAC</th>
<th>Swelling ratio$^a$</th>
<th>$\chi$</th>
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<tbody>
<tr>
<td>0</td>
<td>1.66</td>
<td>0.816</td>
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<tr>
<td>2</td>
<td>2.24</td>
<td>0.694</td>
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<tr>
<td>4</td>
<td>3.20</td>
<td>0.638</td>
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<tr>
<td>6</td>
<td>4.44</td>
<td>0.633</td>
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</table>

$^a$Swelling ratio = (g swollen gel)/(g dry gel)
Table 2. Swelling ratios\textsuperscript{a} in aqueous NaCl for %MAPTAC-varying poly(HEMA co-MAPTAC) hydrogels.

<table>
<thead>
<tr>
<th>M NaCl</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
</tr>
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<tr>
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<td>1.6383</td>
<td>1.7554</td>
<td>1.872</td>
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\textsuperscript{a}Swelling ratio = (g swollen gel)/(g dry gel)