Distribution of Phenols in Thermoresponsive Hydrogels

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ABSTRACT: The effect of three hydrotropic molecules, phenol, resorcinol and phloroglucinol, on the thermodynamic equilibrium and the dynamics of poly(*N*-isopropylacrylamide) (PNIPA) hydrogels is reported. With increasing hydroxyl number of this molecular sequence both the depression of the temperature and the width of the volume phase transition (VPT) increase, reflecting the nonuniform distribution of these molecules inside the gel. Small-angle X-ray scattering detects no notable change in the local structure of the polymer chains in the presence of phenol. Dynamic light scattering observations, however, show that phloroglucinol, unlike phenol and resorcinol, produces a small but significant decrease in the mobility of the polymer in the solvent. Isothermal microcalorimetry reveals an anomalous increase in the exothermic enthalpy of mixing just below the transition, both with phenol and phloroglucinol, which indicates a pretransition state in the gel in which the aromatic molecules partly replace the bound water. This finding is corroborated by small-angle neutron scattering measurements under contrast matched conditions showing that at low phenol concentration the aromatic molecules are uniformly dispersed in the solvent, but in pretransition conditions a sparsely populated layer of phenol forms close to the polymer chains.

Introduction

Over the past 2 decades intense efforts have been deployed in the investigation of polymer gels that exhibit a volume phase transition (VPT). At this transition, under an appropriate stimulus such as a change in temperature, solvent composition or external field, the swollen gel shrinks by expelling the solvent. One of the most studied polymers in this class is poly(*N*-isopropylacrylamide) (PNIPA), which, in pure water, exhibits a VPT close to 34 °C. When, however, the solvent contains guest molecules, the transition temperature generally decreases and the volume change becomes more abrupt.[1−5] The potential applications of these systems are numerous and are generally either of biomedical inspiration or else take advantage of the change in optical or space-filling properties of the material. They still present a scientific challenge, since the interactions that govern the transition are still controversial. For applications in which solvent expulsion plays a central role, such as drug delivery or microfluidic control, an understanding of the interactions and the dynamics of the guest molecules in ternary systems (polymer, water, and guest molecules) is essential.

Certain benzene derivatives are well-known for their hydrotropic behavior.[6] Several of these molecules depress the VPT of the gels,[2,7,8] although no systematic trend between the substituting groups and their effects has been reported. Dynamic light scattering (DLS) measurements on PNIPA gels show that the characteristic decay rate of the osmotic concentration fluctuations becomes slower with increasing phenol or resorcinol content.[5] Within the experimental precision of the DLS measurements, the net effect of these particular phenol molecules is to reduce the thermodynamic interaction between polymer and solvent, rather than to increase the friction coefficient of the network chains by adsorbing on them.

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The interactions prevailing in such ternary systems, however, are complex and the question of the distribution of the aromatic molecules in the gel remains incompletely resolved. The present paper addresses this question by extending previous observations on hydroxybenzene (phenol) and 1,3-dihydroxybenzene (resorcinol) to 1,3,5-trihydroxybenzene (phloroglucinol), shown in Scheme 1.

Isothermal microcalorimetry and small-angle X-ray and neutron scattering (SAXS and SANS) are employed to try to determine directly to what extent the phenol molecules assemble around the polymer chains.

Experimental Section

Gel Preparation. Poly(*N*-isopropylacrylamide) (PNIPA) gels of differing molar cross-link ratios $X = [BA]/[NIPA]$ between 0.005 and 0.013 ($75 \leq 1/X \leq 200$) were prepared from *N*-isopropylacrylamide (NIPA) and *N*,*N*′-methylenebis(acrylamide) (BA) by chemical radical polymerization at 20 °C.[5] Gel films of thickness 2 mm were polymerized and dialyzed in water to remove unreacted chemicals. The films were cut into disks of diameter 7 mm and then air-dried and desiccated above concentrated sulfuric acid. For the SANS measurements gel disks of diameter 16 mm and thickness 1 mm were prepared.

Swelling Measurements and Dynamic Light Scattering. Swelling and DLS measurements were performed following procedures described in ref 5. The dry gel disks were placed in contact with the appropriate aqueous solutions. Phenol (99.5%) and resorcinol of high purity (99%) (Merck) were used to prepare the aqueous solutions of the weak aromatic acids. Swelling was determined by weighing. Volume additivity was assumed. The aromatic concentrations were derived from UV absorption measurements (Kontron Uvikon). The disks were equilibrated at 20.0 ± 0.2 °C for 48 h.

Light scattering measurements were made with an ALV DLS/SLS 5022F goniometer, working with a 22 mW HeNe laser. The swollen gels were placed in 10 mm diameter glass tubes containing the accompanying excess solvent. The temperature of the refractive index matching toluene bath was maintained at 20.0 °C with a precision of better than 0.1 °C. Each gel was measured at 4

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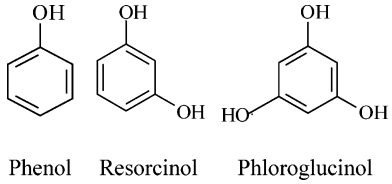
Scheme 1. Formulas for Phenols



Phenol Resorcinol Phloroglucinol

scattering angles, 60, 90, 120, and 150°. The heterodyne mode prevailing in DLS ensured that the measured scattering intensity (Rayleigh ratio R_{dyn}) and collective diffusion coefficient D_c were those of the fast osmotic fluctuations in the gels.

The solvent viscosity η was measured using an Ubbelohde viscometer. Aqueous solutions containing 50 mM of aromatic molecules exhibited a small increase in η with respect to pure water, amounting to 10%, 4%, and 5% for phenol, resorcinol, and phloroglucinol, respectively.

Microcalorimetry. Isothermal and scanning microcalorimetric measurements were made on powdered samples in a MicroDSCIII apparatus (SETARAM, France), as described elsewhere.[9] The DSC scanning rate was 0.02 °C/min.

SAXS. Small-angle X-ray scattering measurements were made at the BM2 beamline of the European Synchrotron Radiation Facility (Grenoble, France) at incident wavelength $\lambda = 0.77$ Å (16 keV). The wavelength spread was $\Delta\lambda/\lambda \approx 1.4 \times 10^{-4}$. The range of wave vectors q explored extended from less than 0.01 Å^{-1} to more than 1 Å^{-1}, where q is defined by

$$q = \frac{4\pi}{\lambda} \sin(\theta/2) \tag{1}$$

θ being the scattering angle. Standard corrections were made for dark current and the background signal of pure water. Measurements were made at 24 °C and at 40 °C.

SANS. These measurements were carried out at 20 °C on the KWS-1 instrument at the IFF Forschungszentrum, (Jülich, Germany) with an incident neutron wavelength $\lambda = 8$ Å and wavelength spread $\Delta\lambda/\lambda = 0.2$. The wave vector range explored was 2.3×10^{-3} Å$^{-1} \leq q \leq 0.2$ Å^{-1}. Deuterated phenol (D6, Polymer Source Inc., Canada) was dissolved in a water mixture containing 18% D_2O and 82% H_2O by volume, the composition that gives contrast matching with the PNIPA.

Results and Discussion

It was found earlier[9] for the range of cross-link ratio $0.005 \leq X \leq 0.013$ that the temperature of the VPT in the PNIPA gels and its associated enthalpy are independent of X. Gels of cross-link ratio defined by $1/X = 150$ were therefore used in the experiments.

Addition of phenols to PNIPA hydrogels lowers the transition temperature.[5,10] The effect is manifested in two ways. With the sample held at a constant temperature $T < T_c$, a VPT is induced when the concentration of aromatic molecules c_L in the surrounding water reaches a certain threshold (Figure 1). The threshold concentration decreases in the sequence phenol > resorcinol > phloroglucinol, i.e., with increasing OH substitution. This result is consistent with the findings of Molyneux and Frank.[11] A reduction of the swelling ratio below the transition, which progresses in the same order, can also be seen in the figure. At constant concentration of the aromatic molecule, low scanning rate DSC measurements reveal the effect of concentration on the temperature of the VPT. Figure 2 shows that with increasing aromatic content or OH substitution the transition temperature decreases and the peaks become broader. The broadening, already visible in Figure 1, is particularly noticeable with resorcinol and phloroglucinol at 25 mM, where multiple peaks begin to develop. Addition of aromatic molecules

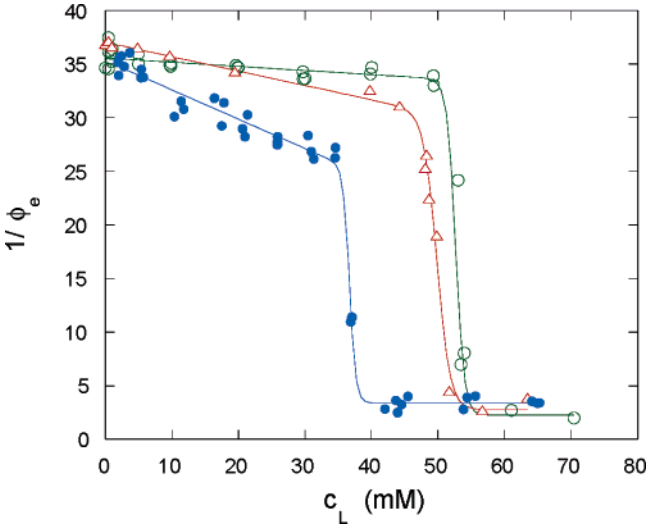


Figure 1. Equilibrium swelling ratio $1/\phi_e$ at 20 °C as a function of aromatic molecule concentration c_L in water, where ϕ_e is the polymer volume fraction of the PNIPA hydrogel. Key: open circles, phenol; triangles, resorcinol; filled circles, phloroglucinol. Continuous lines are guides for the eye.

thus appears to produce an increasingly inhomogeneous distribution of these molecules in the network and to favor multiple relaxation rates.[12] In the dissolution process, the overall enthalpy combines a series of steps involving, e.g., hydration, dehydration, and rehydration of the interacting species.[11] Increased lag times with broadening of the DSC response can arise at the VPT if steric hindrance is involved, e.g., due to the multiple OH substitution in the water-phenol exchange and the phenol−polymer interaction.

Table 1 lists the values of the enthalpy ΔH deduced from the DSC measurements both in pure water and with added phenols. The data show that the aromatic molecules increase the endothermic heat in the VPT process. The dependence on OH substitution is apparent at 25 mM. At this concentration, the observed enthalpy decreases with increasing OH substitution, indicating that the dehydration of the OH group contributes significantly to the energy balance.

The effect of guest molecules on the thermodynamic interactions can be assessed through the swelling pressure ω of the gel in the presence of excess solvent[13]

$$\omega = \Pi - G \tag{2}$$

where G is the elastic modulus. The mixing pressure Π can be described by a Flory−Huggins type expression[14] in which the parameters χ_1 and χ_2 are the first and second-order polymer−polymer interactions. At swelling equilibrium, the polymer volume fraction $\phi = \phi_e$ and

$$\omega = -\frac{RT}{V_1}[\ln(1-\phi_e) + \chi_1\phi_e^{\,2} + \chi_2\phi_e^{\,3}] - G = 0 \tag{3}$$

V_1 is the molar volume of the solvent, R the gas constant, and T the absolute temperature. At the low phenol concentrations investigated here the contribution of the guest molecules to V_1 is negligible. The elastic modulus G of each gel was previously measured[5] as a function of the cross-linking density X. Since the guest molecules take no direct part in the elastic modulus, their only effect on G is through their influence on ϕ

$$G = G_0\phi^{1/3} \tag{4}$$

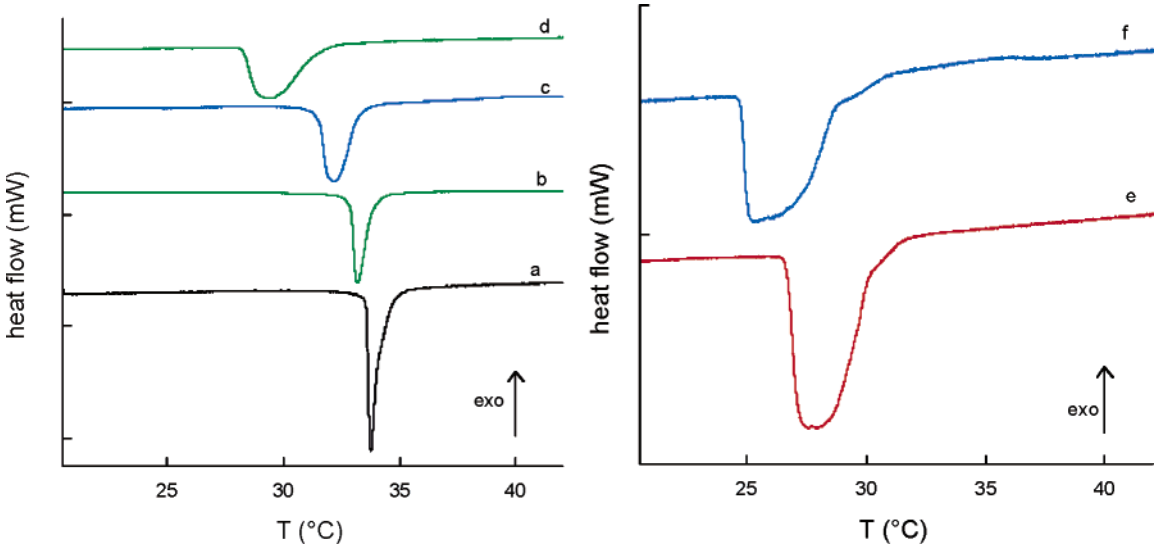


Figure 2. DSC response under heating of PNIPA samples in (a) pure water, (b) 5 mM phenol, (c) 5 mM phloroglucinol, (d) 25 mM phenol, (e) 25 mM resorcinol, and (f) 25 mM phloroglucinol. Heating rate: 0.02 °C/min. Successive curves are shifted vertically for clarity. Interval between graduations on ordinate axis: on left-hand side, 0.2 mW; on right-hand side, 0.1 mW.

Table 1. Parameters Derived from DSC Heating Curves for PNIPA Gels with Aqueous Phenol Solutions of Different Concentrations

solvent	peak position (°C)	integral heat flow (J/g dry gel)
water	33.8	57
5 mM phenol	33.2	60
5 mM phloroglucinol	32.2	61
25 mM phenol	29.5	71
25 mM resorcinol	27.9	68
25 mM phloroglucinol	25.2	64

Table 2. Correlation Lengths Derived from SAXS Curves of PNIPA Samples at 24 °C

sample	ξ (Å)
0 mM phenol	20 ± 2
20 mM phenol	23 ± 2
40 mM phenol	17 ± 2

where G_0 is the nominal shear modulus of the dry network.[15] In this way χ_1 and χ_2 can be determined for each value of aromatic molecule content by least-squares fitting of the data as a function of X to the expression

$$\chi_1 + \chi_2\phi_e = -\frac{1}{\phi_e^2}\left[\frac{V_1 G_0 \phi_e^{1/3}}{RT} + \ln(1-\phi_e)\right] \qquad (5)$$

Figure 3a shows the dependence of χ_1 on phenol and resorcinol content in the swollen region below the VPT at 20 °C. The error bars are the same size as the symbols shown. Within experimental error the first order interaction parameter χ_1 is independent of phenol content and can therefore be assigned a constant value, $\chi_1 = 0.478$. The values of χ_2, found by least-squares fitting to eq 5, are shown for the three phenols in Figure 3, parts b−d. Below the VPT, a regular increase in χ_2 with aromatic concentration and increasing OH substitution is observed. These findings imply that interactions between three polymer segments (three-body interactions) are increasingly favored either with phenol concentration or with OH substitution, while those between two segments (two-body interactions) are unchanged.

SAXS provides information on the polymer chain distribution in the gel, and, if measurements are extended to high enough values of the scattering vector q, on the local chain structure. Figure 4a shows the SAXS response of PNIPA gels in pure water and in water containing 20 or 40 mM phenol. At low q in this figure, small differences can be attributed to excess scattering from the large scale static inhomogeneities that are found in most soft gels.[16] In the region $0.01 < q < 0.1$ Å^{-1} all three curves display a scattering intensity $I(q)$ characteristic of polymer solutions; i.e., they obey an Ornstein−Zernike (OZ) relationship of the form[17]

$$I(q) = \frac{I(0)}{1 + (q\xi)^2} \qquad (6)$$

where ξ is the polymer−polymer correlation length in the gel. The continuous line in Figure 4a is the fit of eq 6 to the data from the 20 mM phenol sample in the region $q < 0.1$ Å^{-1}, with $\xi = 23$ Å. Similar values of ξ are found for the other gels (Table 2). Above $q \approx 0.1$ Å^{-1}, the room-temperature response exhibits a marked deviation from eq 6 that reflects the molecular structure of the polymer segments in the PNIPA chains.[4] The saddle shape of the shoulder implies a preferred distance of approach L between scattering units. When the temperature is raised above the VPT to 40 °C (Figure 4b), microphase separation induces local collapse of the polymer coils, and the OZ contribution vanishes. The low-q region of the spectrum is then dominated by surface scattering, which is the origin of the strong opalescence in these samples.[9] The figure shows the transition from volume to surface scattering at $q < 0.1$ Å^{-1}, with power law behavior of slope −4.[18] At this higher temperature, the shoulder feature transforms into a resolved peak at $q_{max} \approx 0.57$ Å^{-1}. The distance between the correlated groups may be estimated using the approximation[19] $L = 5.76/q_{max}$, which yields $L = 10$ Å at 40 °C. At 24 °C, q_{max} is slightly smaller, giving $L \approx 12$ Å, as can be verified by subtracting the 40 °C SAXS curve from that at 24 °C (not shown here). This implies that the separation distance between adjacent isopropyl groups along the polymer chain is 10−12 Å. Its insensitivity to phenol content, apparent in Figure 4b, indicates that the aromatic molecules do not perturb the relative dispositions of the side groups.

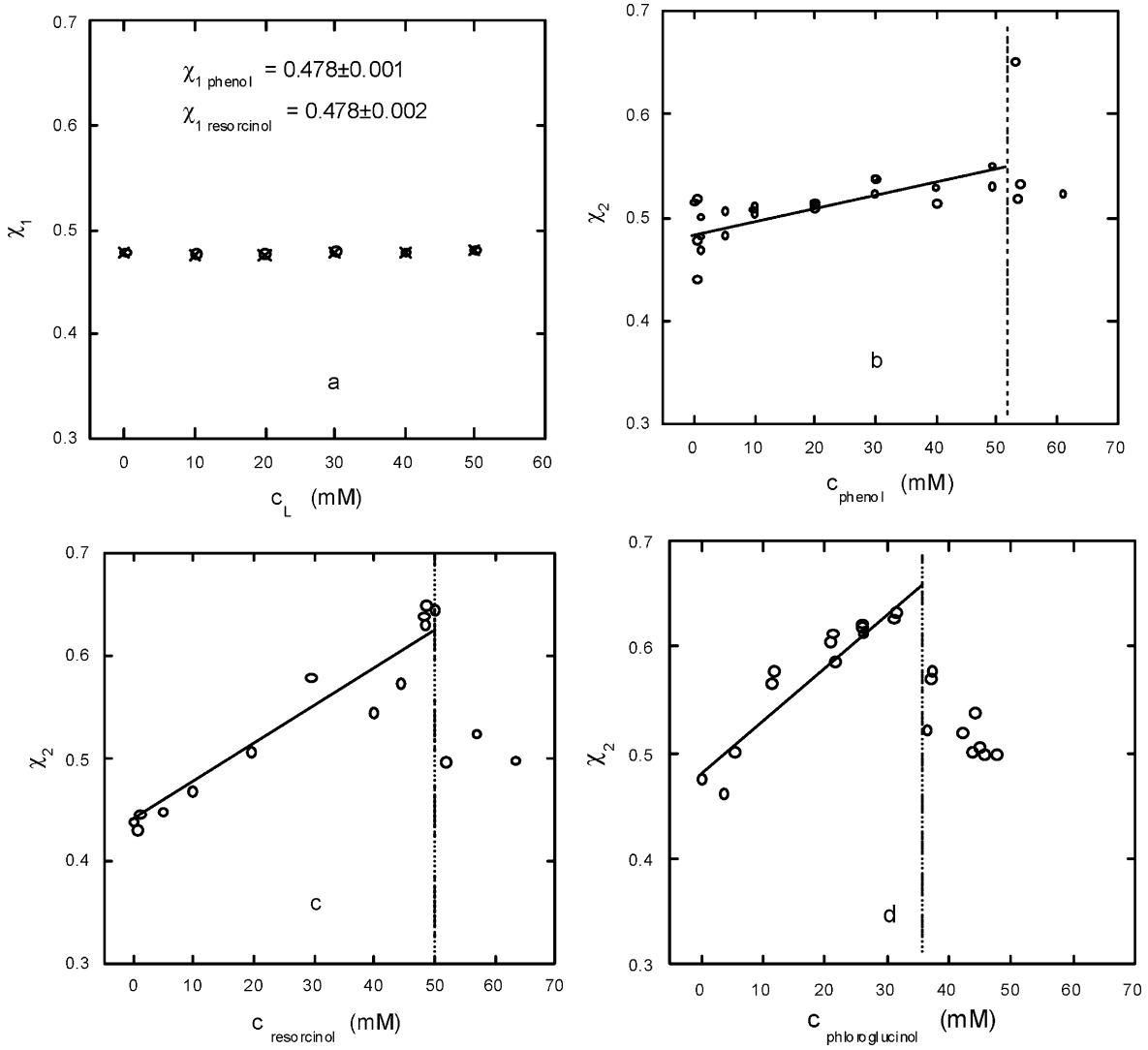


Figure 3. (a) Values of the interaction parameters χ_1 at equilibrium (calculated from least-squares fit to eq 5), as a function of phenol (○) and resorcinol (×) content in the surrounding bath at 20 °C. Second order interaction parameter χ_2 in (b) phenol, (c) resorcinol, and (d) phloroglucinol, on setting $\chi_1 = 0.478$. Dashed lines mark the observed VPT concentration at 20 °C. Data from above the VPT are also shown.

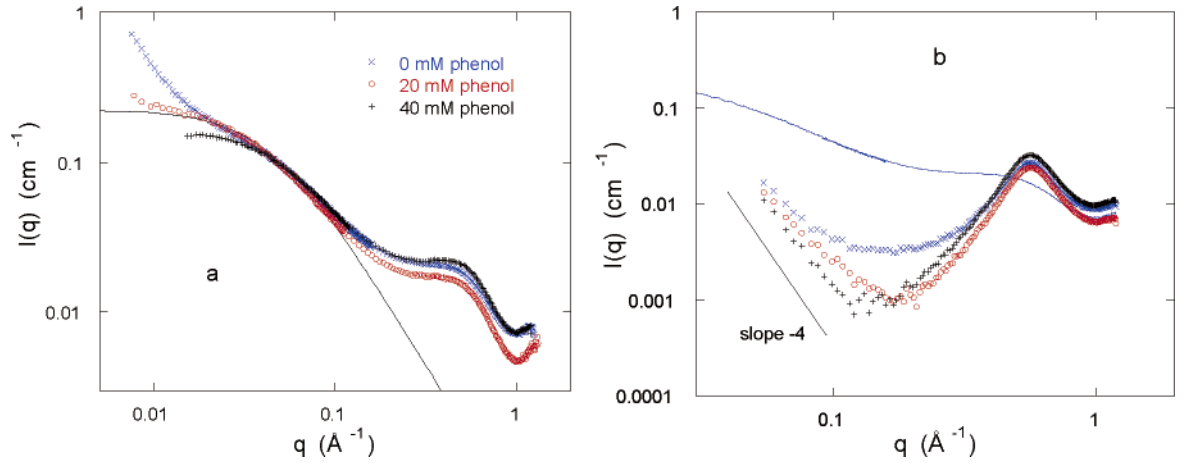


Figure 4. (a) SAXS response of PNIPA gels in pure water and in 20 and 40 mM phenol aqueous solutions at 24 °C. Continuous line is fit to eq 6 where the polymer−polymer correlation length $\xi = 23$ Å. Differences in intensity at low q are due to small variations in the swelling degree of these gels. (b) Detail of high-q region of SAXS response at 40 °C: (×) pure water; (○) 20 mM phenol; (+) 40 mM phenol. Continuous curve is the pure water response at 24 °C from part a, for comparison. For clarity, only 30% of the data are displayed.

Although the above results show that the phenols modify the gel−water interaction, they yield no information about their distribution. In contrast, DLS can in principle provide indirect information through the collective diffusion coefficient D_c and

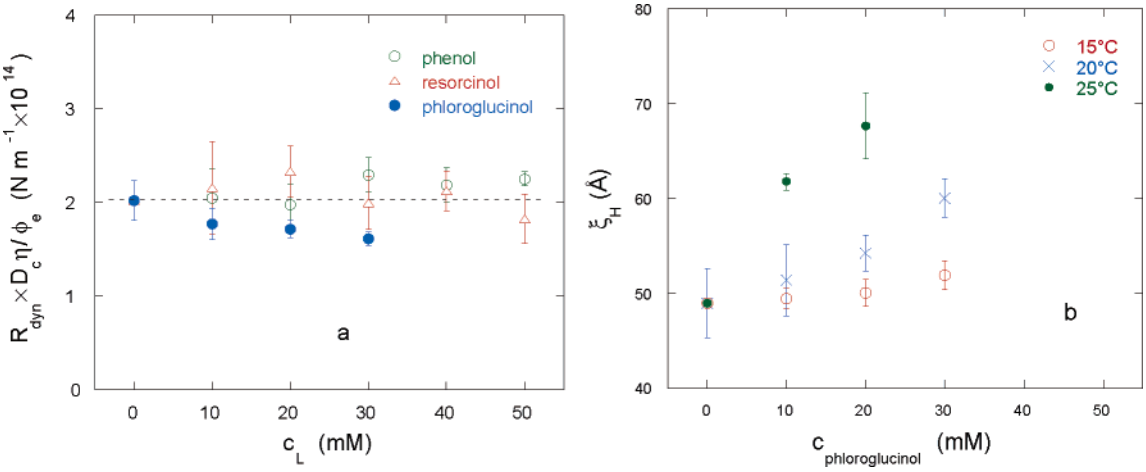


Figure 5. DLS measurements: (a) $D_cR_{dyn}\eta/\phi_e$ in PNIPA gels ($1/X = 150$) as a function of aromatic content c_L; (b) hydrodynamic correlation length ξ_H calculated from eq 8 for PNIPA gels with phloroglucinol at 15, 20, and 25 °C.

the intensity of the dynamically scattered light R_{dyn}. In ref 5, it was shown that at swelling equilibrium

$$\frac{D_cR_{dyn}}{\phi_e} = \frac{K_{light}k_BT}{f} \tag{7}$$

is independent of the osmotic properties. R_{dyn} is the Rayleigh ratio of the light scattered dynamically by the concentration fluctuations, and K_{light} is the optical contrast factor. The friction factor f between the polymer chains and the solvent is proportional both to the solvent viscosity η and to the effective cross-sectional radius ρ of the fluctuating polymer chains. The left-hand side of eq 7 is thus proportional to $1/\rho\eta$ and hence the quantity $R_{dyn}D_c\eta/\phi_e$ is sensitive only to changes in the size of the chain cross-section.

Figure 5a shows the DLS results for PNIPA gels swollen at 20 °C in aqueous solutions of phenol, resorcinol and phloroglucinol of varying concentration c_L. It is clear that $R_{dyn}D_c\eta/\phi_e$, which has the dimensions of surface tension, is approximately constant. This finding implies that the cross section of the polymer chains is practically independent of the phenol concentration, and the only effect of the aromatic molecules is to decrease the overall solvent quality. For phloroglucinol, however, over the range of aromatic concentration c_L in which gel remains swollen, a more pronounced concentration dependence is observed. As there is no reason to attribute this finding to hydrodynamic effects,[20,21] it must be due to a change in the structure of the polymer chains: either aromatic molecules become attached to the network chains, or equivalently, they modify the conformation of the chain.

The hydrodynamic correlation length ξ_H of the concentration fluctuations is defined by the Stokes−Einstein relation

$$\xi_H = k_BT/6\pi\eta D_c \tag{8}$$

Figure 5b shows that increasing the temperature of the gel causes ξ_H to increase, as expected when a critical point is approached. Note that the hydrodynamic size ξ_H is greater than, but of the same order of magnitude as, the static correlation length ξ measured by SAXS.

Isothermal microcalorimetry offers a sensitive method for detecting the energy of interaction. Figure 6a shows the temperature dependence of the heat of mixing of the dry PNIPA gels with pure water,[9] compared with that of the equilibrium swelling ratio of the gel. The principal change in enthalpy of mixing occurs in the close vicinity of the VPT, while below this region the changes are more gradual. In the energy balance, the endothermic/exothermic contribution of the respective elastic swelling/deswelling of the gel is very small (less than 0.1 J/g dry gel) and is therefore negligible. The overwhelming majority of the observed enthalpy difference derives from the stacking of the polymer chains and the exchange and reorganization of the molecules around them.

Parts b and c of Figure 6 show the results of microcalorimetry measurements at 20 °C as a function of aromatic content. With both phenol and phloroglucinol an appreciable increase in the absolute value of the enthalpy (by 24 and 40 J/g dry gel, respectively) occurs immediately prior to the VPT. Absence of a corresponding anomaly in the pure water system (Figure 6a) is evidence that the aromatic molecules trigger a change in the local solvent environment of the polymer already below the transition concentration. The heats of sorption of phenol and phloroglucinol, estimated from Figure 6, parts b and c, and uptake measurements,[5] are −46 and −75 kJ/mol adsorbed molecules, respectively. For comparison, the solvation enthalpy of phenol in water is −58.0 ± 0.7 kJ/mol.[22]

If local solvent ordering occurs in the vicinity of the polymer chains, evidence of the process may be obtained from SANS. This technique is particularly sensitive to molecular associations on a spatial scale extending from 10 to 1000 Å. To reveal the signal from the phenol alone, however, that of the polymer must be eliminated. With a mixture of 18% D_2O and 82% H_2O (v/v), the scattering length density of the water coincides with that of the polymer and the coherent SANS signal from the polymer vanishes, leaving only incoherent scattering, essentially due to the protons. If deuterated phenol is now added to this solvent, the resulting signal will depend on the distribution of the phenol in the system. If the D-phenol is uniformly dispersed in the water, no significant coherent signal will be detected since its amount is too small to modify appreciably the average scattering length density of the solvent. If, however, even a small number of D-phenol molecules decorate the polymer chain, the effective scattering length density of the polymer will be substantially enhanced. This results in a coherent signal from the polymer. Coherent signals, but of a different shape, may also be obtained if the D-phenol molecules undergo self-clustering.

Figure 7 shows the SANS response of the reference sample, namely a PNIPA gel at 20 °C in pure D_2O (open circles). As this polymer−solvent pair is far from the contrast match point,

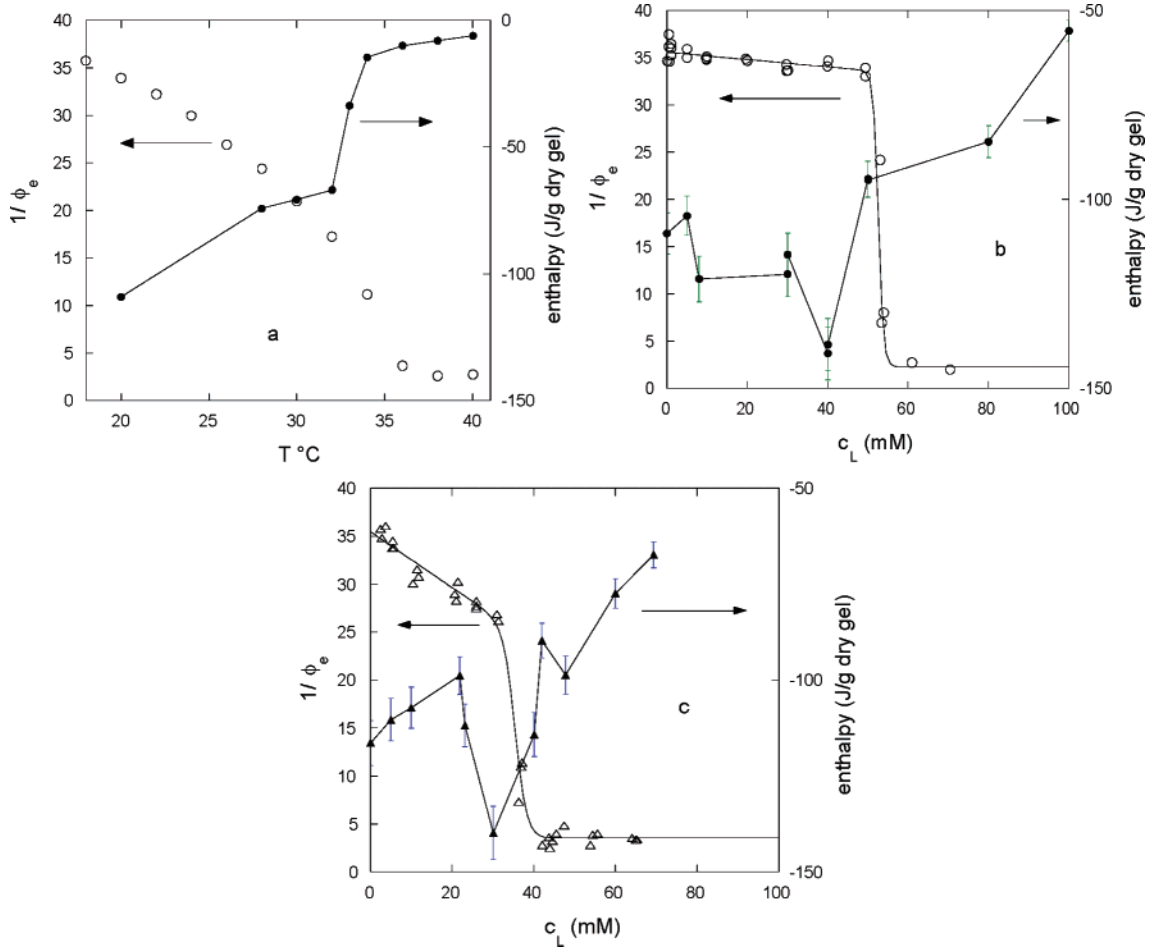


Figure 6. Isothermal heat of mixing of PNIPA gel compared with the swelling ratio in pure water as a function of temperature (a), in aqueous solutions of phenol (b) and phloroglucinol (c) at 20 °C. Reproducibility of the measurements is illustrated by duplicate points at 30 and 40 mM phenol.

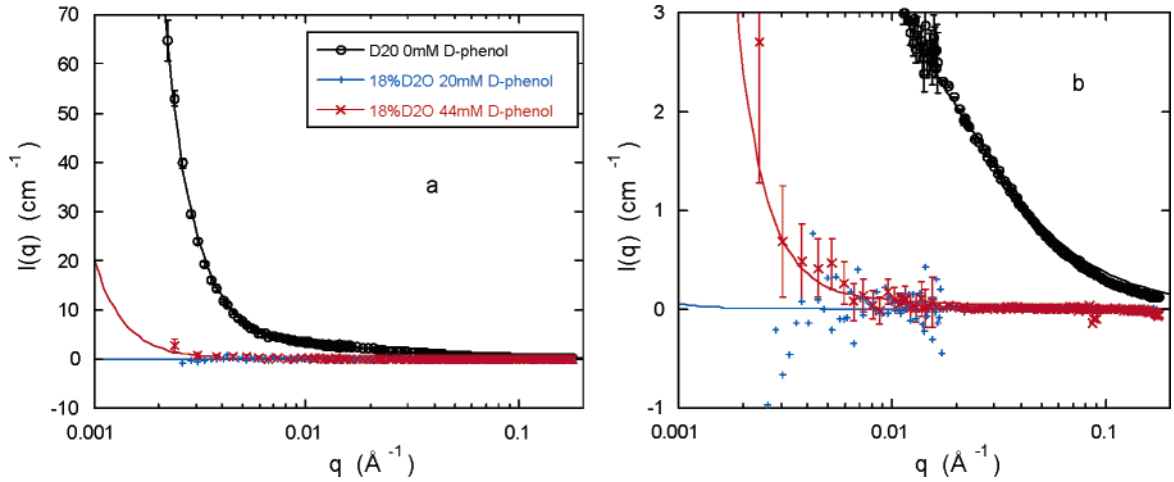


Figure 7. (a) SANS response of PNIPA gels swollen to equilibrium at 20 °C in an 82% H_2O:18% D_2O mixture containing (+) 20 mM aqueous solution of D-phenol. (×) 44 mM D-phenol, and also in pure D_2O (O). (b) Same data on an expanded scale. Continuous lines are fits to a function proportional to the response in D_2O.

it yields the full response from the polymer gel. As expected, the signal from PNIPA in the pure contrast matching water mixture (not shown) is indistinguishable from zero. The signal from the sample with 20 mM D-phenol (+) is also indistinguishable from zero, which implies that phenol sorption is not detected. In the presence of 44 mM D-phenol, however, a coherent signal emerges. Although the signal-to-noise ratio is reduced, the shape of the scattering curve is consistent with that of PNIPA in D_2O. This result implies that the D-phenol adopts the shape of the network chains, i.e., it decorates them. According to the fit shown in Figure 7, the amplitude of the D-phenol signal is about 2.8% of that of the polymer in the reference sample. This information enables an estimate to be made of the fraction of phenol molecules in close association with the network polymer. The difference in neutron scattering length density between D-phenol and the 18% D_2O/82% H_2O

mixture is taken as 4.27×10^{10} cm^{-2}, and that between PNIPA and D_2O as 5.64×10^{10} cm^{-2}. As the PNIPA gel remains swollen at $\phi = 0.03$ in a 44 mM phenol solution at 20 °C, it follows by proportionality that the fraction of sorbed phenol is 0.34 ± 0.10. This result corresponds to approximately 6 phenol molecules for every 100 NIPA units in the network chains. (For comparison, at 20 °C the transition is induced when the number of aromatic molecules confined within the gel is 21, 15, and 12 per 100 monomer units for phenol, resorcinol and phloroglucinol, respectively.) These results show that, already below the VPT, a substantial fraction of the phenol molecules form a sparsely populated shell around the polymer chain, while the majority are more or less evenly distributed in the solvent. The small number of satellite phenol molecules around the polymer chain explains the lack of detectable effect in SAXS and in DLS. By comparison, for the 20 mM solution, the amount of sorbed phenol estimated for the SANS intensity is 2 orders of magnitude smaller than in the 44 mM solution. At low concentrations, therefore, the phenol molecules are uniformly dispersed in the swelling medium, a finding that is consistent with the isothermal calorimetry results.

Conclusions

The behavior of PNIPA hydrogels is investigated in the presence of three aromatic compounds of increasing hydroxyl group number, phenol, resorcinol, and phloroglucinol. These molecules introduce an increasingly large depression in the temperature and a broadening of the volume phase transition. The broadening is believed to reflect inhomogeneous distribution of the aromatic molecules inside the gel and also the effect of steric hindrance. Estimates of the Flory−Huggins interaction parameters χ_1 and χ_2 show that χ_1 remains practically invariant under changes of aromatic molecule content, while χ_2 increases monotonically as the transition is approached. The increase becomes stronger with increasing hydroxyl group number on the phenol. Dynamic light scattering observations indicate that while phenol and resorcinol do not noticeably modify the effective cross section of the polymer, a small but marked increase is nevertheless detected with phloroglucinol. Evidence of a pretransition state is found from isothermal microcalorimetry, in which a clearly resolved enhancement of the enthalpy is visible already below the transition, both with phenol and with phloroglucinol. The aromatic molecules thus appear to trigger a change in the local solvent environment of the polymer below the transition. Measurements by small-angle neutron scattering with contrast matching show that phenol molecules dissolved at low concentrations in PNIPA hydrogels remain dispersed in the aqueous phase between the polymer chains. Closer to the transition, however, a small number of phenol molecules form a sparsely populated cloud around the polymer chains.

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