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# Phase Transition in Poly(*N*-isopropylacrylamide) Hydrogels Induced by Phenols

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ABSTRACT: Poly(*N*-isopropylacrylamide) gels swollen at 20 °C in aqueous solutions of weak aromatic acids (phenol and resorcinol) display a volume transition at aromatic acid concentrations close to 50 mM. Owing to selective solvation, phenol exhibits an excess equilibrium concentration inside the swollen gels that is 7% greater than that in the surrounding bath, while for resorcinol the excess is 20%. The elastic modulus $G$ of the gels at small strains follows the expected behavior of standard network theory, i.e., $G \propto \phi^{1/3}$, where $\phi$ is the polymer volume fraction. Dynamic light scattering measurements, in which light from the thermodynamic fluctuations is heterodyned by that from the large-scale network heterogeneities, show that the collective diffusion coefficient $D_c$ decreases at high aromatic content, while the Rayleigh ratio of the dynamic component of the scattering intensity, $R_{dyn}$, increases. No divergence of $R_{dyn}$ close to the transition is observed, however, in accord with first-order nature of the transition. Within experimental error the product $D_cR_{dyn}$ is independent of aromatic concentration. It follows that the friction coefficient of the polymer chains is not modified in the presence of the binary solvent and that the reduction in the value of $D_c$ is due to the reduction in the osmotic modulus of the system.

## Introduction

Gels swollen in binary solvents have been the subject of many investigations, either in their capacity as index-matching fluids for the polymer[1−5] or for their ability to modify the polymer−solvent interaction.[6−9] Several authors[10−12] have reported that gels made from the thermosensitive polymer PNIPA (poly(*N*-isopropylacrylamide)), swollen in aqueous solutions of aromatic compounds, collapse at aromatic concentrations above a certain threshold, a phenomenon that has been attributed to the approach of the solubility limit of the host molecule in water. By fitting the adsorption curves to a Langmuir equation, Murase et al.[11] deduced that the aromatic molecule investigated (benzyl alcohol) was adsorbed on the PNIPA chains. If adsorption did occur, however, it should increase the cross section of the polymer chains and hence the friction coefficient. This would be reflected in a reduction of the collective diffusion coefficient. The same authors also found that the collapse of the gel occurred in the vicinity of the solubility limit of the aromatic molecule in water.

The aim of the present article is to investigate this volume transition more closely, using two different aromatic molecules, phenol and resorcinol. The former has a solubility limit (0.87 M) in water at room temperature that is an order of magnitude higher than the concentration required to induce the volume transition in PNIPA, while that of resorcinol (9.08 M) is even higher. The observations reported here involve measurements of swelling degree, aromatic uptake, the elastic modulus, and dynamic light scattering.

## Experimental Section

**Gel Preparation.** 18.75 mL of a 1 M aqueous solution of NIPA and 1.225 mL of a 0.1 M solution of *N*,*N*′-methylenebis(acrylamide) (BA) were mixed with 4.9 mL of water and 0.25 μL of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED). Finally, 125 μL of ammonium persulfate (APS) was added to the mixture, and polymerization took place at 20 °C. This yielded gels having a molar ratio of [NIPA]/[BA] equal to 150. For the uptake measurements, gel films of thickness 2 mm were prepared, while for the modulus measurements samples were prepared in 1 × 1 cm isometric cylindrical molds. The samples were then dialyzed in water to remove unreacted chemicals. The films were cut into disks (diameter 7 mm), then dried, and stored above concentrated sulfuric acid. Cylinders were dried and kept in the same way.

To determine the equilibrium uptake of the polymers, the dry 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. The aromatic concentrations were derived from UV absorption measurements (Kontron Uvikon). For the sorption measurements the disks were equilibrated at 20.0 ± 0.2 °C for 48 h, a period determined from preliminary kinetic measurements.

The uptake $n_{eq,aromatic}$ of the small aromatic molecules was determined from the initial and equilibrium molar concentrations, $c_0$ and $c_{liq}$, of the compound in the free liquid, the volumes of which were $V_0$ and $V_{eq}$, respectively. Thus

$$n_{eq,aromatic} = (V_0c_0 - V_{eq}c_{liq})/m_{dry} \qquad (1)$$

in mmol/g of dry gel, where $m_{dry}$ is the mass of the dry gel. The volume of solvent in the swollen gel is

$$V_{eq,gel} = (V_0 - V_{eq}) \qquad (2)$$

The concentration of the aromatic compound in the liquid inside the equilibrated gel is then

$$c_{gel} = (V_0c_0 - V_{eq}c_{liq})/(V_0 - V_{eq}) \qquad (3)$$

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The density of the dry polymer, $d_{\mathrm{PNIPA}}$, was determined by measuring the density of aqueous solutions of PNIPA at 20.00 °C, using a DMA 58 density meter (Anton Paar, Graz, Austria). Volume additivity was assumed. The value obtained was $d_{\mathrm{PNIPA}} = 1.115$ g/cm$^3$.

In addition, measurements of the viscosity of aqueous solutions of phenol and resorcinol were made at 20 °C using a Rheo Stress 100 (Haake, Karlsruhe, Germany). Within experimental error, the viscosity of the solutions was found to be identical to that of pure water over the concentration range explored in this work.

Stress–strain measurements were performed as described by Horkay and Zrínyi.[4] The dry cylindrical samples were equilibrated in the aqueous aromatic solutions for 8 days at $20.0 \pm 0.2$ °C prior to the experiments.

**Dynamic Light Scattering.** Light scattering measurements were made with an ALV DLS/SLS 5022F goniometer equipped with a fiber-optic coupling and an avalanche diode, working with a 22 mW HeNe laser and an ALV 5000E multitau correlator. The swollen gel disks, approximately 8 mm in diameter and of thickness 2 mm, 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 five angles: 30°, 60°, 90°, 120°, and 150°.

Owing to the dominant scattering from large-scale static heterogeneities in these gels, light scattered by the dynamic concentration fluctuations is strongly heterodyned. While the static light is nonergodic in character,[13,14] the mutual overlap of the polymer chains on a local scale ensures that their movement is, in contrast, ergodic. This consideration means that to deduce the contribution to the scattering from osmotic fluctuations, it is sufficient to detect the light from a single speckle in the scattering field, thus avoiding the need for ensemble averages. The resulting intensity correlation function $G(t)$ may then be expressed in terms of the desired field correlation function $g(t)$ as follows:[15–17]

$$G(t) = \frac{\langle I(0)\, I(t)\rangle}{\langle I(t)\rangle^2} = 1 + \beta[2X(1 - X)g(t) + X^2 g(t)^2] \quad (4)$$

where $I(t) = I_{\mathrm{stat}} + I_{\mathrm{dyn}}(t)$ is the sum of the static and dynamic light scattered and

$$X = \langle I_{\mathrm{dyn}}(t)\rangle / \langle I(t)\rangle \quad (5)$$

is the fraction of dynamically scattered light. The optical coherence factor $\beta \approx 1$ depends only on the detection system and is determined by measuring a dilute solution of latex beads. For each intensity correlation function, $G(t)$, the value of $X$ is found from eq 1, using the condition that $g(0) = 1$. The same quadratic equation may then be solved for $g(t)$ at all delay times $t$.[14] The value of the ratio $X$ depends on the brightness of the particular speckle chosen; in the present measurements it varied between about 0.9 (i.e., almost pure homodyne scattering) and 0.05 (almost pure heterodyne scattering). This principle is illustrated in Figure 1. Several measurements of $G(t)$ are shown for $\theta = 90°$, where the sample holder has been successively rotated by a small angle in order to detect speckles of different intensity. Although each speckle yields a different value for the intensity ratio $X$, the field correlation functions $g(t)$ all lie on the same master curve; i.e., within experimental error, they all relax with the same time constant.

It may be noted that slow rearrangements of the macroscopic polymer network sometimes occur, giving rise to slight changes in the speckle pattern. The resulting correlation functions may thus contain long tails in addition to the short-lived concentration fluctuations (cf. Figure 1). Such tails are unrelated to the equilibrium thermodynamics of the system and were consequently discounted in the data analysis.

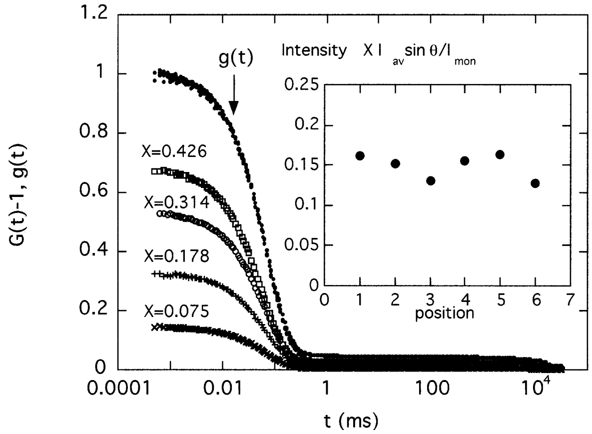

**Figure 1.** Intensity correlation functions $G(t) - 1$ measured at 90° scattering angle at four different positions in a PNIPA sample swollen in pure water (open symbols), with different values of $X$. The corresponding field correlation functions $g(t)$ all fall on the master curve shown. The long tail, which reveals slow macroscopic adjustments in the sample, is unrelated to the thermodynamic concentration fluctuations. Inset: normalized dynamic intensity $I_{\mathrm{dyn}} = XI_{\mathrm{av}} \sin \theta / I_{\mathrm{mon}}$ at six different positions in the same sample.

Although the relaxation of the concentration fluctuations was in all cases practically single exponential, to improve the precision of the analysis, $g(t)$ was fitted to a two-exponent expression

$$g(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \quad (6)$$

in which $a_1 + a_2 = 1$. It is then convenient to describe the average decay rate of $g(t)$ by its first cumulant, $\Gamma$, where

$$\Gamma = -\left[\frac{\mathrm{d} \ln(g(t))}{\mathrm{d}t}\right]_{t\to 0}$$
$$= (a_1/\tau_1 + a_2/\tau_2)/(a_1 + a_2) \quad (7)$$

In swollen polymer gels the diffusion coefficient corresponding to this decay is a collective motion describing the relaxation rate of concentration fluctuations that govern the swelling rate of the gel[18]

$$D_c = \Gamma/q^2 \quad (8)$$

where $q$ is the transfer wave vector

$$q = (4\pi n/\lambda_0) \sin(\theta/2) \quad (9)$$

in which $n$ is the refractive index of the gel, $\lambda_0$ the wavelength of the incident light (6328 Å), and $\theta$ is the scattering angle.

The intensity of the light scattered dynamically by the gel is given by[19,20]

$$I_{\mathrm{dyn}}(q) = X(q) I_{\mathrm{av}}(q) \sin(\theta)/T_s I_{\mathrm{mon}} \quad (10)$$

in which $I_{\mathrm{mon}}$ is the intensity measured by the incident light monitor, $I_{\mathrm{av}}(q) = \langle I(t,q)\rangle$ is the average total scattered intensity, and $T_s$ is the sample transmission. Within experimental error, the values of $T_s$ were equal to unity for all samples, except for those closest to the transition, where $T_s$ was found to be about 0.85. The inset in Figure 1 shows the measured value of $I_{\mathrm{dyn}}$ for six different positions of the same sample (PNIPA in pure water at 20 °C) at the same scattering angle $\theta = 90°$. Within experimental error, $I_{\mathrm{dyn}}$ is independent of the speckle intensity. This result illustrates the ergodic nature of chain dynamics in soft gels.

The absolute value of the dynamic intensity is found by comparison with the Rayleigh ratio of toluene, $R_{\mathrm{tol}}$. The Rayleigh ratio of the dynamic fluctuations in the sample is thus

$$R_{\mathrm{dyn}}(q) = I_{\mathrm{dyn}}(q)R_{\mathrm{tol}}I_{\mathrm{mon,tol}}/I_{\mathrm{tol}} \tag{11}$$

where $I_{\mathrm{tol}}$ and $I_{\mathrm{mon,tol}}$ are respectively the intensity scattered by the standard sample and the corresponding number of counts received on the beam intensity monitor.

## Results and Discussion

Figure 2 shows the concentration of phenol and of resorcinol in the liquid inside the gels for the two series of samples, as a function of the concentration of aromatic compound in the surrounding aqueous solution, at equilibrium. The slope of these lines is greater than unity (1.07 and 1.20, respectively), indicating that these aromatic compounds exhibit preferential affinity for PNIPA.

Parts a and b of Figure 3 show the stress−strain curves for a PNIPA gel swollen in an aqueous solution with phenol concentration $c_{\mathrm{liq}} = 5$ and 50 mM, respectively. The stress $\sigma$ is expressed in terms of applied force per initial surface area. The strain is defined by $\lambda - 1/\lambda^2$, where $\lambda$ is the deformation ratio. The difference between the response during the first compression cycle (open symbols) and the return cycle is caused by loss of solvent expelled during compression. At zero aromatic content these curves are fully reversible. The elastic moduli were determined from the initial slope of the stress−strain curves. Solvent expulsion, as reflected in the hysteresis shown in Figure 3, is expected when the compression cycle is carried out slowly. In such gels, where the value of the osmotic Poisson ratio is close to $^1/_3$ in poor solvent conditions,[21,22] the osmotic response under uniaxial compression is to shrink, while accommodating into the space available along the compression axis. What is striking here is the high rate of deswelling. Application of uniaxial strain causes gels with aromatic concentration $c_{\mathrm{liq}} = 40$ mM immediately to become white and to exude solvent (Figure 4a). With resorcinol the behavior is extreme, in that solvent outflow is so high that not only droplets but also blisters develop at the surface of the gel (Figure 4b).

According to classical theory of neutral gels composed of Gaussian chains, the elastic modulus $G$ is described by[23]

$$G = N_{\mathrm{e}}k_{\mathrm{B}}T(\phi/\phi_0)^{1/3} \tag{12}$$

where $N_{\mathrm{e}}$ is the density of effective elastic chains, $k_{\mathrm{B}}$ Boltzmann's constant, $T$ the absolute temperature, $\phi$ the volume fraction of polymer at a given state of swelling, and $\phi_0$ the polymer volume fraction at preparation. For a given gel, it follows that the ratio $G/(T\phi^{1/3})$ should be independent of the degree of swelling. Figure 5 shows this quantity for the PNIPA gels containing both phenol and resorcinol, as a function of aromatic content in the surrounding bath at equilibrium. Within experimental error, the data lie on a horizontal line, in agreement with the expectation of eq 12.

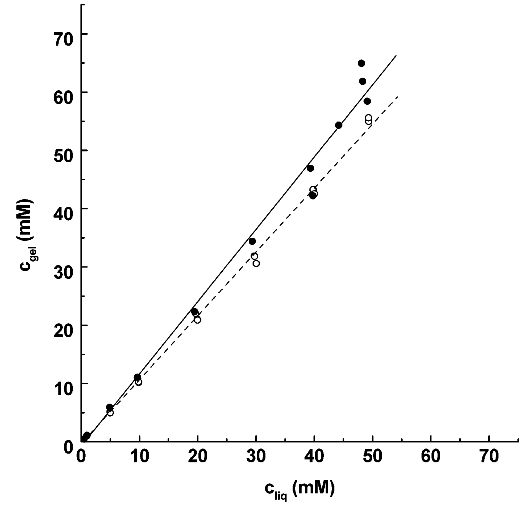

**Figure 2.** Uptake of phenol (open symbols) and resorcinol (filled circles) in PNIPA gels as a function of the equilibrium aromatic concentration in the surrounding fluid.

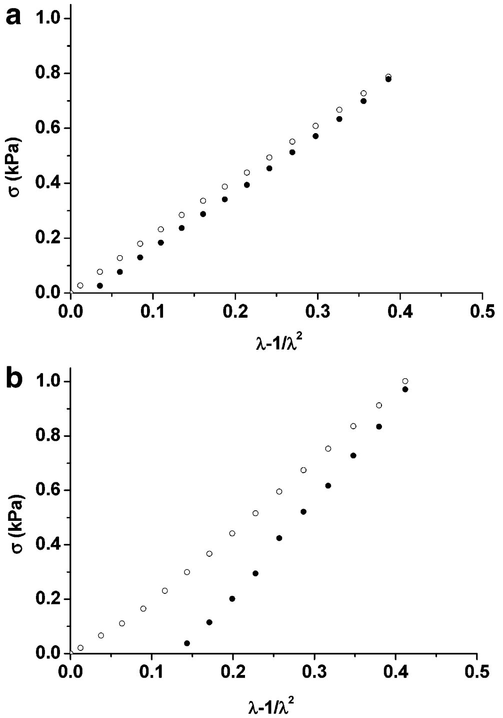

**Figure 3.** Stress−strain curves for PNIPA gels swollen to equilibrium in aqueous solutions of (a) 5 mM phenol and (b) 50 mM phenol. Open symbols: initial compression. Filled symbols: return cycle. The two curves do not superimpose owing to irreversible solvent expulsion. The stress is expressed in terms of force per initial surface area of the sample; $\lambda$ is the axial compression ratio.

Figure 6 shows the equilibrium swelling ratio $1/\phi_{\mathrm{eq}}$ of the gels as a function of phenol or resorcinol concentration, $c_{\mathrm{liq}}$, in the surrounding bath. These measurements, performed at 20 °C, show the abrupt nature of the volume transition close to 50 mM both for phenol and for resorcinol. This concentration is well below the solubility limits of these aromatic compounds in water. Swelling equilibrium for a gel is defined by the condition of zero swelling pressure, i.e., when the osmotic mixing pressure is equal to the retraction pressure exerted by elastic chains. In a modified form of the original expression for the mixing pressure in the Flory−Huggins theory,[23,24] the swelling pressure $\omega$ may be expressed as

$$\omega = -(RT/v_1)[\ln(1-\phi) + \phi + \chi\phi^2 + w\phi^3] - G_0\phi^{1/3} \tag{13}$$

where $R$ is the gas constant, $v_1$ is the molar volume of the solvent, and $\chi$ and $w$ are the second- and third-order interaction parameters. $G_0$ is the value of the shear modulus $G$ extrapolated to the dry state. In Flory's

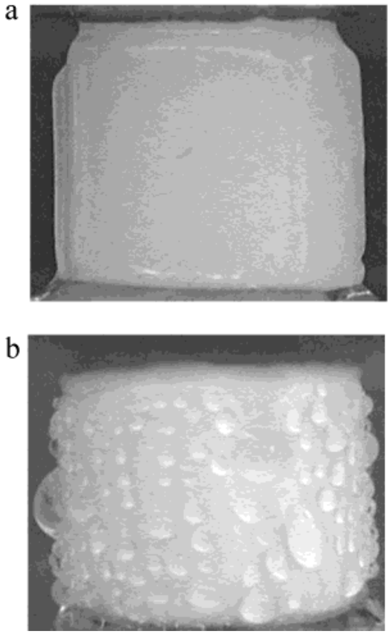

**Figure 4.** (a) PNIPA gel sample in 40 mM phenol, at zero stress after compression to $\lambda = 0.885$. (b) Gel sample in 40 mM resorcinol, at zero stress after compression to $\lambda = 0.877$.

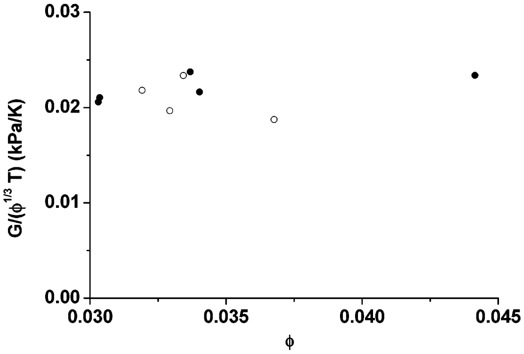

**Figure 5.** Normalized shear elastic modulus of PNIPA gels swollen in aqueous solutions of phenol (open symbols) and resorcinol (solid symbols) at different concentrations.

model of gels, the second term on the right-hand side of eq 13, in addition to the factor $\phi^{1/3}$, contains an extra term proportional to $\phi/2\phi_0$, where, as above, $\phi_0$ is the concentration at preparation. Since, however, its inclusion in expression 13 makes no significant difference to the results, it will be ignored for simplicity. If, as here, $v_1$ and $G$ are known, then a range of values for $\chi$ and $w$ can be found that satisfy the equilibrium swelling condition $\omega = 0$ in pure water. Since the presence of an aromatic compound in the solvent causes the gel to deswell, it can be expected to increase one or other of the interaction parameters $\chi$ or $w$. The effect is most simply simulated in eq 13 by replacing $w$ by $w(1 + Bc_{\text{liq}})$, where $B$ is a constant to be determined and $c_{\text{liq}}$ is the molar concentration of phenol or resorcinol in the reservoir surrounding the gel specimen. The simultaneous condition that $\phi_{\text{eq}} = 0.0280$ in pure water and that the transition occurs at 50 mM aromatic content then defines the permissible values for the three unknown parameters, namely

$$\chi = 0.475, \quad w = 0.558, \quad B = 5.54 \times 10^{-3}\ \text{mM}^{-1}$$

The resulting swelling equilibrium curve is displayed as a continuous line in Figure 6. It can be seen that the simulation describes the qualitative behavior of the resorcinol data but fails to reproduce the square shoulder exhibited by the phenol results. Other variants of the simulation procedure either yield poorer fits or have little physical justification. It can be seen that in the deswollen region the calculated swelling ratio is also too low. Despite such inadequacies, however, the Flory−Huggins expression provides an approximate description of the volume transition. The effect of the solute on the transition thus appears to be best described by a modification of the third-order term $w$, i.e., the three-body polymer interactions. It is therefore natural to ask whether, as suggested by Murase et al.,[11] the polymer chains are decorated by these molecules.

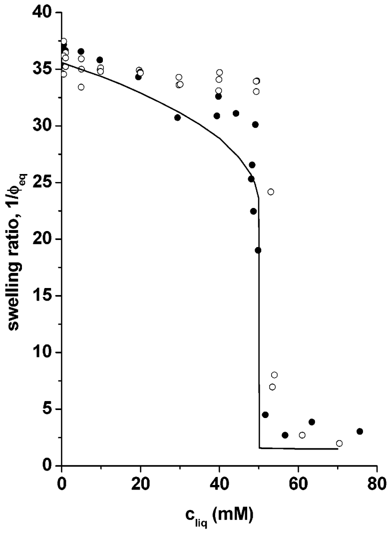

**Figure 6.** Equilibrium swelling ratio of PNIPA gel in aqueous solutions of phenol (open circles) and resorcinol (filled circles) at 20 °C. Continuous curve: solution of eq 13 with $\chi = 0.475$, $w = 0.558(1 + 5.54 \times 10^{-3}c_{\text{liq}})$.

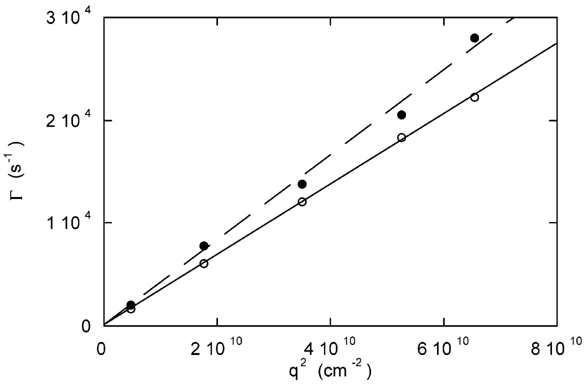

**Figure 7.** Decay rate $\Gamma$ of concentration fluctuations in PNIPA gels as a function of transfer wave vector $q$. Filled circles: gels swollen in pure water. Open circles: gels swollen in aqueous solution with 50 mM phenol.

Dynamic light scattering results are shown in Figure 7, which compares the angular dependence of the mean decay rate $\Gamma$ of the concentration fluctuations in two PNIPA gels at 20 °C, one swollen in pure water and the other in a solution containing 40 mM phenol. In both systems, $\Gamma$ varies as the square of the wave vector $q$, in agreement with eq 8, thus confirming that the concentration fluctuations have a diffusive character. The decay rate is significantly faster in the pure water, even

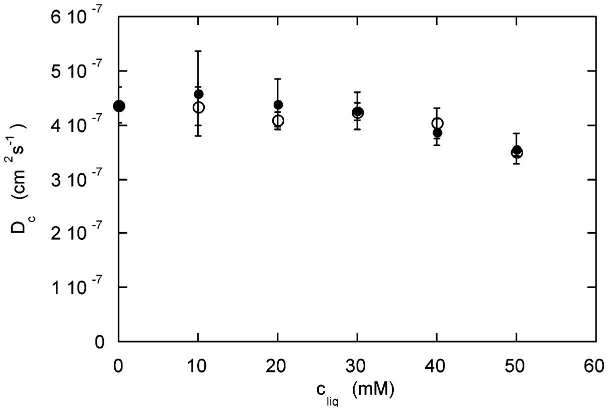

**Figure 8.** Collective diffusion coefficient $D_c = \Gamma/q^2$ in PNIPA gels at 20 °C at equilibrium with aqueous solutions containing different concentrations $c_{liq}$ of phenol (open symbols) and resorcinol (filled symbols).

though the viscosities of the two solvents are identical within experimental error.

Figure 8 shows the collective diffusion coefficient $D_c = \Gamma/q^2$ for the PNIPA gels swollen in aqueous solutions at different equilibrium concentrations $c_{liq}$ of phenol and resorcinol. Both systems display a similar response, with a noticeable, albeit limited, downturn as the limiting concentration $c_{liq} = 50$ mM is approached.

In semidilute solutions, the diffusion coefficient describing the thermal motion of the polymer chains that take part in an osmotic fluctuation in the surrounding solvent may be defined as follows:

$$D_c = \frac{\partial\Pi/\partial\phi}{f} \tag{14}$$

where $f$ is the friction coefficient of the polymer chain moving in the surrounding fluid. In a gel, owing to the permanent elasticity, the term $\partial\Pi/\partial\phi$ is replaced by $M_{os}/\phi$, where the osmotic modulus is[18]

$$M_{os} = \phi\ \partial\omega/\partial\phi + 4G/3 \tag{15}$$

Similarly, the Rayleigh ratio of light scattered by the thermal fluctuations is given by

$$R_{dyn}(q{=}0) = \frac{4\pi n^2\left(\frac{dn}{d\phi}\right)^2}{\lambda_0^{\ 4}}\frac{k_BT\phi^2}{M_{os}} \tag{16}$$

In the present measurements no angular variation of $R_{dyn}$ was observed. The values of $R_{dyn}$ are displayed in Figure 9. In this case the opposite behavior to that of $D_c$ is observed; i.e., the intensity of the scattered light increases moderately as $c_{liq}$ increases. The intensity data, however, exhibit no sign of a divergence at the transition.

The intensity of light scattered by the concentration fluctuations in the gel may also be calculated on the basis of the Flory–Huggins relation in eq 13, using the values of the parameters found from fitting the equilibrium swelling curves. This gives, with eq 15

$$M_{os} = \frac{RT\phi^2}{v_1}\left[\frac{1}{1-\phi} - 2\chi - 3w\phi\right] + G_0\phi^{1/3} \tag{17}$$

Since all measurements were made at swelling equilibrium, the swelling pressure $\omega = 0$. Thus, making use of eq 13, we may write

$$M_{os} = \frac{RT}{v_1}\left[\frac{\phi_{eq}^{\ 2}}{1-\phi_{eq}} - \ln(1-\phi_{eq}) - \phi_{eq} - 3\chi\phi_{eq}^{\ 2} - 4w\phi_{eq}^{\ 3}\right] \tag{18}$$

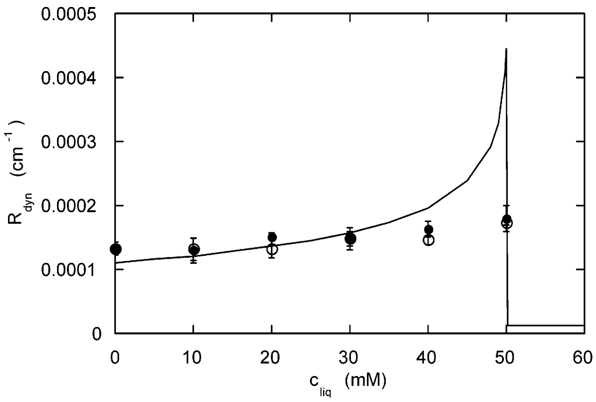

**Figure 9.** Rayleigh ratio $R_{dyn}$ from dynamic light scattering intensity in PNIPA gels 20 °C at equilibrium with aqueous solutions containing different concentrations $c_{liq}$ of phenol (open symbols) and resorcinol (filled symbols). Continuous line is the intensity calculated from eq 19. Unlike Figure 6, measurements could not be made in the collapsed region.

where $\phi_{eq}$ is the equilibrium polymer volume fraction. (Note that $\phi_{eq}$ does not have an analytical expression: it is obtained by solving eq 13 for each value of $c_{liq}$.) The continuous line in Figure 9 is derived from eq 18 for the Rayleigh ratio of the dynamic fluctuations, i.e.

$$R_{theor} = Kk_BT\phi_{eq}^{\ 2}/M_{os} \tag{19}$$

where $K$, the optical constant, is given by

$$K = \frac{4\pi^2 n^2 (dn/d\phi)^2}{N_A\lambda_0^{\ 4}} \tag{20}$$

In eq 20, $N_A$ is Avogadro's number and $dn/d\phi$ is the refractive index increment, expressed in terms of the polymer volume fraction. Its value is determined from the refractive index increment,[25] $dn/dc = 0.167$ mL/g, and the mass density $d_{PNIPA}$ of PNIPA reported in the Experimental Section, $d_{PNIPA} = 1.115$ g cm$^{-3}$.

The weak increase in the experimental value of $R_{dyn}$, displayed in Figure 9, corresponds to a decrease in the osmotic modulus as the transition is approached. This in turn, by virtue of eqs 14 and 15, causes a reduction in $D_c$. The Flory fitting expression, shown by the solid line in this figure, greatly exaggerates the cusp at the transition. The absence of a divergence at the transition, however, both experimentally and in the Flory model, shows that it is of first-order type, in which the osmotic susceptibility undergoes a discontinuity. This finding is consistent with the steplike volume change of Figure 6, another characteristic of first-order transitions. It is also consistent with the observations of Suzuki et al.,[10] according to which addition of an aromatic compound (hydroquinone) lowers the transition temperature and enlarges the volume discontinuity.

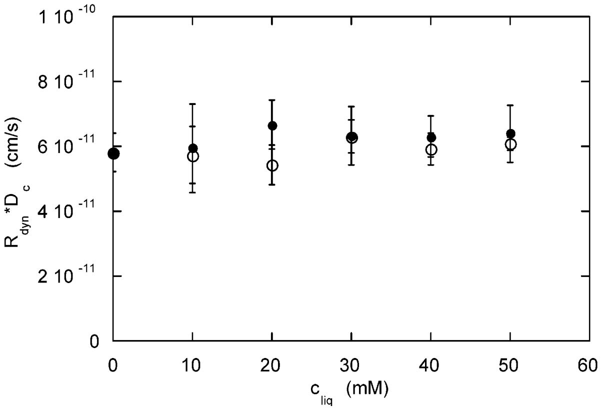

**Figure 10.** Product $R_{\mathrm{dyn}}D_{\mathrm{c}}$ as a function of aromatic content $c_{\mathrm{liq}}$ in the surrounding liquid: phenol (open symbols); resorcinol (filled symbols).

From expressions 14 and 16 it may be remarked that the product $D_{\mathrm{c}}R_{\mathrm{dyn}}$ is proportional to $k_{\mathrm{B}}T\phi/f$ and is therefore independent of the osmotic susceptibility. This quantity is displayed in Figure 10, where, within experimental error, $D_{\mathrm{c}}R_{\mathrm{dyn}}$ is indeed independent of aromatic content. This finding implies that the friction coefficient $f$ of the polymer chains moving in the solvent is independent of the nature of the solvent and the aromatic content. It may therefore be concluded, first, that the cross section of the chains is unaltered, i.e., the aromatic molecules do not significantly interact with the chains, and, second, that the observed decrease in the diffusion coefficient of the gel at higher aromatic content is of purely thermodynamic origin.

A further finding from the observations presented here is that, except in the value of the aromatic uptake (Figure 2), no significant difference appears between the effects of phenol and resorcinol in the swollen region. At the transition, however, the resorcinol solutions show significantly greater repulsion toward the NIPA network.

## Conclusions

The volume transition of PNIPA gels swollen at 20 °C in aqueous solutions of phenol and resorcinol is studied by observations of swelling equilibrium, elastic modulus, and dynamic light scattering. The elastic modulus $G$ of the gels at small strains follows the expected behavior of standard network theory, i.e., $G \propto \phi^{1/3}$, where $\phi$ is the polymer volume fraction. Dynamic light scattering measurements show that the chain motions associated with the osmotic fluctuations in the gel are ergodic. The collective diffusion coefficient $D_{\mathrm{c}}$ decreases at high aromatic content, while the dynamic component of the scattering intensity, $R_{\mathrm{dyn}}$, increases. No divergence of $R_{\mathrm{dyn}}$ close to the transition, however, is observed, as expected in a first-order transition. The light scattering response of the gels swollen in both solvents is closely similar. Within experimental error the product $D_{\mathrm{c}}R_{\mathrm{dyn}}$ is independent of aromatic concentration. It follows that the friction coefficient of the polymer chains is not modified in the presence of the binary solvent and that the reduction in the value of $D_{\mathrm{c}}$ is due purely to the reduction in the osmotic modulus of the system.

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