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The first example of thermochromism of dyes embedded in transparent polymer gel networks

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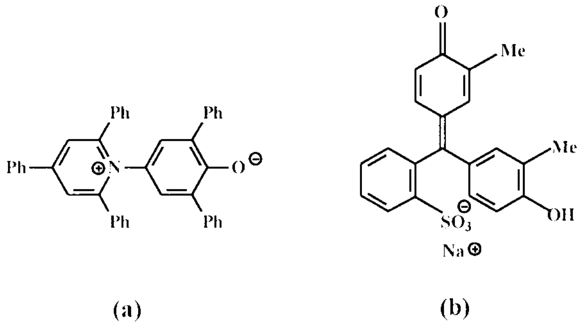
Novel dye containing transparent hydrogels responding to changes in temperature with reversible color changes (thermochromism) are presented. The betaine dye 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate (DTPP), and the well known indicator dye Cresol Red (Fig. 1) exhibit an outstanding thermochromism, if they are embedded in an aqueous polyvinyl alcohol–borax–surfactant gel network. In case of DTPP at pH = 8.5, the color changes gradually from colorless at 10 °C to a deep violet at 80 °C. Similarly, for Cresol Red a change from yellow to wine-red was observed. An explanation for the observed reversible color changes in the closed hydrogel systems is given by a temperature-induced shift of the proton-transfer equilibrium between the phenolate and the phenol form of the dye molecules in the micro-environment of the gel network. The new thermochromic hydrogels can be useful in a wide range of applications, such as temperature sensors, large-area displays, and so-called smart or intelligent windows.

During the last few years, so-called smart or intelligent hydrogels that respond to stimuli such as changes in temperature, pH, electric or magnetic fields have met with growing interest, both regarding their scientific handling and their practical use.[1] Tuneable thermochromic hydrogel films of 125 to 500 µm thickness were created by embedding a crystalline colloidal array of polystyrene spheres within a poly(*N*-isopropylacrylamide)-hydrogel that swells and contracts with temperature.[2] For many applications, *e.g.* as color sensors, for large area displays with higher information density, or for intelligent windows, it is useful to produce fully transparent hydrogels, which can reversibly change their color in the practically relevant temperature range of 10–80 °C along with a constant volume in dependence on temperature. Therefore, we looked for appropriate dyes which would exhibit, for the first time, thermochromism in hydrogels. We began our investigations with the pyridinium *N*-phenolate betaine dye DTPP (Reichardt's Dye), which is well-known as an empirical indicator of solvent polarity because of its strong negative solvatochromism.[3] Not in water but in ethanolic solution thermochromic properties of DTPP were also observed, due to a temperature-induced differential desolvation of the highly zwitterionic ground state of DTPP, relative to its less dipolar first excited state.[4]



(a) (b)

Fig. 1 Molecular structures of the used dyes: (a) DTPP, and (b) Cresol Red.

DTPP is poorly soluble in water ($\approx 2\times10^{-6}$ mol l^{-1}).[5] However, it can be solubilized by adding a suitable surfactant.[3] As surfactant the neutralised *N*,*N*-dimethyl-*N*-tetradecylammonioacetic acid bromide (N-DTB)[6] was selected. In the presence of N-DTB the longest-wavelength Vis-absorption band of DTPP is shifted by $\Delta\lambda = 87$ nm bathochromically compared with its maximum in pure water ($\lambda_{max} = 453$ nm),[7] which is attributed to the lower solvent polarity in the micellar micro-environment of the dye.[8] The gel network was obtained by addition of borax ($Na_2B_4O_{10}\cdot10H_2O$) as gel-network former to a 20% aqueous solution of PVA.[9] The resulting hydrogel[10] possesses a pH-value of 8.5 at room temperature and is colorless as well as transparent. On heating, this hydrogel becomes reversibly more and more violet-colored reaching eventually a deep violet at 80 °C. The absorption intensity of the Vis-absorption band of DTPP in the gel matrix at $\lambda_{max} = 550$ nm (layer thickness $d = 1.00$ cm) increases by about tenfold in the investigated temperature range (Fig. 2). As shown by the bunch of Vis-spectra the color changes continuously with increasing temperature. The increase in absorption intensity is accompanied by a bathochromic shift of the Vis-absorption maximum from $\lambda_{max} = 537$ nm (10 °C) to $\lambda_{max} = 555$ nm (80 °C), *e.g.* of $\Delta\lambda = 18$ nm. This bathochromic bandshift corresponds to the behaviour of DTPP in pure ethanol (bandshift from $\lambda_{max} = 550$ nm at 25 °C to $\lambda_{max} = 568$ nm at 75 °C)[4] and may be caused by a similar temperature-induced differential desolvation of the electronic ground state.

Another phenol-substituted dye, the well-known indicator dye Cresol Red, can also be used to obtain a reversible thermochromic hydrogel. For this hydrogel we used 5% aqueous PVA. As surfactant the commercially available sulfobetaine 3-(*N*,*N*-dimethyl-*N*-dodecylammonio)propanesul-

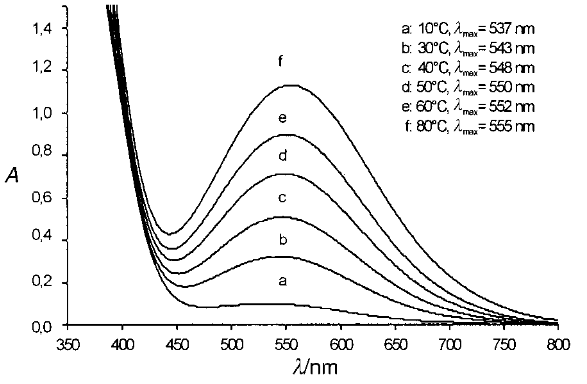


Fig. 2 Visible absorption spectra of the longest-wavelength absorption band of DTPP in the gel network: dependence on temperature (pH = 8.5, $d = 1.00$ cm).

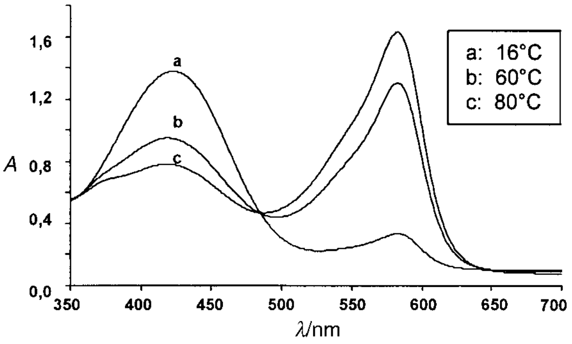


Fig. 3 UV–Vis-absorption spectra of the longest-wavelength absorption band of Cresol Red in the gel network: dependence on temperature (pH = 8.5, d = 1.00 cm).

fonate was chosen since N-DTB leads to turbidity in the gel after a short time. After the gel preparation,[11] we obtained at room temperature (pH = 8.5) an optically clear yellow gel, which on raising the temperature changes reversibly its color to wine-red at 80 °C. In order to obtain this color change the pH-value of the gel mixture must be adjusted to *ca.* 8.5. If the pH-values are below 8.0 or above 9.0, no color changes are observed. With increasing temperature the absorption behaviour in the visible spectral range (Fig. 3) shows an increase of the Vis-absorption band intensity at λ_{max} = 581 nm while the intensity of the second band at λ_{max} = 419 nm is reduced. All spectral curves meet at an isosbestic point at λ = 486 nm.

The color changes are primarily manifested by changes of the absorption intensity and shifts in the absorption maxima are comparatively small, suggesting that solvatochromism is not responsible for the observed behaviour. The absorption behaviour of the dyes at 10 or 16 °C is quite similar to their absorption behaviour under neutral or weak acidic conditions where the longest-wavelength Vis-absorption band disappears because of *O*-protonation. At high temperature (80 °C) the absorption behaviour is similar to the behaviour under weak alkaline conditions (pH = 9.0).[12] Obviously a temperature variation causes a shift in the proton-transfer equilibrium between the phenolate and the phenol forms of the dye molecules (Fig. 4). According to this explanation, by increasing the temperature the amount of the dye in the phenolate form is increased. For DTPP a pK_a-value of 8.63 was measured in water,[5] so that in aqueous solution at pH = 8.5 about 50% of DTPP should be present in the phenol form. Zhou *et al.* reported on the thermochromic properties of lanthanide chelates with the indicator dye Xylenol Orange in aqueous solutions, which are also due to a temperature-dependent shift of the protolytic equilibrium.[13] In contrast to these results, the dyes used in our investigation exhibit no significant color changes with temperature in water, aqueous PVA, surfactant solution, or PVA–surfactant solution under otherwise equal conditions (concentrations, pH). Therefore, the embedding of the dyes into the PVA–borax–surfactant gel network is crucial for the thermochromic behaviour. We assume that in the micro-environment of the dye molecules in the PVA–borax–surfactant gel network at lower temperatures the phenol form of the dye molecules is stabilised over co-operative linkages (amongst others by hydrogen-bond formation to the OH groups of PVA). With increasing temperature, the co-operative linkages are cleared gradually again and the dyes are then preferentially present in the deeply colored phenolate form.

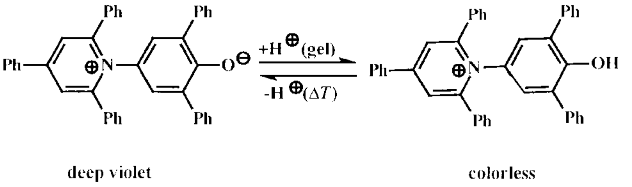


Fig. 4 Proton-transfer equilibrium between the phenol and phenolate form of DTPP.

The existence of a temperature-dependent equilibrium between the phenol and the phenolate form is supported by the occurrence of isosbestic points in the UV–Vis-absorption spectra of DTPP at λ = 355 nm and of Cresol Red at λ = 414 nm.

The investigations presented here demonstrate for the first time the existence of a reversible thermochromism in transparent hydrogels.[14] This phenomenon may have many applications. It can be expected that other phenol-substituted dyes will exhibit a similar behaviour, if the corresponding optimum reaction conditions (concentrations, pH, surfactant) are found.

Notes and references

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6 (*a*) A. Amin-Alami, N. Kamenka and S. Partyka, *Thermochim. Acta*, 1987, **122**, 171; (*b*) Before using the aqueous solution of N-DTB, it was neutralized with the corresponding amount of NaOH to give the zwitterionic inner salt.
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10 The resulting gel was prepared by mixing 30 g of a 20% aqueous solution of PVA (Aldrich, PVA 13 000–23 000, hydrolysed to 85%), 6.0 g of 1 M sodium hydroxide solution, 30 g of an aqueous borate buffer solution (pH = 11), 1.3 g of a 2.2% ethanolic solution of DTPP, 6.0 g of a 30% aqueous N-DTB solution, and leaving the gel mixture for some hours at room temperature.
11 The resulting gel was prepared by mixing 20 g of a 5% aqueous solution of PVA (Dajac Lab., PVA 100 000, 98% hydrolysed), 1.25 g of a 2.2% aqueous borax solution, 0.42 g of an aqueous borate buffer solution (pH = 11), 0.056 g of a 2.2% aqueous solution of Cresol Red, 1.6 g of a 15% aqueous sulfobetaine solution, and leaving the gel mixture for some hours at room temperature.
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