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Color Change of *N*-Isopropylacrylamide Copolymer Bearing Reichardts Dye as Optical Sensor for Lower Critical Solution Temperature and for Host−Guest Interaction with *β*-Cyclodextrin

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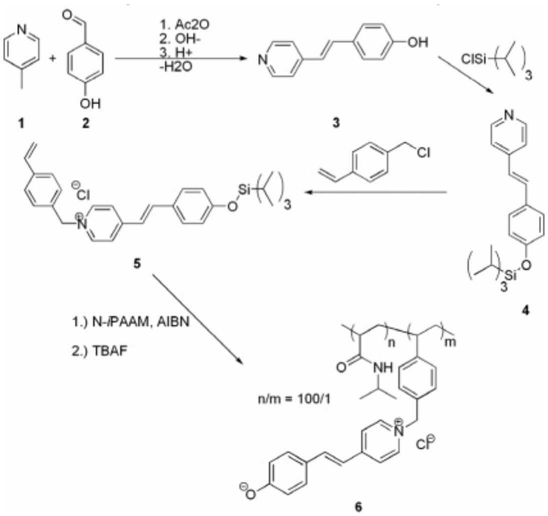
Color change of suitable dyes depending on the polarity of the environment is a well-known photochromic effect. As an example, 4-[(1-methyl-4(1*H*)-pyridinylidene)ethylidene]-2,5-cyclohexadien-1-one hydrate (Reichardts dye) is a special dye showing a so-called negative solvatochromic effect.[1−10] Recently, the solvatochromic behavior of simple physical polymer−dye mixtures in solution[11,12] or films[13] and covalently bound dyes on a Merrifield's peptide resin[14] have been reported. A slight effect on the adsorption bands of a Rose−Bengal-functionalized poly(*N*-isopropylacrylamide) (PN*i*PAAM)[15] or the influence of an attached fluorescent dye to PN*i*PAAM on the phase transition[16] have been studied by spectrometric methods. Furthermore, a previously published patent instructs about the synthesis of some solvatochromic polymers via polymer analogue reactions.[17]

Some hydrophilic polymers such as PN*i*PAAM typically show a lower critical solution temperature (LCST) behavior in aqueous media. This means that the polymer is soluble in water below its LCST (PN*i*PAAM ≈ 34 °C) and becomes insoluble above the LCST.[18] The LCST value may be influenced by supramolecular interaction with cyclodextrin[19,20] and can be influenced also by copolymerization or chemical modification of the acrylamide polymer itself. Covalently cross-linked LCST polymers find some potential application as hydrogels in medical and biochemical fields for controlled drug delivery[21] and as materials for bioreactors.[22] Recently, we synthesized switchable hydrogels consisting of LCST copolymers cross-linked with cyclodextrin dimers.[23]

In the present paper, we wish to report about the behavior of a LCST copolymer bearing a covalently attached solvatochromic dye. Moreover, we investigated the solvatochromism of this polymer in the presence of randomly methylated *β*-cyclodextrin (CD).

The synthesis and copolymerization of a silyl-protected monomer 4-((*E*)-2-{4-[(triisopropylsilyl)oxy]phenyl}ethenyl)-1-(4-vinylbenzyl)pyridinium chloride **5** is described in Scheme 1. Therefore, 4-methylpyridine **1** was condensed with *p*-hydroxybenzaldehyde **2**, the hydroxy group of 4-[(*E*)-2-(4-pyridinyl)ethenyl]phenol **3** was protected with triisopropylsilane, and the pyridinium group was functionalized with 1-(chloromethyl)-4-vinylbenzene to gain monomer **5**. Finally, the solvatochromic copolymer **6** was prepared by radical copolymerization of monomer **5** and *N*-isopropylacrylamide according to Scheme 1.

Scheme 1. Synthesis of Solvatochromic Copolymer **6**



Tetrabutylammonium fluoride was used to deprotect the silylated dye moiety **6**. Because of the phenolic group, the color of the polymer in aqueous solution is strongly pH-sensitive. It turned out that the copolymerized protonated dye is yellow and shows no significant solvatochromism in its UV/vis spectrum. In contrast, the polymer-attached dye becomes orange when deprotonated and shows the typical solvatochromism in its UV/vis spectrum in analogy to low molecular weight dyes as described in the literature[24] (for maximal absorbance of copolymer **6** at various pH compared to the free dye in trichloromethane and water, see the Supporting Information).

As postulated, a characteristic bathochromic shift from orange to dark red could be observed when the aqueous polymer solution at basic pH is heated above the LCST value of about 31 °C (Figure 1). This means that, during precipitation of the polymer due to heating above the LCST value, most of the polar water molecules are pushed out of the polymer coil. This causes a negative change of polarity next to the dye moiety, which results in a color change. This temperature-dependent color change is fully reversible. However, the protonated copolymer showed no color change effect due to the solubility change at its LCST (Figure 2).

The above-described effect might also be caused by dye−dye interaction. To evaluate the effects of the polarity of the environment near by the dye moiety, we also investigated the influence of CD on the absorbance of the polymer-attached dye (pH 10, betaine form). We clearly found that the bathochromic shift due to negative polarity change was also visible after excessive CD addition to the aqueous polymer solution below its LCST. This means that the complexation of the copolymer **6** by CD could also be recognized simply by the naked eye. The unpolar cavity of CD creates an unpolar environment around the dye moiety. The color change due to CD threading is nearly identical compared to the color change caused by phase transition. This proves that the dye−dye interaction plays a minor role. As mentioned above, this effect influenced only the deprotonated polymer at high pH. Addition of CD to the polymer solution with the protonated dye (pH 1) showed only a small effect on the visible spectrum. UV measurements started directly after acid addition. Thus, decomposition of CD is not to be expected. This small effect might be due to weak interaction of

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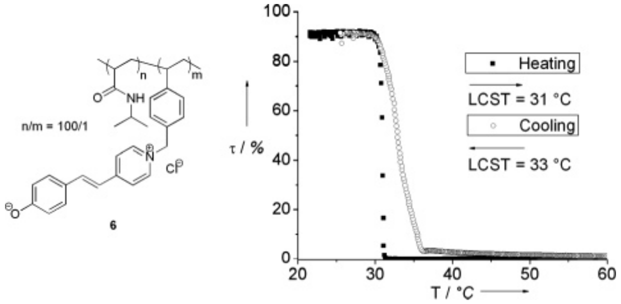

Figure 1. Transmittance (τ) of a solution of polymer **6** in water (5 mg/mL) at pH 10 versus temperature during heating and cooling.

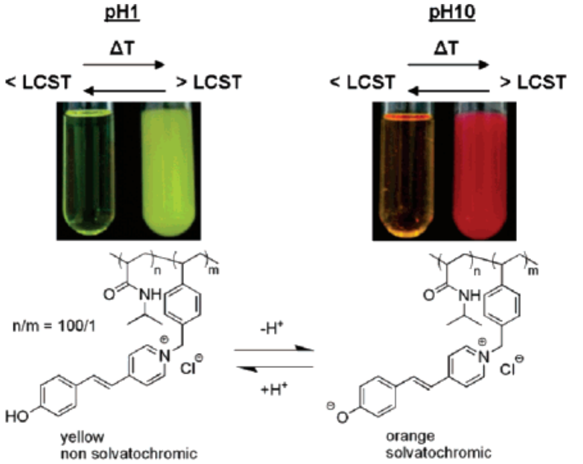

Figure 2. Color effects of copolymer **6** at pH 1 (no shift) and at pH 10 (bathochromic shift).

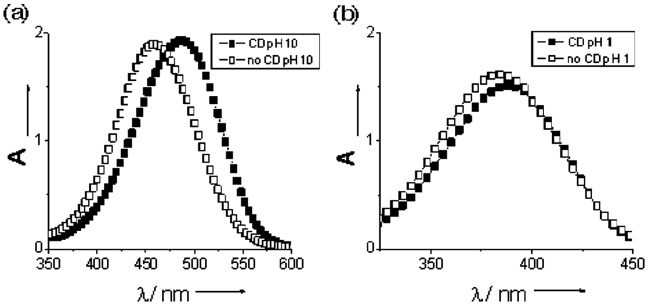

Figure 3. Visible spectra of a 1.25 g/mL aqueous solution of **6** with (■) (addition of 60 mg of CD) or without (□) (addition of 60 mg of glucose) at pH 10 (a) and at pH 1 (b).

CD with the protonated dye. In measurements of an aqueous solution of **6** without CD, glucose was excessively added to this solution to verify the host−guest interactions. As it was expected, no color change could be detected (Figure 3).

Finally, we investigated the relation between the copolymer composition and the resulting LCST in aqueous media. A 1 mol % amount of incorporated dye has no significant influence on the LCST of copolymer **6**. However, if the molar ratio of *N*-isopropylacrylamide to comonomer **5** is changed from 100/1 to 20/1, the LCST of copolymer **6** was reduced from 32 to 23 °C at pH 1 for the protonated dye and from 33 to 29 °C at pH 10 for the betainic dye. This can be explained as the LCST of unfunctionalized PN*i*PAAM is not pH dependent[25] and semiempirical measurements of the dipole moment gave a dipole moment of 4.005 D for the protonated dye in comparison to 10.715 D for the betainic dye. According to this, the protonated dye is less polar than the betainic dye. Thus, the LCST decreases more strongly with increasing amount of the protonated dye in copolymer **6**.

In conclusion, we prepared a colored copolymer **6** with LCST behavior that represents an interesting type of environmental sensitive material. It is possible to change the color of this copolymer via pH, type of solvent, temperature, and host−guest interaction with cyclodextrin. Actually, these effects are completely reversible. Therefore, the behavior of this new polymer-attached solvatochromic dye as an optical sensor in solution and in bulk may be useful for the development of new intelligent signal materials.

Supporting Information Available: Experimental preparations and analysis for **3**, **4**, **5**, and **6** and maximal absorbance of copolymer **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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