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Temperature- and Light-Responsive Polyacrylamides Prepared by a Double Polymer Analogous Reaction of Activated Ester Polymers

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ABSTRACT: Two different series of polyacrylamides containing different amounts of salicylideneaniline moieties have been synthesized via a double polymer analogous reaction of poly(pentafluorophenyl acrylate) (PPFPA). All copolymers were designed to exhibit a lower critical solution temperature (LCST) in aqueous solution, which was dependent on (i) the amount of incorporated chromophoric salicylideneaniline groups and (ii) the isomerization state of the respective salicylideneaniline group. Higher LCST values were measured for UV-irradiated solutions of the copolymers in comparison to the nonirradiated copolymer solutions. A maximum difference in the LCST of up to 13 °C was found for poly(*N*-cyclopropylacrylamide) copolymer containing 15.0 mol % of salicylideneaniline groups. Within this temperature range, a reversible solubility change of the copolymer could be induced by irradiation with light.

Introduction

Stimuli-responsive polymers—so-called smart polymers—have attracted great interest in academic and applied science recently. Most commonly, approaches take advantage of thermally induced, reversible phase transitions. In this context, polymers based on polyacrylamides found great interest as thermoresponsive polymers in aqueous solution. Many polyacrylamides, e.g., poly(*N*-isopropylacrylamide) (PNIPAM)[1,2] or poly(*N*-cyclopropylacrylamide),[3] feature a sharp transition behavior in water in response to changes of the temperature. Accordingly, such polymers featuring a lower critical solution temperature (LCST) in water are expected to find application in many scientific areas. As an example, drug delivery[4−9] or immobilization of enzymes and cells[10−12] can be mentioned.

Besides polymers that are responsive to a single stimulus, recently research on polymers that show a responsive behavior to multiple stimuli has been intensified.[13,14] Other stimuli besides temperature can for example be pH,[15] ionic strength,[16] or light.[17,18] Very appealing and important for applications are polymers that are responsive to light and temperature, and accordingly, there have been several reports on temperature-responsive copolymers that contain a light-responsive moiety, for example azobenzene groups.[19−27]

In the following, the synthesis of temperature- and light-responsive polyacrylamide copolymers featuring salicylideneaniline as a photochromic group is reported. Salicylideneaniline is known to isomerize upon irradiation with UV light from the *enol* form into the *keto* form, which results in a change of the dipole moment.[28−34] Two different series of thermo- and light-responsive polyacrylamide derivates that take advantage of salicylideneaniline as the corresponding photochromic group will be synthesized and characterized. The synthesis extends the thorough investigated polymer analogous reaction of activated ester polymers as tools for functional polymers[35−39] to a double polymer analogous reaction of poly(pentafluorophenyl acrylate) (PPFPA).

Experimental Section

Materials. All chemicals and solvents were commercially available and used as received unless otherwise stated. Tetrahydrofuran (THF), 1,4-dioxane, and diethyl ether were previous distilled over sodium. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from diethyl ether and stored at −7 °C. As dialysis membranes Spectra/Por 3 (MWCO 3500) were used. Benzyl dithiobenzoate was synthesized as described in the literature.[40]

Instrumentation. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer in deutorated solvents. ^{19}F NMR spectra were recorded on a Bruker 400 MHz FT-NMR spectrometer. Chemical shifts (δ) were given in ppm relative to TMS. Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions, M_w/M_n, of polymer samples with respect to polystyrene standards (PSS). GPC measurements were performed in THF as solvent and with the following parts: pump PU 1580, autosampler AS 1555, UV detector UV 1575, RI detector RI 1530 from Jasco, and miniDAWN Tristar light scattering detector from Wyatt. Columns were used from MZ-Analysentechnik: MZ-Gel SDplus 102 Å, MZ-Gel SDplus 104 Å, and MZ-Gel SDplus 106 Å. The elution diagrams were analyzed using the ASTRA 4.73.04 software from Wyatt Technology. Calibration was done using polystyrene standards. The flow rate was 1 mL/min at a temperature of 25 °C. UV/vis spectra were recorded on a Jasco V-630 photospectrometer. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer using an ATR unit. FD masses were measured on a MAT 95 Finnigan mass spectrometer. Cloud points were determined in Millipore water at a concentration of 40 mg/mL and were observed by optical transmittance of a light beam ($\lambda = 632$ nm) through a 1 cm sample quartz cell. The measurements were performed in a Jasco V-630 photospectrometer with a Jasco ETC-717 Peltier element. The intensities of the transmitted light were recorded versus the temperature of the sample cell. The heating rate was 1 °C/min. Irradiation experiments of the polymer solutions were performed in the sample cell of the photospectrometer using an Oriel Instruments 500 W mercury lamp with a 365 nm filter and an optical fiber (see Scheme S2).

Pentafluorophenyl Acrylate (PFPA). 80 g (0.43 mol) of pentafluorophenol and 52.5 g (0.52 mol) of triethylamine (TEA) were

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dissolved in 500 mL of dry diethyl ether, and 47.2 g (0.52 mol) of acryloyl chloride was added dropwise through a funnel under cooling with an ice bath. After stirring an additional 2 h at room temperature, the precipitated salt was removed by filtration. After evaporation of the solvent, the residue was filtered again and purified with column chromatography (column material: silica gel; solvent: petroleum ether). 75 g (0.32 mol, 74%) of a colorless liquid was obtained. The pure PFPA was stored at −7 °C. ^{1}H NMR ($CDCl_3$): δ/ppm: 6.70 (d, 1H), 6.35 (dd, 1H), 6.16 (d, 1H). ^{13}C NMR ($CDCl_3$): δ/ppm: 161.5 (s), 142.8 (m), 141.2 (m), 139.5 (m), 137.9 (m), 136.2 (m), 134.9 (s), 125.1 (s). ^{19}F NMR (CDCl3): δ/ppm: −162.77 (d, 2F), −158.39 (t, 1F), −153.02 (d, 2F). FT-IR (ATR mode): 1772 cm^{-1} (C=O reactive ester band), 1516 cm^{-1} (C=C aromatic band).

Poly(pentafluorophenyl acrylate) (PPFPA). In a typical RAFT polymerization a mixture of 20 g (0.084 mol) of PFPA, 51.5 mg (2.11×10^{-4} mol) of benzyl dithiobenzoate, and 4.3 mg (2.62×10^{-5} mol) of AIBN were placed into a Schlenk flask. After addition of 50 mL of dry 1,4-dioxane, four freeze−pump−thaw cycles were performed to degas the solution. The flask was filled with argon, immersed in a preheated oil bath of 80 °C, and stirred overnight. After cooling to room temperature, the polymer was isolated by precipitation in hexane. The crude polymer was dissolved in THF, precipitated again twice into hexane, centrifuged, and finally dried in a vacuum oven at 40 °C. Yield 13 g (65%) of a pink powder. ^{1}H NMR ($CDCl_3$): δ/ppm: 3.10 (br s), 2.51 (br s), 2.13 (br s). ^{13}C NMR ($CDCl_3$): δ/ppm: 169.28 (s), 142.24 (m), 138.93 (m), 135.77 (m), 40.11 (br s), 34.27 (br s). ^{19}F NMR ($CDCl_3$): δ/ppm: −162.28 (br s), −157.15 (br s), −153.56 (br s). FT-IR (ATR mode): 1783 cm^{-1} (C=O reactive ester band), 1515 cm^{-1} (C=C aromatic band), 1090 cm^{-1} (C−O ester band).

Synthesis of the Copolymers P1. To two different solutions containing each 1.5 g of PPFPA and 2 mL of TEA in 20 mL of THF were added dropwise 7.6 mg (**P1a**: 6.30×10^{-5} mol) and 30.8 mg (**P1b**: 2.52×10^{-4} mol) of 4-aminobenzylamine were dissolved in 5 mL of THF. The solutions were stirred for 2 h under a nitrogen atmosphere at room temperature. Afterward, 2 mL of isopropylamine (0.023 mol) was added into each flask. After additional 18 h of stirring, the solvent of each sample was removed by evaporation in vacuum. The colorless residues were suspended in 10 mL of water and dialyzed against diluted ammonia overnight. The dialyzed solutions were evaporated, and the residues were three times dissolved in 5 mL of THF and precipitated into hexane. Usually, after centrifugation and drying in a vacuum oven at 40 °C, 0.35 and 0.39 g of colorless polymers were obtained. ^{1}H NMR (CD_2Cl_2): δ/ppm: 7.06 (s), 6.64 (s), 6.27 (br s), 4.23 (br s), 3.98 (s), 2.10 (br s), 1.60 (br s), 1.12 (s). FT-IR (ATR mode): 3306 cm^{-1} (amide N−H valence), 2971 cm^{-1} (C−H valence band), 1640 cm^{-1} (C=O amide band I), 1533 cm^{-1} (C=O amide band II), 838 cm^{-1} (aromatic 1,4-disubstitution).

Synthesis of the Copolymers P2. To four different solutions containing each 1.5 g of PPFPA and 2 mL of TEA in 20 mL of THF were added dropwise 15.4 mg (**P2a**: 1.26×10^{-4} mol), 38.4 mg (**P2b**: 3.15×10^{-4} mol), 76.9 mg (**P2c**: 6.30×10^{-4} mol), and 115.3 mg (**P2d**: 9.45×10^{-4} mol) of 4-aminobenzylamine dissolved in 5 mL of THF. The solutions were stirred for 2 h under a nitrogen atmosphere at room temperature. Afterward, 2 mL of cyclopropylamine (0.029 mol) was added into each flask. After additional 18 h of stirring, the solvent of each sample was removed by evaporation in vacuum. The colorless residues were suspended in 10 mL of water and dialyzed against diluted ammonia overnight. The dialyzed solutions were evaporated, and the residues were three times dissolved in 5 mL of methanol and precipitated into diethyl ether. Usually, after centrifugation and drying in a vacuum oven at 40 °C, between 0.33 and 0.54 g of colorless polymers was obtained. ^{1}H NMR (MeOD): δ/ppm: 8.03 (br s), 7.09 (s), 6.73 (s), 4.25 (br s), 2.72 (s), 2.07 (br s), 1.59 (br s), 0.66 (d). FT-IR (ATR mode): 3293 cm^{-1} (amide N−H valence), 2971 cm^{-1} (C−H valence band), 1646 cm^{-1} (C=O amide band I), 1517 cm^{-1} (C=O amide band II), 826 cm^{-1} (aromatic 1,4-disubstitution).

Synthesis of the Temperature- and Light-Sensitive Copolymers P3. To two different solutions containing each 300 mg of **P1a** and **P1b** in 10 mL of ethanol were added dropwise 2 mL (0.019 mol) of salicylaldehyde. The solutions were stirred for 2 h under a nitrogen atmosphere at room temperature. Afterward, the solvent of each sample was removed by evaporation in vacuum. The yellow residues were three times dissolved in 5 mL of THF and precipitated into hexane. Usually, after centrifugation and drying in a vacuum oven at 40 °C, 0.18 and 0.27 g of yellow polymers were obtained. ^{1}H NMR (CD_2Cl_2): δ/ppm: 13.20 (s), 8.67 (s), 7.38 (br s), 6.95 (s), 6.37 (br s), 4.41 (br s), 4.00 (s), 3.35 (br s), 2.08 (br s), 1.65 (br s), 1.12 (s). FT-IR (ATR mode): 3302 cm^{-1} (amide N−H valence), 2981 cm^{-1} (C−H valence band), 1644 cm^{-1} (C=O amide band I), 1540 cm^{-1} (C=O amide band II), 747 cm^{-1} (aromatic 1,2-disubstitution).

Synthesis of the Temperature- and Light-Sensitive Copolymers P4. To four different solutions containing each 300 mg of **P2a**, **P2b**, **P2c**, and **P2d** in 10 mL of ethanol were added dropwise 2 mL (0.019 mol) of salicylaldehyde. The solutions were stirred for 2 h under a nitrogen atmosphere at room temperature. Afterward, the solvent of each sample was removed by evaporation in vacuum. The yellow residues were three times dissolved in 5 mL of methanol and precipitated into diethyl ether. Usually, after centrifugation and drying in a vacuum oven at 40 °C, between 0.21 and 0.26 g of yellow polymers was obtained. ^{1}H NMR (MEOD): δ/ppm: 8.78 (br s), 7.38 (br s), 6.95 (s), 4.39 (br s), 2.70 (s), 2.07 (br s), 1.60 (br s), 0.67 (d). FT-IR (ATR mode): 3287 cm^{-1} (amide N−H valence), 2968 cm^{-1} (C−H valence band), 1645 cm^{-1} (C=O amide band I), 1527 cm^{-1} (C=O amide band II), 756 cm^{-1} (aromatic 1,2-disubstitution).

Synthesis of 4-(2-Hydroxybenzylideneamino)benzoic Acid. 5.42 g (0.0396 mol) of 4-aminobenzoic acid was dissolved in 120 mL of ethanol, and 4.83 g (0.0396 mol) of salicylaldehyde in 80 mL of ethanol was added rapidly under magnetically stirring. After several minutes, the final yellow product started to precipitate. The mixture was totally stirred 2 h at room temperature, and the precipitated solid was isolated by filtration through a glass frit. The product was washed with ethanol and dried in a vacuum oven at 40 °C. 8.5 g (0.0353 mol, 89%) of yellow 4-(2-hydroxybenzylideneamino)benzoic acid was obtained. ^{1}H NMR (DMSO): δ/ppm: 12.79 (br s, 1H), 8.98 (s, 1H), 8.01 (d, 2H), 7.68 (d, 1H), 7.47 (d, 2H), 7.42 (d, 1H), 6.99 (m, 2H). FT-IR (ATR mode): 1679 cm^{-1} (C=O aryl acid band), 1600 cm^{-1} (C=C aromatic valence), 1569 cm^{-1} (C=C aromatic valence), 1287 cm^{-1} (C−O band), 860 cm^{-1} (aromatic 1,4-disubstitution), 751 cm^{-1} (aromatic 1,2-disubstitution). MS (FD) *m*/*z* (%): 241.8 (12.97), 240.8 (100.00).

Results and Discussion

First, poly(pentafluorophenyl acrylate) (PPFPA) was synthesized by a reversible addition−fragmentation chain transfer (RAFT) polymerization utilizing benzyl dithiobenzoate as a chain transfer agent in 1,4-dioxane. The resulting polymer was obtained by precipitation and had molecular weight $M_n = 24\,900$ g/mol with a narrow molecular weight distribution ($M_w/M_n = 1.36$). PPFPA was then subjected to a first polymer analogous reaction with different amounts of 4-aminobenzylamine in tetrahydrofuran at room temperature (see Scheme 1). After 2 h of reaction, the remaining pentafluorophenyl ester groups were converted with an excess amount of isopropylamine or cyclopropylamine, respectively, yielding two series of temperature-responsive polyacrylamide derivates. 4-Aminobenzylamine will react selectively with its aliphatic amino group because the nucleophility of the aromatic amino group is not sufficient to attack the activated ester polymer, as we have reported recently.[35] The two resulting copolymer series **P1** and **P2** were purified by dialysis against dilute ammonia as well as precipitation to remove any pentafluorophenol salts.

All polymers were analyzed by FT-IR spectroscopy, GPC measurement, and NMR spectroscopy. As an example, the IR spectrum of copolymer **P1b** is shown in Figure 1. The quantitative conversion of the polymer analogous reaction was confirmed by the complete vanishing of the activated ester polymer band at 1783 cm^{-1} of the PPFPA and the appearance of two amide bands at 1640 and 1533 cm^{-1} of the copolymer **P1b**, respectively. Additionally, the appearance of the NH group valence vibrations in the infrared spectrum appeared at 3306 cm^{-1}. In Figure 2, the GPC elugram of PPFPA and the copolymer **P1b** are shown. After the first polymer analogous reaction, the GPC trace of **P1b** (M_n(**P1b**) = 9400 g/mol) is shifted to lower molecular weights in comparison to the GPC trace of PPFPA (M_n(PPFPA) = 24 900 g/mol) due to the decrease of molecular weight per repeating unit. However, the obtained value for the molecular weight of the polymer **P1b** (M_n(**P1b**) = 9400 g/mol) is slightly lower than the theoretical value (M_n(theor) = 11 800 g/mol) calculated from the ^{1}H NMR data of the copolymer composition taking the molecular weight of PPFPA into account. A suitable explanation for this divergence might result from the calibration of the GPC with respect to polystyrene standards. Nevertheless, a successful conversion could be demonstrated from the GPC shift of the polymer **P1b**. Noteworthy, the molecular weight distribution did not change after the postmodification. The conversion was also followed by ^{1}H NMR spectroscopy, and as an example, the ^{1}H NMR of copolymer **P1b** is shown in Figure 3. All characteristic proton signals from the polyacrylamide sidegroup (in CD_2Cl_2: δ/ppm: 6.27, 3.98, 1.12) and from the aromatic aniline protons (in CD_2Cl_2: δ/ppm: 7.06, 6.64) can be identified. Further, ^{19}F NMR spectroscopy was not able to detect a fluorine signal anymore, indicating a complete conversion of all pentafluorophenyl ester

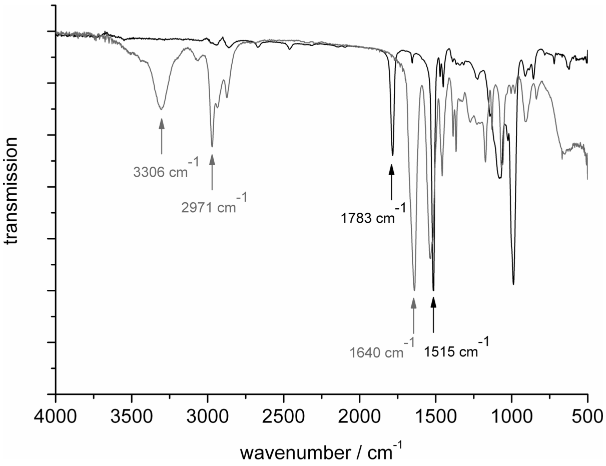

Figure 1. FT-IR spectra of poly(pentafluorophenyl acrylate) (black line) and the copolymer **P1b** (gray line).

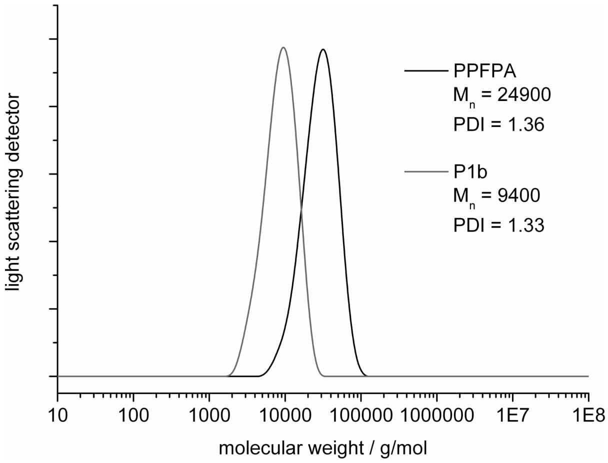

Figure 2. GPC elugram of poly(pentafluorophenyl acrylate) (black line) and the copolymer **P1b** (gray line).

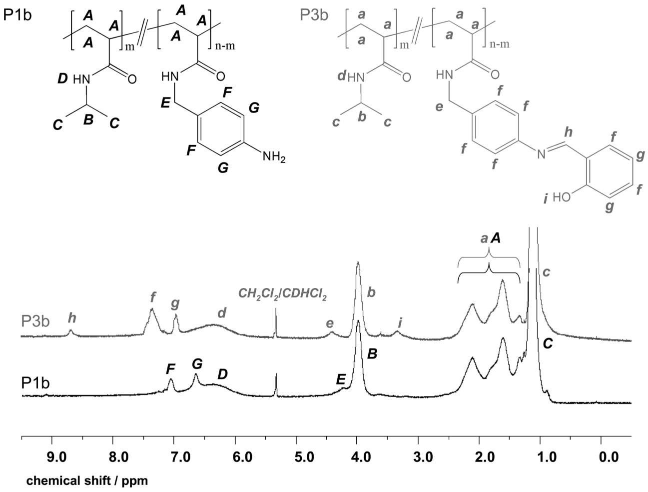

Figure 3. ^{1}H NMR of the copolymer **P1b** (black line) and the thermo- and light-responsive copolymer **P3b** (gray line) in CD_2Cl_2.

Scheme 1. Synthetic Scheme of Two Polyacrylamide Series (P3 and P4) Containing Salicylideneaniline Moieties in Varying Amounts Prepared by a Double Polymer Analogous Reaction of the Reactive Precursor Polymer Poly(pentafluorophenyl acrylate) (PPFPA)

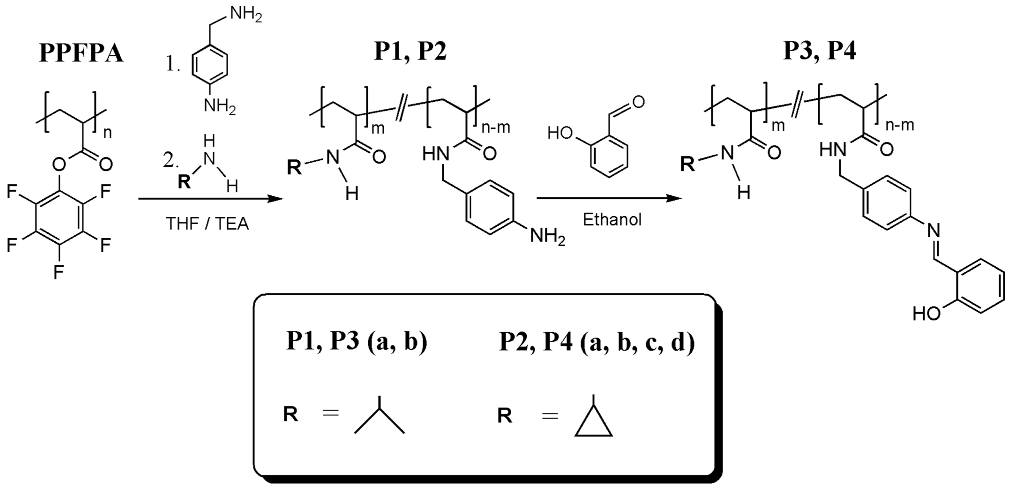

Table 1. Composition and LCST Values for the Copolymer Series P3 and P4

polymer	amount of salicylideneaniline [mol %] (calculated)	amount of salicylideneaniline [mol %] (measured by UV/vis)	amount of salicylideneaniline [mol %] (measured by ^{1}H NMR)	LCST before irradiation [°C] (measured by turbidimetry)	LCST during irradiation [°C] (measured by turbidimetry)	ΔLCST [°C]
P3a	1.0	0.4	1.0	29.7	30.6	0.9
P3b	4.0	3.8	4.0	26.3	30.6	4.3
P4a	2.0	2.4	2.0	41.8	46.4	4.6
P4b	5.0	3.3	4.0	36.5	38.5	2.0
P4c	10.0	9.6	9.0	33.9	36.0	2.1
P4d	15.0	13.7	15.0	25.1	38.1	13.0

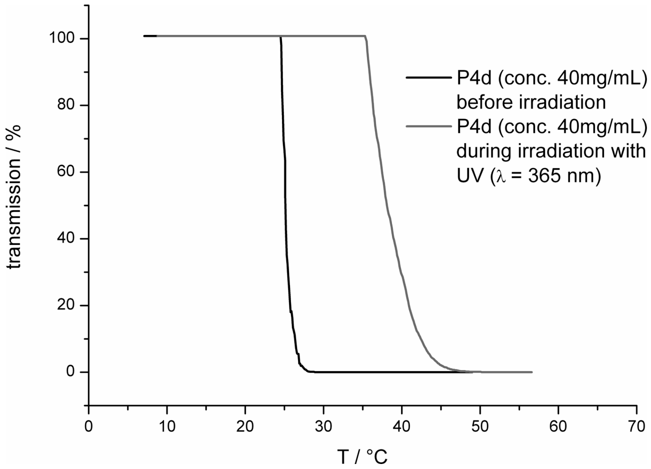

Figure 4. LCST curves of the copolymer sample **P4d** before (black curve) and during irradiation (gray curve) with UV light of 365 nm. The concentration was 40 mg/mL in Millipore water and the heating rate 1 °C/min.

groups. It also showed that all pentafluorophenol salts were removed during the purification by dialysis.

In the second polymer analogous reaction (see Scheme 1), the aniline functional group of the copolymer series **P1** and **P2** was converted selectively with salicylaldehyde in ethanol solution at room temperature to yield the photoswitchable salicylideneaniline group. The solution turned immediately yellow upon addition of salicylaldehyde, indicating the successful formation of salicylideneaniline chromophores. The resulting copolymer series **P3** and **P4** were isolated by precipitation into hexane or diethyl ether and dried in vacuum. A successful conversion of this second polymer analogous reaction has been confirmed by ^{1}H NMR spectroscopy and UV/vis spectroscopy. The ^{1}H NMR spectrum of **P3b** is shown in Figure 3, and the characteristic proton signals of the formed salicylideneaniline Schiff's base can be assigned (in CD_2Cl_2: δ/ppm: 8.67, 7.38, 6.95). Additionally, the signals of the aromatic aniline protons (in CD_2Cl_2: δ/ppm: 7.06, 6.64) of **P1b** totally disappeared, indicating a complete conversion. As an example, the UV/vis spectrum of the copolymer **P3b** in ethanol was measured (see Supporting Information, Figure S1) and compared to the UV/vis spectrum of 4-(2-hydroxybenzylideneamino)benzoic acid. Both spectra showed the characteristic absorption peaks at 270, 302, 320, and 340 nm of the respective salicylideneaniline, indicating the formation of the chromophore. Table 1 summarizes the list of synthesized copolymers with varying contents of salicylideneaniline ranging from 1 to 15 mol %.

The amount of incorporated chromophore has been determined by ^{1}H NMR spectroscopy. The integrals of the aromatic signals (7.38, 6.95 ppm) of the salicylideneaniline group and the single signal of the polyacrylamide protons (**P3** series: 4.00 ppm; **P4** series: 2.70 ppm) were used for the calculation. The composition of the copolymers was additionally determined by UV/vis spectroscopy, assuming that the absorption coefficient of polymer bound salicylideneaniline was identical to that of 4-(2-hydroxybenzylideneamino)benzoic acid at 277 nm. A calibration curve of 4-(2-hydroxybenzylideneamino)benzoic acid was calculated by measuring the absorption maximum at different concentrations in ethanol. Comparison to the absorption maxima at 277 nm of the copolymers solutions **P3** and **P4** in ethanol yielded the incorporation ratio of chromophore. The determined chromophore incorporation ratios of the copolymers were close to the theoretically calculated values and did not significantly differ from the values measured by ^{1}H NMR spectroscopy (see Table 1), demonstrating the efficiency of the two polymer analogous reactions.

The LCSTs of the copolymer series **P3** and **P4** were determined by turbidimetry; thus, the optical transmittance of a light beam (λ = 632 nm) through the sample cell of the photospectrometer was monitored as a function of temperature. The concentration of all copolymer solutions was 40 mg/mL in Millipore water, and the heating rate was 1 °C/min. The cloud points were measured before and during irradiation with UV light (λ = 365 nm) using an optical fiber (see Scheme S2, Supporting Information). The LCST was defined as the temperature at which a transmission of 50% was observed. The LCSTs of the aqueous solutions of the copolymer series **P3** and **P4** exhibited a strong dependence upon the content of incorporated salicylideneaniline. In general, the LCST of all copolymers decreased almost linear with increasing amount of salicylideneaniline, due to the hydrophobic character of the chromophore. The LCSTs are listed in Table 1. In all cases, higher LCST values were observed during irradiation with UV light. Therefore, the LCST shift upon irradiation can be explained by the isomerization of the salicylideneaniline groups from the *enol* to the *keto* form, accompanied by an increase in dipole moment and thus an increased local polarity present at the polymer backbone, which results in the increase of LCST. Accordingly, within the temperature range of the LCSTs before and after irradiation, an isothermal, light-induced precipitation of the copolymers was possible. By turning off the UV light, the respective LCSTs values remained higher than before irradiation which might be explained by an intramolecular stabilization of the exited *keto* form in high polar media such as water. After evaporation of the samples solutions and redissolving in water, the values for the LCST as before irradiation was performed were measured again. Any decomposition of the salcylideneaniline moieties during the irradiation experiment could be excluded by a careful investigation via ^{1}H NMR spectroscopy, UV/vis spectroscopy, and GPC measurement of the samples before and afterward. No changes could be detected. However, the chromophores were instable in acidic media as the yellow color of the polymer solution faded away immediately upon addition of concentrated hydrochloric acid. As an example the LCST curve of **P4d** before and during irradiation has been recorded (see Figure 4).

For the copolymer series **P3**, we observed a higher LCST shift (4.3 °C) for an amount of 4.0 mol % salicylideneaniline (**P3b**) compared to the LCST shift of 0.9 °C for 1.0 mol % salicylideneaniline (**P3a**). However, for the copolymer series **P4**, the polymers with the lowest (**P4a**: 2.0 mol %) and the highest amount (**P4d**: 15.0 mol %) of incorporated salicylideneaniline showed the highest differences in LCST before and during irradiation. A maximum LCST shift of 13.0 °C was observed for copolymer **P4d**. Normally, a linear increase of the LCST shift with increasing amount of chromophoric groups would be expected. A reasonable explanation might be the statistical incorporation of the salicylideneaniline moieties in the polymer that may result in a neighboring effect of the photoswitchable units incorporated. A similar effect was already reported by our group for copolymer series based on poly(*N*-cyclopropyacrylamide) with azobenzene as a chromophoric group.[27]

Conclusion

In summary, we were able to prepare thermo- and light-responsive copolymers containing different amounts of salicylideneaniline chromophores. The synthesis was based on a double polymer analogous reaction of poly(pentafluorophenyl acrylate) precursor polymers with the respective amines. Within the investigated polymers, the molecular weight distribution had been kept constant while maintaining a narrow molecular weight distribution, which was achieved by RAFT polymerization. The obtained copolymer series **P3** and **P4** exhibited a LCST in aqueous solution that depended strongly on the amount of incorporated chromophore. Furthermore, the isomerization of the salicylideneaniline chromophore in the copolymers, which was induced by irradiation with UV light, had an influence on the LCST. Higher LCST values up to 13.0 °C were measured during irradiation, and thus in the temperature region between the LCST of the nonirradiated and the irradiated solution, a light controlled reversible solubility change was observed. In our approach, the chromophore is not directly attached as a preformed chromophore to the polymer but is rather build right at the polymer backbone, which opens the route to combine it with other immobilization chemistry, which may yield potential multifunctional and multiresponsive materials.

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Supporting Information Available: Graphical setup for the LCST experiments and UV/vis spectra of 4-(2-hydroxybenzylideneamino)benzoic acid and the copolymer **P3b**. The material is available free of charge via the Internet at http://pubs.acs.org.

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