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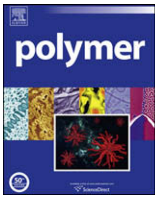

Temperature and light sensitive copolymers containing azobenzene moieties prepared via a polymer analogous reaction

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ABSTRACT

Four different series of polyacrylamides containing different amounts of azobenzene moieties have been synthesized via a polymer analogous reaction of poly(pentafluorophenylacrylate) (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 azobenzene groups and (ii) the isomerization state of the respective azobenzene group. Higher LCST values were measured for UV-irradiated solutions of the copolymers in comparison to the non-irradiated copolymer solutions. A maximum difference in the LCST of up to 7 °C was found for the copolymer poly(*N*,*N*-dimethylacrylamide) containing 8.5 mol% of azobenzene groups. Within this temperature range, a reversible solubility change of the copolymer could be induced by irradiation with light.

1. Introduction

Some water-soluble polymers show an unusual behavior in aqueous solution, as these synthetic materials undergo a phase separation upon heating. In this context, especially polyacrylamide derivates, such as poly(*N*-isopropylacrylamide) (PNIPAM) found great interest, because PNIPAM features a sharp transition behavior in water in response to temperature changes [1]. This lower critical transition temperature (LCST) appears for PNIPAM in water at 32 °C. Besides PNIPAM also other polymers exhibit such a temperature induced transition in water. Examples are poly(*N*-ethyl-*N*-methylacrylamide) [2], poly(*N*-cyclopropylacrylamide) [3] or poly(*N*,*N*-diethylacrylamide) [4]. Accordingly, such polymers featuring an LCST are expected to find application in many scientific areas, such as drug delivery [5] or the immobilization of enzymes and cells [6], because the LCST is close to body temperature.

The area of polymers responsive to a single stimulus has been extended to polymers, which show a responsive behavior to multiple stimuli. Other stimuli besides temperature can for example be pH [7], ionic strength [8] or light [9,10]. Of special importance seem polymers that are responsive to light and temperature and accordingly, there have been several reports on temperature-responsive polymers, for example those containing a light-responsive azobenzene moiety [11–18]. In all these reports, appropriate azobenzene containing monomers have been copolymerized with either *N*-isopropylacrylamide (NIPAM) or *N*,*N*-dimethylacrylamide (DMA) yielding light- and temperature-responsive copolymers. The LCST of these azobenzene containing copolymers depends not only on the amount of chromophoric groups but also on the degree of isomerization of the azobenzene. Azobenzene groups are known to undergo reversible isomerization from *trans*- to *cis*-configuration upon irradiation [19,20]. In the excited *cis*-configuration, the higher dipole moment leads to an increase of local polarity of the polymer chain, which causes an increase of the LCST [21]. And as a result, these copolymers can be precipitated upon irradiation with light within a certain temperature range.

As we could describe in previous publications, the polymer analogous reaction of activated ester polymers provides many synthetic advantages [22–25]. In combination with modern methods of controlled radical polymerization, like the reversible addition-fragmentation chain transfer (RAFT) polymerization, one can receive precisely defined reactive polymer structures [26]. This procedure enables the synthesis of polymeric architectures, which cannot be realized by the classical way of radical copolymerization. Poly(pentafluorophenylacrylate) PPFPA is known to react quantitatively with aliphatic amines yielding the respective polyacrylamide polymers and copolymers [22]. Additionally, this post-modification of activated polymers has the advantage that the synthesis is totally independent from the copolymerization parameters of the respective acrylamide monomers. Furthermore, with this method one can even obtain copolymers in the case where the corresponding monomers would be impossible to be copolymerized.

In this manuscript, we report on the synthesis and characterization of four different series of thermo- and light-responsive

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polyacrylamides that use azobenzenes as the corresponding photochromic groups. In contrast to previous reports, all copolymers will be prepared via a polymer analogous reaction of activated ester precursor polymers on the basis of (PPFPA) [22], which will be synthesized by the RAFT polymerization [26]. The LCST behavior of the resulting polyacrylamides with different amounts of azobenzenes will be investigated in detail.

2. Experimental section

2.1. Materials

All chemicals and solvents were commercially available and used as received unless otherwise stated. Tetrahydrofuran (THF), 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 [27].

2.2. Instrumentation

All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer in deuterated 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, auto sampler 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 Shimadzu UV PC 2102 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 20 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 of polymer samples was performed in a quartz cell with a diameter of 1 cm using an Oriel Instruments 500 W mercury lamp with a 365 nm filter. For the real-time photoswitch experiment an optical fiber from Oriel Instruments and a filter for visible light irradiation ($\lambda > 400$ nm) were additionally used.

2.3. Pentafluorophenylacrylate (PFPA)

80 g (0.43 mol) pentafluorophenol and 52.5 g (0.52 mol) triethylamine (TEA) were dissolved in 500 mL dry diethyl ether and 47.2 g (0.52 mol) acryloyl chloride was added dropwise through a funnel under cooling with an ice bath. After stirring 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 colourless liquid were 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 ($CDCl_3$): 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 (C=C aromatic band).

2.4. Poly(pentafluorophenylacrylate) (PPFPA)

In a typical RAFT polymerization a mixture of 20 g (0.084 mol) PFPA, 51.5 mg (2.11×10^{-4} mol) benzyl dithiobenzoate and 4.3 mg (2.62×10^{-5} mol) AIBN were placed into a Schlenk flask. After addition of 50 mL dry 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 for 20 h. After cooling down to room temperature, the polymer was isolated by precipitation in to 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).

2.5. Pentafluorophenyl 4-(2-phenyldiazenyl)benzoate

2.5 g (0.011 mol) 4-(2-phenyldiazenyl)benzoic acid and 2.9 g (0.029 mol) TEA were dissolved in 50 mL THF and 7.7 g (0.028 mol) pentafluorophenyl trifluoracetate in 30 mL THF were added slowly through a dropping funnel. After stirring for 2 h at room temperature, 150 mL of dichloromethane were added and the solution was extracted twice with 30 mL of water. The organic layer was isolated and dried with sodium sulfate. After evaporation of most of the solvent, the final product was obtained by precipitation into hexane. After filtration and drying in vacuum at 40 °C, a red colored solid was obtained in 2.7 g yield (0.0069 mol –63%). ^{1}H NMR ($CDCl_3$): δ/ppm: 8.34 (d, 2H), 8.03 (d, 2H), 7.96 (m, 2H), 7.54 (m, 3H); FT-IR (ATR-mode): 1759 cm^{-1} (C=O reactive ester band), 1516 cm^{-1} (C=C aromatic band).

2.6. N-(2-Aminoethyl)-4-(2-phenyldiazenyl)benzamide

2.3 g (0.038 mol) 1,2-diamino ethane were dissolved in 50 mL THF and 1.5 g (0.0038 mol) pentafluorophenyl 4-(2-phenyldiazenyl)benzoate dissolved in 30 mL THF were added slowly at room temperature through a dropping funnel. After 3 h of stirring at room temperature, 120 mL of dichloromethane were added and the solution was washed four times with 30 mL water. The organic layer was isolated and dried with sodium sulfate. After complete evaporation of the solvent, 0.83 g (0.0031 mol –82%) of orange colored *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide were obtained. ^{1}H NMR (DMSO): δ/ppm: 8.63 (s, 1H), 8.06 (d, 2H), 7.93 (m, 4H), 7.60 (m, 3H), 3.30 (q, 2H), 2.72 (t, 2H); FT-IR (ATR-mode): 3292 cm^{-1} (N–H valence band), 1634 cm^{-1} (C=O amide band I), 1540 cm^{-1} (C=O amide band II); MS (FD) *m/z* (%): 270.4 (0.39), 269.4 (9.89), 268.4 (100.00).

2.7. Synthesis of the temperature and light sensitive copolymers P1

To three different solutions containing each 1.5 g of PPFPA and 2 mL TEA in 20 mL THF were added dropwise 16.9 mg (P1a: 6.30×10^{-5} mol), 50.7 mg (P1b: 1.89×10^{-4} mol) and 84.5 mg (P1c: 3.15×10^{-4} mol) of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide dissolved in 10 mL THF. The solutions were stirred for 3 h under nitrogen atmosphere at room temperature. Afterwards, 2 mL of isopropylamine (0.023 mol) were added into each flask. After additional

18 h of stirring, the solvent of each sample was removed by evaporation in vacuum. The orange colored residues were suspended in 10 mL of water and dialyzed against diluted ammonia over night. The dialyzed solutions were evaporated and the residues were twice dissolved in 5 mL of THF and precipitated into hexane. Usually, after centrifugation and drying in a vacuum oven at 40 °C, between 0.54 g and 0.65 g of yellow-orange polymers were obtained. ^{1}H NMR (MeOD): δ/ppm: 8.00 (br s), 7.66 (br s), 3.99 (s), 2.13 (br s), 1.63 (br s), 1.19 (s); FT-IR (ATR-mode): 3302 cm^{-1} (amide N–H valence), 1644 cm^{-1} (C=O amide band I), 1540 cm^{-1} (C=O amide band II).

2.8. *Synthesis of the temperature and light sensitive copolymers P2*

To four different solutions containing each 1.5 g of PPFPA and 2 mL TEA in 20 mL THF were added dropwise 16.9 mg (P2a: 6.30×10^{-5} mol), 50.7 mg (P2b: 1.89×10^{-4} mol), 84.5 mg (P2c: 3.15×10^{-4} mol) and 135.2 mg (P2d: 5.04×10^{-4} mol) of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide dissolved in 10 mL THF. The solutions were stirred for 3 h under nitrogen atmosphere at room temperature. Afterwards, 2 mL of cyclopropylamine (0.029 mol) were added into each flask. After additional 18 h of stirring, the solvent of each sample was removed by evaporation in vacuum. The orange colored residues were suspended in 10 mL of water and dialyzed against diluted ammonia overnight. The dialyzed solutions were evaporated and the residues were twice dissolved in 5 mL of methanol and precipitated into diethyl ether. Usually, after centrifugation and drying in a vacuum oven at 40 °C, between 0.49 g and 0.58 g of yellow-orange polymers were obtained. ^{1}H NMR (MeOD): δ/ppm: 8.01 (br s), 7.58 (br s), 2.72 (s), 2.07 (br s), 1.58 (br s), 0.66 (d); FT-IR (ATR-mode): 3291 cm^{-1} (amide N–H valence), 1652 cm^{-1} (C=O amide band I), 1539 cm^{-1} (C=O amide band II).

2.9. *Synthesis of the temperature and light sensitive copolymers P3*

To three different solutions containing each 1.5 g of PPFPA and 2 mL TEA in 20 mL THF were added dropwise 16.9 mg (P3a: 6.30×10^{-5} mol), 50.7 mg (P3b: 1.89×10^{-4} mol) and 84.5 mg (P3c: 3.15×10^{-4} mol) of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide dissolved in 10 mL THF. The solutions were stirred for 3 h under nitrogen atmosphere at room temperature. Afterwards, 2 mL of ethylmethylamine (0.023 mol) were added into each flask. After additional 18 h of stirring, the solvent of each sample was removed by evaporation in vacuum. The orange colored residues were suspended in 10 mL of water and each dialyzed against diluted ammonia over night. The dialyzed solutions were evaporated and the residues were twice dissolved in 10 mL of THF and precipitated in diethyl ether. Usually, after centrifugation and drying in a vacuum oven at 40 °C, between 0.54 g and 0.65 g of yellow-orange polymers were obtained. ^{1}H NMR (D$_2$O): δ/ppm: 7.76 (br s), 3.33 (br s), 2.84 (s), 1.63 (br s), 1.05 (s); FT-IR (ATR-mode): 3452 cm^{-1} (amide N–H valence), 1623 cm^{-1} (C=O amide band I).

2.10. *Synthesis of the temperature and light sensitive copolymers P4*

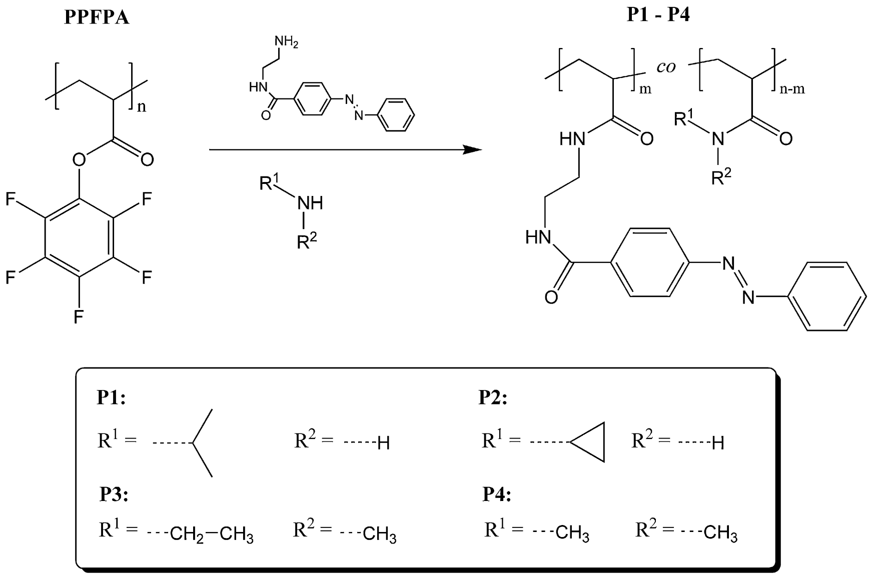
To three different solutions containing each 1.5 g of PPFPA and 2 mL triethylamine in 20 mL THF were added dropwise 84.5 mg (P4a: 3.15×10^{-4} mol), 135.1 mg (P4b: 5.04×10^{-4} mol) and 202.7 mg (P4c: 7.56×10^{-4} mol) of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide dissolved in 10 mL THF. The solutions were stirred for 3 h under nitrogen atmosphere at room temperature. Afterwards, 8 mL of a 2.0 M solution of dimethylamine in THF (0.016 mol) were added into each flask and the solutions. After additional 18 h of stirring, the solvent of each sample was removed by evaporation in vacuum. The orange colored residues were suspended in 10 mL of water and each dialyzed against diluted ammonia overnight. The dialyzed solutions were evaporated and the residues were twice dissolved in 5 mL of a methanol/THF mixture (1:4) and precipitated in diethyl ether. Usually, after centrifugation and drying in a vacuum oven at 40 °C, between 0.32 g and 0.52 g of yellow-orange polymers were obtained. ^{1}H NMR (D$_2$O): δ/ppm: 7.55 (br s), 2.90 (s), 2.62 (br s), 1.63 (br s), 1.34 (br s); FT-IR (ATR-mode): 3446 cm^{-1} (amide N–H valence), 1622 cm^{-1} (C=O amide band I).

3. Results

To synthesize thermo- and light-responsive polymers with varying amounts of azobenzene chromophores but maintaining the degree of polymerization, we made use of the polymer analogous reaction of poly(pentafluorophenylacrylate) (PPFPA) with amines. For that purpose, pentafluorophenylacrylate (PFPA) was synthesized as an activated ester monomer and polymerized under RAFT conditions yielding the corresponding reactive precursor polymer PPFPA. We conducted four polymerization experiments, which were carried out under the same conditions to obtain PPFPA polymers with the same molecular weight. All resulting polymers had a narrow molecular weight distribution around 1.3, a molecular weight of around 25 000 g/mol and were slightly pink colored due to their dithiobenzoate end group. A defined degree of polymerization of 100 was chosen in order to exclude any influence of the molecular weight on the LCST. In contrast to recent publication [26] the polymerization was performed for 20 h to guarantee full conversion due to the large amount of 20 g of PFPA monomer. A broadening of the molecular weight distribution was not observed for longer polymerization times.

First, an azobenzene possessing an aliphatic amine-functionality necessary for a following polymer analogous reaction was synthesized in two steps. 4-(2-Phenyldiazenyl)benzoic acid was activated in the first step using commercial available pentafluorophenyl trifluoroacetate to yield the activated pentafluorophenyl 4-(2-phenyldiazenyl)benzoate in 63% yield, which was then allowed to react in the next step with an excess amount of 1,2-diamino ethane. The final product was purified with several steps of washing with water to remove any excess of 1,2-diamino ethane and the pentafluorophenol salts. The resulting *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide was obtained in 82% yield and had the required aliphatic amino-functionality to react with PPFPA activated precursor polymers in the next step.

The polymer analogous reaction is shown in Scheme 1. PPFPA polymers were dissolved in THF and allowed to react at room temperature with different amounts of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide in the presence of triethylamine (TEA). After 3 h an excess amount of isopropylamine (P1a–P1c), cyclopropylamine (P2a–P2d), ethylmethylamine (P3a–P3c) or dimethylamine (P4a–P4c) was added and allowed to react for 12 h to guarantee complete conversion, respectively. All resulting copolymers were dialyzed against diluted ammonia after the reaction to remove any formed pentafluorophenol salts. The pure copolymers differed in the amount of incorporated azobenzene chromophore and the chemical compositions of the polyacrylamides are listed in Table 1. Complete conversion of all reactions had been detected by IR-spectroscopy. As an example, the IR spectrum of polymer P1c is shown in Fig. 1. Full conversion of the polymer analogous reaction could be observed due to the complete vanishing of the activated ester polymer band at 1783 cm^{-1} and the appearance of the amides bands at 3302 cm^{-1}, 1644 cm^{-1} and 1537 cm^{-1}, respectively. Additionally, ^{1}H NMR spectroscopy was used to characterize the copolymers. For example, the ^{1}H NMR of the copolymer P1c (see Fig. 2) showed the characteristic proton signals from the polyacrylamide



Scheme 1. Synthetic scheme of four polyacrylamide series (P1–P4) containing azobenzene moieties in varying amounts prepared by a polymer analogous reaction of the reactive precursor polymer poly(pentafluorophenylacrylate) with *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide and isopropylamine, cyclopropylamine, diethylamine or ethylmethylamine, respectively.

backbone (in CD_2Cl_2: δ/ppm: 3.97, 1.11) and from the azobenzene protons (in CD_2Cl_2: δ/ppm: 8.07, 7.93, 7.52). Further, using ^{19}F NMR spectroscopy it was not possible to detect a fluorine signal anymore, indicating a complete conversion of all pentafluorophenyl ester groups. It also showed that the formed pentafluorophenol salts were totally removed through dialysis. The GPC elugram in Fig. 3 shows the PPFPA and the copolymer P1c. The curve of P1c is shifted to higher elution volumes due to the lower molecular weight. Noteworthy, the molecular weight distribution did not change after the post-modification.

The composition of the copolymers was additionally determined by UV/vis spectroscopy assuming that the absorption coefficient of polymer bound azobenzene was identical to that of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl) benzoate. First, a calibration curve of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl) benzamide was calculated by measuring the absorption maximum at different concentrations in ethanol, and was then compared to the absorption maxima of the respective copolymers solutions of P1–P4 in ethanol, respectively. The determined absorbances of the chromophoric copolymers were close to the theoretically calculated values and did not differ from the values measured by ^1H NMR spectroscopy. For the determination of the degree of substitution via ^1H NMR spectroscopy, the ratio of the integrals of the signals *d* (amide-signal) to *a* and *b* (azobenzene-signal) were used (see Fig. 2). All calculated and determined compositions of the copolymers are listed in Table 1. In summary, we have been able to prepare copolymers with varying amounts of azobenzene chromophore between 1 and 8.5 mol%.

Next, the light-induced isomerization of the azobenzene group of the chromophoric copolymers was investigated in water. The UV/vis spectrum of P1c in water, shown in Fig. 4, serves as an example for the kinetics of the light-induced isomerization of the chromophores of all copolymers. Prior irradiation all azobenzene groups were in the *trans*-configuration, which can be deduced from the characteristic absorption band at 326 nm. After irradiation of the sample with UV light at 365 nm in a quartz cell for 1 h, the absorption band at 326 nm decreased and the band for the exited *cis*-azobenzene at 256 nm appeared. The relaxation of the excited azobenzenes back into the *trans*-configuration occurred quickly ($\tau_{1/2} = 30$ min) under visible light and reached equilibrium after

Table 1
Composition and LCST values for the copolymer series P1–P4.

Polymer	Amount of azobenzene [mol%] (calculated)	Amount of azobenzene [mol%] (measured by UV/vis)	Amount of azobenzene [mol%] (measured by ^1H NMR)	LCST before irradiation [°C] (measured by turbidometry)	LCST after irradiation [°C] (measured by turbidometry)	Δ LCST [°C]
P1a	1.0	1.0	0.3	29.3	29.9	0.6
P1b	3.0	2.0	2.4	29.1	29.6	0.5
P1c	5.0	3.9	3.0	20.5	23.7	3.2
P2a	1.0	1.2	1.0	42.6	46.0	3.4
P2b	3.0	2.7	2.5	34.1	35.1	1.0
P2c	5.0	5.5	5.0	26.9	28.1	1.2
P2d	8.0	6.1	7.2	23.6	27.4	3.8
P3a	1.0	1.4	1.3	53.5	58.0	4.5
P3b	3.0	2.5	2.2	41.9	43.5	1.6
P3c	5.0	4.5	4.1	32.7	33.1	0.4
P4a	5.0	4.4	4.9	80.5	87.0	6.5
P4b	8.0	6.0	6.7	66.0	72.0	6.0
P4c	12.0	8.5	8.3	37.9	45.2	7.3

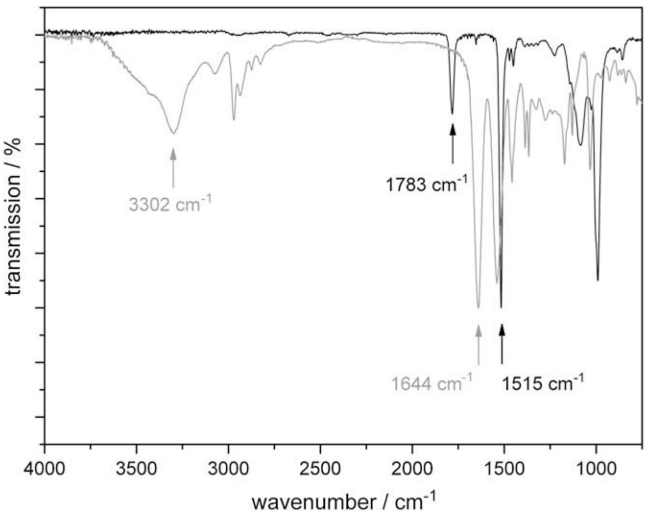


Fig. 1. FT-IR spectra of poly(pentafluorophenylacrylate) (black line) and the thermo- and light-responsive copolymer P1c (grey line).

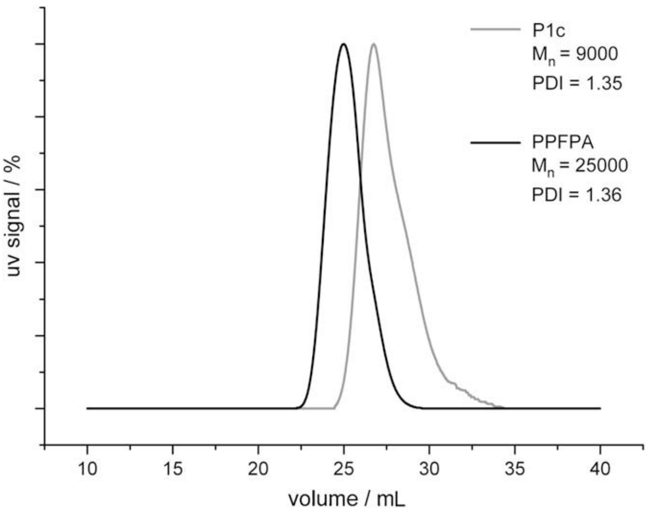


Fig. 3. GPC elugram of poly(pentafluorophenylacrylate) (black line) and the copolymer P1c (grey line).

2 h, with the majority of all chromophoric azobenzene side groups in the *trans*-configuration. In contrast to the light-induced re-isomerization, the thermal relaxation in the dark was very slow at room temperature and had a half time of 11 days. In comparison to the re-isomerization observed for free azobenzene in chloroform, the values of the half times obtained for the polymer series P1–P4 did not differ in more than 5 min.

The isomerization of azobenzene is always combined with a change in dipole moment of the molecular structure. Azobenzene groups are known to have a dipole moment of 0 Debye in the *trans*-configuration, while azobenzene molecules in the *cis*-configuration have a dipole moment of 3 Debye [21]. For the synthesized copolymers containing azobenzene groups, this means that the LCST can be shifted through irradiation with UV light. Due to the increased dipole moment of *cis*-azobenzene, the respective copolymers showed a higher LCST for a *cis*-azobenzene containing polymer than for copolymers containing *trans*-azobenzene [11–13]. The LCSTs of the copolymer solutions were determined by turbidimetry, thus the optical transmittance of a light beam ($\lambda = 632$ nm) through the sample cell of the photospectrometer was monitored as a function of temperature. The concentration of all copolymer solutions was 20 mg/mL and the heating rate was 1 °C/min. The cloud points were measured before and after irradiation with UV light at 365 nm, respectively, and the LCST was defined as the temperature at which a transmission of 50% was observed. The LCSTs of the aqueous solutions of the copolymers P1–P4 exhibited a strong dependence upon the content of azobenzene moieties. In general, the LCST of all the copolymers decreased with increasing amount of azobenzene due to the hydrophobic character of *trans*-azobenzene. The LCSTs are listed in Table 1. In all cases, higher LCST values were observed after irradiation with UV light. This LCST shift upon irradiation can be explained by the isomerization of the azobenzene groups accompanied with an increase in dipole moment and thus an increased local polarity present at the polymer backbone.

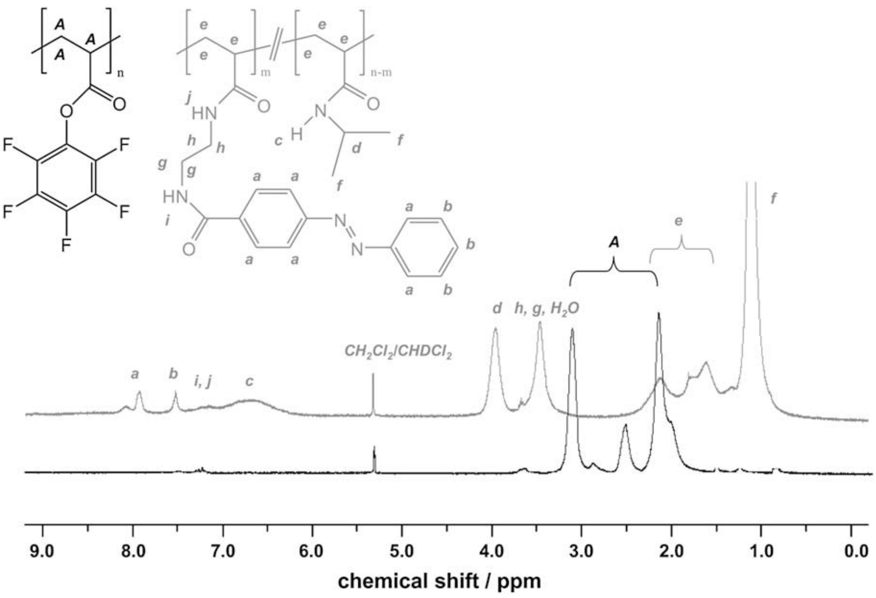


Fig. 2. ^{1}H NMR of poly(pentafluorophenylacrylate) (black line) and the thermo- and light-responsive copolymer P1c (grey line) in CD_2Cl_2.

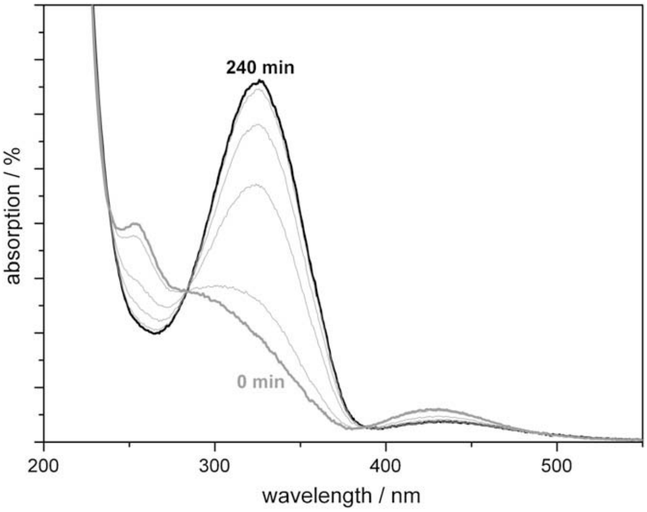


Fig. 4. Evolution of the UV/vis spectra of P1c in water (0.16 mg/mL) after irradiation at 365 nm for 1 h. The curves were measured at 0, 5, 30, 60, 120 and 240 min after irradiation.

Accordingly, within this temperature range an isothermal, light-induced precipitation of the copolymers is possible.

As an example, the real-time photoswitching of the thermo- and light sensitive copolymers was demonstrated for the polymer P4c (see Fig. 5). A polymer solution of P4c (10 mg/mL) in a quartz cell was irradiated inside the spectrometer from above with UV light of 365 nm by using an optical fiber at a constant temperature higher than the LCST ($T = 40$ °C). The optical transmittance of the light beam ($\lambda = 632$ nm) was recorded versus the irradiation time. During the irradiation time of 4 h with UV light, the transmittance of the solution at 40 °C increased from 8% up to 92% intensity due to higher solubility of the polymer with azobenzene groups in the *cis*-configuration. This shows the light-responsive phase transition behavior of the polymer. With the azobenzene groups in the *cis*-configuration, re-isomerization is possible through thermal relaxation in the dark, as can be seen by the slow decrease of the transmittance intensity after the irradiation with UV light has been turned off (see Fig. 5, curve A). The process occurred very slow and had a lifetime of several days. In contrast to the thermal relaxation, the light-induced re-isomerization occurred very fast. The optical transmittance of the solution decreased quickly while irradiating the sample cell with visible light ($\lambda > 400$ nm) using an optical filter (see Fig. 5, curve B). Consequently, a halftime of 40 min for the light-induced re-isomerization could be calculated. This value fits to the results from the UV/vis kinetic experiment mentioned above. Therefore the real-time light controlled solubility change of polymer P4c could be demonstrated.

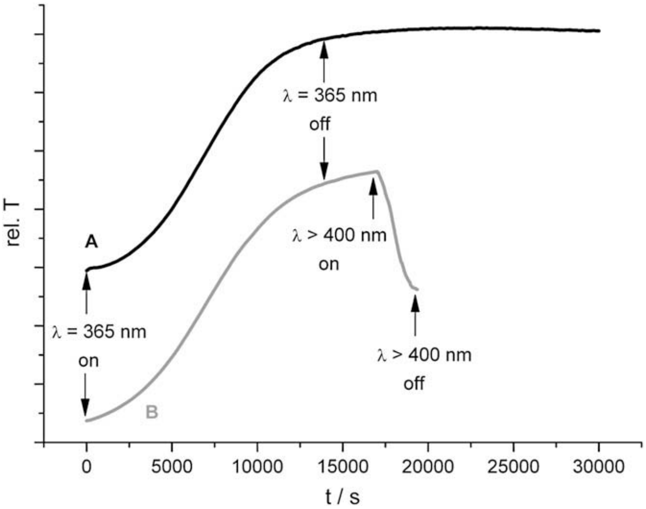


Fig. 5. Real-time photoswitching experiment of the copolymer P4c at 40 °C. (A) The black curve shows the change of the transmittance during irradiation with UV light (from 0 to 14 000 s) and following thermal relaxation in the dark (from 21 000 to 30 000 s). (B) The grey curve shows the change of the transmittance during irradiation with UV light (from 0 to 14 000 s) and following light-induced re-isomerization ($\lambda > 400$ nm, from 16 700 to 19 000 s).

4. Discussion

For the copolymer series P1, we observed the highest LCST shift (3.2 °C) for an amount of 3.9 mol% azobenzene (P1c) compared to the LCST shift of 0.6 °C (1.0 mol% azobenzene) for P1a and 0.5 °C (2.0 mol% azobenzene) for P1b. In contrast, the LCST for *trans*-azobenzene polymers did not differ in more than 0.2 °C for a content between 1.0 mol% (P1a) to 2.0 mol% (P1b) of azobenzene. Only with higher content of *trans*-azobenzene of 3.9 mol% (P1c), the LCST was decreased tremendously. This phenomenon of a sudden change of the LCST at a critical azobenzene content of 3 mol% was already described and reported by Irie and Kungwatchakun [17]. By incorporation of azobenzene chromophores into the polymer, the hydrophobic interaction is enforced, and the polymer becomes less soluble. This resulted in a decrease of the LCST from P1a to P1c. Accordingly, at higher contents of azobenzene the light-induced isomerization into the less hydrophobic *cis*-azobenzenes increased the phase separation temperature up to 3.2 °C.

For the copolymer series P2 no tendency for the LCST shifts in correlation to the amount of azobenzene chromophores was found. The LCSTs of the series of *trans*-azobenzene copolymers P2 decreased almost linear with increasing amount of chromophores. However, the polymers with the lowest (1.2 mol%) and the highest amount (6.1 mol%) of incorporated azobenzene showed the highest differences in LCST before and after irradiation.

The copolymers P3 also showed a linear decrease of the LCSTs with increasing amount of hydrophobic *trans*-azobenzene. But in the case of P3a with an incorporated azobenzene amount of 1.4 mol%, the highest LCST shift of 4.5 °C before and after irradiation was observed. In contrast to the copolymer series P1 the shifts of the LCST decreased with increasing amounts of chromophore.

The copolymer series P4, based on poly(*N*,*N*-dimethylacrylamide), showed the highest differences in the LCST between the irradiated and non-irradiated samples. For copolymer P4c with an amount of 8.5 mol% of incorporated azobenzene, the highest difference in the LCST of 7.3 °C was measured. Further, it has to be mentioned that the LCST shifts of all copolymers P4a–P4c seemed to be almost independent of the amount of incorporated azobenzene, as the shift of LCST did not differ in more than 1.3 °C for varying amounts of incorporated azobenzene between 4.4 and 8.5 mol%. Even though, similar to the copolymer series P2 and P3, the LCSTs showed a linear decrease with increasing amount of incorporated chromophore. In general, the shift in the LCST seemed to be dependent from the chemical structure of the different copolymers P1–P4 and from the amount of incorporated azobenzene.

In comparison to the thermo- and photoresponsive poly(acrylamides) that had been prepared by free radical polymerization, our measured values correspond very well with those measured by Kroeger et al. [11] and thus are a beautiful example of the synthetic versatility of the polymer analogous reaction of PPFPA with functional amines.

5. Conclusion

In summary, we have presented the synthesis of copolymers that exhibit a thermo- and light-responsive behavior in aqueous solution. Within the investigated polymers, the degree of polymerization had been kept constant, which could be achieved by RAFT polymerization of pentafluorophenylacrylate yielding reactive precursor polymers with defined molecular weight, i.e. degree of polymerization and a narrow molecular weight distribution. Four series of polyacrylamides containing azobenzene moieties in varying amounts have been prepared by a polymer analogous reaction of the reactive precursor polymer poly(pentafluorophenylacrylate) with *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)-benzamide and isopropylamine, cyclopropylamine, diethylamine or ethylmethylamine, respectively. The obtained copolymer series P1–P4 exhibited an LCST in aqueous solution that depended strongly on the amount of incorporated azobenzene. Furthermore, the reversible isomerization of the azobenzene groups in the copolymers, which was induced by irradiation with UV light, had an influence on the LCST. Higher LCST values were measured after irradiation and thus, in the temperature region between the LCST of the non-irradiated and the irradiated solution, a light controlled reversible solubility change was observed. The light controlled solubility change could be demonstrated in a real-time experiment. In general, it can be concluded that the copolymers, which have been prepared by polymer analogous reaction with the azobenzene derivate *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide showed a similar response behavior than the previously reported copolymerization of e.g. *N*-isopropylacrylamide with *N*-(4-phenylazophenyl)acrylamide, demonstrating that the presented polymer analogous synthesis of light- and temperature-responsive polymers provides a much more versatile synthetic route.

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