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ARTICLE

Thermo- and Light-Responsive Polymers Containing Photoswitchable Azobenzene End Groups

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ABSTRACT: Telechelic thermo- and light-responsive polymers based on poly(oligo(ethylene glycol) methyl ether methacrylate) P(OEGMA) with azobenzene functionalities at the end groups were synthesized. In a reversible addition−fragmentation chain transfer (RAFT) polymerization using a functionalized chain transfer agent (CTA) containing a pentafluorophenyl (PFP) activated ester, oligo(ethylene glycol) methyl ether methacrylate (OEGMA, $M_n \sim 300$ g mol^{-1}) could successfully be polymerized with good control over molecular weight, very high conversions, and narrow molecular weight distributions. Polymers derived from this CTA possessed an activated ester at the α-end of the polymer chain as well as a dithioester ω-terminus. The ω-dithioester group of each polymer chain could quantitatively be either removed with AIBN treatment or substituted with a PFP ester by using a modified diazo compound. As a consequence, a postmodifiaction of the telechelic reactive end groups was possible through a polymer analogous reaction with amino-functionalized azobenzene. P(OEGMA) polymers containing azobenzene end groups showed a reversible light- and temperature-controlled phase transition in water. Higher values for the lower critical solution temperature (LCST) were measured after irradiation of the aqueous polymer solutions due to the higher polarity of *cis*-azobenzene. The LCST differences between irradiated and nonirradiated solutions increased linearly upon the ratio of azobenzene units up to 4.3 °C.

Introduction

Stimuli-responsive polymers, also called smart polymers, have been attracting great interest in academic and applied science recently. For instance, water-soluble polymers exhibiting a lower critical solution temperature (LCST) are potentially useful for several biomedical applications such as smart bioactive surfaces, selective bioseparation, phase separation immuno-assays, or hyperthermia-induced drug delivery.[1−4] Many poly(*N*-alkylacrylamides) feature an LCST in aqueous solution,[5−7] and so far, poly(*N*-isopropylacrylamide) (PNIPAM) has been the most studied thermosensitive polymer because its LCST of 32 °C is close to the human body temperature.[1,8] Another class of thermally responsive systems is based on oligo(ethylene glycol) methyl ether methacrylates (OEGMA).[9−12] As many other methacrylate monomers, OEGMA can be polymerized under controlled radical polymerization methods yielding well-defined materials. Polymers constructed from these PEG (macro)monomers exhibit fascinating solution properties in aqueous media. Depending on the molecular structure of their monomer units (i.e., nature of the polymerizable moiety, length of the PEG side chain, end group of the PEG side chain), the polymers can be insoluble in water and readily soluble up to 100 °C or even show a thermoresponsive behavior.

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,[13] ionic strength,[14] or light.[15,16] Of special importance seem to be polymers that are responsive to light and temperature, and accordingly, there have been several reports on temperature-responsive poly(*N*-alkylacrylamide) copolymers, for example, those containing light-responsive azobenzene in the side groups of the polymer chain.[17−22] Azobenzene groups are known to undergo a reversible isomerization from trans- to cis-configuration upon irradiation.[23,24] In the excited cis-configuration, the higher dipole moment[25] leads to an increase of local polarity of the polymer chain, which causes an increase of the LCST.[17−22] As a result, these copolymers can be precipitated upon irradiation with UV light within a certain temperature range. To the best of our knowledge, in most reports, the azobenzene chromophores were incorporated as side groups in the polymer backbone and not at the chain end. Upon increasing the number of azobenzene units, the photoinduced shift increased up to a certain value but decreased thereafter. These phenomena might be due to the variety in the number of azobenzene moieties and side-group effects of the photofunctional units. Akiyama et al. demonstrated that photoisomerization of a single terminal unit of a polymer could also trigger a phase transition of a polymer chain.[26] They prepared an end-functionalized PNIPAM by atom transfer radical polymerization (ATRP) with an azobenzene derivative initiator. A linear increase of the LCST shifts with increasing amount of azobenzene located at the end group was found by this group which was in contrast to the transition behavior of azobenzene-functionalized PNIPAM copolymers.

Telechelic polymers are polymers with the same functional group at both chain ends. Accordingly, it is synthetically a challenge to introduce azobenzene functionalities at the both end groups of a polymer exhibiting an LCST. However, the investigation of the light-controlled solubility change in the case of telechelic polymers and its potential application are as exciting. The linear chain of an LCST polymer such as P(OEGMA) then acts as a spacer between the α- and ω-end groups. A variety of methods to obtain end-group-functionalized polymers by controlled radical polymerization,[27−33] especially those by reversible addition−fragmentation chain transfer polymerization (RAFT),[34−39] have been reported. The RAFT polymerization[40] uses a dithioester

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chain transfer agent (CTA) and thus results in polymer chains that carry a CTA residue on their α-end and a dithioester at their ω-terminus. These dithioesters are very promising for a subsequent end-group functionalization.[36,37,39,41]

Herein, we want to extend the investigation of thermoresponsive polymers with azobenzene at the end group. In the following, the synthesis and characterization of thermoresponsive poly(oligo(ethylene glycol) methyl ether methacrylates), P(OEGMA), in two different molecular weights with either azobenzene at one end group or telechelic azobenzene moieties at both chain ends are described. All polymers were designed to exhibit an LCST in aqueous solution, which was known to be dependent on the amount of incorporated chromophoric azobenzene end groups, the molecular weight of the polymer, and the isomerization state of the respective azobenzene end group. The synthesis is based on the RAFT polymerization of OEGMA monomer ($M_n \sim 300$ g mol^{-1}) with four ethylene oxide units followed by postmodification of the respective α- and ω-chain end groups. As CTA, pentafluorophenyl-(4-phenylthiocarbonylthio-4-cyanovalerate) (PFP-CTA) will be used, which was described as a reasonable reagent for the synthesis of narrow distributed polymers with reactive terminus recently.[42-44] The LCST behavior of the resulting P(OEGMA) polymers with azobenzenes α- and ω-end group and the light-controlled phase separation will be investigated in detail.

Experimental Section

Materials. All chemicals and solvents were commercially available and used as received unless otherwise stated. Oligo(ethylene glycol) methyl ether methacrylate (OEGMA) available as poly(ethylene glycol) methyl ether methacrylate from Aldrich ($M_n \sim 300$ g mol^{-1}) was distilled under high vacuum over 2,6-di-*tert*-butyl-*p*-cresol (DBPC) before use. Tetrahydrofuran (THF) and 1,4-dioxane were 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. 4-Phenylthiocarbonylthio-4-cyanovaleric acid[45] and *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide[22] were synthesized as described in the literature.

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 performed in THF to determine molecular weights and molecular weight distributions, M_w/M_n, of polymer samples with respect to polystyrene standards. Calibration was done using polystyrene standards. 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. Cloud points were determined in Millipore water at a concentration of 10 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 with an Oriel Instruments 500 W mercury lamp with a 365 nm filter and an average output of 6.5 mW/cm^2 in a 1 cm diameter quartz cell (total volume 2.5 cm^3). Mass spectra were acquired by using a Shimadzu Axima CFR MALDI-TOF (matrix-assisted laser desorption/ionization time of flight) mass spectrometer equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. Samples using α-cyano-4-hydroxycinnamic acid (CHCA) as matrix and KI as additive were prepared by dissolving the polymer in THF at a concentration of 10 g/L. First, an aliquot of 2 μL of the matrix solution (10 mg of CHCA dissolved in 1 mL of 50% acetonitrile in 0.05% trifluoroacetic acid) was placed on a multistage target plate. In the following, 2 μL of the polymer solution (10 mg of the polymer dissolved in 1 mL of THF) and then 2 μL of the cationization agent solution (10 mg of KI dissolved in 1 mL of methanol) were added. The target plate was left to dry in air. The samples were analyzed with the operator manually and measured in positive reflectron ion mode. The laser was adjusted slightly above the ionization/desorption threshold.

Pentafluorophenyl-(4-phenylthiocarbonylthio-4-cyanovalerate) (PFP-CTA). 6.31 g (0.0226 mol) of 4-phenylthiocarbonylthio-4-cyanovaleric acid and 4.81 g of triethylamine (TEA) (0.0475 mol) were dissolved in 150 mL of THF with magnetic stirring. The flask was sealed with a septum, and 13.3 g (0.0475 mol) of pentafluorophenyl trifluoracetate was added slowly through a syringe. The solution was stirred for 3 h at room temperature and was then diluted with 150 mL of dichloromethane. Afterward, the solution was transferred into a separating funnel and washed three times with 50 mL of water. The organic phase was separated and dried with sodium sulfate, and after filtration, it was concentrated in vacuum. The product was purified by column chromatography (column material: silica gel; solvent: petroleum ether/ethyl acetate 5:1) and finally dried under high vacuum overnight. 7.62 g (0.0171 mol, 76%) of pure red pentafluorophenyl-(4-phenylthiocarbonylthio-4-cyanovalerate) was obtained. ^{1}H NMR (CDCl$_3$): δ/ppm: 7.91 (d, 2H), 7.57 (t, 1H), 7.39 (t, 2H), 3.08−3.01 (m, 2H), 2.80−2.70 (m, 1H), 2.59−2.49 (m, 1H), 1.97 (s, 3H). ^{13}C NMR (CDCl$_3$): δ/ppm: 219.7, 167.8, 144.3, 142.7, 139.4, 136.3, 134.4, 133.2, 128.6, 126.7, 118.2, 45.5, 32.9, 29.1, 24.2. ^{19}F NMR (CDCl$_3$): δ/ppm: −162.28 (t, 2F), −157.69 (t, 1F), −152.88 (d, 2F). FT-IR (ATR mode): 2927 cm^{-1} (C−H valence band), 1785 cm^{-1} (C=O reactive ester band), 1516 cm^{-1} (PFP C=C aromatic band).

Bis(pentafluorophenyl)-4,4′-azobis(4-cyanovalerate) (PFP-ACV). 3.85 g (0.0137 mol) of 4,4′-azobis(4-cyano valeric acid) and 5.55 g (0.0549 mol) of TEA were dissolved in 150 mL of dry THF. 15.38 g (0.0549 mol) of pentafluorophenyl trifluoracetate was added slowly through a dropping funnel, and the solution was allowed to stir for 5 h at room temperature. Afterward, 150 mL of dichloromethane was added; the solution was transferred into a shaking funnel and was washed three times with 50 mL of water. The organic phase was separated and dried with sodium sulfate, and after filtration it was concentrated in light vacuum at 30 °C. The raw product was dissolved in 20 mL of dichloromethane and precipitated into cold hexane. After filtration and washing with cold hexane, the colorless solid was dried under vacuum at room temperature. 6.54 g (0.0107 mol, 78%) of bis(pentafluorophenyl)-4,4′-azobis(4-cyanovalerate) was obtained and stored at −7 °C. ^{1}H NMR (CDCl$_3$): δ/ppm: 3.00−2.48 (m, 8H), 1.78 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (CDCl$_3$): δ/ppm: 167.5, 142.6, 141.4, 139.5, 138.1, 136.2, 117.0, 71.7, 32.7, 28.3, 23.9. ^{19}F NMR (CDCl$_3$): δ/ppm: −162.20 (t, 4F), −157.56 (t, 2F), −152,88 (d, 4F). FT-IR (ATR mode): 2929 cm^{-1} (C−H valence band), 1786 cm^{-1} (C=O reactive ester band), 1517 cm^{-1} (PFP C=C aromatic band).

General RAFT Polymerization Procedure (P1a and P1b). Both RAFT polymerizations followed the same procedure. PFP-CTA, AIBN, and freshly distilled OEGMA monomer were placed into a Schlenk tube with varying ratios (see Table 1). After addition of 20 mL of dry 1,4-dioxane, four freeze−pump−thaw cycles were performed to degas the solution. The flask was filled with argon, immersed into 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 three times into hexane, centrifuged, and finally dried under vacuum. Usually, 90% of red viscous PFP-P(OEGMA) (**P1a** and **P1b**) was obtained. ^{1}H NMR (CDCl$_3$): δ/ppm: 7.81 (d), 7.46 (t), 7.30 (t), 4.03 (br s), 3.83 (br s), 3.59 (br d), 3.49 (br t), 3.39 (s), 3.32 (s), 3.25 (s), 3.08 (s), 3.04 (s), 2.81 (br s), 2.18 (br s), 1.82 (br m), 1.22 (br m), 0.90 (br d). ^{13}C NMR (CDCl$_3$): δ/ppm: 177.0, 128.1, 126.4, 71.6, 70.3, 68.2, 63.6, 58.7, 54.1, 44.4, 18.3,

Table 1. Characteristic Data for the P(OEGMA) Polymers P1a and P1b

polymer	PFP-CTA	AIBN	OEGMA monomer	M_n(calcd), g mol^{-1}	M_n(GPC), g mol^{-1}	M_n(NMR), g mol^{-1}	M_w/M_n (GPC)
P1a	456 mg (1.025×10^{-3} mol)	21 mg (1.280×10^{-4} mol)	7.38 g (0.0265 mol)	7800	8600	7900	1.18
P2b	826 mg (1.856×10^{-3} mol)	38 mg (2.317×10^{-4} mol)	6.40 g (0.0230 mol)	3700	5000	3800	1.15

16.1. ^{19}F NMR (CDCl$_3$): δ/ppm: −162.5 (t, 2F), −158.1 (m, 1F), −153.0 (d, 2F). FT-IR (ATR mode): 2875 cm^{-1} (C−H valence band), 1789 cm^{-1} (C=O reactive ester band), 1727 cm^{-1} (C=O ester band), 1519 cm^{-1} (PFP C=C aromatic band), 1250 cm^{-1} (C−O ester band), 1097 cm^{-1} (C−O ether band).

General Procedure for Dithioester Removal of PFP-P(OEGMA) Polymers with AIBN (P2a and P2b). In a typical run, PFP-P(OEGMA) polymers (**P1a** and **P1b**) containing a dithioester end group at the *ω*-position and 30 equiv of AIBN were dissolved in a Schlenk tube in dry dioxane. 18 mL of dioxane was used for 5 mmol of diazo component. After addition of AIBN, the Schlenk tube was sealed with a septum, placed immediately into a preheated oil bath at 80 °C, and stirred for 3.5 h. After cooling to room temperature, the polymer was isolated by precipitation into hexane. The crude polymer was dissolved in THF, precipitated again three times into hexane, centrifuged, and finally dried in vacuum. Usually, between 76 and 85% of colorless and viscous polymers (**P2a** and **P2b**) was obtained. ^{1}H NMR (CDCl$_3$): δ/ppm: 4.04 (br s), 3.83 (br s), 3.62 (br d), 3.50 (br t), 3.40 (s), 3.33 (s), 3.26 (s), 3.10 (s), 3.05 (s), 2.83 (br s), 2.02 (s), 1.86 (br m), 1.22 (br m), 0.92 (br d). ^{13}C NMR (CDCl$_3$): δ/ppm: 177.0, 71.7, 70.3, 68.3, 63.6, 58.8, 54.3, 44.6, 18.3, 16.1. ^{19}F NMR (CDCl$_3$): δ/ppm: −162.4 (t, 2F), −158.0 (m, 1F), −153.0 (d, 2F).

General Procedure for the Synthesis of P(OEGMA) Polymers with PFP-Ester at the *ω*- and α-Position (P3a and P3b). In a typical run, PFP-P(OEGMA) polymers (**P1a** and **P1b**) containing a dithioester end group at the *ω*-position and 30 equiv of PFP-ACV were dissolved in a Schlenk tube in dry dioxane. 18 mL of dioxane was used for 5 mmol of diazo component. After addition of the PFP-ACV, the Schlenk tube was sealed with a septum, placed immediately in a preheated oil bath at 80 °C, and stirred for 3.5 h. After cooling to room temperature, the polymer was isolated by precipitation in hexane. The crude polymer was dissolved in THF, precipitated again three times into hexane, centrifuged, and finally dried in vacuum. Usually, between 75 and 81% of colorless and viscous polymers (**P3a** and **P3b**) was obtained. ^{1}H NMR (CDCl$_3$): δ/ppm: 4.04 (br s), 3.68 (s), 3.61 (br d), 3.52 (br t), 3.40 (s), 3.35 (s), 3.26 (s), 3.20 (s), 3.10 (s), 2.83 (br s), 1.83 (br m), 1.22 (br m), 0.91 (br d). ^{13}C NMR (CDCl$_3$): δ/ppm: 177.0, 71.7, 70.3, 68.3, 63.6, 58.8, 54.1, 44.7, 18.4, 16.5. ^{19}F NMR (CDCl$_3$): δ/ppm: −162.4 (t, 4F), −158.0 (m, 2F), −153.0 (d, 4F).

General Procedure for the Synthesis of P(OEGMA) Polymers with Azobenzene at the α-Position (P4a and P4b). P(OEGMA) polymers containing azobenzene end groups in the α-position were obtained by reaction of the polymers **P2a** and **P2b** with *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide. Therefore, **P2a** and **P2b** were dissolved with 5 equiv of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide and 1 equiv of TEA in dry THF. 10 mL of THF was used for 0.2 mmol of the azobenzene compound. The solutions were stirred for 12 h under a nitrogen atmosphere. Then, the solvent was evaporated in vacuum, and the residues were suspended in cold water. After filtration of the insoluble excess *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide, the orange-colored filtrates were filled into dialysis membranes and dialyzed against diluted aqueous ethanol (30−60%) for 2 days to remove the remaining *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide and the pentafluorophenol salts. Every 6 h the solvent was refreshed. Afterward, the contents of the membranes were transferred into a flask and concentrated under vacuum. The polymer residues were redissolved in THF and isolated by precipitation into hexane. After centrifugation and drying in vacuum, usually between 71% and 76% of orange-colored viscous polymers (**P4a** and **P4b**) was obtained. ^{1}H NMR (CDCl$_3$): δ/ppm: 7.94 (m), 7.72 (br s), 7.47 (d), 6.81 (br s), 4.04 (br s), 3.83 (br s), 3.61 (br d), 3.51 (br t), 3.33 (s), 3.10 (s), 2.33 (br s), 1.83 (br m), 1.22 (br m), 0.91 (br d). FT-IR (ATR mode): 2875 cm^{-1} (C−H valence band), 1727 cm^{-1} (C=O ester band), 1657 cm^{-1} (C=O amide band I), 1542 cm^{-1} (C=O amide band II), 1250 cm^{-1} (C−O ester band), 1097 cm^{-1} (C−O ether band).

General Procedure for the Synthesis of P(OEGMA) Polymers with Telechelic Azobenzene Functionality (P5a and P5b). P(OEGMA) polymers containing azobenzene end groups in the α- and *ω*-position were obtained by reaction of the polymers **P3a** and **P3b** with *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide. Therefore, **P3a** and **P3b** were dissolved with 10 equiv of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide and 2 equiv of TEA in dry THF. 10 mL of THF was used for 0.2 mmol of the azobenzene compound. The solutions were stirred for 12 h under a nitrogen atmosphere. In the following the solvents were evaporated in a vacuum, and the residues were suspended in cold water. After filtration of the insoluble excess *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide, the orange-colored filtrates were filled into dialysis membranes and dialyzed against diluted aqueous ethanol (30−60%) for 2 days to remove the remaining *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide and the pentafluorophenol salts. Every 6 h the solvent was refreshed. Afterward, the contents of the membranes were transferred into a flask and concentrated in vacuum. The polymer residues were redissolved in THF and isolated by precipitation into hexane. After centrifugation and drying in vacuum, usually between 60 and 69% of orange-colored viscous polymers (**P5a** and **P5b**) were obtained. ^{1}H NMR (CDCl$_3$): δ/ppm: 7.94 (m), 7.72 (br s), 7.47 (d), 6.81 (br s), 4.04 (br s), 3.83 (br s), 3.61 (br d), 3.51 (br t), 3.33 (s), 3.10 (s), 2.33 (br s), 1.83 (br m), 1.22 (br m), 0.91 (br d). FT-IR (ATR mode): 2875 cm^{-1} (C−H valence band), 1727 cm^{-1} (C=O ester band), 1657 cm^{-1} (C=O amide band I), 1542 cm^{-1} (C=O amide band II), 1250 cm^{-1} (C−O ester band), 1097 cm^{-1} (C−O ether band).

Results and Discussion

The scope of the present study was the preparation of telechelic thermoresponsive P(OEGMA) polymers that possessed azobenzene moieties either on one or on both end groups of the chain. In order to reach this goal, several individual techniques to prepare α- or *ω*-end-group-functionalized polymers were combined. As former investigations had shown, the pentafluorophenyl (PFP) ester is a very versatile and reactive functionality. Accordingly, pentafluorophenyl-(4-phenylthiocarbonylthio-4-cyanovalerate) (PFP-CTA) was obtained in a slightly different way as already previously reported by our group.[42] For that, first 4-phenylthiocarbonylthio-4-cyanovaleric acid was synthesized as described in the literature[45] and treated with pentafluorophenyl trifluoracetate. The final product was obtained after purification through column chromatography in 76% yield.

Synthesis of PFP-P(OEGMA) Polymers (See Scheme 1, Route A). PFP-CTA was used as a chain transfer reagent for RAFT polymerization of oligo(ethylene glycol) methyl ether methacrylate (OEGMA). The two resulting red viscous polymers PFP-P(OEGMA) **P1a** and **P1b** were analyzed by NMR spectroscopy, FT-IR spectroscopy, UV/vis spectroscopy, and GPC. ^{1}H NMR polymers (see Figure 1) showed the characteristic aromatic signals of the dithioester *ω*-end group at 7.81, 7.46, and 7.30 ppm. ^{19}F NMR spectroscopy

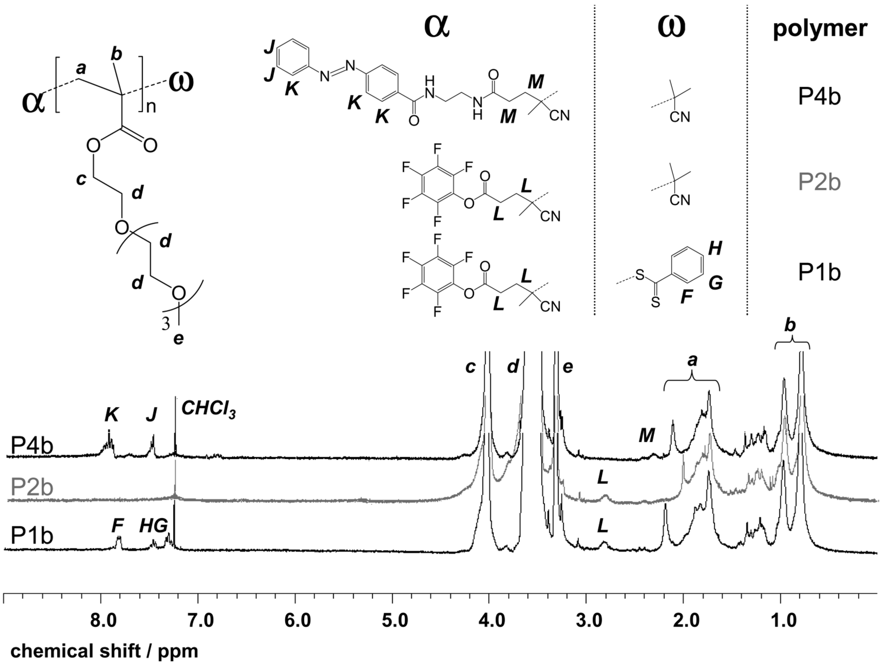
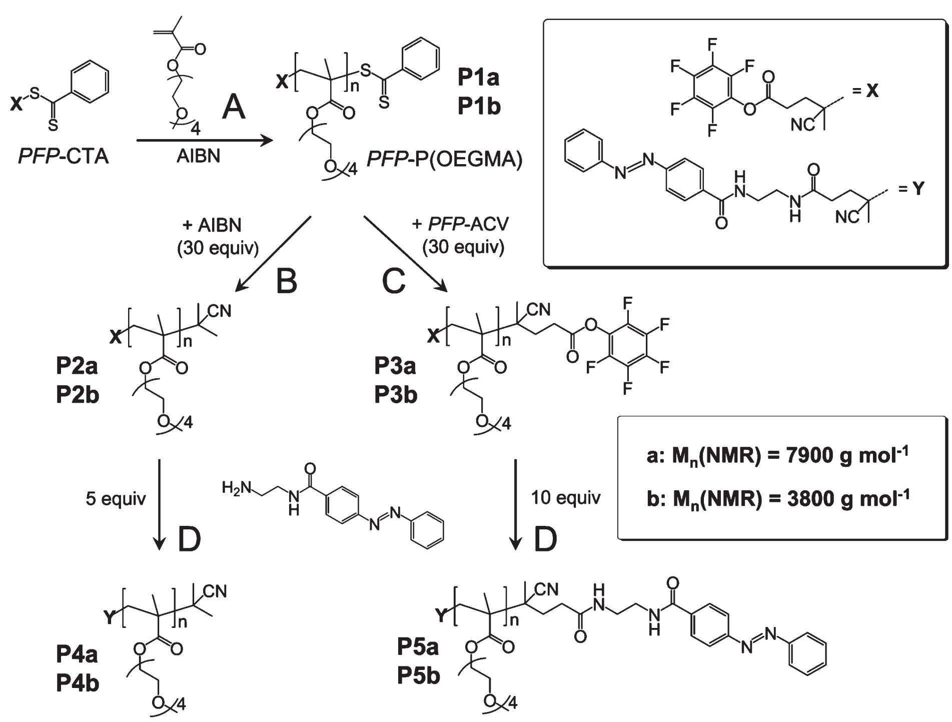


Figure 1. ^{1}H NMR spectra measured in deuterated chloroform of polymers **P1b**, **P2b**, and **P4b**.

Scheme 1. Overview of Reactions Described in Detail in the Text



was performed to analyze the end group of both polymers. The fluorine signals at a chemical shift of −162.5, −158.1, and −153.0 ppm of the PFP-ester proved the existence of reactive α-terminus. Additionally, the FT-IR spectrum (see Figure 2) showed an ester band at 1727 cm^{-1} and also the characteristic bands at 1789 and 1519 cm^{-1} of the PFP-ester end group. The UV/vis spectrum, as illustrated in Figure 3, showed the characteristic absorption bands of the dithioester at 302 and 503 nm.[41] The molecular weight of polymers **P1a** and **P1b** was determined by GPC and in addition by end-group analysis using ^{1}H NMR spectroscopy. The values for the molecular weights are listed in Table 1. For the calculation of the molecular weight by ^{1}H NMR spectroscopy, the ratio of the aromatic dithioester signals (7.81, 7.46, and 7.30 ppm) and the single signal of the methoxy protons (3.32 ppm) was calculated. The values for the number-average of the molecular mass M_n determined by GPC (**P1a**: M_n = 8600 g mol^{-1}; **P1b**: M_n = 5000 g mol^{-1}) were slightly higher than the calculated values and the ones measured by NMR (**P1a**: M_n = 7900 g mol^{-1}; **P1b**: M_n = 3800 g mol^{-1}). The reason for this divergence was the calibration of the GPC with respect to polystyrene standards. However, the polydispersity M_w/M_n of 1.15 and 1.18 indicated a narrow molecular weight distribution for both PFP-P(OEGMA) polymer samples. As an

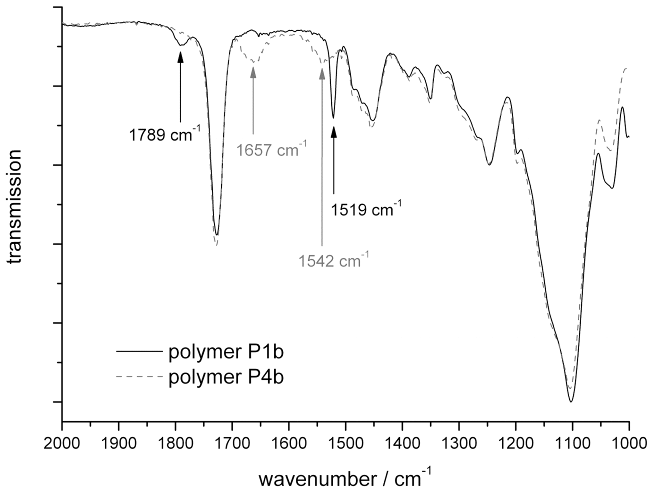


Figure 2. FT-IR spectra of polymers **P1b** (black solid line) and **P4b** (gray dashed line).

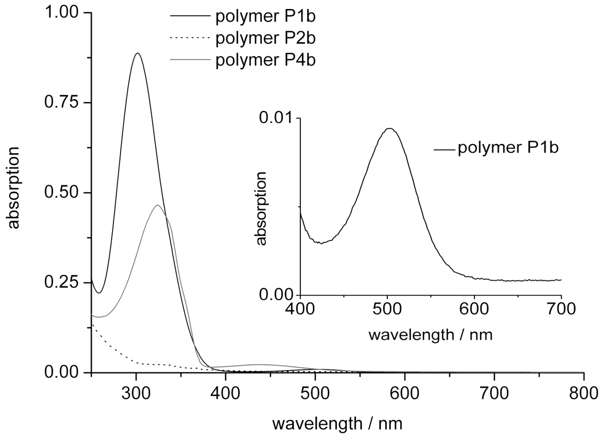


Figure 3. UV/vis spectra of polymers **P1b** (black solid curve, concentration 0.400 mg/mL acetonitrile), **P2b** (black dotted curve, concentration 0.349 mg/mL acetonitrile), and **P4b** (gray solid curve, concentration 0.125 mg/mL acetonitrile).

example, the GPC curve of the PFP-P(OEGMA) polymer **P1b** with the UV/vis detector set to the absorption maximum of the dithioester (302 nm) is illustrated in Figure 4. Altogether, two different PFP-(POEGMA) polymers with different molecular weights, which means two different ratios between the OEGMA-repeating units and the α- and *ω*-end group, were obtained in a narrow molecular weight distribution.

Dithioester Removal of PFP-P(OEGMA) Polymers with AIBN (See Scheme 1, Route B). Next the PFP-P(OEGMA) polymers **P1a** and **P1b** containing a reactive ester functionality at the α-end group and a dithioester at the *ω*-end group were postmodified. The removal of the dithioester was crucial to prevent the formation of disulfide coupling reactions which might occur during a polymer analogous reaction of the α-end group. The dithioester of the PFP-P(OEGMA) polymers **P1a** and **P1b** was removed with an excess amount of AIBN in a slightly different procedure as reported by Perrier et al.[37] For that, two samples of the **P1a** and **P1b** were stirred with 30 equiv of AIBN for 3.5 h at a constant temperature of 80 °C. A preheated oil bath with a constant temperature of 80 °C was crucial for a successful reaction and to inhibit high molecular disulfide formation. The obtained polymers **P2a** and **P2b** were analyzed by ^{1}H NMR, ^{19}F NMR, UV/vis spectroscopy, and GPC measurements. The ^{1}H NMR as illustrated in Figure 1 showed the complete removal of the dithioester group as the aromatic protons of the *ω*-end group at 7.81, 7.46, and 7.30 ppm were vanished completely. The UV/vis spectrum (see Figure 3) did not show the dithioester absorption band at 302 nm any longer. Additionally, samples of polymers **P2a** and **P2b** were analyzed by ^{19}F NMR to exclude any decomposition of the α-functionality. The PFP-ester was not harmed by this treatment, as PFP-esters are stable toward radicals and elevated temperature in the absence of nucleophiles. Clearly, the ^{19}F NMR spectra of the polymers obtained after AIBN treatment still showed the typical PFP ester signals. The GPC curve of polymers **P2a** and **P2b** showed no shoulder at twice the molecular weight, indicating that no disulfide coupling reaction had occurred (see Supporting Information). The molecular weights and the molecular weight distribution were still the same as measured for the polymers **P1a** and **P1b**.

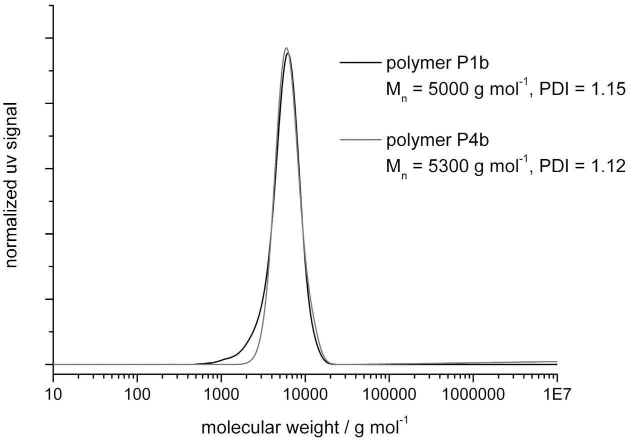


Figure 4. Normalized GPC elugrams of **P1b** (black line) measured at 302 nm and **P4b** (gray line) measured at 323 nm.

Synthesis of P(OEGMA) Polymers with PFP-Ester at the *ω*- and α-Position (See Scheme 1, Route C). To introduce a pentafluorophenyl ester end group at the *ω*-position, the dithioester end group of the polymers had to be exchanged in a reaction described in detail by the group of Theato.[42] This method enabled the synthesis of P(OEGMA) polymers with telechelic PFP-ester functionality. Quite similar to the conditions reported there, two samples of the dithioester-terminated PFP-P(OEGMA) polymers **P1a** and **P1b** were treated with an excess amount bis(pentafluorophenyl)-4,4′-azobis(4-cyanovalerate) (PFP-ACV). The PFP-ACV was therefore previously synthesized by activating the commercial available 4,4′-azobis(4-cyanovaleric acid) with pentafluorophenyl trifluoracetate. In analogy to the procedure for the dithioester removal with AIBN, both PFP-P(OEGMA) polymers **P1a** and **P1b** were stirred with 30 equiv of PFP-ACV for 3.5 h at a constant temperature of 80 °C. Full conversion of the end-group modification was confirmed for the polymers **P3a** and **P3b** again by ^{1}H NMR, ^{19}F NMR, and UV/vis spectroscopy and GPC measurements. The aromatic signals of the dithioester *ω*-end group in the proton NMR spectrum had completely vanished while the typical fluorine signals of the PFP ester in the fluorine spectra were still present. The UV/vis spectrum did not show anymore the characteristic absorption band at 302 nm, indicating the formation of telechelic polymers with activated ester functionality at both sides of the chain. Again, the GPC curve of polymers **P3a** and **P3b** showed no shoulder at twice the molecular weight, indicating that no disulfide coupling reaction had occurred. The molecular weights and the molecular weight distribution were still the same as measured for polymers **P1a** and **P1b**.

Synthesis of Thermo- and Light-Responsive Polymers with Azobenzene End-Group Functionality (See Scheme 1, Route D). In order to address the terminal activated ester either on one side or on both sides of the polymer chains, four samples of the postmodified PFP-P(OEGMA) polymers **P2a,b** and **P3a,b**, respectively, were reacted with an excess amount of aliphatic amino-functionalized azobenzene. For that, *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide was synthesized in a reaction according to a previous publication.[22] In a typical polymer analogous reaction the polymers were stirred in THF solution with 5 equiv of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide for the polymers **P2a,b** with one PFP-ester at the α-end and 10 equiv of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide for the polymers **P3a, b** with telechelic PFP-ester functionality. All polymer samples were purified through filtration and dialysis against diluted aqueous ethanol, in order to remove the remaining excess *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide and the formed pentafluorophenol salts. The obtained polymers **P4a,b** and **P5a,b** were all orange-colored in different intensity, and a GPC measurement with the UV/vis detector set to the absorption maximum of azobenzene (323 nm) indicated that azobenzene was successfully attached to the polymer chain end and any excess *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide had been completely removed by dialysis (see Figure 4). The GPC curve of the azobenzene-functionalized polymers showed no shoulder at twice the molecular weights; however, fractions with a lower molecular weight than 3500 g/mol were totally removed through the dialysis. The molecular weight and the molecular weight distribution M_w/M_n had not changed significantly, indicating that no disulfide coupling had occurred during the dithioster removal reaction. MALDI-TOF mass spectrometry was used in addition to determine the molecular weight in the case of the polymer **P4b** (see Supporting Information). Noteworthy, the average molecular weight of 4500 g mol^{-1} was in the range between the mass values as measured by ^{1}H NMR (M_n = 3800 g mol^{-1}) and GPC (M_n = 5300 g mol^{-1}). Additionally, NMR spectroscopy was performed to analyze the synthesized **P4a,b** and **P5a,b** polymers. The ^{1}H NMR spectra (see Figure 1) showed the characteristic signals of the aromatic azobenzene protons at 7.94 and 7.47 ppm. Further, ^{19}F NMR spectroscopy was not able to detect any fluorine signals, indicating a complete conversion of all pentafluorophenyl ester end groups. The FT-IR spectroscopy confirmed the successful modification of the end groups as the bands at 1789 and 1519 cm^{-1} of the PFP-ester end group had totally vanished and two amide bands of the azobenzene end group at 1657 and 1542 cm^{-1} had appeared (see Figure 2). In the UV/vis spectrum of the **P4b** as illustrated in Figure 3 the characteristic absorption band at 323 nm of the azobenzene chromophore could be assigned.

Figure 5 shows exemplary a section of the MALDI-TOF mass spectrum of **P4b** in order to demonstrate the high efficiency during the end-group transformation (full MALDI-TOF spectrum, see Supporting Information). Clearly two statistical distributions can be observed: (a) distribution of the ethylene glycol side chain length, with the typical peak separation of 44 (equivalent to the mass of an ethylene gylcol unit), and (b) the distribution of the main chain repeating units, with the typical peak separation of 276 (equivalent to the mass of a repeating unit with 4 ethylene glycol units in the side chain). All peaks can clearly be assigned to the polymer exhibiting the proposed end groups. For example, polymer **P4b** with n = 15 repeating units in the backbone and m = 4 side-chain ethylene glycol units gives a theoretical mass of 4623, which can be clearly assigned to the peak located at 4620 in the MALDI-TOF.

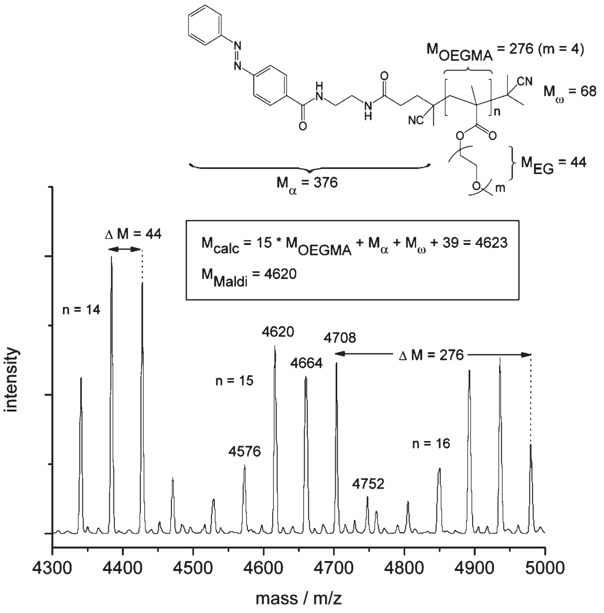


Figure 5. Section of the MALDI-TOF spectrum of polymer **P4b**, demonstrating the high end-group functionalization efficiency.

Each of the four polymers **P4a,b** and **P5a,b** differed in the amount of incorporated azobenzene chromophores as the polymers had a varying ratio between the end groups and the molecular weight. The conversion of the end groups of the respective polymers was determined by UV/vis spectroscopy assuming that every polymer chain end had precisely one reactive ester group for the polymers **P2a,b** and two reactive ester groups in the case of the telechelic polymers **P3a,b**. Further, the ratio between end group and the repeating units was used from the molecular weight values measured by ^{1}H NMR as listed in Table 1. The absorption coefficient of the polymer bound azobenzene was assumed to be identical to that of free *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide at 323 nm. For that, a calibration curve of *N*-(2-aminoethyl)-4-(2-phenyldiazenyl)benzamide was calculated by measuring the absorption maximum at different concentrations in ethanol. Comparison to the absorption maxima at 323 nm of the different polymer solutions in ethanol yielded the incorporated amount of chromophore (see Table 2). Altogether, the values showed that the polymer analogous reaction of the PFP-ester end-functionalized polymers was performed successfully with high conversions. For the polymers **P4a** and **P4b** with one functional end group at the α-terminus, an almost quantitative conversion of the PFP-ester (≥93%) was measured. However, the values for the polymers **P5a** and **P5b** with telechelic azobenzene functional group were lower and in the range between 79 and 80%. These values with an estimated error of 10% represent reasonable data which we could also observe in a recent publication.[42]

As the P(OEGMA) polymers **P4a,b** and **P5a,b** containing azobenzene chromophores at the chain end were designed to exhibit a light- and temperature-controlled phase separation in aqueous solution, cloud point measurements were performed to determine the LCST. The cloud points were measured before and after irradiation with UV-light (λ = 365 nm) for 1 h. The LCST was defined as the temperature at which a transmission of 50% was observed. However, the LCST is dependent on the concentration of the polymer

Table 2. Composition and Conversions for the PFP-Ester End Groups of the P(OEGMA) Polymers

polymer	amount of azobenzene [mol %] (calculated)	amount of azobenzene [mol %] (measured by UV/vis)	conversion of the end groups [%]
P4a	3.8	3.5	93
P5a	7.6	6.1	80
P4b	7.9	7.8	98
P5b	15.8	12.5	79

Table 3. Composition and LCST Values for the P(OEGMA) Polymers

polymer	amount of azobenzene [mol %] (measured by UV/vis)	LCST before irradiation [°C]	LCST after irradiation [°C]	ΔLCST [°C]
P4a	3.5	59.9	60.9	1.0
P5a	6.1	58.4	60.2	1.8
P4b	7.8	49.9	52.3	2.4
P5b	12.5	43.4	47.7	4.3

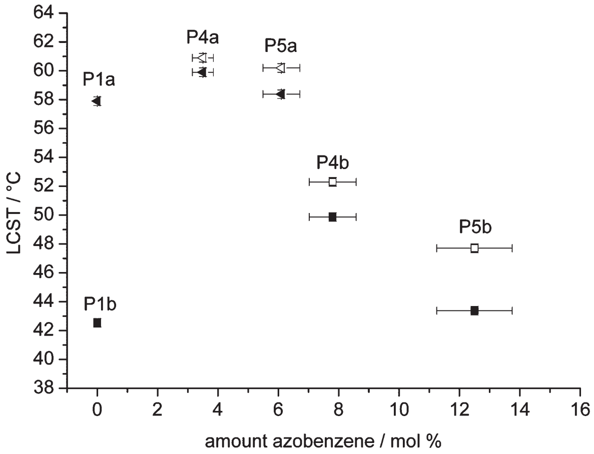


Figure 6. Dependency of the LCST values of the two P(OEGMA) polymer series a (triangle) and b (rectangle) on the amount of azobenzene end groups. The polymers **P4a**, **P5a**, **P4b**, and **P5b** showed higher LCST values after irradiation (white dots) than before irradiation (black dots) with UV light.

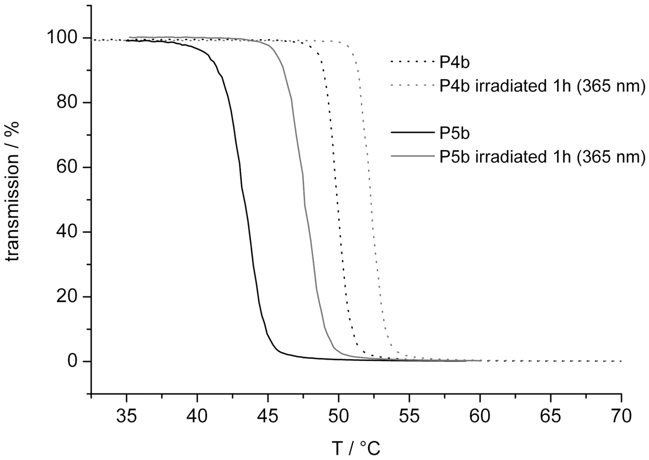


Figure 7. LCST heating curves of the polymers **P4b** (dotted curves) and **P5b** (line curves) before (black) and after irradiation with UV light of 365 nm for 1 h (gray). The concentration was 10 mg/mL in Millipore water and the heating rate 1 °C/min.

solution, the molecular weight of the polymer, and effects of salts. Therefore, a defined concentration of 10 mg/mL polymer in Millipore water was chosen, which had already been demonstrated in a recent publication as a suitable concentration to determine the LCST of P(OEGMA) polymers.[9] In all measurements, a slight temperature hysteresis shifted to lower LCST values during the cooling period was observed. Typically, the LCST values of the heating cycle were 0.5 °C higher than the values of the cooling cycle. The LCSTs values for the heating period are listed in Table 3. The LCSTs of the polymer solutions exhibited a strong dependence upon the content of incorporated azobenzene to the chain length of the polymer. For polymers with increasing amount of hydrophobic azobenzene chromophore, the LCST decreased, and a broadening of the curves was observed. While the LCSTs of **P4a** and **P5a** differed in 1.5 °C, the LCSTs of **P4b** and **P5b** showed a difference of 6.5 °C. Additionally, polymers **P4b** and **P5b** had lower cloud points than the polymers **P4a** and **P5a**, respectively. This showed that the end-group functionality exhibited a stronger influence on the LCST in the case of polymers with a lower molecular weight. The LCST values of the polymers **P4a**, **P5a**, **P4b**, and **P5b** were plotted versus the amount of azobenzene (see Figure 6). However, polymers **P1a** and **P1b** had the lowest LCST values within a polymer series with the same molecular weight due to the hydrophobic effect of the dithioester and PFP-ester end groups.

The content of azobenzene had been calculated by several methods combining ^{1}H NMR spectroscopy and UV/vis measurements. Therefore, a total error of 10% was assumed for each calculated amount of azobenzene end group, while the errors for the LCST values measured were in a range of ±0.3 °C.

As the polymers contained photoswitchable azobenzene either on one side (**P4a**, **P4b**) or on both sides of the chain end (**P5a**, **P5b**), a light-controlled solubility change was investigated. The isomerization of azobenzene is always accompanied by a change in dipole moment of the molecular structure. For the synthesized polymers containing azobenzene groups, this means that the LCST can be shifted through irradiation with UV light. For that, the respective samples were irradiated with UV light of 365 nm for 1 h, and the cloud point of the solutions was measured again. In all cases, higher LCST values were observed after irradiation with UV light (see Figure 6). As an example, the LCST curves of the polymers **P4b** and **P5b** before and after irradiation are illustrated in Figure 7. The LCST shift can be explained by the isomerization of the azobenzene groups accompanied by an increase in dipole moment and thus an increased local polarity present at the polymer backbone. Accordingly, within this temperature range an isothermal, light-induced precipitation of the copolymers was possible. The values for the LCST of the irradiated solutions and the LCST shifts are listed in Table 3. Noteworthy, the LCST shifts between irradiated and nonirradiated solution increased linearly with increasing amount of azobenzene chromophore (see Figure 8), which is in strong contrast to the transition behavior of copolymers based on poly(*N*-alkylacrylamides) with azobenzene side groups.[18,22] This finding is, however, in accordance with a similar linear LCST increase which was

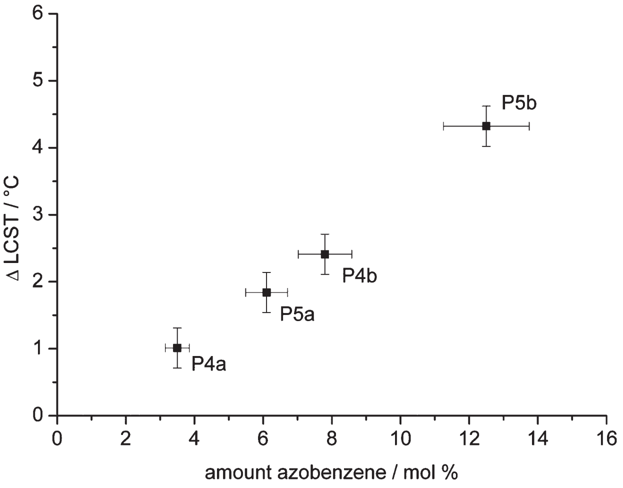


Figure 8. LCST shifts of the P(OEGMA) polymers versus the amount of azobenzene end groups. The differences in the LCST between the irradiated and nonirradiated solutions increased linearly with increasing amount of azobenzene end groups.

already reported by Akiyama et al. for PNIPAM-based thermoresponsive polymer with one azobenzene end group.[26] In general, we observed the same effect for P(OEGMA) polymers with either one or two terminal azobenzene end-group functionality. Noteworthy, polymer **P5a** with azobenzene at both end groups showed an almost twice higher LCST shift (1.8 °C) than polymer **P4a** with one azobenzene terminus (1.0 °C). The same effect was observed for the polymer pairs **P5b** (4.3 °C) and **P4b** (2.4 °C). We believe that the presence of azobenzene at the terminus of each polymers results in the controlled LCST shifts, as the photoisomerization is totally independent from side-group effects which might occur in copolymers. To prove the reversibility of the light-induced solubility change, the samples were allowed to stand for several hours in daylight. LCST measurements were performed again and showed the same values for the cloud points as measured before irradiation with UV light. Additionally, UV/vis kinetics of the irradiated solutions were measured (see Supporting Information). While the light (daylight)-induced reisomerization of the azobenzene occurred very fast ($\tau_{1/2}$ = 5 min), the thermal (room temperature) reisomerization in the dark had a half-time of 14 days.

Conclusion and Outlook

In summary, we have presented the synthesis of P(OEGMA) polymers with either α- or telechelic azobenzene functionalities exhibiting a thermo- and light-responsive behavior in aqueous solution. Within the investigated polymers, the molecular weight distribution was narrow, which could be achieved by RAFT polymerization using a PFP-functionalized chain transfer agent (CTA) yielding polymers with defined molecular weight and one activated end group per chain. The two polymers synthesized had different molecular weights (**P1a**: M_n(NMR) = 7900 g mol^{-1}; **P1b**: M_n(NMR) = 3800 g mol^{-1}) and consequently a different ratio between the repeating units to the end groups. By using the PFP-functionalized azo compound, we were able to substitute the dithioester end group of the polymers into an PFP-ester, thus allowing active ester functionalization at the ω-end of the polymer chain. Both the α and the ω PFP-ester end groups could be addressed with primary amino-functionalized azobenzene with high conversion yielding in light- and temperature-responsive polymers. The obtained polymers **P4a,b** and **P5a,b** exhibited a LCST in aqueous solution that depended strongly on the amount of incorporated azobenzene as well as the ratio between azobenzene end group and the molecular weight of the polymer. Furthermore, the reversible isomerization of the azobenzene end groups in the polymers, 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 nonirradiated and the irradiated solution, a light-controlled reversible solubility change was found. A maximum LCST shift of 4.3 °C was measured for the polymer **P5b**. Additionally, a linear increase in the LCST shifts with an increasing amount of azobenzene in the P(OEGMA) polymers was observed, which was in contrast to the phase transition behavior of thermoresponsive polymers with azobenzene side groups.

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Supporting Information Available: GPC elugram of **P2b**, evolution of UV/vis spectrum of **P4a** after irradiation, and MALDI-TOF spectrum of **P4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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