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Phototunable Temperature-Responsive Molecular Brushes Prepared by ATRP

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ABSTRACT: Molecular brushes with *trans*-4-methacryloyloxyazobenzene (MOAB) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) units in the side chains were successfully synthesized by grafting from a poly(2-(2-bromopropionyloxy)ethyl methacrylate) (pBPEM) macroinitiator using atom transfer radical polymerization (ATRP). Molecular weight, molecular weight distribution, and the DP of the side chains containing different distributions of DMAEMA and MOAB were determined by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy. The number-average molecular weight (M_n) of the brushes ranged from 4.7×10^5 to 1.1×10^6 depending on molecular architecture. The molecular weight distribution of the brushes was narrow ($M_w/M_n = 1.23-1.36$). UV−vis spectra of the brush copolymers in either chloroform or aqueous solution showed reversible isomerization of azobenzene units in the side chains upon irradiation with UV (365 nm) or visible light (442 nm). The transmission spectra of the aqueous solutions of the brush copolymers at 600 nm were measured as a function of temperature and showed that the lower critical solution temperature (LCST) can be affected by photoirradiation. The particle size in aqueous solution measured by dynamic light scattering ranged from 30 to 120 nm depending on temperature, concentration, and structural state of the azobenzene units. This variation of particle size gave additional evidence for photoresponsive thermal transition.

Introduction

Molecular brushes with a long backbone and densely grafted side chains are copolymers with an interesting architecture.[1−5] Atom transfer radical polymerization (ATRP)[6,7] has been successfully used to prepare molecular brushes with poly(methacrylate) backbones and various polyacrylates, polymethacrylates, polyacrylamides, and polystyrene side chains using the "grafting from" approach.[8−10] Molecular architecture of brushes was additionally manipulated, resulting in starlike multiarm structures[11−13] and copolymers with block structures in the side chains and main chains[2,14−17] as well as with a gradient in grafting density along the copolymer backbone.[18−20]

The properties and conformation of molecular brushes are determined by the chemical structure and density of the grafted side chains. In solution, because of steric repulsion between the closely packed side chains, the backbone adopts the entropically unfavorable chain extended conformation, leading to cylindrically shaped brush molecule.[8,21] The persistence length increases with the length of the side chains and their grafting density. This leads to special properties of these materials not only in solution but also in bulk[10,22,23] and at interfaces.[1,2,12,19,24−31]

Recently, "stimuli responsive" materials receive increasing attention. Various types of stimuli, e.g., temperature,[32] pH,[33] ionic strength, solvent vapors,[34−36] light, or an electrical field,[37] can affect properties and conformation of polymer chains. Of special interest are water-soluble polymers whose solubility depends on temperature, leading to materials with either lower or upper critical solution temperature (LCST or UCST). These temperatures can be additionally adjusted by copolymerization with more or less hydrophilic/hydrophobic comonomers. Even more interesting are systems responsive to two different stimuli. For example, the preparation of a linear block copolymer, poly(*N*-isopropylacrylamide)-*block*-poly(acrylic acid), which was responsive to both temperature and pH stimuli was reported.[38] The lower critical solution temperature (LCST) of poly(*N*-isopropylacrylamide) in aqueous solution was additionally influenced by the pH of the medium.

Azobenzene units respond to light and undergo cis−trans isomerization, which results in large changes in the size and polarity of the units.[39−44] Therefore, copolymers composed of azobenzene containing monomer units and DMAEMA units should respond to both light and temperature.[45] Recently, the synthesis of diblock copolymers composed of DMAEMA and azobenzene units and the effect of photoinduced trans−cis isomerization on the LCST was reported.[46] The LCST of the diblock copolymers increased upon UV irradiation due to the *cis*-azobenzene being less hydrophobic than the trans conformation. The formation of core−shell micelles from the amphiphilic block copolymers was also observed, and the effect of photoirradiation on micellization was studied.

In this study, we report the synthesis of the densely grafted molecular brushes with *trans*-4-methacryloyloxyazobenzene (MOAB)[40] and DMAEMA units in the side chains and the response of an aqueous solution of the brush copolymers to photostimuli and thermal stimuli. The hydrophobic azobenzene groups can be isomerized photochemically, providing an additional control over the LCST of the brush macromolecules.

Experimental Section

Materials. 4-Hydroxyazobenzene (98%), methacryloyl chloride (97%), triethylamine (98%), DMAEMA (97%), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%) were purchased from Aldrich Chemical Co. 2-(Trimethylsilyloxy)ethyl methacrylate (HEMA-TMS) was purchased from Polysciences and purified by distillation before use. All other reagents were used without further purification.

Analysis. Apparent molecular weight and molecular weight distributions were measured on a GPC system consisting of a Waters 510 HPLC pump, three Waters UltraStyragel columns (100, 10^3, and 10^5 Å), and a Waters 410 differential refractive index detector, with a DMF flow rate of 1.0 mL/min; poly(methyl

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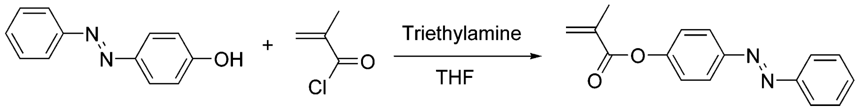
Scheme 1. Synthesis of *trans*-4-Methacryloyloxyazobenzene (MOAB)



methacrylate) was used as calibration standards employing WinGPC software from Polymer Standards Service. ^1H NMR spectra of MOAB and the copolymer brushes were examined in deuterated chloroform at 30 °C using a Bruker 300 MHz spectrometer. Conversion of DMAEMA was determined by gas chromatography (GC) using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector and ValcoBond 30 m VB WAX Megabore column. To investigate the effects of UV and visible light irradiation, a high-power mercury arc lamp (200 W) which covers from UV to visible light was used. The intensity was 50 mW after passing through a wavelength filter and IR block filter. 365 and 442 nm wavelength filters were used for UV and visible light irradiation, respectively.

UV−vis spectra were recorded using a Cary 50 Bio UV−vis spectrophotometer equipped with a digital temperature controller. The wavelength of 600 nm was used for the determination of the LCST. The range of temperature was from 25 to 55 °C, and the heating rate was 0.1 °C/s. The particle size was measured using dynamic light scattering (DLS) (high performance particle sizer, model HPP5001, Malvern Instruments). Measurements were taken from 25 to 55 °C at 4 °C intervals, and each measurement was finished in 2 min.

Synthesis. p(HEMA−TMS) and PBPEM were prepared as previously reported.[1]

***trans*-4-*Methacryloyloxyazobenzene* (MOAB)**: *trans*-4-Methacryloyloxyazobenzene was prepared by the condensation reaction of 4-hydroxyazobenzene and methacryloyl chloride in THF, in the presence of triethylamine (TEA) to trap HCl. 4-Hydroxyazobenzene (10 g, 0.05 mol) was dissolved in 100 mL of THF in a 250 mL flask, to which triethylamine (5.05 g, 0.05 mol) was added. Methacryloyl chloride (5.86 mL, 0.06 mol) was added dropwise to the solution for 1 h via a dropping funnel while the solution was kept in an ice bath. The triethylammonium salt started to accumulate immediately after the addition of methacryloyl chloride. The reaction mixture was stirred for 12 h. The resulting precipitate was filtered off, and the solvent was evaporated to give a yellow solid, which was purified by passage through a silica chromatography column (silica gel) using $CHCl_3$/hexane (3:7) as the solvent. The solvent was removed under vacuum, and then the solid was recrystallized twice from *n*-hexane and dried under high vacuum. A yield of 65% was obtained after purification. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 8.05−7.25 (9H, aromatic); 6.4 (1H, $-C\mathit{H}_2-C-CH_3$); 5.79 (1H, $-C\mathit{H}_2-C-CH_3$); 2.1 (3H, $-CH_2-C-C\mathit{H}_3$).

Brush I: Poly(BPEM-*graft*-DMAEMA). 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) (35 μL, 0.13 mmol), $CuCl_2$ (4.5 mg, 0.033 mmol), DMAEMA (8.0 mL, 47 mmol), PBPEM (0.0247 g, 0.094 mmol, $M_n = 86\,300$ g/mol, $M_w/M_n = 1.12$), and acetone (2.0 mL) were added to a 50 mL Schlenk flask equipped with a magnetic stir bar. Oxygen was removed by three freeze−pump−thaw cycles, and CuCl (9.6 mg, 0.090 mmol) was added under nitrogen. The polymerization was conducted at 25 °C for 24 h. The reaction was stopped by opening the flask to air, and the catalyst was removed by passing the solution through a neutral alumina column. The polymer was precipitated by addition to hexane, filtered, and dried under high vacuum at room temperature for 12 h (DP_{sc} of DMAEMA = 45, as determined gravimetrically). M_n(GPC) = 1 110 000 g/mol, $M_w/M_n = 1.23$.

Brush II: Poly[BPEM-*graft*-(DMAEMA-*stat*-MOAB)]. A brush copolymer with random distribution of MOAB and DMAEMA in the side chains. In a 25 mL Schlenk flask, PBPEM (0.0132 g, 0.05 mmol), DMAEMA (2.75 g, 17.5 mmol), $CuCl_2$ (0.00033 g, 0.0025 mmol), and MOAB (0.67 g, 2.5 mmol) were added, and the solution was purged with nitrogen. Deoxygenated acetone (3 mL) and HMTETA (6.8 μL, 0.025 mmol) were added, and the reaction mixture was degassed by three freeze−pump−thaw cycles. After stirring for 0.5 h at room temperature, CuCl (0.0025 g, 0.025 mmol) was added under nitrogen, and the flask was placed in a preheated oil bath at 35 °C. The polymerization was stopped after 10 h by cooling to room temperature and opening the flask to air. The resulting polymer was purified by passing through a column (2 cm × 10 cm) of neutral alumina, precipitated into hexane, filtered, and dried under high vacuum at room temperature for 12 h (DP_{sc} of MOAB = 5, DP_{sc} of DMAEMA = 25, as determined by ^1H NMR spectroscopy). $M_n = 475\,000$ g/mol, $M_w/M_n = 1.36$. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 7.9−7.25 (9H, aromatic); 4.05 (2H, $-C\mathit{H}_2-CH_2-N-(CH_3)_2$); 2.63 (2H, $-CH_2-C\mathit{H}_2-N-(CH_3)_2$); 2.21(6H, $-CH_2-CH_2-N-(C\mathit{H}_3)_2$); 1.9−1.15 (overlapped, $-CH_3-C-C\mathit{H}_2$); 1.15−0.78 (overlapped, $C\mathit{H}_3-C-CH_2$).

Brush III: Poly[BPEM-*graft*-(MOAB-*block*-DMAEMA)]. *Step 1*: poly(BPEM-*graft*-MOAB): In a 10 mL Schlenk flask, PBPEM (0.0264 g; 0.1 mmol), MOAB (2.68 g, 10 mmol), dNbpy (0.082 g, 0.2 mmol), and anisole (5 mL) were added, and the reaction mixture was degassed by three freeze−pump−thaw cycles. After stirring for 0.5 h at room temperature, CuCl (0.01 g, 0.1 mmol) was added under nitrogen, and the flask was placed in a preheated oil bath at 70 °C. The polymerization was stopped after 20 h by cooling to room temperature and opening the flask to air. The resulting polymer was purified by passing through a column (2 cm × 10 cm) of neutral alumina, precipitated into methanol, filtered, and dried under high vacuum at room temperature for 12 h (DP_{sc} of MOAB = 5 determined by ^1H NMR spectroscopy). $M_n = 183\,000$ g/mol, $M_w/M_n = 1.26$. ^1H NMR (300 MHz, DMSO, δ in ppm): 7.95−7.05 (9H, aromatic); 4.52 (2H, $-O-CH_2-C\mathit{H}_2-OCO-CH-$); 4.28 (2H, $-O-C\mathit{H}_2-CH_2-O-CO-CH-$); 2.65 (1H, $-OCO-C\mathit{H}-CH_3-$); 1.98 (3H, $-OCO-CH-C\mathit{H}_3-$); 1.8−1.31 (overlapped, $-CH_3-C-C\mathit{H}_2$); 1.3−0.7 (overlapped, $C\mathit{H}_3-C-CH_2$).

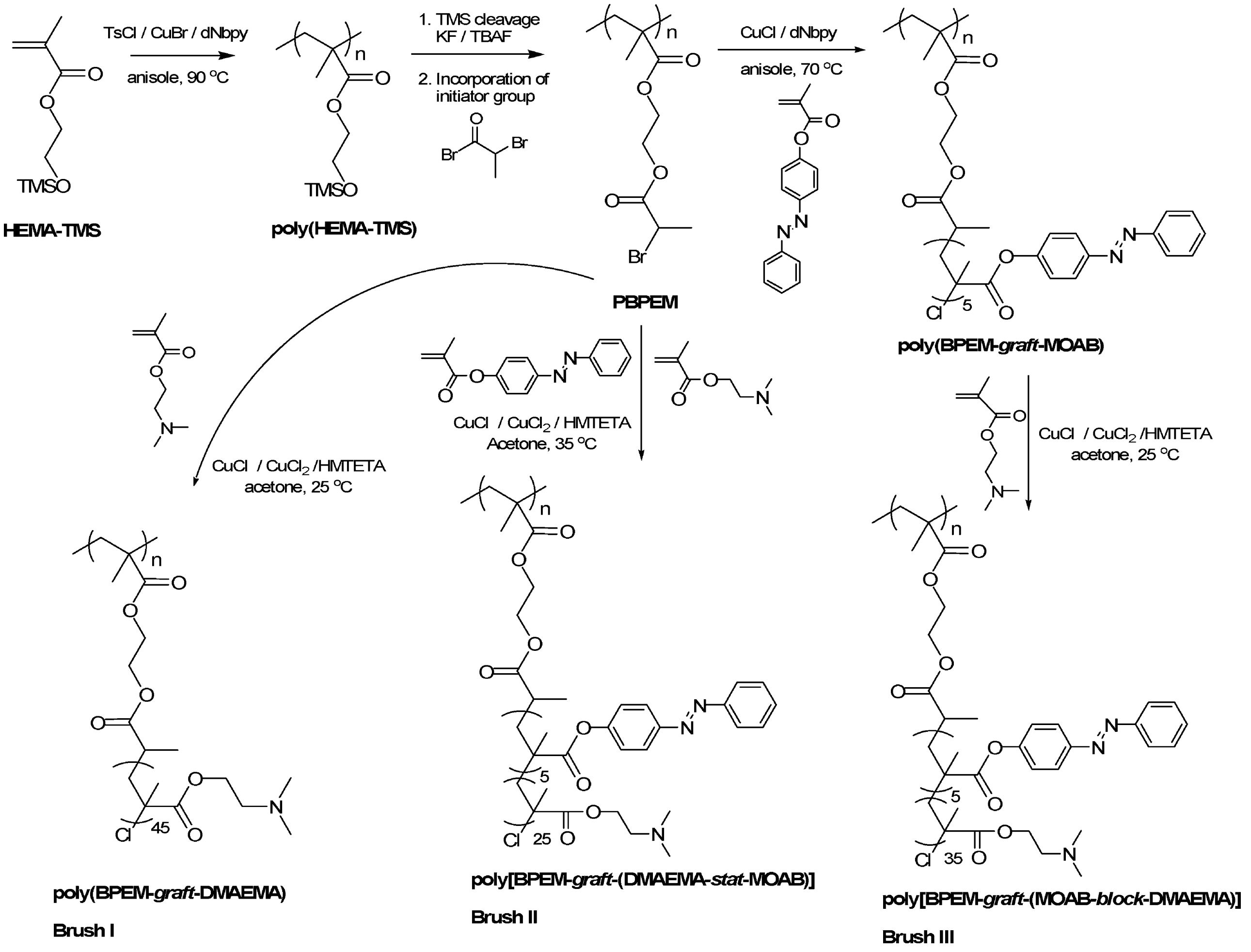
Step 2: Poly[BPEM-*graft*-(MOAB-*block*-DMAEMA)]: In a 10 mL Schlenk flask, poly(BPEM-*graft*-MOAB) (0.094 g, 0.05 mmol), $CuCl_2$ (0.00033 g, 0.0025 mmol), and DMAEMA (3.14 g, 20 mmol) were added, and the solution was purged with nitrogen. Deoxygenated acetone (3.5 mL) and HMTETA (6.8 μL, 0.025 mmol) were added, and the reaction mixture was degassed by three freeze−pump−thaw cycles. After stirring for 0.5 h at room temperature, CuCl (0.0025 g, 0.025 mmol) was added under nitrogen, and the flask was placed in a preheated oil bath at 25 °C. The polymerization was stopped after 10 h by cooling to room temperature and opening the flask to air. The resulting polymer was purified by passing through a column (2 cm × 10 cm) of neutral alumina, precipitated into hexane, filtered, and dried under high vacuum at room temperature for 12 h (DP_{sc} of MOAB = 5, DP_{sc} of DMAEMA = 35, as determined by ^1H NMR spectroscopy). $M_n = 804\,000$ g/mol, $M_w/M_n = 1.23$.

Results and Discussion

Synthesis and Characterization. The synthesis of *trans*-4-methacryloyloxyazobenzene (MOAB), depicted in Scheme 1, involves the reaction of methacryloyl chloride with 4-hydroxyazobenzene in the presence of triethylamine.[41] ^1H NMR confirmed synthesis of MOAB; the integration ratios of aromatic and vinyl signals showed the stoichiometry of azobenzene to vinyl groups to be 1:1.

Water-soluble brush copolymers, responsive to light and temperature, were prepared by ATRP according to Scheme 2. Temperature-responsive DMAEMA units and the light-responsive MOAB units were incorporated into the side chains in a "grafting from" ATRP reaction from the PBPEM macroinitiator. Halogen exchange, where the bromine in the PBPEM macroinitiator was replaced by chlorine from CuCl, was employed in order to ensure fast initiation from the secondary macroinitiator-

Scheme 2. Synthesis of the Molecular Brushes Containing MOAB and DMAEMA in the Side Chains from the Backbone (PBPEM) by ATRP



derived radicals and controlled propagation of the methacrylate monomers.[47−50] $CuCl_2$ was added to the initial reaction mixture to reduce spontaneously generated radical−radical termination reactions, normally required to develop the necessary amount of deactivator for operation of the persistent radical effect.[51,52]

Figure 1a shows the progressive increase in the molecular weight during the polymerization of DMAEMA side chains from a PBPEM backbone. A small shoulder in high molecular weight region, most likely arising from coupling during the polymerization of the HEMA-TMS precursor, is visible in the macroinitiator traces. This shoulder became largely undetectable as the polymerization proceeded due to decreased chromatographic resolution. The molecular weight distribution remained relatively narrow throughout the polymerization of DMAEMA. Since the molecular weight was determined by GPC using linear PMMA standards for calibration, the molecular weights reported for the brush copolymers are apparent molecular weights because their highly compact nature do not correspond well to the linear standards. It is therefore more accurate to estimate the length of the brush side chains from conversion data determined gravimetrically, assuming quantitative initiation. The random copolymerization of DMAEMA and MOAB was initiated with a PBPEM backbone, as shown in Scheme 2. The complete shift of the GPC traces during the synthesis of the brushes confirmed that well-defined molecular brushes with statistical copolymer side chains were prepared (brush II), as shown in Figure 1b. Figure 1c shows the GPC traces of the polymer backbone (PBPEM), intermediate poly(BPEM-*graft*-MOAB), and the end product poly[BPEM-*graft*-(MOAB-*block*-DMAEMA)] (brush III). The polymerization of MOAB using PBPEM as a macroinitiator proceeded in a controlled way. The increase of the molecular weight of the intermediate graft copolymer is shown by the shift in the GPC trace (Figure 1c). The isolated intermediate poly(BPEM-*graft*-MOAB) brush was used as a macroinitiator for the polymerization of DMAEMA, leading to brushes with block copolymer side chains (brush III). The GPC trace of brush III is monomodal and shows no evidence of brush coupling products. Side chain extension from poly(BPEM-*graft*-MOAB) with DMAEMA proceeded in a controlled fashion as shown by shift of the GPC traces entirely toward higher molecular weight, and no intermolecular brush−brush coupling reactions were detected.

Table 1 presents the results of conducting ATRP of DMAEMA and MOAB monomers from the PBPEM macroinitiators. Brush syntheses appeared to proceed in a controlled fashion since the polydispersities of the final copolymers, in all cases, remained similar to that of the backbone copolymer.

^1H NMR was used to analyze the structure of the synthesized copolymer brushes. Figure 2 shows the structural assignments for the ^1H NMR spectrum of poly(BPEM-*graft*-MOAB) and poly[BPEM-*graft*-(MOAB-*block*-DMAEMA)] (brush III). The spectrum provides evidence of incorporation of both DMAEMA and MOAB into the side chains of brush III. In Figure 2A, there were two broad peaks of aromatic protons between 7 and 8 ppm. The peaks (b and c) at 4.52 and 4.28 ppm represent the methylene protons adjacent to the ester group in PBPEM. The ratios of the integral for the signal from the aromatic protons

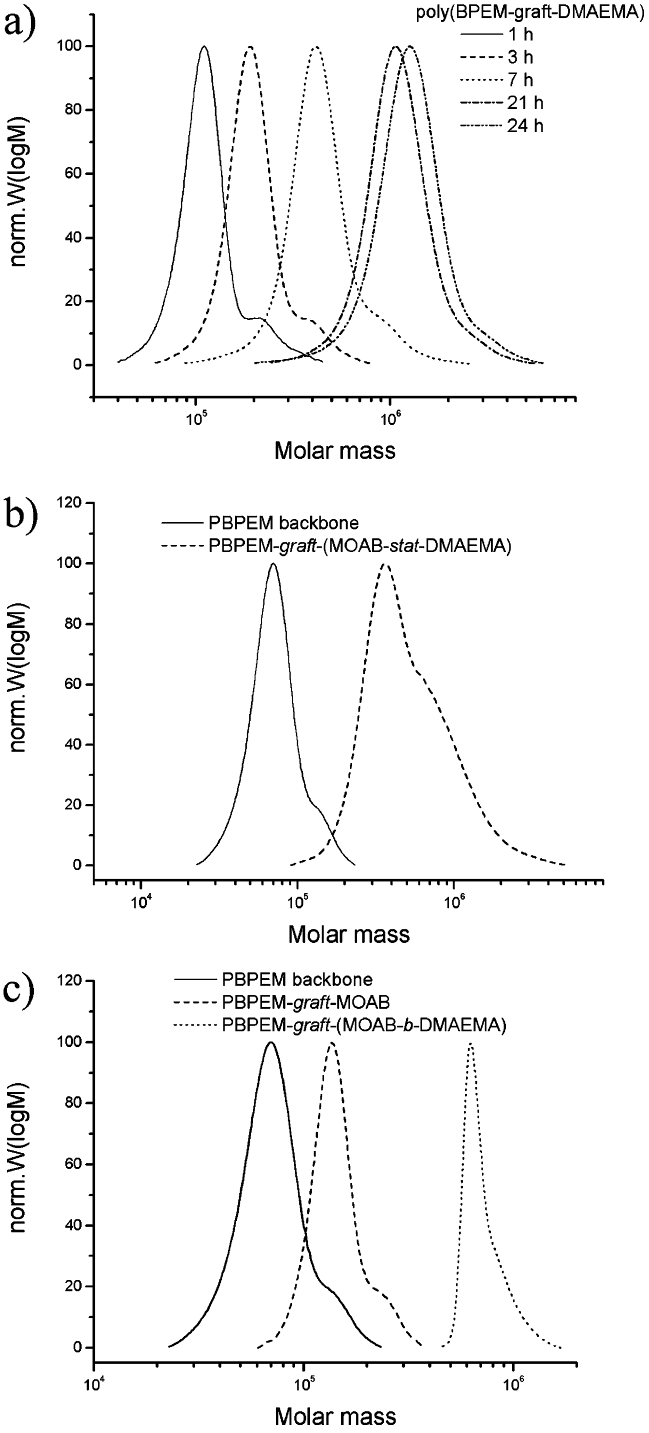


Figure 1. GPC traces of synthesis of (a) poly(BPEM-*graft*-DMAEMA) (brush I), (b) poly[BPEM-*graft*-(MOAB-*stat*-DMAEMA)] (brush II), and (c) poly[BPEM-*graft*-(MOAB-*block*-DMAEMA)] (brush III) from a PBPEM backbone.

of MOAB and the methylene protons from PBPEM backbone were used to calculate the DP of MOAB units. After chain extension with the second monomer, DMAEMA, two peaks from methylene protons (b and c) disappeared while new peaks, d, e, and f from DMAEMA units, appeared as shown in Figure 3B, indicating successful block extension with p(DMAEMA). The DP of DMAEMA units was calculated from the integral ratio between the aromatic protons of MOAB and the methylene protons from DMAEMA. The DP of DMAEMA units and MOAB units for poly[BPEM-*graft*-(DMAEMA-*stat*-MOAB)] (brush II) was calculated by the same way.

Table 1. Characterization of Double-Responsive Brush Copolymers

brush	time (h)	DP DMAEMA	DP MOAB[4]	mole fraction MOAB[4]	$M_{\mathrm{n,theory}} \times 10^{-5}$	$M_{\mathrm{n,app}}{}^{e} \times 10^{-5}$	$M_{\mathrm{w}}/M_{\mathrm{n}}{}^{e}$
I[a]	24	45[c]		0	16.8[c]	11.1	1.23
II[b]	10	25	5	0.16	12.5[d]	4.75	1.36
III[b]	20	35	5	0.125	14.7[d]	8.04	1.23

[a] From PBPEM ($M_n = 86\,300$ g/mol, $M_w/M_n = 1.12$, DP = 330). [b] From PBPEM ($M_n = 78\,100$ g/mol, $M_w/M_n = 1.17$, DP = 300). [c] Determined from gravimetry. [d] Determined from ^{1}H NMR spectroscopy. [e] Apparent values determined by GPC in DMF with PMMA calibration.

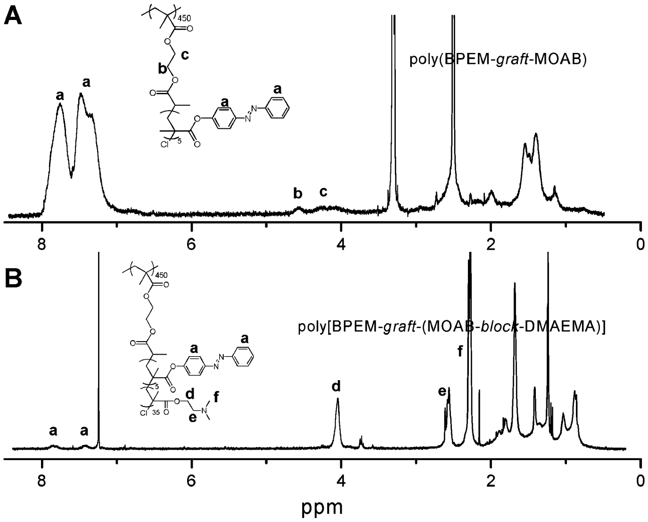


Figure 2. ^{1}H NMR spectra for the polymer brushes: (A) poly(BPEM-*graft*-MOAB); (B) poly[BPEM-*graft*-(MOAB-*block*-DMAEMA)] (brush III).

Phototunable Thermal Transition: UV−Vis, % Transmission, and Dynamic Light Scattering Studies. Polymers containing azobenzene units change their conformation in response to light and this influences the polymer properties. The photochemical isomerization of an azobenzene moiety can be followed by UV−vis absorption spectroscopy. The initial solution of brush II in $CHCl_3$ (0.1 wt %) was stored in the dark for 48 h to ensure the presence of 100% trans isomers. Then the solution was irradiated with (a) UV (365 nm) and (b) visible light (442 nm) until photostationary states were reached. Figure 3 shows representative spectra from the solution of brush II with varying irradiation time. The trans-to-cis isomerization of the azo chromophores was confirmed by the changes in the spectra. The azobenzene unit of brush II was initially in the thermodynamically stable trans form, which has a strong absorbance at 323 nm due to a $\pi-\pi^*$ transition, but upon UV irradiation, the intensity of this band decreased and the intensity of the $n-\pi^*$ transition band at 440 nm gradually increased. The resulting *cis*-azobenzene solution was placed in oil bath at 50 °C for 1 h. It was verified that *cis*-azobenzene kept its conformation since there was no significant change in the UV−vis spectrum. Irradiation with visible light isomerizes the *cis*-azobenzene back to the *trans*-azobenzene conformation, as evidenced by the spectra gradually reverting to the original curve. While the same general isomerization trends are observed in aqueous solutions, interpretation of the spectra is complicated by contributions to the absorption spectra arising from aggregation of the azobenzene units.

It has been reported that the *cis*-azobenzene unit is less hydrophobic than the *trans*-azobenzene unit.[53,54] Therefore, the change in transmission as a function of temperature was monitored at 600 nm for aqueous solutions of brush II and brush

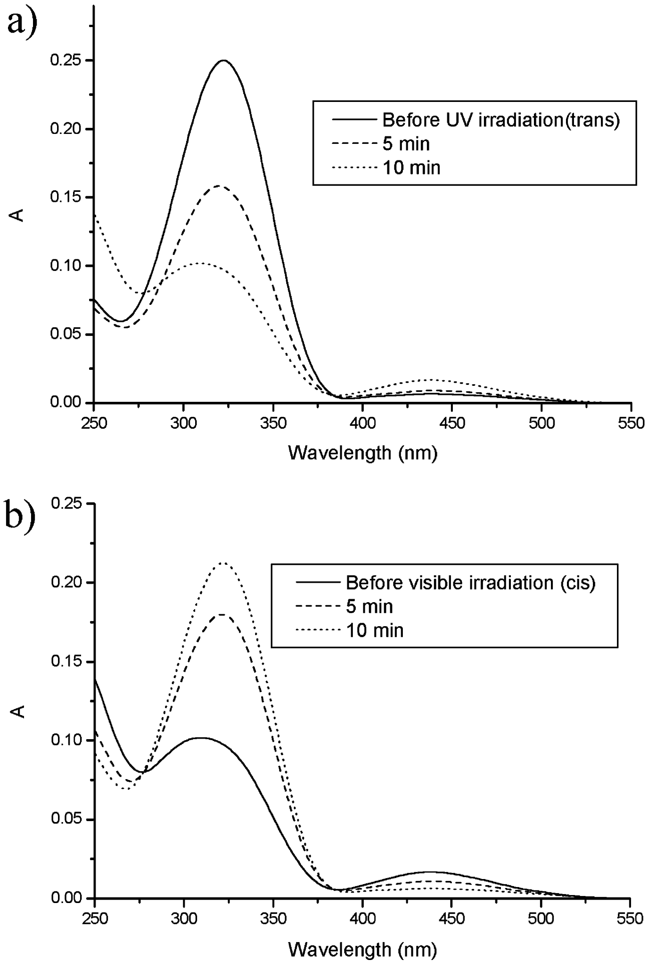


Figure 3. UV−vis spectra of brush II upon (a) UV (365 nm) and (b) visible (442 nm) irradiation in chloroform solution (0.1 wt %).

III, as shown in Figure 4. The % transmission of 600 nm light through the aqueous solution of brush II, with *trans*-azobenzene units, started to decrease at 35 °C (Figure 4a), indicating a LCST, but for the *cis*-isomer of brush II, there was no evidence for a LCST below 55 °C. Visually, it was easy to observe that for a solution of the *trans*-azobenzene brush there was a sharp transition between a transparent and cloudy solution with increasing temperature. However, for brush II with the *cis*-azobenzene units, the solution remained transparent regardless of an increase in temperature. On the other hand, as seen from Figure 4b, no significant difference was observed between the trans and cis isomers of brush III over the examined range of temperature. This is a consequence of the core−shell cylindrical structure of brush III. The structural variation of the azobenzene units, induced by photoisomerization, changes the hydrophobicity of the core region, but this does not have much effect on the thermal transition of PDMAEMA segments which are in direct contact with water molecules. It appears that the less hydrophobic environment provided by trans-to-cis isomerization was greatly enhanced by random distribution of the azobenzene units along the side chains rather than in a core−shell diblock structure.

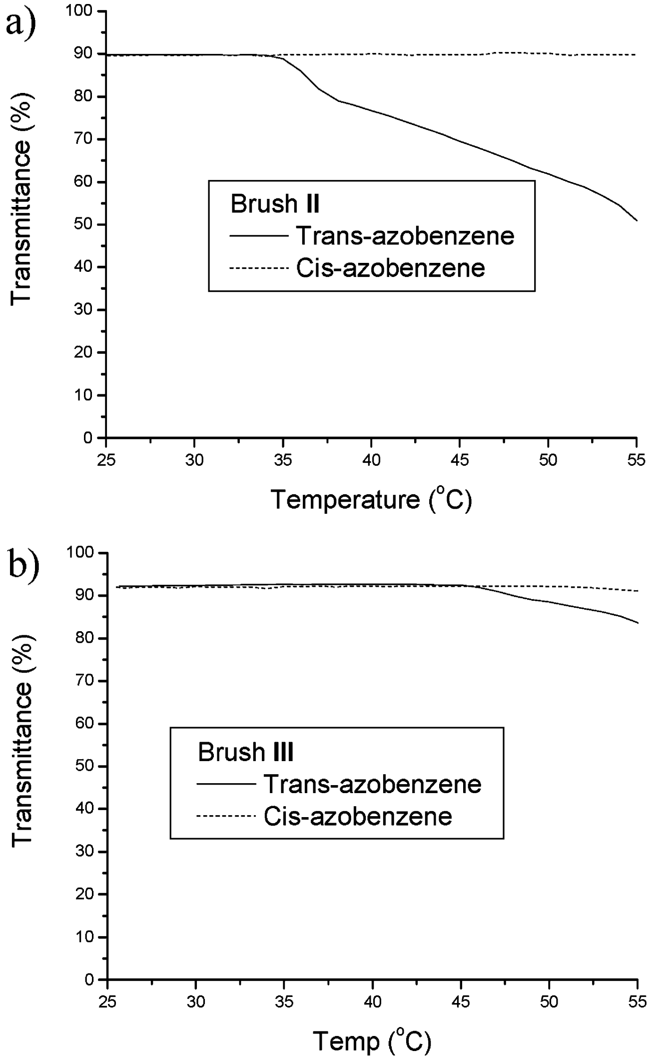


Figure 4. % transmission at 600 nm of 1.0 wt % aqueous solutions of (a) brush II and (b) brush III with *trans*-azobenzene (solid) and *cis*-azobenzene (dash) at different temperature.

The apparent hydrodynamic diameter of brush I was measured as a function of solution temperature for three different concentrations of the brush macromolecule in water. As shown in Figure 5a, the results from the thermal transformation of the DMAEMA units were concentration dependent. There was a significant increase in the hydrodynamic diameter of the molecules for the solution with higher concentration (solution 3, 5.0%) upon increase of temperature, which can be explained by intermolecular aggregation. The opposite behavior was observed for the dilute solutions (solution 1 and 2, 0.1% and 0.5%, respectively). The hydrodynamic diameter of the brush molecules in the 0.1% solution decreased with increasing temperature, from 61 nm at 20 °C to 34 nm at 55 °C, which was driven by intramolecular aggregation due to the low concentration of the molecules in solution. Similar behavior was observed for a 0.5% solution. No further change in the hydrodynamic diameter of the molecules was observed when the solutions were held at 55 °C for 24 h, which indicates that the individually collapsed brushes were stable during this period.

To confirm the dual photothermal transition behavior, the particle size of brush II in an aqueous solution was also measured by dynamic light scattering and a concentration dependence of the hydrodynamic diameter was also observed. Photochemical isomerization of the azobenzene units had little effect on the hydrodynamic diameter of brush II in a 0.1% solution. Regardless of the presence of the trans or cis isomers, the hydrodynamic diameter decreased with temperature as a result of intramolecular aggregation due to the low concentration of the molecules in the solution. However, it was observed the onset temperature for the decrease in the hydrodynamic diameter of the molecules with the trans isomer was lower than that for copolymers with the cis isomer, indicating that, as expected,

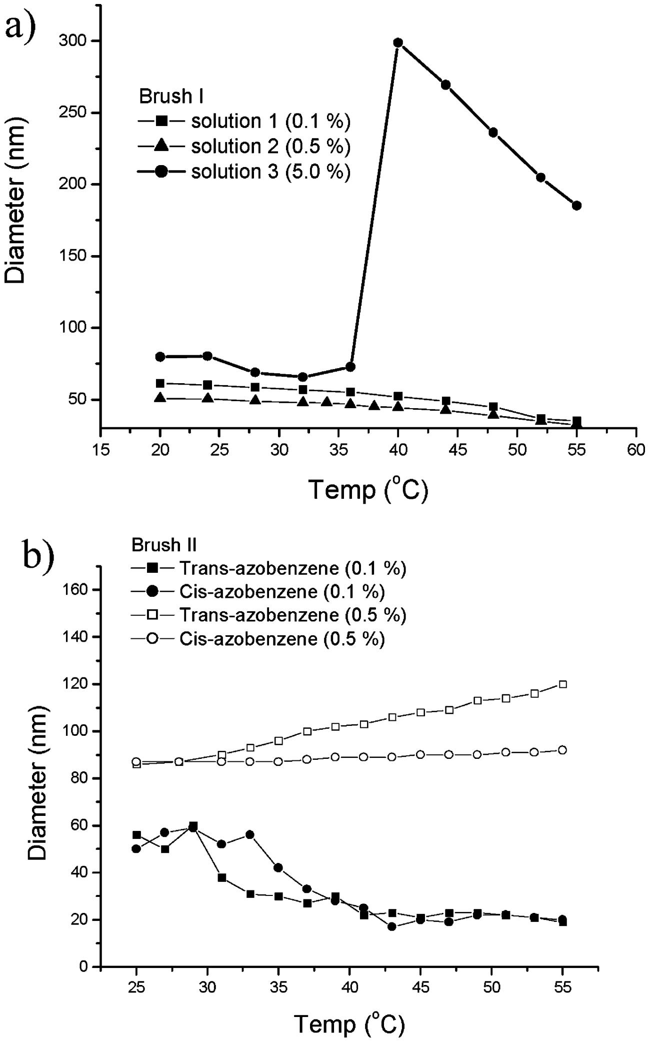


Figure 5. Apparent hydrodynamic diameter of (a) brush I and (b) brush II as a function of temperature at various solution concentrations.

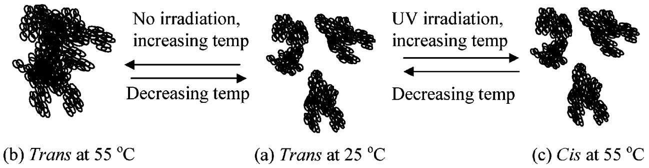


Figure 6. Possible modes of aggregation behaviors of brush II in aqueous solution as a dependence of the photochemical isomerization and temperature.

the more hydrophobic trans isomer shifted the LCST toward lower temperature. On the other hand, for the more concentrated 0.5% solution of brush II, the hydrodynamic diameter of the brush with *trans*-azobenzene increased with temperature as a result of intermolecular aggregation. There was no aggregation behavior for the brush with *cis*-azobenzene because the size of the particles did not change over the examined temperature range (Figure 5b). It can be concluded that, for the more concentrated 0.5% solution, the lower hydrophobicity provided by trans-to-cis isomerization played a greater role in disturbing the aggregation of DMAEMA units at high temperature, resulting in a shift of LCST to higher temperatures.

Figure 6 schematically illustrates a plausible simplified explanation of the behavior of an aqueous solution brush II at higher concentration, above 0.5%, and how the aggregation behavior of the individual molecules depends on which isomers are present as temperature changes. Initially there is no intermolecular aggregation of the DMAEMA units present in an aqueous solution of brush II with *trans*-azobenzene units in the side chains (a). However upon heating, without UV irradiation, intermolecular aggregation can be observed (b). This was confirmed by an increase in turbidity and an increase in hydrodynamic diameter of the molecules. As the temperature decreases below the LCST intermolecular aggregation was broken, and the solution became transparent, indicating reversible recovery to the original state (a). In the case of the aqueous solution of brush II with *cis*-azobenzene units in the side chains, even upon heating (c), intermolecular aggregation is not observed because the less hydrophobic *cis*-azobenzene units interfere with dehydration of the DMAEMA units, as confirmed by no change in turbidity or hydrodynamic diameter.

Structural Effect on Phototunable Thermal Transition. It has been reported that the LCST of linear polymers containing photoresponsive azobenzene groups and thermoresponsive units can be shifted by a few degrees upon photoisomerization.[46,54] However, the study on turbidity and DLS of brush II has shown that the LCST behavior can be completely eliminated in brush macromolecules with branch segments containing a copolymer of azobenzene monomer units and thermoresponsive monomer units. The prime reason for this behavior might be that the polarity of brush II in an aqueous solution can be significantly altered by photochemical isomerization of the azo units. In other words, the more hydrophobic *trans*-azobenzene groups accelerate the aggregation of the side chains of brush II at higher temperatures, while the less hydrophobic *cis*-azobenzene units presumably raise the LCST of the brush to a higher temperature than that measured. Several factors may contribute to such a large polarity change upon isomerization. First of all, because of the relatively large ratio of MOAB to DMAEMA (MOAB: DMAEMA = 5:25) in the side chains of brush II, photoisomerization has a significant effect on the polarity of the molecule in the aqueous solution. The less hydrophobic environment, provided by trans-to-cis isomerization, could be maximized by random distribution of azobenzene units along the side chains. Further, because of the congested structure of molecular brushes, the side chains are in such a close contact with each other that the structural rearrangement of azobenzene units was amplified by being constrained in a single molecular level. As a result, the arrangement of the azobenzene units in the multigraft macromolecule are significantly influenced by the structural state of the isomers, with the trans isomers being more closely packed and the cis isomers being less densely packed between the side chains.[12,55−57] Thus, the reversible structural rearrangement due to isomerization within the locally confined side chains of the brushes could influence the overall aggregation behavior at high temperature.

Conclusions

Well-defined molecular brushes containing MOAB and DMAEMA units in the side chains were successfully synthesized using an ATRP "grafting from" approach. UV−vis spectroscopy showed that a reversible isomerization of azobenzene units occurred upon alternating irradiation with UV and visible light. The transmission spectra of an aqueous solution of a brush copolymer with copolymer graft segments measured at 600 nm as a function of temperature proved that the lower critical solution temperature (LCST) of the molecule was affected by photoisomerization of the azobenzene units. Particle size distribution, measured by dynamic light scattering, showed that there was a concentration dependency for aggregation of the brush molecules in solution. The statistical copolymer brush (brush II) with *trans*-azobenzene units showed LCST behavior, but after isomerization to *cis*-azobenzene, this brush did not show a LCST within the examined temperature range. In conclusion, the LCST of this brush was changed by photoirradiation, indicating that a dual responsive macromolecule had been prepared.

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