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Polyacrylamide Containing Weak Temperature Labile Azo Links in the Polymer Backbone

Emilia Kot and Alexander Bismarck*

Department of Chemical Engineering, Polymer and Composite Engineering (PaCE) Group, Imperial College London, South Kensington Campus, London, SW7 2AZ, U.K.

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ABSTRACT: Degradable polyacrylamide (PAAm) was prepared by incorporating temperature-sensitive azo groups into the polymer backbone. Ceric ions (Ce(IV)) and 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)-propionamide] were used as a redox couple to initiate the polymerization of acrylamide. The presence of azo groups in the backbone of the synthesized polyacrylamide was confirmed by ^{1}H NMR spectra, DSC, and by the fact that the polymerization of acrylonitrile could be initiated using the synthesized polyacrylamide with built-in azo groups as a macroinitiator. Drag reduction properties of the synthesized polyacrylamide with incorporated azo groups were quantified. It was found that polyacrylamide with azo links in the polymer backbone is as good a drag reducing agent as pure polyacrylamide. However, PAAm with azo links in the backbone degrades into smaller molecular weight fragments and, therefore, loses its drag reduction properties once subjected to elevated temperature, which for some applications is seen as an advantage. The degradation behavior of the PAAm with temperature-sensitive azo groups was characterized using GPC.

Introduction

Water-soluble polymers are widely used in a range of industries and products. They are predominantly used as rheology modifiers, stabilizers, and emulsifiers to improve effectiveness of a number of products.[1] Water-soluble polymers are used in detergents, shampoos, food, skin lotions, textiles, paints, water purification, and pharmaceuticals. They are also used in oil industry as viscosifiers, flocculants, drag reducing agents, or mobility control fluids.[2,3] One of the biggest challenges of the modern world is the environment. Conventional polymers, except their oligomers, are stable in the environment; thus, they are retained in water or the ground for many years.[2] It appears that production of degradable water-soluble polymers could be the ultimate answer to this issue.

Apart from the environmental motive, a reason for the production of degradable water-soluble polymers is also related to particular applications of a product, for instance, in the case of drag reducing agents and viscosifiers used in the oil field servicing industry. For these applications, the availability of water-soluble polymers containing weak links that can be degraded upon experiencing a trigger such as temperature, pH, or a reducing agent would be very advantageous. Because of ability of weak links to degrade under certain conditions, the polymer could be used for its intended application, and then afterward it degrades in a controlled and predetermined manner. The resulting lower molecular weight fractions of that polymer lead to a reduced viscosity and quick partitioning into the water phase, and they are also less likely adsorb onto formation surfaces.

Generally, water-soluble polymers with a hydrocarbon backbone are not degradable due to their resistance to hydrolysis, oxidative cleavage, temperature, or enzymatic attack,[4] whereas heteroatom-containing polymers such as amides, esters, orthoesters, carbonates, anhydrides, and phosphazenes do degrade but they are usually insoluble in water.[5] Depending on the character of the labile group, a polymer can degrade by oxidation, photodegradation, thermal degradation, and hydrolysis or by microbial degradation.[6] The incorporation of various degradable groups into the polymer backbone allows tailoring the degradation conditions and kinetics. Azo linkages have drawn a lot of attention due to their thermal, chemical, photochemical, and biological properties.[7−9] Aromatic azo groups confer biodegradability, which enables to use them as a delivery vehicle in targeted drug delivery.[10−12] Aliphatic azo groups are thermally cleavable, creating free radicals which are used for the synthesis of block or graft copolymers.[13] The incorporation of azo compounds into a polymer backbone opens the way to thermo- and photodegradable polymers.[14−16]

Azo-containing polymers can be prepared by condensation, radical, cationic, and anionic polymerization.[17,18] An alternative strategy is based on using bifunctional initiators compromising azo groups to polymerize vinyl monomers. The redox reaction between an oxidizing metal ion such as Ce(IV), Mn(III), V(V), Co(III), Cr(VI), and Fe(III) and a reducing agent such as alcohols, aldehydes, amines, or acids generates free radicals, which can be used to initiate a free radical polymerization.[19,20] We show in this paper that, using an azo initiator with two hydroxyl groups on both ends and Ce(IV) ions as a redox couple, degradable polyacrylamide can be synthesized.

Experimental Section

Reagents. Acrylamide (98%, BDH) was purified by recrystallization from acetone (99.5%, Fluka). Polymerization was carried out in deionized water in an oxygen-free nitrogen (BOC) atmosphere. Deionized water, from water purifier Option 4 (Elga, UK), was used for all experiments. Other chemicals, such as acrylonitrile (99%, Aldrich), vinyl acetate (≥99%, Fluka), 2,2′-azobis[2-methyl-(2-hydroxyethyl)propionamide] (98%, Wako Chemicals), ceric ammonium nitrate (98,5%, Fluka), 70% nitric acid (Aldrich), hydroquinone (≥99%, Aldrich), poly(ethylene glycol) (PEG) 2000 (Aldrich), polyacrylamide, 5−6 million Da (PAAm) (Polysciences, Inc.), sodium nitrate

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*Corresponding author. E-mail: a.bismarck@imperial.ac.uk.

Table 1. Polymerization Conditions of Acrylamide Initiated by the 2,2′-Azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]/Ce(IV) Redox System and Polymerization Yield, Molecular Weight, Content of the Incorporated Reducting Agent into the Polymer Backbone, and Number of Weak Links within PAAm

sample ID	[reducing agent] [mmol/L]	[Ce(IV)] [mmol/L]	time [h]	yield [%]	M_w [kDa]	reducing agent content in polymer [mol %]	N_l
1	0.2	0.4	2.5	45	2850	0.17	17
2	0.85	1.7	2.5	21	390	0.58	8
3	0.85	1.7	3.5	25	400	0.56	8
4	2	1	3.0	19	190	1.95	13
5	2	2	3.0	12	140	1.56	8

(≥98%, BDH), sodium azide (≥99%, Fluka), and phosphorus pentoxide (≥98%, Aldrich) were used as received.

For NMR analysis the deuterated solvents d_6-DMSO (99.9%, Merk) and D_2O (99.9%, Aldrich) were used.

Preparation and Purification of PAAm Initiated from 2,2′-Azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] and PEG. 2.5 g (35 mmol) of acrylamide with 0.12 g (1.4 mmol) of vinyl acetate and 0.06 g (0.2 mmol) to 0.6 g (2 mmol) of 2,2′-azobis-[2-methyl-*N*-(2-hydroxyethyl)propionamide] were dissolved in 12 mL of deionized water and charged into a round-bottom flask. The solution was purged with nitrogen for 20 min. Ceric solution was prepared by dissolving ceric ammonium nitrate (1/1 to 1/4 molar ratio with respect to the hydroxyl end groups of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide], Table 1) in 1 mL of 1 N nitric acid. The ceric solution was purged with nitrogen for 1 min, before it was injected into the monomer solution containing 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)-propionamide]. The whole reaction was carried out in the dark under nitrogen at 26 °C from 2 to 3.5 h. The synthesized product was recovered by precipitation in methanol, which was followed by filtration and multiple washing with methanol in order to remove most of the nonreacted initiator, monomers, and oligomers. Finally, the precipitate was dried to the constant weight over P_2O_5 in a desiccator under reduced pressure. The yield of the reaction Y was determined gravimetrically:

$$Y\,[\%] = \frac{W_p}{W_m + W_i} \times 100 \qquad (1)$$

W_p is the weight of the precipitated product, and W_m and W_i are the weights of the monomers and the initiator used, respectively.

Based on ^{1}H NMR spectra, the 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] content in the polymer backbone was calculated using following equation:

$$\text{reducing agent content} = \frac{I_{1.06}}{6I_{1.56} + I_{1.06}} \times 100\ [\text{mol}\ \%] \qquad (2)$$

where $I_{1.06}$ is integrated peak area of the CH_3 protons of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] at 1.06 ppm and $I_{1.56}$ is integrated peak area of the CH_2 of polyacrylamide at 1.56 ppm. The calculated content of the reducing agent was used to determine number of weak links per PAAm chain (N_l):

$$N_l = \frac{M_w \times \text{reducing agent content}}{100 \times M_{Ra}} \qquad (3)$$

where M_w is the weight-average molecular weight of PAAm containing azo functionalities and M_{Ra} is the molecular weight of the reducing agent 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)-propionamide].

Before conducting further experiments, the polymer was purified further by dialysis in deionized water. For the dialysis a dialysis tube with a molecular weight cut off of 3500 Da (Fisher Scientific) was used.

As a control, polyacrylamide was synthesized using poly(ethylene glycol)/Ce(IV) as redox couple and used for drag reduction test and degradation experiments. Poly(ethylene glycol) was chosen as a nondegradable reducing agent which is also well-known to form a redox system with Ce(IV).[21−23] The same polymerization procedure as outlined above was followed in order to produce nondegradable PAAm at the same conditions as PAAm containing azo groups in the backbone. 0.1 g (0.05 mmol) of poly(ethylene glycol) was used with the same amount of monomers as for the polymerization of acrylamide initiated using 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]. Ceric solution (0.055 g (0.1 mmol) of Ce(IV) in 1 mL of 1 N nitric acid) was added to the reaction vessel after purging the monomer solution containing the reducing agent for 20 min with nitrogen. The whole reaction was carried out in the dark under nitrogen at 35 °C for 2.5 h. The synthesized product was recovered and purified the same way as PAAm initiated using 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide].

Synthesis of Polyacrylamide−Polyacrylonitrile Block Copolymers Using PAAm Containing Azo Functionalities as Macroinitiator. 0.04 g of purified azo group containing PAAm was dissolved in 20 mL of water together with 0.08 g (1.5 mmol) of acrylonitrile. The solution was purged with nitrogen for 20 min and placed in an oven at 86 °C for 15 h to initiate the polymerization. Acrylonitrile was selected because it is water-soluble while polyacrylonitrile precipitates from water solution, which allows observing whether the polymerization was successful or not without using any analytical technique.

In order to determine the number of chain scissions per molecule during the polymerization of acrylonitrile, a solution of PAAm containing azo functionalities was heated at 86 °C for 15 h with 200 ppm of hydroquinone as a radical scavenger. The number of chain scission (N_s) in the polymer backbone can be calculated using following equation[24]

$$N_s = \frac{M_{wbd}}{M_{wad}} - 1 \qquad (4)$$

where M_{wbd} and M_{wad} are weight-average molecular weight of the polymer before and after degradation.

Thermolysis of PAAm Containing Thermosensitive Azo Groups in the Backbone. Thermolysis of PAAm containing azo groups was carried out at a temperature of 86 °C. The choice of the temperature was based on the decomposition temperature of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]. A water solution with a polymer concentration of 2 mg/mL was prepared, and 200 ppm of hydroquinone was added in order to scavenge any radicals created. The percentage degradation of the polyacrylamide was calculated using the following equation

$$\text{degradation}\ [\%] = \frac{M_{pt_0} - M_{pt_x}}{M_{pt_0}} \times 100 \qquad (5)$$

where M_{pt_0} is the peak molecular weight of the polymer before degradation and M_{pt_x} is the peak molecular weight of the polymer after heating it at 86 °C for a certain time. M_p was determined using triple detection GPC.

Characterization of the Drag Reducing Ability of PAAm Containing Azo Functionalities in the Backbone. Polymer samples for the drag reduction measurements were prepared by dissolving a predetermined amount of PAAm in deionized water. In order to obtain good polymer dissolution, samples were shaken at 200 oscillations/min on a shaker tray overnight. Prior to the measurements, the polymer solutions were filtered using a syringe filter with a pore size of 0.45 μm. A sample volume of 17 mL was always used for all drag reduction measurements. The drag reduction efficiency, the percentage drag reduction (%DR), was calculated using the following equation[25,26]

$$\mathrm{DR}\ (\%) = \left(100 - \frac{\eta_{\mathrm{N}}^{\mathrm{solution}}}{\eta_{\mathrm{N}}^{\mathrm{solvent}}} \times 100\right)_{n_{\mathrm{N}} = \mathrm{constant}} \qquad (6)$$

where $\eta_{\mathrm{N}}^{\mathrm{solution/solvent}}$ is the normalized viscosity of the solvent and solution, respectively, and are defined as follows:

$$\eta_{\mathrm{N}}^{\mathrm{solution}} = \eta_{\mathrm{Taylor\ area}}^{\mathrm{solution}} - \eta_{\mathrm{Taylor\ onset}}^{\mathrm{solution}} \qquad (7)$$

$$\eta_{\mathrm{N}}^{\mathrm{solvent}} = \eta_{\mathrm{Taylor\ area}}^{\mathrm{solvent}} - \eta_{\mathrm{Taylor\ onset}}^{\mathrm{solvent}} \qquad (8)$$

$$n_{\mathrm{N}} = n_{\mathrm{Taylor\ area}} - n_{\mathrm{Taylor\ onset}} \qquad (9)$$

where $\eta_{\mathrm{Taylor\ area}}^{\mathrm{solution/solvent}}$ and $\eta_{\mathrm{Taylor\ onset}}^{\mathrm{solution/solvent}}$ are the apparent viscosity in the Taylor area and at the Taylor onset, respectively, and n_{N} is the normalized rotor speed.

Characterization of PAAm Containing Azo Functionalities in the Backbone. ^{1}H NMR spectra of the synthesized polymers and their initiators were recorded on a two-channel DRX-400 spectrometer (Bruker, Germany) using d_6-DMSO and D_2O as solvent. Chemical shifts are expressed in parts per million (ppm, δ). Tetramethylsilane (TMS) was used as a generally accepted internal standard.

Thermal behavior of the PAAm initiated from 2,2′-azobis-[2-methyl-*N*-(2-hydroxyethyl)propionamide] was examined using differential scanning calorimetery (DSC Q2000, TA Instruments). The differential scanning calorimeter was calibrated using indium and zinc standards to cover whole temperature range. Samples were weighted into aluminum Tzero pan with a hermetic Tzero lid and characterized in the temperature range of 25−220 °C in a helium atmosphere.

The molecular weight and polydispersity index (PDI) of the synthesized polymers were determined by gel permeation chromatography (GPC) PL-GPC 50 (Polymer Laboratories, UK) with integrated triple detection system, including refractive index (PL-RI), viscometer (PL-BV 400RT), and light scattering (PL-LS) detectors using two TSK-GEL columns (TOSOH, Japan). A 0.1 N $NaNO_3$ containing 200 ppm of NaN_3 water solution at 25 °C was used as a mobile phase. A flow rate of 0.7 mL/min was used. Samples were filtered (0.25 μm) before analysis. Poly(ethylene glycol) standards (Polymer Laboratories, UK) were used for calibration. The data were analyzed using PL Cirrus GPC software (version 3.0) (Polymer Laboratories, UK).

Drag reduction measurements of commercial polyacrylamide (Polysciences) and polyacrylamide containing azo functionalities in the backbone were carried out using a universal dynamic rheometer Physica UDS 200 (Paar Physica, Inc., Germany) equipped with a double-gap Coquette geometry. The aspect ratio $\Gamma = (H/\delta^*)$ was 222, where δ^* is the gap between the rotor and stator $\delta^* = 0.5$ mm. For all drag reduction measurements 17 mL samples were used. The temperature was fixed to 25.0 ± 0.5 °C using a water circulatory thermostat.

Results and Discussion

Synthesis of PAAm Initiated Using a Redox System. Polyacrylamide with azo functionalities in the backbone was synthesized via redox polymerization where 2,2′-azobis-[2-methyl-*N*-(2-hydroxyethyl)propionamide]/Ce(IV) was used as a redox couple. The expected polymerization mechanism is shown in Figure 1.

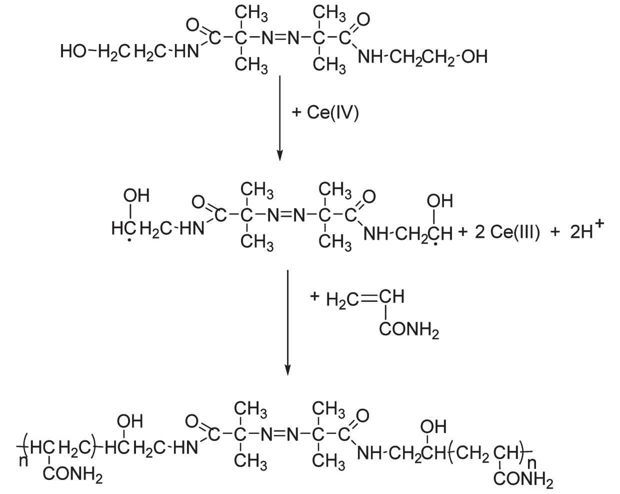

Figure 1. Mechanism of the acrylamide polymerization initiated from 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide].

The polymerization conditions and yield of the polymerization are tabulated in Table 1. The effect of ceric concentration on the yield of the redox-initiated polymerization has been widely studied and is in agreement with our obtained results.[27,28] For most of the experiments the 2,2′-azobis-[2-methyl-*N*-(2-hydroxyethyl)propionamide]/Ce(IV) molar ratio was kept constant in order to initiate polymerization from both ends of the reducing agent. However, it can be noticed that for lower concentrations of Ce(IV) higher yields are obtained. For this reason, when a higher concentration of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] was used for the polymerization, the ratio of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]/Ce(IV) was reduced.

The ^{1}H NMR spectra of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide], commercial polyacrylamide, and polyacrylamide initiated by redox initiation using the Ce(IV)/2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] redox pair were recorded in D_2O and are shown in Figure 2. Protons characteristic for polyacrylamide and 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] were identified and assigned (Figure 3). In the spectrum of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (Figure 2a) chemical shifts for protons from the methylene groups (CH_2) marked as C and B can be distinguished in the 3.52−3.57 and 3.30−3.35 ppm ranges, respectively. The strong singlet from the protons of the methyl groups A appears at 1.24 ppm. In the spectrum of the commercial polyacrylamide (Figure 2b) peaks in the ranges of 1.2−1.8 and 2.0−2.4 ppm correspond to the protons of the methylene (D) and methine (E) groups of PAAm. All protons for PAAm and 2,2′-azobis[2-methyl-(2-hydroxyl)proponamide] could be identified and assigned in the ^{1}H NMR spectrum of PAAm initiated from 2,2′-azobis-[2-methyl-*N*-(2-hydroxyethyl)propionamide] (Figure 2c), confirming the successful incorporation of azo groups into PAAm.

The ^{1}H NMR spectrum of control polyacrylamide initiated from poly(ethylene glycol) was recorded and can be found in Figure 1 of the Supporting Information. The ^{1}H NMR spectrum of the product showed characteristic peaks of PAAm and a very low intensity peak characteristic for the main chain methylene units within poly(ethylene glycol) at 3.6 ppm.

DSC Analysis of PAAm with Azo Functionalities in the Backbone. In order to further confirm the presence of azo functionalities in the polyacrylamide backbone, differential

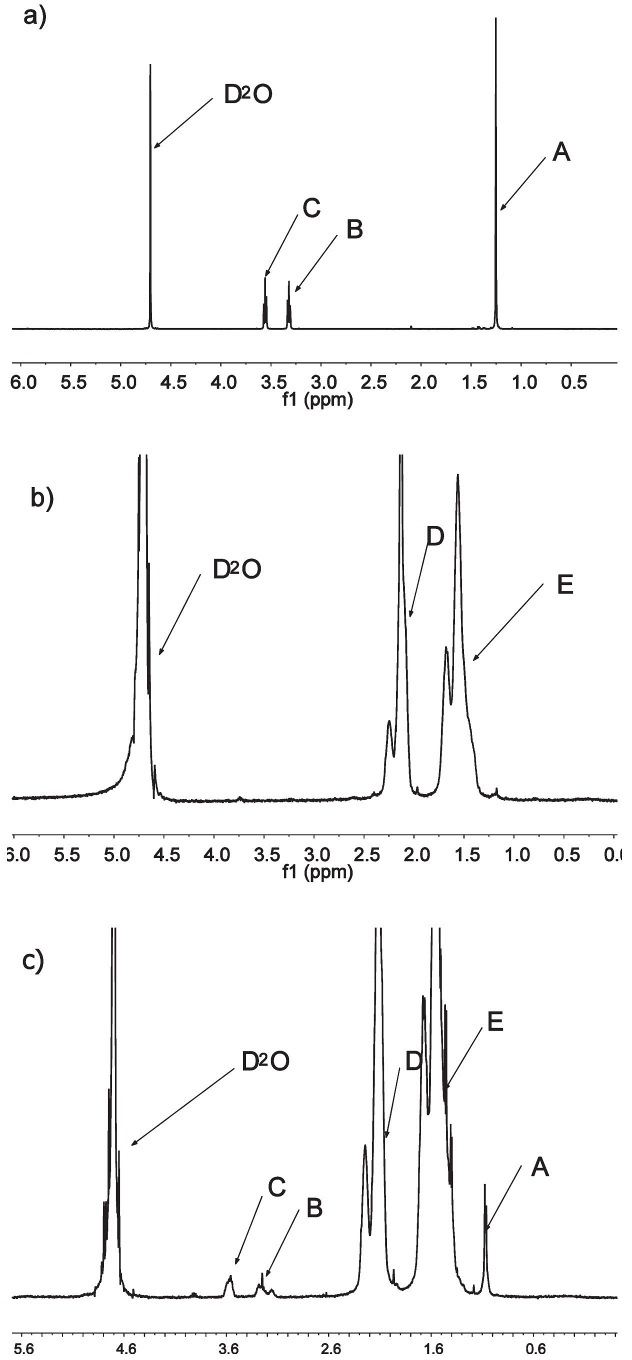

Figure 2. ^{1}H NMR spectra of (a) 2,2′-azobis[2-methyl-(2-hydroxyl)-propionamide], (b) commercial polyacrylamide, M_w 5−6 million Da, and (c) polyacrylamide initiated using the 2,2′-azobis[2-methyl-(2-hydroxyl)propionamide]/Ce(IV) redox pair (sample 3) (solvent: D_2O).

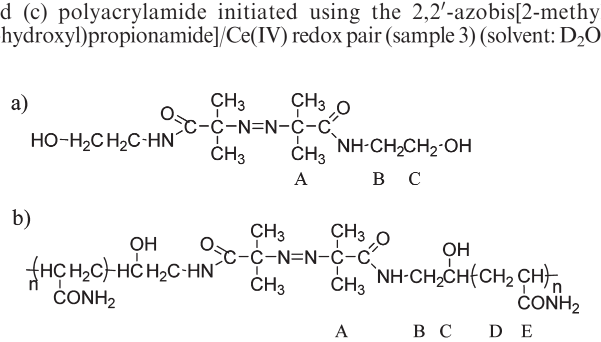

Figure 3. Chemical Structure of (a) 2,2′-azobis[2-methyl-(2-hydroxyl)-propionamide] and (b) polyacrylamide initiated using the 2,2′-azobis-[2-methyl-(2-hydroxyl)propionamide]/Ce(IV) redox pair.

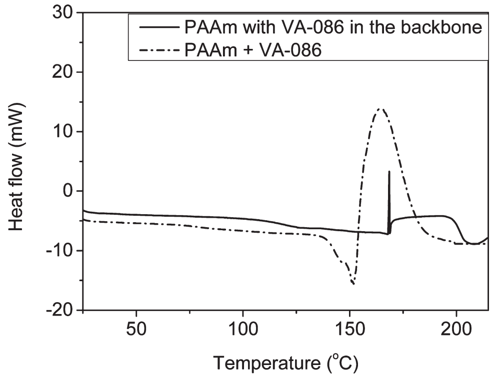

Figure 4. DSC thermogram: first heating curve of 9 mg of commercial PAAm, M_w 5−6 million Da, mixed with 0.6 mg of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] and PAAm containing incorporated azo groups (sample 4).

scanning calorimetry has been used. The thermal behavior of commercial polyacrylamide and commercial polyacrylamide mixed with the original azo-initiator 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] were compared with polyacrylamide containing degradable 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] links (Figure 4). An amount of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] equivalent to that covalently incorporated into PAAm was mixed with pure PAAm and used for the DSC analysis. In both cases an apparent exothermic peak due to decomposition of the azo groups was observed; however, the shape and the maxima of these peaks are different. The maximum degradation temperature for PAAm containing azo functionalities in the backbone was observed at 192 °C, whereas for PAAm mixed with 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] at 164 °C. The shift and the shape of the exothermic peak, in the thermogram of PAAm containing azo functionalities in the backbone, are caused by the different chemical environment due to the covalent incorporation of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] into PAAm.

Initiation of Polymerization of Acrylonitrile from PAAm Containing Incorporated Azo Functionalities. Acrylonitrile was polymerized using PAAm containing azo- functionalities in the backbone (sample 3) as an initiator. The mechanism of the polymerization of acrylonitrile initiated from polyacrylamide containing azo group is illustrated in Figure 5.

Because of insolubility of polyacrylonitrile (PAN) in water, the synthesized acrylonitrile−acrylamide copolymer precipitated from the solution in the form of very fine white powder. For comparison, acrylonitrile in the presence of the azoinitiator 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] and acrylonitrile without any initiator was subjected to the same polymerization conditions. Polyacrylonitrile produced by normal free radical polymerization initiated using 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] precipitated as a yellow powder, while pure acrylonitrile did not polymerize within the time of the experiment (Figure 2 in the Supporting Information).

The number of chain scissions of the backbone of PAAm caused by the degradation of temperature labile azo functionalities was also calculated using eq 4. Based on the initial molecular weight of the PAAm with azo functionalities in the backbone (400 kDa) and that of the degraded polymer after heating for 15 h at 85 °C in the presence of hydroquinone (189 kDa), the number of chain scissions was calculated and was found to be on average 1.1. According to the ^{1}H NMR spectrum of sample 3, however, on average eight thermally

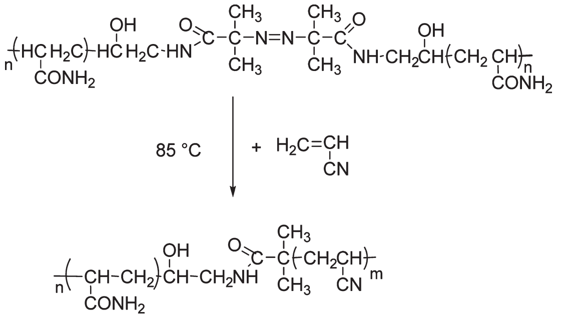

Figure 5. Mechanism of the polymerization of acrylonitrile initiated from the azo group containing PAAm.

cleavable azo groups are available per single molecular chain. On the basis of this fact and possibility of both unimolecular and bimolecular termination, a mixture of BA−, BAB−, and BABAB−poly(acrylamide-*co*-acrylonitrile) block copolymers is very likely.

The solubility of poly(acrylamide-*co*-acrylonitrile) block copolymer was tested in order to find a solvent for NMR analysis. Poly(acrylamide-*block*-acrylonitrile) was soluble in dimethyl sulfoxide (DMSO), which is also a solvent for pure polyacrylonitrile, but it did not dissolve in any solvents for pure polyacrylamide, such as water, formamide, or ethylene glycol.

The ^{1}H NMR spectra of poly(acrlonitrile) and poly(acrylamide-*block*-acrylonitrile) synthesized using polyacrylamide containing thermosensitive azo groups in the backbone are shown in Figure 6. The ^{1}H NMR spectrum of the copolymer shows peaks for methylene (D) and methine (C) protons characteristic for PAAm at 1.39 and 2.09 ppm, respectively. The methylene protons of polyacrylonitrile (B) overlapped with methine protons of polyacrylamide (C) at 2.09 ppm, whereas the characteristic methine protons of polyacrylonitrile (A) can be clearly seen as a quite broad peak at 3.15 ppm.

The presence of peaks of both PAAm and PAN in spectrum c in Figure 6 proves that poly(acrylamide-*block*-acrylonitrile) was indeed synthesized; thus, it again confirms that polyacrylamide used for copolymerization contained covalently incorporated azo groups in its backbone.

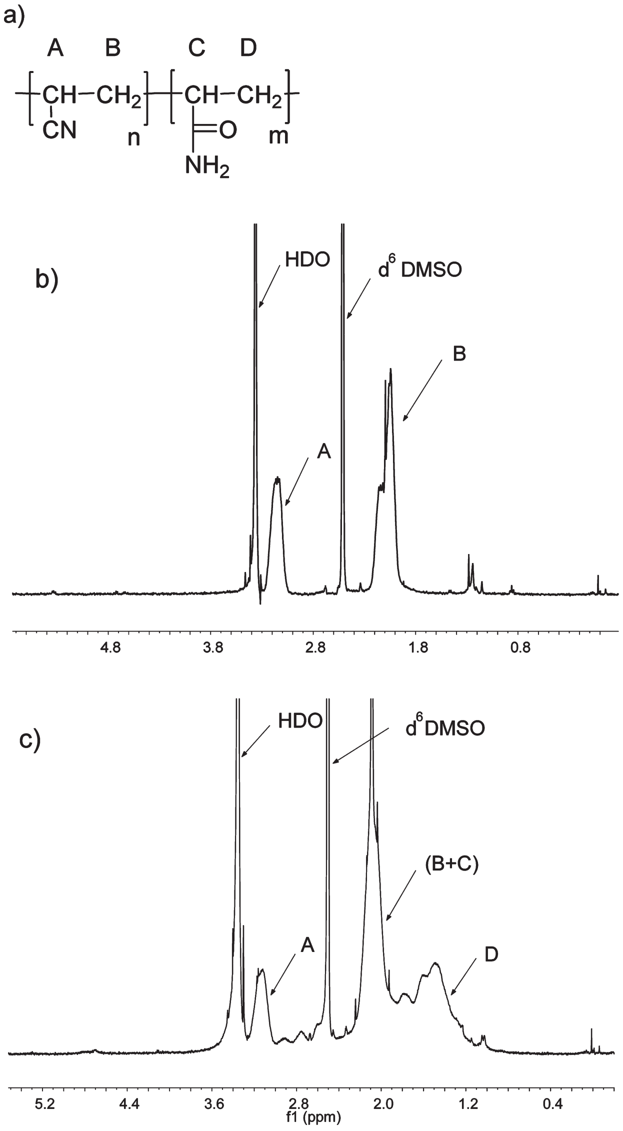

Figure 6. (a) Chemical structure of poly(acrylamide-*block*-acrylonitrile), (b) ^{1}H NMR spectrum of polyacrylonitrile, and (c) ^{1}H NMR spectrum of poly(acrylamide-*block*-acrylonitrile) (solvent: d_6-DMSO).

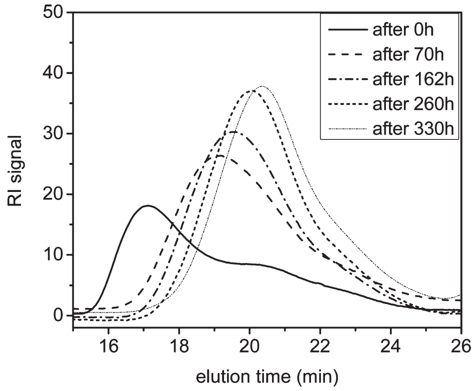

Figure 7. Response of the GPC RI detector for PAAm containing azo groups (sample 1) before and after being subjected to 86 °C for various times.

Degradation Behavior of PAAm Containing Azo Groups in the Backbone. Degradation of the PAAm containing azo functionalities in the backbone was studied using GPC. Figure 7 shows exemplarily the response of the RI detector of the triple detection GPC system for PAAm containing temperature-sensitive azo groups before and after subjecting it to a temperature of 86 °C. The higher response of the detector and an increase of the elution time were due to the cleavage of the temperature sensitive azo groups in the polymer backbone. Because 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] contains hydroxyl groups on both ends, the polymerization of acrylamide was most likely initiated from both sides of the reducing agent, allowing for incorporation of at least one azo group into the polymer. The number of azo groups in the backbone and hence the molecular weight of the polymer after degradation depend on the termination step of the polymerization. In case of bimolecular termination one expects at least two azo groups in the polymer backbone, whereas in case of disproportionation or unimolecular termination only one azo group would be incorporated. Peak molecular weight M_p and weight-average molecular weight M_w calculated from the response of all detectors of the GPC system of PAAm containing azo functionalities during the degradation process are tabulated in Table 2. The M_p of the polymer before degradation was around 4400 kDa. In the first 70 h M_p decreased to 600 kDa, which was about 14% of the original polymer molecular weight. Over next 270 h the molecular weight of the PAAm

Table 2. M_p, M_w, and PDI As Obtained from GPC Measurements of PAAm Containing Azo Functionalities in the Backbone and Percentage M_p Reduction after Degradation

degradation time [h]	M_p [kDa]	M_w [kDa]	PDI	percentage degradation [%]
0	4430	2850	3.1	0
70	600	650	2.7	86
162	480	500	2.5	89
260	270	300	2.1	93
330	260	250	1.5	94

with azo groups in the backbone decreased further, but at a lower rate, and stabilized when M_p of the polymer reached 260 kDa (about 6% of the original molecular weight of the polymer).

The systematic decrease of the polydispersity of the degraded polymer implies random scission of the polymer backbone. From the result of the degradation it can be assumed that on average the spacing between weak links for the sample 1 was about 250 kDa. On the basis of weight-average molecular weight of the polymer before degradation and after, it was calculated that the number of chain scissions in the polymer backbone was around 11. Hence, it was assumed that at least 11 weak links were successfully built in to the PAAm backbone. However, the amount of 2,2′-azobis-[2-methyl-*N*-(2-hydroxyethyl)propionamide], calculated for the same polymer, from the ^{1}H NMR spectrum (Table 1) implies that actually 17 labile azo-functionalities were built into the polymer backbone. This discrepancy can be caused either by an error due to very small intensity of the peaks from 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] or the recombination of some radicals, which would affect the molecular weight of the polymer after degradation. We also attempted to characterize the degradation products by ^{1}H NMR; the results, which can be found in Figures 3 and 4 of the Supporting Information, broadly confirm our conclusions stated above. The degradation behavior of PAAm containing azo groups in the backbone was confirmed by repeating the synthesis of the tested polymer (sample 1) and subjecting it to the same degradation conditions. As expected, the same degradation behavior was observed. Additionally, these results were compared with degradation behavior of PAAm initiated from PEG. After subjecting this polymer to 86 °C, it was found that the molecular weight changed slightly from M_p 3200 kDa to 2700 kDa. According to Kulicke et al.[29,30] this, however, could be related to conformational changes of the polymer chains rather than cleavage of the polymer backbone.

Ability of PAAm Containing Azo Groups in Their Backbone To Reduce Turbulent Drag. The influence of the concentration of PAAm containing azo groups in the backbone on the drag reduction of water solutions was studied and compared to the results obtained for PAAm initiated from PEG. For both polymers the percentage of drag reduction increased with increasing concentration, leveling off at 300 ppm; both polymers follow the same trend (Figure 8). Frictional drag was reduced by about 30% even at polymer concentrations as low as 25 ppm. A further increase in the concentration of the PAAm containing azo groups enabled to reduce the drag up to 56%, while PAAm with a molecular weight of 4.6 million Da reduces the drag by 55%.

The ability of PAAm containing azo groups to reduce frictional drag should diminish or disappear after exposure to high temperature. Studied PAAm solutions were subjected to a temperature of 86 °C. After 170 h at 86 °C, the polymer solutions were tested for the second time for its ability to reduce drag using exactly the same procedure as before. As expected for such a massive decrease of the molecular weight of the polymer, the percent of the drag reduction decreased as well from 56% DR to a level of 1% DR. The control experiment, using PAAm synthesized by initiation from the PEG/Ce(IV) pair, was carried out in order to test the DR behavior of PAAm without containing weak, temperature-sensitive links in the backbone once subjected to the same conditions (86 °C for 170 h). A negligible decrease in drag reducing abilities of PAAm without azo groups in the backbone was observed; the drag reduction ability for 500 ppm concentration dropped from 53% ± 1.6% to 50% ± 0.8% after exposure to 86 °C.

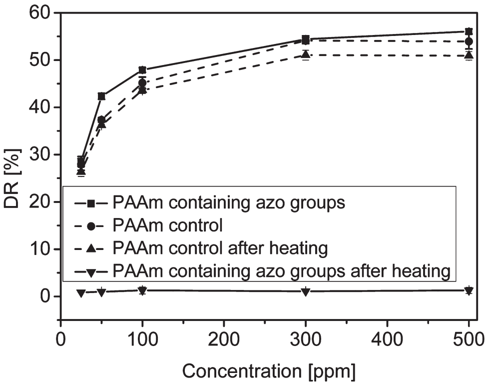

Figure 8. Percentage drag reduction as a function of polymer concentration for both PAAm initiated from PEO and PAAm containing azo groups in the polymer backbone (sample 1).

Conclusions

Azo functional groups were successfully incorporated into the polyacrylamide backbone by redox polymerization using the water-soluble azo-initiator 2,2′-azobis[2-methyl-(2-hydroxyethyl)-propionamide] as a reducing agent and Ce(IV) as oxidizing ion. ^{1}H NMR spectra of the synthesized polymer confirm the presence of azo functionalities in the polymer backbone. This result was supported by DSC where an exothermic peak from the degradation of azo groups can be observed in the PAAm initiated from 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]. The synthesized PAAm containing azo group in the backbone was used as an initiator for the free radical polymerization of acrylonitrile, which resulted in the synthesis of PAAm-*block*-PAN. This also proved that active azo groups were incorporated into the PAAm backbone. PAAm with temperature-sensitive azo groups in the backbone can degrade when subjected to a temperature above the degradation temperature of azo groups, in this case 86 °C. A significant decrease of the molecular weight of PAAm containing temperature-sensitive azo groups in the backbone from 4430 to 260 kDa and very little change in the molecular weight of "normal" PAAm were observed, after subjecting both polymers to 86 °C. Drag reduction tests carried out for the PAAm with and without built in azo groups proved that this polymer synthesized by redox polymerization is a useful drag reducing agent. We have also demonstrated that after exposure to 86 °C the polymer loses its drag reducing ability, whereas PAAm without azo groups retains almost the same drag reducing properties. This experiment proves once again the effectiveness of redox polymerization in incorporating degradable groups into polymer backbone.

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Supporting Information Available: Figures 1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

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