Cationic Polymer Grafted Starch from Nonsymmetrically Substituted Macroinitiators

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ABSTRACT: The aim of this work was the synthesis of starch macroinitiators for cationic polymer grafted starches that: (i) are free of cationic homopolymer, and (ii) display a high degree of conversion of the cationic monomer. We show that this can be achieved by a free-radical polymerization reaction using the cationic monomer *N*-methacryloyloxyethyl-*N*,*N*-dimethyl-*N*-benzylammonium chloride (MADAM-BQ) and a new starch-based macroazoinitiator. For this purpose, the acid chloride of 4-*tert*-butylazo-4-cyanovaleric acid was synthesized and bound covalently to starch (predominantly in the C6 position) to form a nonsymmetrically substituted macroinitiator that was used to polymerize MADAM-BQ in aqueous media. Essentially no MADAM-BQ homopolymer was formed. The initiator decomposes thermally to starch radicals of high reactivity and low-molar mass radicals that do not initiate polymerization. The reason for the different reactivities of the radicals is presumably due to the nonsymmetric constitution of the starch-bound azo groups. The graft polymerization of MADAM-BQ in aqueous solution performs according to an ideal overall kinetic. The structure of the synthesized starch-*graft*-poly(MADAM-BQ) products is similar to that of block copolymers because of the low radical efficiency of the starch initiators in aqueous solution. Especially, starch substrates with a higher content of azo groups did not lead to graft products with shorter graft distances because the state of solution of these macroinitiators becomes worse and aggregation occurs with an increasing degree of substitution.

1. Introduction

The physical and chemical modification of starch offers many possibilities to adjust its properties to those required in tailor-made products. One attractive method of chemical modification of starch is the grafting of synthetic polymer chains from starch (e. g. starch-*graft*-polystyrene).[1,2] Most of these graftings are radical-initiated reactions.[3−6] Here, the graft polymers are generated by the formation of radicals on the starch backbone from which the polymerization of vinylic monomers is initiated. The formation of the initiating radicals by γ, β, or UV radiation is nonspecific and results in the formation of a significant amount of homopolymer.[7−10] Classical initiating systems for the chemical formation of starch radicals are permanganates in the presence of acids,[11−14] the Fenton agent,[15−17] and peroxodisulfates.[18−20] Large amounts of homopolymers are formed in all of these systems because the primary radicals, which are not bound to starch, also initiate homopolymerization. The unwanted side reactions can be suppressed by generating radicals with the help of Ce(IV)[21−26] or Mn(III),[27−29] but it is difficult to remove these metal ions from the colored products. However, even in this case, the formation of homopolymer cannot be excluded. In particular, the grafting of cationic monomers leads exclusively to homopolymers unless the graft process is not promoted by the use of an uncharged comonomer like acrylamide. This is also evident for grafting cellulose.[30]

A further possibility of initiating the graft polymerization is to bind initiating groups directly to the starch molecule, which can be activated thermally or chemically. For example, a thiocarbamate derivative of starch can be grafted by the addition of H_2O_2[31,32] or iron peroxodisulfate.[33] Peroxy,[34−36] azonium,[37,38] and azo groups are the common thermally cleavable groups; starch derivatives of these groups are typical starch macroinitiators. All these starch macroinitiators show the same disadvantages as the above-named initiating systems, such as the formation of low-molar mass radicals inducing homopolymers.

Azo compounds of starch have been described in the patent literature in which two anhydroglucose units were linked by symmetrically substituted azobis groups.[39−42] An advantage of these starch initiators is that their thermal decomposition exclusively produces macroradicals. A strong disadvantage, however, is that the polymer analogue reaction of such bifunctionalized azo compounds leads generally to cross-linked structures whose accessibility to the graft monomer is hindered. This limits a homogeneous graft polymerization in solution.

The two aims of this work are to avoid the formation of a cationic homopolymer and to graft a cationic vinyl monomer without the need to add noncharged monomers such as acrylamide, which gives grafted copolymer chains.[43] Our idea was that these aims can be achieved with a starch macroinitiator that contains nonsym-

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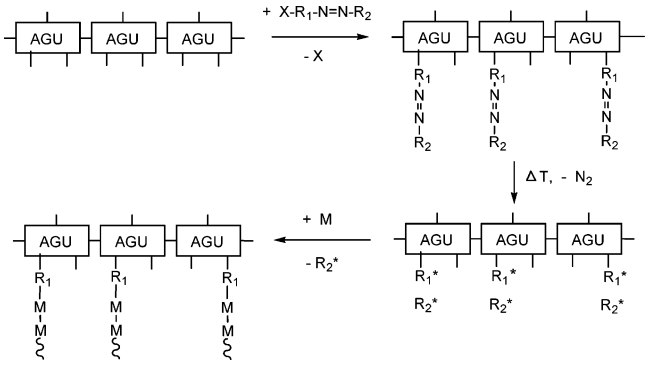

Figure 1. Concept for the synthesis of cationic grafted starch. A starch-based nonsymmetrically substituted macroazoinitiator is formed in a first step whose groups R_1 and R_2 have different symmetries. Its thermal decomposition (second step) produces highly reactive radicals R_1* that are bound to the anhydroglucose units (AGU) of the starch and the low-molar mass radicals R_2* that do not initiate polymerization. The cationic monomer M polymerizes exclusively initiated by R_1* (third step), while the amount of polymerization initiated by R_2* can be neglected (no cationic homopolymer is formed).

metrically substituted azo groups. It should decompose thermally into highly reactive radicals R_1* being bound to the starch and into low-molar mass radicals R_2*, which do not initiate polymerization. There were indications in the literature that R_2* can be a *tert*-butyl radical that unexpectedly does not initiate polymerization of homopolymer.[37] Presuming that no initiating species are formed by transfer reactions, this should give a graft polymer that is essentially free of cationic homopolymer. Our concept is shown schematically in Figure 1. To verify this concept, we synthesized a suitable nonsymmetrically substituted azo compound, **5**, and bound it to starch, which resulted in the starch macroazoinitiator **7** (cf. Figure 2). The polymerization products and the polymerization kinetics were investigated systematically.

2. Materials and Methods

Materials. All chemicals were obtained from Fluka unless otherwise stated. Laevulinic acid (≥97%), *tert*-butylhydrazonium chloride (≥97%), potassium cyanide (≥98%), and 0.01 mol L^{-1} hydrochloric acid prepared by 1:10 dilution of 0.1 N HCl (Merck, standard solution), phosphor pentoxide (Sicapent), sodium hydroxide (98%), nitrogen (Linde, 5.0), chlorine (Linde, 2.8), pentane (≥95%), toluene (≥99.5%), thionyl chloride (≥99.5%), *N,N*-dimethyl-acetamide (Merck, for synthesis ≥99%), triethylamine (≥99.5%), *N*-methacryloyloxyethyl-*N,N*-dimethyl-*N*-benzylammonium chloride (Ato-Chem, 75% aq solution, determined by potentiometry of Cl), 2,3-dimethyl-1-vinylimidazolium chloride (Röhm), hydroquinone (≥99.5%), 4,4′-azobis-4-cyanovaleric acid (WAKO, V-501), 4-*tert*-butylazo-4-cyanovaleric acid, and 4-*tert*-butylazo-4-cyanovaleric starch ester.

Starch. We used a commercially available enzymatic waxy maize starch hydrolysate from Roquette (France). This was chosen for the starch modification in homogeneous aqueous solution because its aqueous solutions are stable for long periods of time, showing a low tendency of retrogradation due to its high content of amylopectin.[44] The broad molar mass distribution of this starch (cf. Figure 3, solid line) with molar masses in the range of 10^3-10^7 g mol^{-1} and a polydispersity of 14.1 was fractionated by ultrafiltration (Minisette Omega, FA. Pall Filtron, cutoff was 10^5 g mol^{-1}) to a starch with a molar mass in the range of 10^5-10^7 g mol^{-1}, $M_w = 660 \times 10^3$ g mol^{-1} and a polydispersity of 1.5 (cf. Figure 3, dotted line).

Synthesis of Nonsymmetrically Substituted Starch Azo Initiators. 4-*tert*-Butylhydrazono-4-cyanovaleric Acid (cf. structure **3** in Figure 2). An amount of 11.6 g (0.1 mol) of laevulinic acid was dissolved in 50 mL of water, and 17.5 g (0.14 mol) of *tert*-butylhydrazonium chloride and 6.5 g (0.1 mol) of potassium cyanide were added. A white precipitate was formed while stirring the solution at room temperature overnight. The precipitation was separated, washed with diluted hydrochloric acid, and dried over phosphor pentoxide. The yield was over 90%. CHN analysis found: C 56.7%, H 8.9%, N 19.6%; calcd: C 56.3%, H 9.0%, N 19.7%. Melting point: 104.5 ± 0.5 °C.

4-*tert*-Butylazo-4-cyanovaleric Acid (cf. structure **4** in Figure 2). An amount of 4.0 g (0.1 mol) of sodium hydroxide

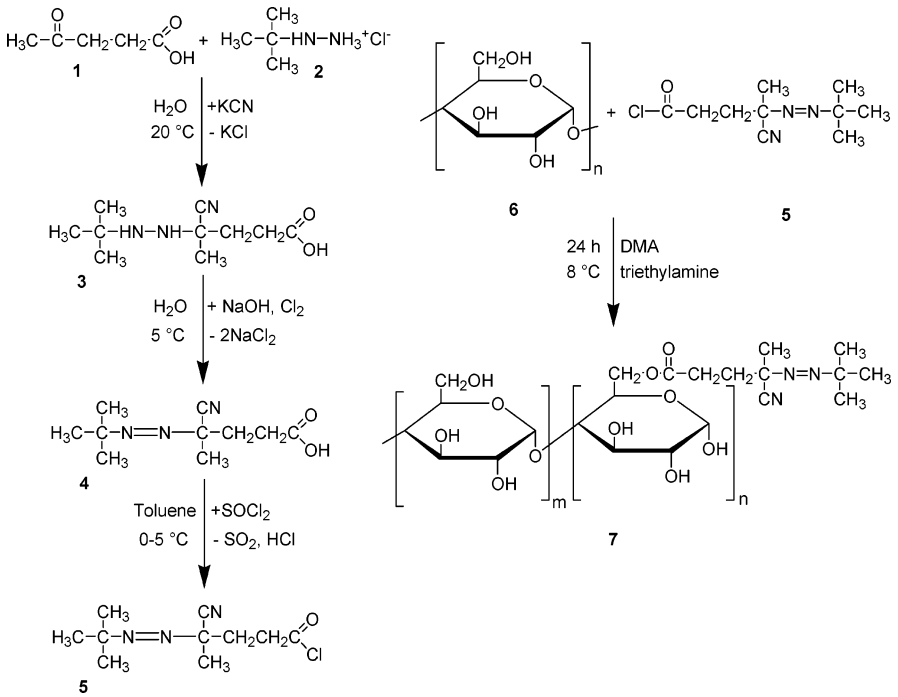

Figure 2. Three-step synthesis of a low-molar mass azo compound **5** suitable for covalent binding to starch (left-hand figure). Synthesis of the nonsymmetrically substituted starch-based macroazoinitiator **7** using the acid chloride **5** and amylopectin **6** (right-hand figure).

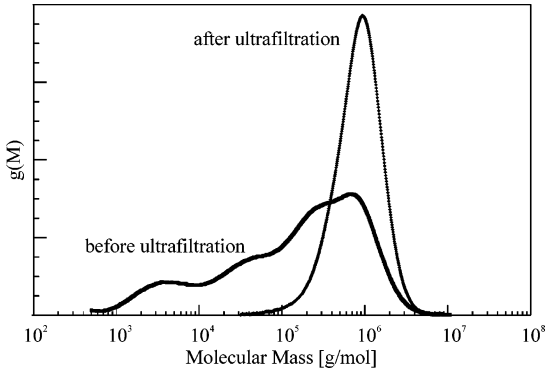

Figure 3. Molar mass distribution of the waxy maize starch hydrolysate in its state as received (solid line) with a polydispersity of 14.1 and after ultrafiltration (dotted line) with a polydispersity of 1.5 ($M_w = 660 \times 10^3$ g mol^{-1}).

was dissolved in 50 mL of water, and 21.3 g (0.1 mol) of **3** was added while stirring. The solution was cooled to 5 °C under nitrogen atmosphere. Then chlorine was introduced until a thick-yellow flocculation was formed while the reaction temperature was kept to between 5 and 10 °C. The product was separated and crystallized in a pentane/toluene solvent mixture (50:10). Analysis of **4**: ^{13}C NMR ($CDCl_3$, δ in ppm): 23.81 (q, 1C); 26.54 (q, 3C); 28.87 (t, 1C); 32.82 (t, 1C); 68.61 (s, 1C); 70.72 (s, 1C); 118.89 (s, 1C); 177.78 (s, 1C). The yield was in the range of 50−70%. CHN analysis found: C 55.8%. H 8.0%, N 18.5%; calcd: C 56.9%, H 8.1%, N 19.9%. FT-IR (KBr, selected bands): 2974 cm^{-1} (ν_{as} CH_3), 2937 cm^{-1} (ν_{as} CH_2), 2237 cm^{-1} (ν CN, weak), 1712 cm^{-1} (ν C=O), 1580 cm^{-1} (ν N=N, weak). Melting point: 82.5 ± 0.5 °C.

4-*tert*-Butylazo-4-cyanovaleric Acid Chloride (cf. structure **5** in Figure 2). An amount of 21.1 g (0.1 mol) of **4** was dissolved in 100 mL of water-free toluene and adjusted to 0−5 °C. Then 9 mL (0.12 mol) of thionyl chloride was added in droplets, and the reaction mixture was stirred at room temperature for 4 h. The obtained product was a yellow-brownish liquid after the distillation of the excess thionyl chloride and solvent. The yield was 80%. It had to be cooled for storage at 4 °C to avoid decomposition. FT-IR (KBr, selected bands): 2977 cm^{-1} (ν_{as} CH_3), 2937 cm^{-1} (ν_{as} CH_2), 2237 cm^{-1} (ν CN, weak), 1798 cm^{-1} (ν C=O), 1580 cm^{-1} (ν N=N, weak).

4-*tert*-Butylazo-4-cyanovaleric Acid Starch Ester (cf. structure **7** in Figure 2, Table 1). An amount of 5.0 g of starch (corresponding to 0.03 mol anhydroglucose units) was dissolved in 100 mL of *N*,*N*-dimethyl-acetamide (DMA) and heated to 170 °C. Then 30 mL of DMA was distilled in a nitrogen stream to remove the water from the starch. The solution was cooled to room temperature and transferred to a 150 mL double-wall reactor. A mixture of 3.6 g (0.036 mol) of triethylamine and 10 mL of DMA was added. The solution was cooled to 8 °C, and 1.2 g (0.0052 mol) of 4-*tert*-butylazo-4-cyanovaleric acid chloride, which was dissolved in 10 mL DMA, was added slowly, and the reaction mixture was stirred for 24 h at 8 °C. The starch derivative was precipitated in 1 L of methanol, dissolved in water, and dialyzed for 4 days at 4 °C (membrane: regenerated cellulose, cutoff was 6×10^3 g mol^{-1}) and then freeze-dried. The degree of substitution of the resulting starch macroinitiator (compound 7 in Figure 2) was 0.05, as revealed by ^{1}H NMR signal intensity ratios of starch (4.2−6.0 ppm) to methyl group protons (1.0−1.8 ppm) (cf. Figure 4). The degree of substitution varied in the range of 0.04−0.72 by adjusting the reaction conditions (cf. Table 1). The starch initiator with the low degree of substitution (DS = 0.05, $\mathbf{I}_5$ of Table 1) was characterized by SEC-MALLS ($M_w = 637 \times 10^3$ g mol^{-1} and $M_n = 504 \times 10^3$ g mol^{-1}), while the higher-substituted initiators showed adsorption effects on the SEC columns. CHN analysis of I_{70} (DS = 0.72) calcd: C 52.5%, H 6.9%, H 9.5%; found C 51.5%, H 7.5%,N 8,7%. Water content (Karl Fischer titration): 2.87% (w/w).

Homopolymerization of *N*-Methacryloyloxyethyl-*N*,*N*-dimethyl-*N*-benzylammonium Chloride (MADAM-BQ).

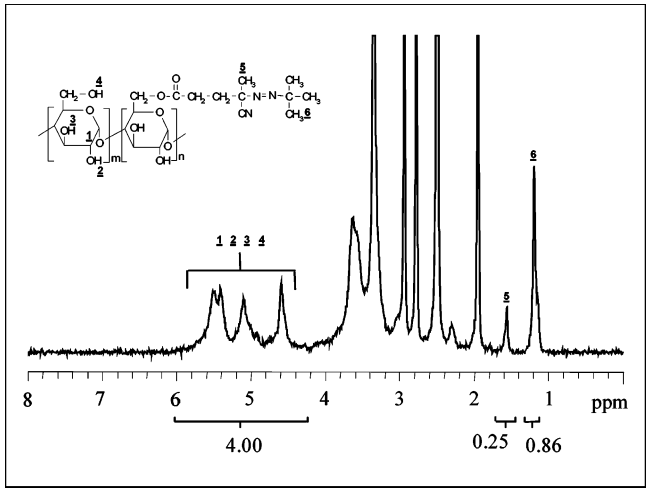

Figure 4. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of the starch macroazoinitiator $\mathbf{I}_{10}$ for the determination of the degree of substitution (DS) which is here 0.10. The DS was determined from the ^{1}H NMR signal intensity ratios of the starch (4.2−6.0 ppm) to the protons of the tertiary butyl group (1.0−1.8 ppm).

An amount of 3.78 g (0.01 mol) of 75% aq solution of MADAM-BQ, 0.1057 g (0.5 mmol) of 4-*tert*-butylazo-4-cyanovaleric acid (or 0.1402 g (0.5 mmol) of 4,4′-azo-bis-4-cyanovaleric acid) were weighed in a 100 mL measuring flask, solved in deionized water, and filled up to the calibration mark. The solution (20 mL) was filled into a reaction ampule (Schlenk tube). The ampule was frozen with an ethanol/dry ice mixture, degassed with a vacuum pump, and defrosted inside a water bath of room temperature. After repeating this process four times, the clear solution was overlaid with argon. The thermal initiation of the polymerization solution was performed by heating the reaction ampule in a water bath at 70 °C. After stirring for 180 min, 0.010 g of hydroquinone (500 ppm) was added and the solution was diluted with cold deionized water, filled into a dialysis tube (regenerated cellulose, cutoff was 6×10^3 g mol^{-1}), and dialyzed against water for 5 days to remove unreacted cationic monomer (control of conductivity). After freeze-drying a white, cottonlike solid was obtained.

^{1}H NMR (400 MHz, D_2O): δ (in ppm) = 0.5−1.4 (C−CH_3), 2.7−3.4 (N−CH_3), 3.5−4.2 (N−CH_2–), 7.2−8.0 (−C_6H_5).

The proton signal intensities do not correspond completely to the structure of poly(MADAM-BQ). This may due to the different state of solution/solvation and mobility of the polymer protons, especially the signals of protons being attached to hydrophobic backbone are partially broadened and suppressed. This phenomenon is known and described for other ionic methacrylate structures by Laschewsky and Zerbe.[45]

Graft Polymerization of (MADAM-BQ) *N*-Methacryloxyethyl-*N*,*N*-dimethyl-*N*-benzylammonium Chloride (MADAM-BQ) (cf. Figure 7, Example no. 2 of Table 3). A 4-*tert*-butylazo-4-cyanovaleric acid starch ester of DS = 0.05 ($\mathbf{I}_5$) (0.648 g, 4 mmol) and 0.756 g of a 75% aq solution of MADAM-BQ (2 mmol) were solved in 20 mL of deionized water. The solution was filled into a reaction ampule (Schlenk tube), frozen with an ethanol/dry ice mixture, degassed via a vacuum pump, and defrosted inside a water bath to room temperature. After repeating this process four times, the clear solution was overlaid with argon. The thermal initiation of the polymerization solution was performed by heating the reaction ampule in a water bath at 70 °C. After stirring for 180 min, 0.010 g of hydroquinone (500 ppm) was added and the solution was diluted with cold deionized water, filled into a dialysis tube (regenerated cellulose, cutoff was 6×10^3 g mol^{-1}), and dialyzed against water for several days to remove unreacted cationic monomer (control of conductivity). After freeze-drying a white, cottonlike solid was obtained, showing an intrinsic viscosity of 35 cm^3 g^{-1} (0.2 mol L^{-1} aq solution of Na_2SO_4 + 1% (w/w) acetic acid). The synthetic mass ratio of the obtained

product was quantified by densiometry (37%, see section on graft polymerization kinetics) and also by UV−vis measurements at a wavelength of 268 nm (43%), resulting in an average amount of 40% (w/w). The synthetic molar ratio of the graft product was additionally determined with ^{1}H NMR. It was calculated to 26.5% mol/mol by means of comparing the signal intensities of the acetal starch protons and the aromatic protons of MADAM-BQ. This value is equal to a synthetic mass fraction (w_U) of 39% (w_U = (0.265 g mol^{-1} × 283.4 g mol^{-1})/(0.265 g mol^{-1} × 283.4 g mol^{-1}) + (0.735 × 162.1)).

^{1}H NMR (400 MHz, D_2O): δ (in ppm) = 0.5−1.4 (C−CH3), 2.7−3.3 (N−CH3), 3.4−4.2 (protons of the starch ring at C2−C6), 5.2−5.6 (acetal proton at C1), 7.2−8.0 (−C6H5).

To get different synthetic products, the initiator and monomer concentrations were varied as shown in the Tables 3 and 4. In addition, we also used a corresponding starch initiator ($\mathbf{I}_{10}$) of DS = 0.10 to graft MADAM-BQ.

Graft Process Characterization. Because of the absence of homopolymer, the **graft efficiency** of the polymerization experiments was in each case 100%. The **conversion** U was calculated by the use of equation $U = (1/w_{100\%} - 1)/(1/w_U - 1)$, where w_U represents the synthetic mass ratio of the dialyzed reaction product determined by UV−vis measurements (268 nm), and $w_{100\%}$ is the corresponding value for 100% conversion. It must be taken into account that nongrafted starch remains after polymerization, and the purified product is a mixture of the starch graft copolymer and free starch. Its mass fraction is $w_{starch} = (1 - w_U/w_{P-MADAM-BQ})$.

Molecular Characteristics of Starch-*graft*-poly(MADAM-BQ). $w_{P-MADAM-BQ}$ represents the synthetic add-on of the pure graft copolymer, which is the ratio of the mass of grafted poly(MADAM-BQ) and the total mass of the starch backbone and its grafts. SEC was used to determine $w_{P-MADAM-BQ}$ by the coupling of RI and UV detection. The ratio of the simultaneously measured UV and RI signals ($c(\lambda = 268$ nm) and c(RI), respectively) was calculated. It was found that the ratio c(268 nm)/c(RI) is approximately constant for small elution volumes, where graft copolymer fractions elutes exclusively and decreases at higher volumes where graft copolymer fractions and free starch elutes at the same time (not shown).

The $w_{P-MADAM-BQ}$ is equal to the c(268 nm)/c(RI) ratio in the constant region, presuming that the correct refractive index increment is used. Refractive index increments were calculated from the polymer composition according to Bushuk and Benoit,[46] which is $dn/dc = (w_{P-MADAM-BQ} \times (dn/dc)_{P-MADAM-BQ}) + ((1 - w_{P-MADAM-BQ}) \times (dn/dc)_{starch})$ for the grafted starch. An interferometric refractometer was used for the (dn/dc) determination of poly(MADAM-BQ) and starch. The increment $(dn/dc)_{P-MADAM-BQ}$ was 0.182 mL g^{-1}, and $(dn/dc)_{starch}$ is 0.147 mL g^{-1} at a wavelength of 633 nm in an aq solution of 0.2 mol/L Na_2SO_4 with 1% (w/w) acetic acid. The determination of $w_{P-MADAM-BQ}$ or dn/dc was carried out iteratively.

The **graft length** P_l represents the average number of monomer units per grafted poly(MADAM-BQ). P_l was determined by SEC-MALLS after the complete hydrolysis of the starch (5% (w/w) of the dialyzed graft product in 0.1 mol L^{-1} HCl at 80 °C for 4 h) using P_l = *number-average molar mass of the cationic graft chains* $M_{n,P-MADAM-BQ}$/*molar mass of the monomer unit* $M_{MADAM-BQ}$. The ester structure of the poly(MADAM-BQ) is not affected by the applied conditions of hydrolysis. The **graft frequency** ν_{graft} reflects the average distance between two graft chains quantified by the average number of anhydroglucose units (AGU) per grafted poly(MADAM-BQ) chain. $M_{n,P-MADAM-BQ}$ and $w_{P-MADAM-BQ}$ were used to calculate the graft frequency via $\nu_{graft} = ((1 - w_{P-MADAM-BQ}) \times M_{n,P-MADAM-BQ})/(w_{MADAM-BQ} \times M_{AGU})$. It was assumed that no recombination of growing side chains occur during the graft polymerization. This is well-known for the (graft) polymerization of methacrylics with bulky substituents such as MADAM-BQ. The average number of grafted chains per starch molecule, N_{graft}, was calculated from ν_{graft} and $M_{n,\,starch}$, the number-average molar mass of the starch backbone $N_{graft} = M_{n,starch}/(\upsilon_{graft} \times M_{AGU})$.

Measurements. ^{1}H NMR (400 MHz) and ^{13}C NMR (400 MHz) spectroscopy (solvent DMSO-d_6, $CDCl_3$, inverse gated decoupling, without NOE decoupling) was carried out with a UNITY 400 (Varian, Germany). The UV−vis spectroscopy was performed with an UVIKON 939 photometer (Kontron, UK) using a temperature-controlled quartz cuvette (d = 10 mm). Solvents were *N*,*N*-dimethyl-acetamide and water, respectively. Analytical ultracentrifugation was performed with a XL-I (Beckman, Germany) at 20 ± 0.1 °C and a rotation rate of 4 × 10^4 min^{-1}. The sedimentation of the macromolecules was detected by interference measurements using water containing 0.2 mol L^{-1} Na_2SO_4 and 1% (w/w) acetic acid as solvent and different sample concentration of 1−5 g L^{-1}. The calculation of the relative molar mass M_r followed the method of Linow and Phillip using[47]

$$M_r = 2.406 \times 10^{25}\ \text{mol}^{-1}\left(\frac{s_0\eta_0}{1 - \bar{\upsilon}_{St}\,\rho_0}\right)^{3/2}([\eta]\,k_{SB})^{1/2}$$

where s_0 is the Svedberg constant in 10^{-13} s, η_0 is the viscosity of the solvent in g cm^{-1}, ρ_0 is the density of the solvent in g/cm^3, $[\eta]$ is the intrinsic viscosity in cm^3/g, k_{SB} is the Schulz−Blaschke constant, and $\bar{\upsilon}_{St}$ is the partial specific volume of the starch substrate in cm^3/g.

The weight- and number-average molar masses (M_w and M_n, respectively) of the polymers were determined by size exclusion chromatography with multiangle laser light scattering detection (SEC-MALLS: degaser SCM 400, isocratic pump P1000 and auto sampler AS 1000 from Spectra Physics, Egelsbach, Germany; TSK columns (polyglycidyl(meth)acrylate gel) PWH-Guard + 6000 (7.5 × 300 mm, 17 μm) 5 × 10^5 to 5 × 10^7 g/mol, + 5000 (7.5 × 300 mm, 17 μm) 5 × 10^4 to 7 × 10^6 g/mol, + 3000 (7.5 × 300 mm, 10 μm) 10^2 to 6 × 10^4 g/mol by Tosohaas, Stuttgart, Germany; Hema Bio column (hydroxyethyl methacrylate gel) (8.0 × 300 mm, 10 μ) 10^2 to 2 × 10^4 g/mol Polymer Standards Service GmbH, Mainz, Germany; laser light scattering detector Dawn DSP, 632.8 nm, cell type K5; 18 detectors from 22.5° up to 147° from Wyatt, Woldert, Germany; OPTILAB DSP interferometric refractometer, 632.8 nm, cell type P10 from Wyatt, Woldert, Germany; UV−vis detector UV 2000 by Spectra Physics, Egelsbach, Germany; software Astra 4.7 from Wyatt, Woldert, Germany). The accuracy of the determined molar masses is about ±10%. MADAM-BQ was detected at a wavelength of 268 nm. A mixture of 0.2 mol L^{-1} Na_2SO_4 and 1% (w/w) acetic acid in deionized water was used as eluent. The flow rate was 0.65 mL min^{-1} at 20 °C using a sample loop of 100 μL and sample concentrations of 1−4 g L^{-1}.

Viscosity measurements were performed using an Ubbelohde viscometer with automatic dilution (Viscoboy 2 from Lauda) at 30 ± 0.1 °C. An aqueous mixture of Na_2SO_4 (0.2 mol L^{-1}) and 1% (w/w) acetic acid with a pH of 3−4 was used as solvent. The thickness of the capillary used was 0.58 mm.

The kinetic measurements were performed with a density meter (DMA 60/602, Paar, Austria). It is based on a vibrating mass whose resonance frequency is influenced by the density of the polymer solution (oscillating U-tube principle).[48] The correctness as given for the density of degassed water was ±0.5·10^{-6} g/cm^3 and the temperature was held constant at ±0.01 °C.

3. Results and Discussion

3.1. Starch Macroinitiator. The synthesis of **5** was carried out in three steps, as shown in Figure 2. First, the reaction of *tert*-butylhydrazonium chloride (**2**) with laevulinic acid (**1**) in the presence of cyanide results in 4-*tert*-butylhydrazono-4-cyanovaleric acid (**3**). Second, **3** was oxidized by chlorine to the azo compound **4**. Third, compound **4** was reacted with thionyl chloride to the low-molar mass azo initiator **5**, which is a brownish liquid. The coupling of **5** to starch (**6**) to produce the starch macroinitiator (**7**) was carried out analogous to a tosylating procedure for cellulose in *N*,*N*-dimethylacetamide in the presence of triethylamine.[49,50] A low

Table 1. Reaction Parameters for the Synthesis of the Starch Macroinitiators (I_5 to I_{70}), Their Degree of Substitution (DS), Intrinsic Viscosities ([η]), and Huggins Constants (k_H)

number	4-*tert*-butylazo-4-cyanovaleric acid chloride [mol]	triethylamine [mol]	starch [mol]	DS	k_H	$[\eta]^b$ [cm^3 g^{-1}]
starch				0	0.6	26
I_5	0.010	0.100	0.030	0.05	1.4	23
I_7	0.015	0.090	0.035	0.07	4.1	18
I_{10}	0.020	0.080	0.040	0.10	6.0	17
I_{13}	0.025	0.070	0.045	0.13	11.9	14
I_{60}	0.030	0.075	0.035	0.60	*a*	*a*
I_{70}	0.040	0.070	0.030	0.72	*a*	*a*

[a] Turbid aqueous solutions (viscosities were not measured). [b] Determined at 25 °C in 0.2 M Na_2SO_4 with 1% (w/w) acetic acid.

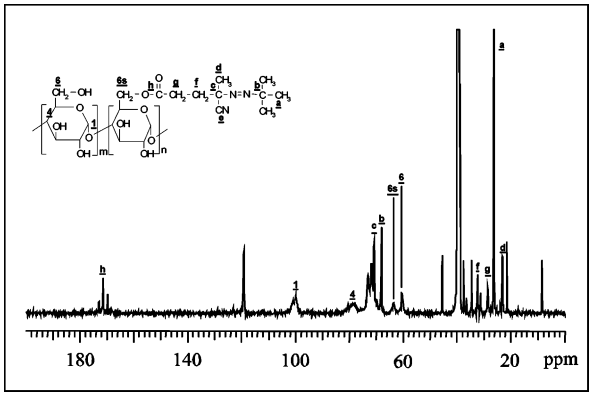

Figure 5. ^{13}C NMR spectrum (400 MHz, DMSO-d_6) of the starch macroinitiator $\mathbf{I}_{10}$ for the determination of the preferred position of the substitution. The signals of the substituted carbon C6 (6s, 61.5 ppm) and the nonsubstituted C6 (6, 60.5 ppm) are clearly separated.

reaction temperature of 8 °C should give predominantly a selective C6 substitution of the anhydroglucose units and should also avoid the thermal decomposition of the azo groups. No gelation was observed during the reaction, indicating the absence of intermolecular reactions of starch molecules. The questions arose how the degree of substitution depends on the composition of the reaction mixture and whether the substitution of **5** at the starch in C6 position is the most likely. The properties of the synthesized macroinitiators are summarized in Table 1.

Degree of Substitution (DS). The degree of substitution of the starch macroinitiator was determined using ^{1}H NMR spectroscopy (400 MHz, DMSO-d_6). An example is given in Figure 4. The signals between 4.2 and 6.0 ppm can be assigned to the three protons of the hydroxyl groups and the proton of the semiacetal of the starch. The characteristic signal of the tertiary butyl group occurs at 1.2 ppm and the signal of the methyl group at 1.6 ppm. We determined the degree of substitution from the ratio of the signal area of the anhydroglucose unit to that of the substituent, which is 0.10 in the example shown in Figure 4. The degree of substitution of the starch macroinitiators was in the range of 0.05−0.72 (cf. Table 1).

Position of the Azo Groups. ^{13}C NMR measurements of the starch macroinitiators were carried out to determine the position of the substitution. An example is shown in Figure 5. The signal of the carbons can be distinguished clearly whether the carbon in the C6 position is substituted (6s, 61.5 ppm) or not (6, 60.5 ppm). The substitution at the C2 and C3 positions cannot be quantified because of the strong superposition of other signals in the region of 70−76 ppm. Nevertheless, we can conclude that the binding of **5** was predominantly to carbon C6 from the high intensity of the substituted C6 signal and its comparison to the whole DS as measured by ^{1}H NMR spectroscopy. This finding is similar to the result of Katsura et al.,[51] who revealed a preferred functionalization of C6 for the etherification of amylopectin with diethylaminoethyl chloride and 3-chloro-2-hydroxypropyltrimethylammonium chloride using aqueous alkaline conditions.

Properties in Solution. The functionalization of the starch with the azo compound **5** corresponds to a hydrophobization of the starch, and we expected that the solution properties of the starch and the starch macroinitiator differ significantly. Therefore, we measured the viscosity of their aqueous salt solutions (0.2 mol L^{-1} Na_2SO_4 and 1% (w/w) acetic acid) and determined their intrinsic viscosities, [η], as well as their Huggins constants, k_H, (see Table 1). The k_H, which is 0.6 for the pristine starch ($M_w = 660 \times 10^3$ g mol^{-1}), increases strongly with an increasing degree of substitution (1.4 for $\mathbf{I}_5$ to 11.9 for $\mathbf{I}_{13}$). The initiators with the highest degree of substitution ($\mathbf{I}_{60}$ and $\mathbf{I}_{70}$) were not measured because they formed turbid aqueous solutions. Typical coiled polymers with linear chains in a good solvent have a k_H in the range of 0.3−0.6, while higher values of 0.6−0.8 are known for branched structures such as amylopectin.[52] We assume that the reason for the increasing k_H values of the macroinitiators result from less water solubility with an increase of DS. Probably, an increasing DS leads to more compact structures of the initiators compared to those of the pristine starch. This assumption is consistent with the values of the intrinsic viscosities that decrease from 26 cm^3 g^{-1} (starch, DS = 0) to 14 cm^3 g^{-1} ($\mathbf{I}_{13}$, DS = 0.13). Indications of the formation of aggregates were observed by analytical ultracentrifugation, e.g., for the macroinitiator I_{10}; its molar mass M_r was calculated as 470 × 10^3 g mol^{-1} for the molecular soluble part and 1500 × 10^3 g mol^{-1} for the aggregates.

Decomposition of the Initiator. The thermal decomposition of the initiators in aqueous solution was measured at 85 °C by UV−vis detection at 356 nm, where **4** has its absorption maximum. The decomposition constants, k_d, were then determined from the initial slope of the logarithmic absorption curves (i.e., ln *Absorbance(t)* = $-k_d t$, not shown). The k_d values are (9.5 ± 0.2) 10^{-6} s^{-1} (4-*t*-butylazo-4-cyanovaleric acid), (31.7 ± 14.4) 10^{-6} s^{-1} ($\mathbf{I}_5$), (93.3 ± 18.9) 10^{-6} s^{-1} ($\mathbf{I}_{10}$), and (180.5 ± 37.5) 10^{-6} s^{-1} ($\mathbf{I}_{13}$) (for thermal decomposition curves see also Figure S1 in Supporting Information). It is surprising that the macroinitiators decompose faster than their low-molar mass analogue and faster with increasing DS. The reason for this is not clear. Possibly, the decomposition of the azo groups along the starch backbone is a cooperative process. We observed

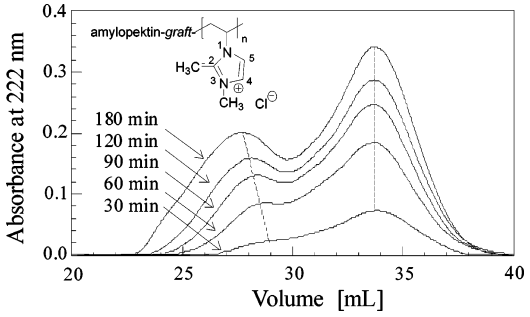

Figure 6. SEC traces of products of poly(2,3-dimethyl-1-vinylimidazolium chloride) (MV) grafted from the starch macroinitiator $\mathbf{I}_5$ at different reaction times. The straight lines indicate the peak maxima positions at different reaction times. Reaction conditions were monomer concentration [MV] = 0.2 mol L^{-1}, [I_5] = 0.2 mol L^{-1}, T = 90 °C, termination with 500 ppm hydroquinone, UV detection at 222 nm.

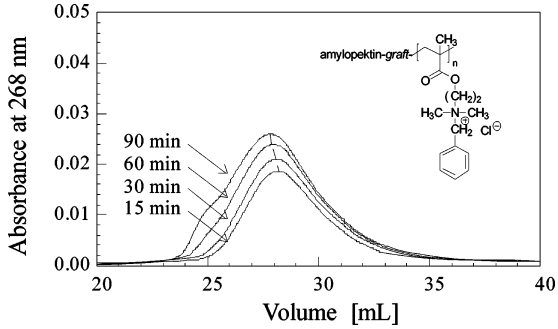

Figure 7. SEC traces of products of poly(MADAM-BQ) grafted from the starch macroinitiator $\mathbf{I}_5$ at different reaction times. The straight line shows the peak maxima positions. Reaction conditions were [M] = 0.1 mol L^{-1}, [I_5] = 0.1 mol L^{-1}, T = 90 °C, termination with 500 ppm hydroquinone, UV detection at 268 nm.

the formation of gels for longer decomposition times, which is promoted for higher DS.

3.2. Graft Polymerization of Different Cationic Vinyl Monomers. To estimate the initiating properties of the starch initiators as well as the structure of the resulting polymers, we investigated the polymerization of the two cationic monomers 2,3-dimethyl-1-vinylimidazolium chloride (MV) and 2-*N*-methacryloyloxyethyl-*N*,*N*-dimethyl-*N*-benzylammonium chloride (MADAM-BQ) when initiated with $\mathbf{I}_5$.

Figure 6 shows the SEC traces of the products from a polymerization mixture that contained equimolar amounts of $\mathbf{I}_5$ and MV (equimolar with respect to monomer units). The reaction was carried out at 90 °C and stopped at different times with hydroquinone so that the products could be investigated by SEC. The cationic polymer structures of MV were detected specifically at a wavelength of 222 nm. The presence of bimodal distributions can be seen clearly in the SEC traces (see Figure 6). This indicates the formation of the aspired graft polymers as well as cationic homopolymers. The graft polymers are expected to be found at lower elution volumes than that of homopolymers due to their higher molar masses. This was verified by the nearly constant position of the peak maxima of the homopolymer, which is especially expected for low conversions of a free-radical polymerization (neglecting the consumption of monomer). By contrast, one has to expect a shift of the peak maxima to lower elution volumes for the graft polymer as a result of its increasing molecular mass with reaction time. The high amount of homopolymer formed is probably a result of a radical transfer to the monomer, which has a reactive carbon at position 5.

A comparable experiment was carried out again with MADAM-BQ using analogue procedures of polymerization and SEC analysis. The molar monomer concentration was reduced to 50% to produce similar molar masses, only, because of the significantly higher reactivity of MADAM-BQ compared to MV. It can be seen in Figure 7 that, in this case, only a single peak, which was detected at 268 nm, is present in the SEC traces. The peak maximum shifts to lower elution volumes with increasing reaction times, as expected for increasing molecular masses with time due to successful grafting. Consequently, we can exclude the formation of significant amounts of MADAM-BQ homopolymer on the basis of the SEC traces. But it must be mentioned that some amount of initiator may not have started a polymerization and remained as nongrafted starch. With that, our working hypothesis is proven. Cationic starch grafted polymers are available without the formation of homopolymers, provided that the macroinitiated polymerization will be carried out with vinyl monomers of very low transfer activity.

Further information about the specific properties of starch in solution, poly(MADAM-BQ), and the corresponding graft copolymer are also available from SEC-MALLS measurements. Figure 11 describes the increase of the radius of gyration with increasing molecular mass. The slope increases from starch (0.26) to the graft copolymer (0.41) to poly(MADAM-BQ) (0.63 for the grafted chains), which was obtained after hydrolysis (5% (w/w) of the dialyzed graft product in 0.1 mol L^{-1} HCl at 80 °C for 4 h) of the graft copolymers. This indicates a more compact structure of the starch backbone and a remarkable swelling after the graft reaction. The ^{1}H NMR-spectra in D_2O of poly(MADAM-BQ) and starch-*graft*-poly(MADAM-BQ) are shown, for comparison, in Figure S2 of Supporting Information.

3.3. Different Reactivities of the Radicals. It contradicts the a priori expectation that R_1* (*iso*-butyronitrile radical bound to the starch, Figure 2) should be less reactive in initiating the polymerization than R_2* (*tert*-butyl radical). The latter displays a strong nucleophilic character and is known to react fast with substituted alkenes.[53] However, it was shown experimentally by Simionescu et al.[54] that this expected behavior is, for example, not observed for a poly(dimethylsiloxane) macroazoinitiator containing terminal 4-*tert*-butylazo-4-methylcyanobutyryl groups. In their system, the macroinitiated polymerization of vinyl monomers yields exclusively block copolymers. As demonstrated by SEC and extraction experiments, no homopolymer is observed, which has to be produced if the *tert*-butyl radicals were able to initiate the polymerization. Simionescu suggested that the reason for the absence of homopolymer formation is the rapid recombination of *tert*-butyl radicals due to their high reactivity. This explanation is not satisfactory, though their experimental results are convincing. Therefore, we hoped also to observe a similar behavior for the starch macroazoinitiator **7**, i.e., the *tert*-butyl radical does not initiate polymerization of cationic homopolymers.

To examine whether the *tert*-butyl radical initiates polymerization when it is a fragment of a nonsymmetrically substituted initiator, we compare the polymerization of MADAM-BQ when: (i) initiated with 4-*tert*-

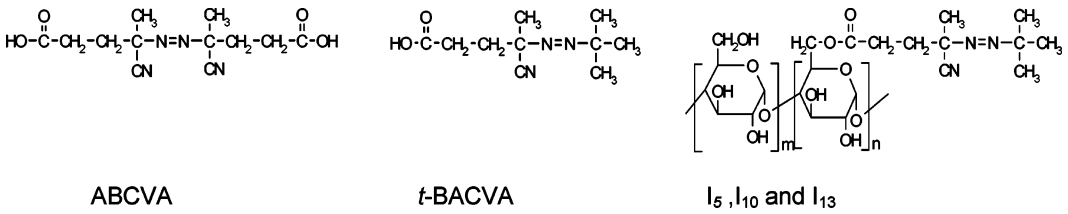

Figure 8. Chemical structures of low-molar mass initiators 4,4′-azobis-4-cyanovaleric acid (ABCVA) and 4-*tert*-butylazo-4-cyanovaleric acid (*t*-BACVA) and their corresponding starch macroinitiators (I_5, I_{10}, and I_{13}) for the investigation of the radical efficiency of the *tert*-butyl radical and the cyanovaleric acid radical.

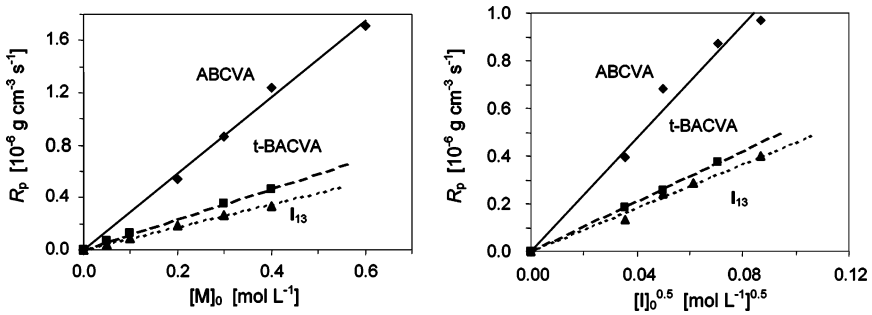

Figure 9. Rate of polymerization, R_p, for MADAM-BQ when initiated with ABCVA (solid lines), *t*-BACVA (dashed lines), and starch macroinitiator $\mathbf{I}_{13}$ (dotted lines). It shows an ideal kinetic in aqueous solution, i.e., R_p (determined by density measurements) increases linearly with the initial monomer concentration $[M]_0$ and the square root of initiator concentration $[I]_0^{0.5}$. Reaction conditions were $[M]_0 = 0.05-0.60$ mol L^{-1}, $[I]_0 = 5.00 \times 10^{-3}$ mol L^{-1} for the variation of $[M]_0$ and $[M]_0 = 0.30$ mol L^{-1}, $[I]_0 = 1.25-7.50 \times 10^{-3}$ mol L^{-1} for the variation of $[I]_0$, $T = 70$ °C.

butylazo-4-cyanovaleric acid (*t*-BACVA), the low-molar mass analogue to **7**, and (ii) 4,4′-azobis-4-cyanovaleric acid (ABCVA), the corresponding symmetric azo compound (cf. Figure 8).

We chose MADAM-BQ because it is known as a monomer showing an ideal kinetic polymerization in aqueous solution when initiated, for example, with a commercial initiator 2,2′-azobis(2-amidinepropane) hydrochloride.[55] The rate of the free-radical polymerization of MADAM-BQ in that study follows $R_p = K[I]_{t=0}^{0.5}[M]_{t=0}$ with $K = k_p(f \times k_d \times k_t^{-1})^{0.5}$. The K is the overall rate constant in (L mol^{-1}s^{-2})$^{0.5}$, k_p is the rate constant of the chain propagation in L mol^{-1} s^{-1}, k_t is the rate constant of the chain termination in L mol^{-1} s^{-1}, k_d is the rate constant of the initiator decomposition in s^{-1}, and f is the radical efficiency. The $[I]_{t=0}$ and $[M]_{t=0}$, respectively, are the concentrations of initiator and monomer when the polymerization starts ($t = 0$). We rearrange the expression for K to $K^2/(f \times k_d) = k_p^2 \times k_t^{-1}$, which is constant. Then we determined K and k_d experimentally. Figure 9 shows the rates of polymerization of ABCVA, *t*-BACVA, and $\mathbf{I}_{13}$ (i.e., **I** with DS = 0.13) as a function of the initial monomer concentration and initiator concentration, respectively. The temperature was always 70 °C. It can be seen that the rate of polymerization increases linearly with $[M]_{t=0}$ and $[I]_{t=0}^{0.5}$. The results show clearly that the R_p of ABCVA is much larger than those of *t*-BACVA and $\mathbf{I}_{13}$. Further, the R_p of the low-molar mass initiator *t*-BACVA is close to that of the macromolecular one, $\mathbf{I}_{13}$. We determined the overall rate constants by linear interpolation (slopes in Figure 9) to be $K = (6.67 \pm 0.44) \times 10^{-3}$ (L$^{0.5}$ mol$^{-0.5}$) s^{-1} for *t*-BACVA, and K = $(16.58 \pm 0.41) \times 10^{-3}$ (L$^{0.5}$ mol$^{-0.5}$) s^{-1} for ABCVA.

The k_d values are $(9.5 \pm 0.2) \times 10^{-6}$ s^{-1} for *t*-BACVA and $(31.1 \pm 0.6) \times 10^{-6}$ s^{-1} for ABCVA. The ratio of the radical efficiencies was calculated as $f_{t-\mathrm{BACVS}}/f_{\mathrm{ABCVA}} = (K_{t-\mathrm{BACVA}}^2/k_{\mathrm{d},t-\mathrm{BACVA}})/(K_{\mathrm{ABCVA}}^2/k_{\mathrm{d,ABCVA}}) = 0.53$. We can presume that the radical efficiency of the initiator is given as sum of the radical efficiencies of its two fragments, i.e., of the *tert*-butyl radical ($f_{t-\mathrm{butyl}}$) and the cyanovaleric acid radical (f_{CVA}). Then we get the ratio $f_{t-\mathrm{BACVA}}/f_{\mathrm{ABCVA}} = (f_{\mathrm{CVA}} + f_{t-\mathrm{butyl}})/(2f_{\mathrm{CVA}})$, which can only be close to the calculated value of 0.53 if $f_{t-\mathrm{butyl}}$ is close to zero. Accordingly, we proved that the *tert*-butyl radical does not initiate the polymerization of MADAM-BQ in aqueous solution. This is in agreement with the finding of Simionescu et al.[37] and our SEC experiments (cf. Figure 7). Nevertheless, the reason why the *tert*-butyl radical does not initiate the polymerization of MADAM-BQ is not clear yet. Probably, the highly reactive *tert*-butyl radicals recombine. However, this hypothesis seems impossible if the local concentration is low. Alternatively, the highly reactive *tert*-butyl radical could abstract hydrogen atoms from starch. This would lead also to a grafting from the starch that cannot be distinguished analytically from the expected graft positions.

3.4. Graft Polymerization Kinetics of MADAM-BQ. Determination of the Rate of Polymerization. Conversion and rate of the graft polymerization were estimated by measuring the change of the density of the reaction mixture in situ using a very precise density meter based on the oscillating U-tube principle to monitor the polymerization of MADAM-BQ (partial specific volumes of monomer and polymer differ). Details of the use of the oscillating U-tube capillary for the investigation of polymerization kinetics are given elsewhere.[56,57]

In principle, this method is applicable by a foregoing calibration of density versus conversion of a given polymerizing system. We will show the possibility of making precise measurements without such calibration. The density of the solution, ρ, is given by

$$\rho = \rho_0 + \sum_i (1 - v_i\rho_0)c_i$$

where ρ_0 is the density of the solvent (water) in g cm^{-3}, c_i is the mass concentration of the analyte i in g cm^{-3},

and v_i is the partial specific volume of the analyte i in $cm^3\ g^{-1}$. Here, we have the three analytes MADAM-BQ, poly(MADAM-BQ), and starch. It must be mentioned that whether polymeric MADAM-BQ is bound to starch or not cannot be distinguished by the density measurement. This has to be proved by SEC. The sum of the concentrations of MADAM-BQ and poly(MADAM-BQ) (in monomer units) is always equal to the starting monomer concentration, $c_{M,0}$. The density of the polymer reaction mixture as a function of time, $\rho(c_{p,t})$, is given by

$$\rho(c_{p,t}) = \rho_0 + (1 - v_{st}\rho_0)c_{st} + (1 - v_M\rho_0)c_{M,0} + (v_M - v_P)\rho_0 c_{P,t}$$

where the v represents the specific volumes of starch (v_{st}), MADAM-BQ (v_M), and poly(MADAM-BQ) (v_P). After summarizing the terms that stay constant during the polymerization and after introducing the conversion, $U = (c_{M,0} - c_{M,t})/c_{M,0} = c_{P,t}/c_{M,0}$, we get

$$\rho(U) = A + Bc_{M,0}U \quad \text{with}$$

$$A = \rho_0 + (1 - v_{st}\rho_0)c_{st} + (1 - v_M\rho_0)c_{M,0} \quad \text{and } B = (v_M - v_P)\rho_0$$

The density can be rewritten as a function of the molar monomer concentration, $[M]$, of the time t:

$$\rho([M]) = A' - BM_M[M](10^{-3}\ \text{L cm}^{-3}) \quad \text{with}$$

$$A' = \rho_0 + (1 - v_{st}\rho_0)c_{st} + (1 - v_p\rho_0)c_{M,0} \quad \text{and } B = (v_M - v_P)\rho_0$$

M_M is the molar mass of MADAM-BQ (283.4 g mol^{-1}). Differentiation with respect to time results in

$$\frac{d\rho([M])}{dt} = -BM_M(10^{-3}\ \text{L cm}^{-3})\frac{d[M]}{dt}$$

which is equivalent to the overall reaction rate of the polymerization, R_p. Assuming ideal kinetics for a free-radical polymerization, the initial reaction rate, R_{p0}, is given by

$$R_{p0} = -\left(\frac{d[M]_{t=0}}{dt}\right)_{t=0}$$

$$R_{p0} = K[I]_{t=0}^{0.5}[M]_{t=0} \quad \text{with } K = k_p\left(\frac{fk_d}{k_t}\right)^{0.5}$$

where K is the overall rate constant in $(\text{L mol}^{-1}\ \text{s}^{-2})^{0.5}$, k_p is the rate constant of the chain propagation in L $mol^{-1}\ s^{-1}$, k_t is the rate constant of the chain termination in L $mol^{-1}\ s^{-1}$, k_d is the rate constant of the initiator decomposition in s^{-1}, and f is the radical efficiency of the initiator. The $[I]_{t=0}$ and $[M]_{t=0}$, respectively, are the concentrations of initiator and monomer when the polymerization starts. Combining both equations results in

$$\left(\frac{d\rho([M]_{t=0})}{dt}\right)_{t=0} = BM_M(10^{-3}\ \text{L cm}^{-3})K[I]_{t=0}^{0.5}[M]_{t=0}$$

which describes ideal radical polymerization kinetics. Further, $R_p = K[I]_{t=0}^{0.5}[M]_{t=0}$. It was shown earlier that the polymerization of MADAM-BQ in solution using 2,2′-azobis-(2-amidinopropane) dihydrochloride as an initiator displays this ideal behavior.[58] Therefore, it was reasonable to assume that the polymerization kinetics of MADAM-BQ would show a similar behavior when started with the starch macroinitiators.

Table 2. Partial Specific Volumes of MADAM-BQ Polymer (v_p) and Monomer (v_m), the Density of Water, and the Constant B at Temperatures of 20 and 70 °C

temperature [°C]	v_p [$cm^3\ g^{-1}$]	v_m [$cm^3\ g^{-1}$]	ρ_0 [g cm^{-3}][a]	$B = (v_m - v_p)\ \rho_0$
20	0.7850	0.8547	0.99820	0.06957
70	0.8071	0.8954	0.97784	0.08634

[a] The values given in the literature are 0.99820 g cm^{-3} for 20 °C and 0.97776 g cm^{-3} for 70 °C[61]

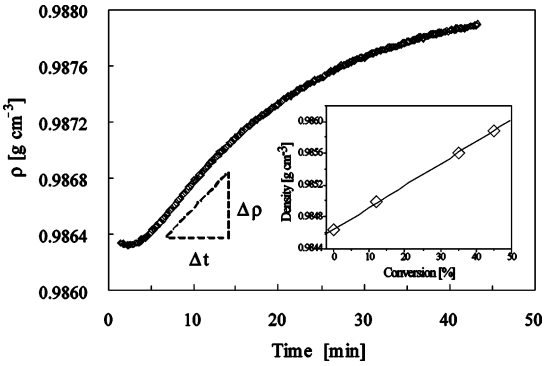

Figure 10. (Inset) Density of the reaction mixture as a function of the conversion at a temperature of 70 °C. The monomer concentration of MADAM-BQ was $[M]_{t=0} = 0.1$ mol L^{-1}, and the macroazoinitiator concentration was $[I_{10}]_{t=0} = 5 \times 10^{-3}$ mol L^{-1}. From the linear fit (straight line), we calculated $B = (v_m - v_p)\ \rho_0 = 0.09655$. The density of the reaction mixture as a function of reaction time during the polymerization of MADAM-BQ at 70 °C (large figure). The monomer concentration at reaction start was 0.1 mol L^{-1}, the initiator concentration (*tert*-butylazocyanovaleric acid) was 10^{-2} mol L^{-1}.

The applicability of the linear relation between density and conversion for understanding the graft polymerization of MADAM-BQ from starch was proved. We measured first the partial specific volumes of monomeric and polymeric MADAM-BQ at 20 and 70 °C in water (Table 2). The high value of B at 70 °C calculated with these data explains why a precise density measurement is also sensitive for the measurement in the ratio of monomer to polymer. Furthermore, B is positive, which means that the density of the polymer is higher than that of the monomer, and therefore, as expected, the density of the reaction mixture increases during the polymerization also in this special case.

Confirmation of the validity of the upper equation B was determined by both conversion and density measurements of a graft polymerization (70 °C, $[M]_{t=0} = 0.1$ mol L^{-1}, $[\mathbf{I}_{10}]_{t=0} = 5 \times 10^{-3}$ mol L^{-1}). After polymerization, we measured the conversion by SEC separation of monomer and graft product (ratio of the peak areas of the UV signal at a wavelength of 268 nm). It was found that the conversion, as well as the density, increases linearly with time as expected (see Figure 10, insert). The conversation data and density data were used to determine how the density of the solution depends on the conversion of the monomer after the elimination of the variable time. The result is shown in Figure 10. From the slope, we calculated $B = 0.09655$, which is about 10% higher than given in Table 2. Both values are within the expected experimental error.

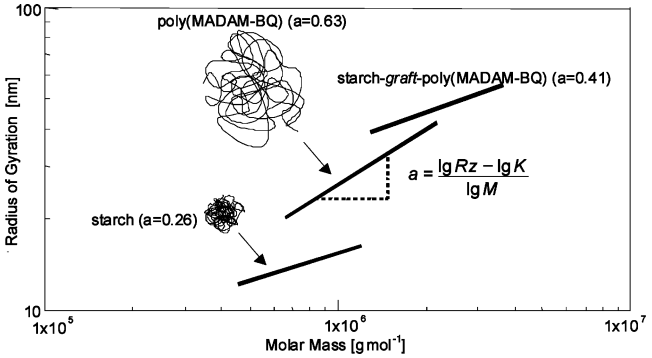

Figure 11. lgR_z-lg$M$-plot, as determined by SEC-MALLS, shows that the slope (a = d lgR_z/d lg$M$) increases with increasing M of starch-*graft*-poly(MADAM-BQ), starch and poly(MADAM-BQ). The low value of $a = 0.26$ found for starch is indicative for a compact structure of the graft substrate in aqueous solution and an increased swelling after graft polymerization.

Overall Rate and Transfer Constants. One aim of this section is to prove whether transfer reactions occur. Therefore, homopolymerizations of MADAM-BQ were carried out by using different concentrations of a low-mass initiator and also with the addition of starch. The molar masses were determined by SEC-MALLS in order to compare the polymerization when using different initial concentrations of the monomer, $[M]_{t=0}$, initiator, $[I]_{t=0}$, and the presence of chain-transfer agents. The evaluation was carried out assuming kinetics as described by the Mayo equation,[59] which was applied to the graft polymerization of MADAM-BQ from starch by the expression:

$$\frac{1}{P_n} = K'\frac{\sqrt{[I]_0}}{[M]_0} + C_M + C_{st}\frac{[St]_0}{[M]_0}$$

$$\text{with } K' = \frac{2(fk_dk_t)^{1/2}}{ak_p} = \frac{2fk_d}{aK}$$

P_n is the degree of polymerization of the grafted poly(MADAM-BQ) chains (i.e., graft length), C_M and C_{st} are the chain-transfer constants of MADAM-BQ and starch, respectively. $[St]_0$ is the starch concentration at the beginning of the polymerization, and K' is a combined constant. f is the initiator efficiency, k_p is the rate constant of chain propagation in L mol^{-1} s^{-1}, K is the overall rate constant of the polymerization in (L mol^{-1} s^{-2})$^{0.5}$, and a is an integer ($a = 1$ for termination by disproportionation and $a = 2$ for recombination).

For simplicity, we assume that neither water nor the initiating azo group have chain-transfer properties. The same assumption cannot be made a priori for the MADAM-BQ monomer and starch because both are capable of hydrogen abstraction. Therefore, we performed the homopolymerization of MADAM-BQ with and without the presence of starch using 4-*tert*-butylazo-4-cyanovaleric acid as low-molar mass initiator.

First, the homopolymerization was carried out with different initial concentrations of the monomer $[M]_{t=0}$ without starch and the same concentration of 4-*tert*-butylazo-4-cyanovaleric acid. The transfer constant C_M was then determined from a Mayo plot of P_n^{-1} vs $1/[M]_{t=0}$ (not shown). It was found that C_M is in the range of 4.8×10^{-5} to 6.5×10^{-5}, which is comparable to the values of methyl methacrylate (1×10^{-5} at 70 °C) and styrene (6×10^{-5} at 60 °C).[60] The low C_M value of MADAM-BQ proves that the transfer activity of MADAM-BQ can be neglected.

Second, we investigated the homopolymerization of MADAM-BQ, initiated with 4-*tert*-butylazo-4-cyanovaleric acid in the presence of different concentrations of starch (0.0−0.4 mol L^{-1}). We found a constant value for $(d\rho[M]/dt)_{t=0}$ of $(0.35 \pm 0.02) \times 10^{-6}$ g cm^{-3} s^{-1} and a constant molar mass of $M_w = (2.7 \pm 0.2) \times 10^6$ g mol^{-1} when starting with $[M]_{t=0} = 0.30$ mol L^{-1} and $[I]_{t=0} = 5 \times 10^{-3}$ mol L^{-1} at $T = 70$ °C. This proves that the transfer activity of starch can also be neglected ($C_M \approx 0$) and that starch has no significant degrading influence, i.e., reduction of the polymer mass of poly(MADAM-BQ).

Next, we determined the overall rate constants for the polymerization of MADAM-BQ using starch macroinitiators with different DS. The values for K are $(6.0 \pm 0.6) \times 10^{-3}$ (L mol^{-1} s^{-2})$^{0.5}$ for $\mathbf{I}_5$, $(6.3 \pm 0.6) \times 10^{-3}$ (L mol^{-1} s^{-2})$^{0.5}$ for $\mathbf{I}_{10}$, and $(5.7 \pm 0.7) \times 10^{-3}$ (L mol^{-1} s^{-2})$^{0.5}$ for $\mathbf{I}_{13}$. Obviously, all the *Ks* are identical within the error range. For comparison, the K of the low-molar mass initiator 4-*tert*-butylazo-4-cyanovaleric acid is slightly higher $(6.7 \pm 0.4) \times 10^{-3}$ (L mol^{-1} s^{-2})$^{0.5}$. In contrast to *K,* we found that the decomposition constant of the initiators k_d increases with higher DS. The k_d values are $(9.5 \pm 0.1) \times 10^{-6}$ s^{-1} for 4-*tert*-butylazo-4-cyanovaleric acid, $(31.7 \pm 4.4) \times 10^{-6}$ s^{-1} for $\mathbf{I}_5$, $(93.3 \pm 18.9) \times 10^{-6}$ s^{-1} for $\mathbf{I}_{10}$, and $(180.5 \pm 37.4) \times 10^{-6}$ s^{-1} for $\mathbf{I}_{13}$. When k_d increases and K is constant, it can be concluded that the radical efficiency f decreases significantly with an increase of DS ($k_d \times f \sim$ constant). This seems to be evident when we assume that the higher the DS of starch substrate, the more compact is its structure in aqueous media such as monomer solutions (cf. Section 3.1 on viscosity and SEC-MALLS measurements). The thermally induced starch radicals are probably not accessible enough for the monomers to react and initiate graft polymerization efficiently. We expected, therefore, that a higher DS does not necessarily result in a shorter distance between two graft chains (decrease of graft frequency). To investigate the influence of the initiator and MADAM-BQ concentration on the polymer characteristics, we used $\mathbf{I}_5$ with DS 0.05, which is the macroinitiator with the lowest DS showing best solubility in water.

3.5. Polymer Structure. Variation of the Initiator Concentration. The initial concentration of $\mathbf{I}_5$ was varied for the graft polymerization at 70 °C in the range of 0.10−0.40 mol L^{-1} (5−20 $\times$ 10^{-3} mol L^{-1} concentration of azo groups), while the concentration of MADAM-BQ was constant at 0.1 mol L^{-1}. The results of the molecular characteristics are summarized in Table 3. It can be seen that the molar mass $M_{n,P-MADAM-BQ}$ of the grafted poly(MADAM-BQ) chains decreases from 289×10^3 g mol^{-1} to 202×10^3 g mol^{-1} with increasing initiator concentration. These correspond to graft lengths, P_l, of 1020−714 monomer units per chain. For initiator concentration above 0.2 mol L^{-1}, the monomer conversions are similar (90−94%) and do not depend significantly on the initiator concentration. The mass fraction of poly(MADAM-BQ), $w_{P-MADAM-BQ}$, decreases from 58 to 32%, and the fraction of starch that was not grafted with poly(MADAM-BQ), w_{starch}, increases from 10 to 25% with increasing initiator concentration. The graft frequency, ν_{graft}, representing the average distance between two graft chains, exceeds from 1290 to 2650 with increasing initiator concentration. This means

Table 3. Graft Polymerization of MADAM-BQ with Different Concentrations of the Starch Azo Initiator I_5 (DS = 0.05)[a]

polymer no.	$[I_5]$ [mol L^{-1}]	U	$M_{n,P-MADAM-BQ}$ [10^3 g mol^{-1}]	P_l	$w_{P-MADAM-BQ}$ [%]	w_{starch} [%]	ν_{graft}	N_{graft}
1	0.10	74	289	1020	58	10	1291	2.41
2	0.20	91	260	916	48	17	1735	1.79
3	0.30	94	243	851	45	31	1819	1.71
4	0.40	90	202	714	32	25	2654	1.17

[a] Monomer concentration of MADAM-BQ was 0.1 mol L^{-1}, the polymerization was carried out at a temperature of 70 °C and stopped after 180 min. U is the conversion of MADAM-BQ, $M_{n,P-MADAM-BQ}$ is the number-average molar mass of the graft chains, P_l is the graft length (number of MADAM-BQ monomers units per grafted chain), $w_{P-MADAM-BQ}$ is the mass fraction of poly(MADAM-BQ) in starch-*graft*-poly(MADAM-BQ), w_{starch} is the mass fraction of nongrafted starch, ν_{graft} is the graft frequency, and N_{graft} is the number of grafted chains per starch molecule.

Table 4. Graft Polymerization of MADAM-BQ with Different Concentrations of the Monomer[a]

polymer no.	[M] [mol L^{-1}]	U	$M_{n,P-MADAM-BQ}$ [10^3 g mol^{-1}]	P_l	$w_{P-MADAM-BQ}$ [%]	w_{starch} [%]	ν_{graft}	N_{graft}
5	0.05	58	107	377	16	34	3463	0.90
6	0.10	82	260	918	47	26	1810	1.72
7	0.15	86	396	1399	61	23	1564	1.99
8	0.20	89	445	1569	66	32	1413	2.20

[a] Initiator concentration (I_5, DS = 0.05) was 0.25 mol L^{-1} (12.5×10^{-3} mol L^{-1} concentration of azo groups), the polymerization was carried out at a temperature of 70 °C and stopped after 180 min. U is the conversion of MADAM-BQ, $M_{n,P-MADAM-BQ}$ is the number-average molar mass of the graft chains, P_l is the graft length (number of MADAM-BQ monomers units per grafted chain), $w_{P-MADAM-BQ}$ is the mass fraction of poly(MADAM-BQ) in starch-*graft*-poly(MADAM-BQ), w_{starch} is the mass fraction of nongrafted starch, υ_{graft} is the graft frequency, N_{graft} is the number of grafted chains per starch molecule.

that, in any case on the starch backbone, only less than one of a thousand anhydroglucose units is grafted. By combining the graft frequency with the molar mass numbers, we calculated the number of poly(MADAM-BQ) chains per starch molecule, N_{graft}, which was found to decrease from 2.41 to 1.17 with increasing concentration of starch initiator. This means that, on average, we have only one to two grafted poly(MADAM-BQ) chains per starch molecule. Consequently, the structure of the starch-*graft*-poly(MADAM-BQ) can be assumed to be similar to block copolymers of the AB and ABA type, but with nondefined positions of the A blocks (poly(MADAM-BQ)) on the B blocks (starch). Structures similar to polymer brushes, which may be assumed a priori for the grafting from starch, can be excluded on the basis of the present data. It was of interest to see whether the variation of the monomer concentration gives similar results.

Variation of the Monomer Concentration. For this purpose, the concentration of MADAM-BQ was varied in the range of 0.05−0.20 mol L^{-1}, while the molar concentration of azo groups of I_5 was held constant at 12.5×10^{-3} mol L^{-1}. The results of the molecular characteristics are summarized in Table 4. It can be seen there that the $M_{n,P-MADAM-BQ}$ of the grafted poly(MADAM-BQ) chains increases from 107×10^3 g mol^{-1} to 445×10^3 g mol^{-1} with increasing monomer concentration. These correspond to graft lengths, P_l, of 377−1569 monomer units per graft chain. The conversions of MADAM-BQ increase with increasing MADAM-BQ concentration from 58 to 89%. The percentage of poly(MADAM-BQ) by mass, $w_{P-MADAM-BQ}$, increases from 16 to 66%, and the percentage of starch that was not grafted with poly(MADAM-BQ) varies nonsystematically between 23 and 34%. The graft frequency decreases from 3463 to 1413 with increasing MADAM-BQ concentration. Again, less than one of a thousand anhydroglucose units is grafted. The number of poly(MADAM-BQ) chains per starch molecule increases from 0.90 to 2.20 with increasing monomer concentration. Again, on average, we have only one to two grafted poly(MADAM-BQ) chains per starch molecule. In summary, the results of the polymerization with varying the initiator and monomer concentrations are consistent.

Variation of DS. One may assume that a higher DS of the initiator gives products with more grafted poly(MADAM-BQ) chains per starch molecules. Therefore, we used I_{10} to start the polymerization using the same conditions as for I_5 in polymerization number 2 (see Table 3). Because of the higher DS of I_{10}, we used for comparison a concentration of 0.10 mol L^{-1} instead of 0.20 mol L^{-1}. We found that the conversion is slightly higher (93% instead of 91%) and, therefore, also the mass fraction of poly(MADAM-BQ) (57% instead of 48%). Surprisingly, the length of the grafted poly(MADAM-BQ) chains increases (1220 instead of 916), but the graft frequency is almost the same (1611 instead of 1735); also, the number of grafted chains per starch molecule remaining almost the same (1.93 instead of 1.79). Obviously, the use of a starch macroinitiator with a higher DS does not result in graft products with a significantly lower graft frequency. We assume that the reason for this unexpected result is a reduction in the efficiency of the macroradicals with increasing DS due to the decrease in solubility and tendency to aggregate of higher-substituted starch initiators. Regarding the amount of decomposed azo groups of I_{10} as a function of the polymerization time t with $\Delta DS(t) = DS \times (1 - e^{-k_d \times t})$, the specific value of ΔDS (180 min) is equal to 0.0635 for DS = 0.10 and $k_d = 93.3 \times 10^{-6}$ s^{-1}.

Thus, the reciprocal of 0.0635 (∼16) represents the minimal graft distance, which can be obtained at this point of the graft process, i.e., 100% radical efficiency. Because we observed a hundred times larger graft distance of 1611, the radical efficiency of I_5 is expected to be in the region of 10^{-2}. The loss of radical efficiency, especially for higher-substituted starch initiators, was also verified by the previous kinetic measurements.

4. Conclusions

The object of this work has been the design of a new starch-based macroinitiator for the synthesis of cationic polymer grafted starch. It was shown that the binding of a nonsymmetric azo group is suitable by reaction of

starch with 4-*tert*-butylazo-4-cyanovaleric acid chloride. The azo compound is linked to the starch predominantly at carbon in the C6 position. This functionalization leads to a hydrophobization of the starch, resulting in decreasing water solubility with increasing degree of substitution as revealed by viscometry in solution.

The azo macroinitiator starts the polymerization of MADAM-BQ, resulting in graft products with a high monomer conversion and which are essentially free of cationic homopolymers. In contrast to MADAM-BQ, it was shown that the use of 2,3-dimethyl-1-vinylimidazolium chloride results in significant amounts of cationic homopolymer due to high transfer activity of this monomer. It was found that, independent of the DS of the macroinitiator, the number of grafted poly(MADAM-BQ) chains from starch is nearly constant in the case of the used starch substrate between one and two. Therefore, the structures of the formed graft products were always similar to that of block copolymers. Polymer brush structures can be excluded. Obviously only few azo groups of the starch initiators are able to start the polymerization of MADAM-BQ. Their radical efficiency is significantly lower than those of low-mass initiators and decreases with increasing DS. This is mainly due to the compactness of the starch substrate and the corresponding initiator, which in addition, leads to some aggregation. We expect that the synthesized starch-initiators could be useful as stabilizer and also as initiator in emulsion polymerization. Investigations of these applications are in progress.

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Supporting Information Available: Thermal decomposition of ABCVA, *t*-BACVA and $\mathbf{I}_{13}$ in aqueous solution; ^{1}H NMR-spectra in D_2O of poly(MADAM-BQ) and starch-*graft*-poly(MADAM-BQ). This material is available free of charge via the Internet at http://pubs.acs.org.

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