Controlled Synthesis of Coordination Block Copolymers with β-Dicarbonyl Ligating Segments

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Metal chelates and coordination compounds play an extraordinary role in very diverse areas like the chemistry of living matter and biominerals, wastewater treatment, industrial-scale polymer synthesis, catalysis, and hydrometallurgy, to mention just a few.[1] Over the past three decades, macromolecular science has strongly been entering this field of organic−inorganic hybrid materials, aiming to combine potential applications of metal compounds with the special features of copolymers, namely the formation of nanometer-scale structured materials, the electrosteric stabilization of colloids, and good mechanical performance.[1−3]

Up to the present, a large number of coordination polymers with O-, S-, and N-containing ligands and polymer−metal complexes have been described. The majority of studies investigated homopolymers, random copolymers and resins which were mainly obtained from conventional free radical polymerization techniques.[1] However, radical reactions polymerize many monomers and tolerate most functional groups, but they often yield chemically disperse products which are not suited for accurate systematic studies on phase behavior and material properties. The synthesis of well-defined materials and block copolymers, on the other hand, requires advanced polymerization techniques (e.g., living/controlled radical or ionic polymerization methods)[4,5] or polymer modification reactions starting from well-defined precursor polymers involving quantitative and side reaction-free conversion.[6]

We are focusing on amphiphilic block copolymers with bidentate β-dicarbonyl moieties because of their strong affinity to multivalent cations and their expected interesting aggregation behavior.[2] Polymers with β-dicarbonyl repeating units have so far been obtained from the free radical polymerization of (meth)acroylacetone,[7,8] ethylacrylolyl acetate,[8] and acetoacetoxyethyl (meth)acrylate[9] or by the controlled oxidation of poly(vinyl alcohol).[10] Procedures for a living and controlled synthesis of block copolymers from acetoacetyl- or ketal-functional monomers have not been reported yet. We therefore employed this alternate route to prepare coordinating polymers with pendant β-dicarbonyl ligands that involves the chemical modification of suitable precursor block copolymers. Considering established methods of synthetic organic chemistry, β-dicarbonyl compounds can be obtained from (1) the transesterification of *tert*-butyl acetoacetate with alcohols (transacetoacetylation)[11] or (2) the Claisen acylation of esters with sodium acetonate.[12] Poly(2-hydroxyethyl methacrylate) and poly(2-hydroxyethyl ethylene), which can both be prepared via anionic polymerization of readily available monomers and subsequent modification, were therefore taken as the precursor segments for transacetoacetylation. Poly(*tert*-butyl methacrylate) was used for the modification via Claisen acylation because of its good *tert*-butoxide leaving groups.

Structures and chemical compositions of the prepared precursor polymers, all having a narrow molecular weight distribution (polydispersity index, PDI = 1.03−1.09), are given in Table 1; samples were characterized, employing standard size exclusion chromatography (SEC)[13] and NMR spectroscopy.[14] All solvents and reagents used for polymerization and modification reactions were high-purity reagent-grade materials (Aldrich, Fluka) and were purified following standard procedures. Sample **A-1**, poly(*n*-butyl methacrylate)-*block*-poly(2-hydroxyethyl methacrylate), was synthesized via sequential group transfer polymerization (GTP) of *n*-butyl methacrylate and 2-(trimethylsilyloxy)ethyl methacrylate at 20 °C in tetrahydrofuran (THF) employing 1-methoxy-1-trimethylsiloxy-2-methylprop-1-ene (MTS) and tetrabutylammonium bibenzoate as the initiator/catalyst;[15] the trimethylsilyl protecting groups were quantitatively removed by HCl-catalyzed hydrolysis at room temperature. Sample **B-1**, poly(ethylene oxide)-*block*-poly(2-hydroxyethyl ethylene), was obtained via the sequential anionic polymerization of 1,3-butadiene (−70 °C) and ethylene oxide (+40 °C) in THF with *sec*-butyllithium/*t*-BuP_4 phosphazene as the initiator;[16] the butadiene units were hydroxylated in 90% yield via hydroboration/oxidation.[17] Sample **C-1**, poly(*tert*-butyl methacrylate), was obtained from the anionic polymerization of *tert*-butyl methacrylate in THF at −78 °C, employing lithium diisopropylamide as the initiator in the presence of LiCl.[18]

Since transesterifications between *tert*-butyl acetoacetate (*t*BAA) and alcohols are equilibrium reactions, the released *tert*-butyl alcohol (*t*BuOH) should be removed from the reaction mixture in order to achieve maximum yields of the desired esters. As proposed by Witzeman and Nottingham,[11] the alcohol could be distilled off the reaction mixture in xylene at 120 °C. However, we developed another—in our opinion more convenient—procedure that employs the removal of *t*BuOH within a ternary azeotrope with benzene and water (bp 67.3 °C).[19] A mixture of *t*BAA (0.36 mL, 2.10 mmol; 99%, Aldrich) and either **A-1** (0.95 g, 0.06 mmol) or **B-1** (0.50 g, 0.11 mmol) ([*t*BAA]/[-OH] = 1.5) in 30 mL of benzene was stirred for 1 h at room temperature. After the addition of ∼10 mL of water, the reaction solution was refluxed in a liquid−liquid extraction apparatus to remove the aqueous phase (H_2O + *t*BuOH). The products **A-2** and **B-2** were precipitated in hexane and diethyl ether, respectively, and the isolated colorless materials were dried in a vacuum at 40 °C for at least 24 h. ^{1}H NMR and characteristic FT-IR data[20] of the acetoacetylated polymers are summarized in Table 1; the exemplary NMR spectra of **A-2** and the corresponding precursor **A-1** are shown in Figure 1. The NMR and IR spectra agreed with the structures proposed in Table 1 (**A-2**: poly(*n*-butyl methacrylate)-*block*-poly(2-(acetoacetoxy)ethyl methacrylate), **B-2**: poly(ethylene oxide)-

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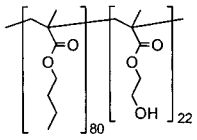
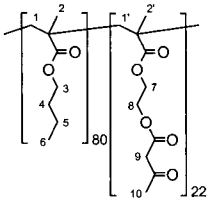
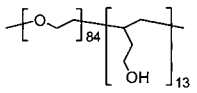
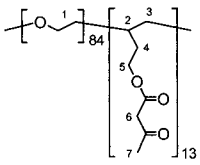
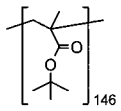
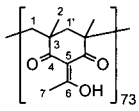
Table 1. Structures of Precursor Polymers and Coordination Polymers with β-Dicarbonyl Ligating Segments Obtained from Transacetoacetylation (A-2 and B-2) and Claisen Acylation (C-2)

precursor polymer	acylated product	
A-1 	**A-2** 	*^{1}H NMR*, δ/ppm: 0.75–1.05 (2, 6), 1.38 (5), 1.59 (4), 1.70–2.00 (1), 2.27 (10), 3.54 (9), 3.92 (3), 4.15 (7), 4.33 (8). *FT-IR*, $\tilde{\nu}$/cm^{-1}:[#] 3100–2800 (s; C–H), 1720 (vs), 1650 (w; C=O), 1140 (vs; C–O).
B-1 	**B-2** 	*^{1}H NMR*: 0.80–1.40 (2, 3, 4), 2.23 (7), 3.45 (6), 3.60–3.80 (1), 4.12 (5). *FT-IR*: 3000–2700 (s; C–H), 1737 (s), 1711 (s), 1642 (w; C=O), 1103 (vs; C–O).
C-1 	**C-2** 	*^{1}H NMR*: 0.75–1.40 (2), 1.70–2.35 (1, 7), 5.86 (5, keto). *^{13}C NMR*: 27.3–33.0 (1, 2), 37.5, 45.2–52.3 (3), 72.1 (5, keto), 136.0 (6), 158.4 (5), 201.7 (4). *FT-IR*: 3000–2800 (s; C–H), 1720 (s), 1659 (s), 1643 (s; C=O), 1579 (w; =C–OH), 1131 (s; C–O).

[#] vs = very strong; s = strong; w = weak.

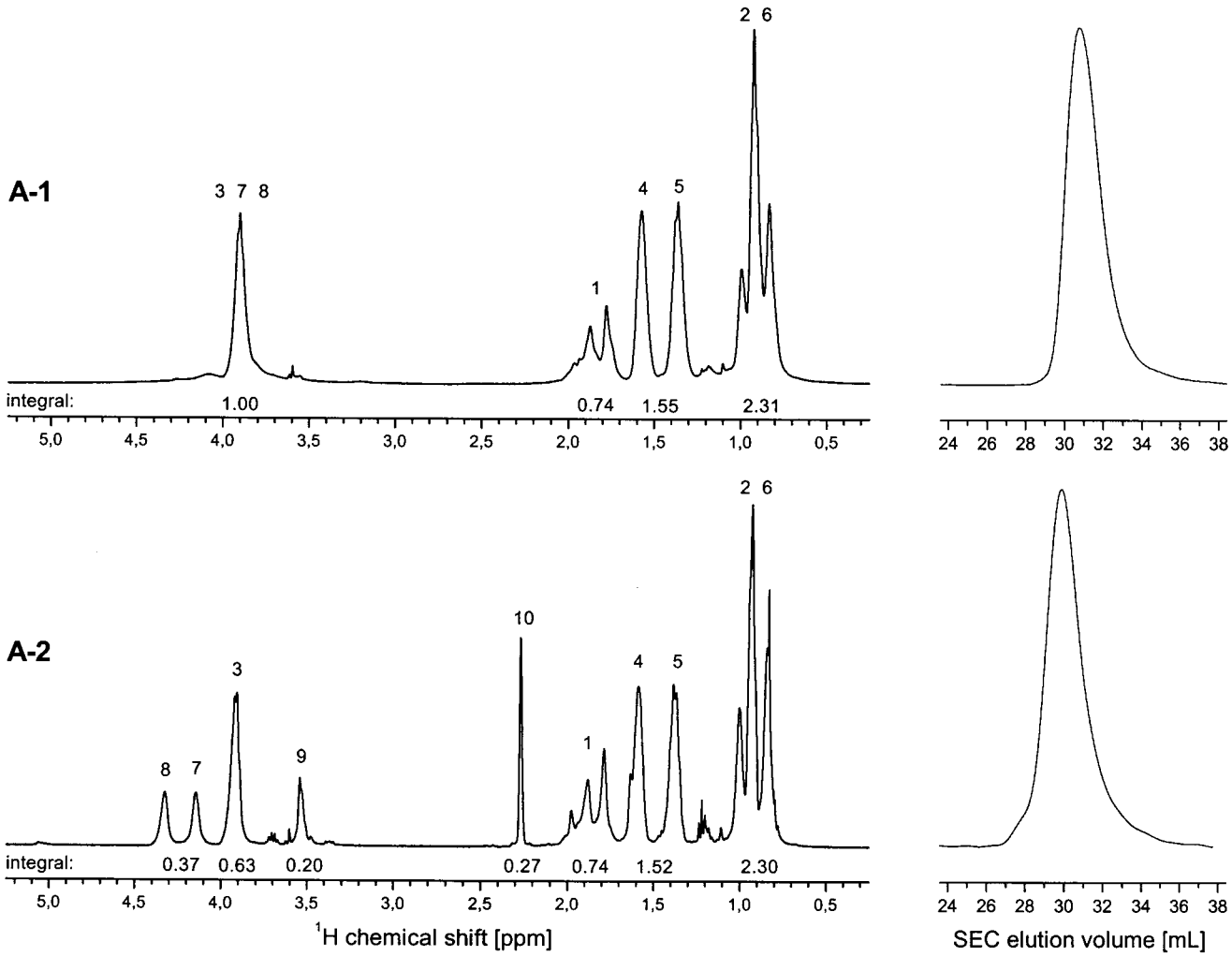


Figure 1. ^{1}H NMR spectra ($CDCl_3$) (left) and SEC chromatograms (DMA, DRI detector signal) (right) of the block copolymer precursor **A-1** and the acetoacetylated product **A-2**. For assignment of NMR signals, see Table 1.

block-poly(2-(acetoacetoxy)ethyl ethylene)) representing the β-dicarbonyl moieties in the favored ketonic tautomeric form.[9] The degree of acetoacetylation of **A-2** and **B-2** was calculated from the peak areas under the ^{1}H NMR signals of $-CH_2O-$ (8)/$-CH_3$ (2, 6) and $-CH_2O-$ (5)/(1), respectively, to be greater than 90%. SEC analyses suggest that the narrow molecular weight distribution of precursor copolymers was maintained during the transesterification (see Figure 1); therefore, the PDI of **A-2** and **B-2** should be less than 1.1. Also, the acetoacetylated samples elute faster in the SEC mode than the hydroxylated precursor block copolymers because of a somewhat larger hydrodynamic volume of the derivatized functional segment.[6]

The Claisen acylation of sample **C-1** was performed as follows: acetone (2 mL, 27.2 mmol; 99.5%, Aldrich) was slowly added to a suspension of NaH (0.17 g, 6.8 mmol; 95%, Aldrich) in 3 mL of THF under a dry argon atmosphere at 0 °C. After stirring for 50 min, a solution of **C-1** (0.50 g, 0.024 mmol) in 5 mL of acetone was added dropwise, and the mixture was slowly heated to reflux and stirred overnight. The resulting red reaction mixture was quenched with aqueous HCl at room temperature, and then the organic solvents were evaporated and replaced by benzene. The organic layer was washed thoroughly with H_2O and freeze-dried to yield a deeply red material, **C-2**. According to ^{13}C NMR analysis (see Table 1), the product is free of ester carbonyl units ($\delta \sim 177$ ppm), indicating complete acylation of **C-1**. However, the NMR and FT-IR spectra lack characteristic signals of the expected poly(methacroylacetone) (^{13}C: $\delta \sim 100$ and 191 ppm (acetylacetone); IR:[7] $\tilde{\nu} = 1605$ cm^{-1}). Any methacroylacetone unit formed during the reaction should have been immediately deprotonated by either sodium acetonate or sodium butoxide and should then have attacked a neighboring ester group to yield a acetyl-substituted cyclic β-diketone (see the structure plot of the respective enol tautomer in Table 1). The spectroscopic data seem to support the structure of **C-2** as is proposed in Table 1, but further investigations will be necessary to confirm this. The SEC chromatogram of **C-2** is virtually identical to that of the precursor polymer **C-1** (PDI = 1.03), indicating the absence of any intermolecular chain coupling products.

Initial studies on the micellization behavior of **A-2** and its ability to solubilize inorganic metal salts in hydrophobic media were performed employing dynamic light scattering (DLS)[21] and analytical ultracentrifugation (AUC).[22] Upon adding **A-2** to a stirred suspension of $FeCl_3 \cdot 6H_2O$ in cyclohexane (**A-2/Fe^{III}**, [Fe]/[β-dicarbonyl] $\approx$ 0.5), the salt dissolves readily, and the color of the solution changes from colorless to purple ($\lambda_{max} = 250 \rightarrow 500$ nm), which indicates that a polymer−metal complex has been formed. DLS analyses revealed the presence of spherical micelles with a hydrodynamic diameter of ~25 nm for both **A-2** and **A-2/Fe^{III}** samples. We propose that the micellar aggregates of **A-2/Fe^{III}** consist of a poly(*n*-butyl methacrylate) solvating corona and a β-dicarbonyl ligating core being loaded with the ferric salt; i.e., **A-2/Fe^{III}** should be a sterically stabilized colloidal hybrid material. Because of the different densities of organic and inorganic components, AUC provides information on the chemical composition of the **A-2/Fe^{III}** colloids. In fact, sedimentation−velocity analysis (Figure 2) not only confirms the loading of the **A-2** micelles with Fe^{III} but also indicates that the salt is evenly distributed among the aggregates.

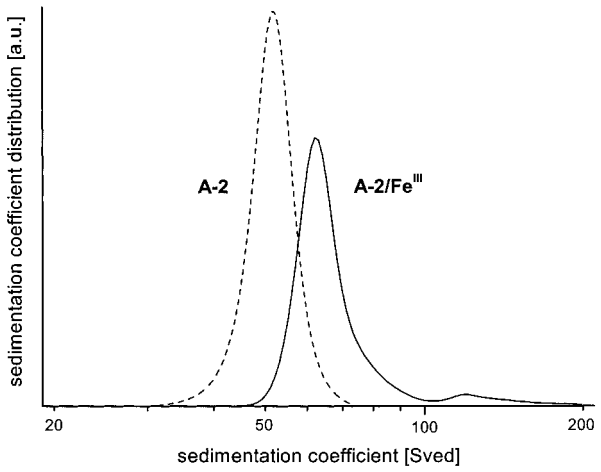


Figure 2. Sedimentation coefficient distribution of the **A-2** and **A-2/Fe^{III}** micellar solutions in cyclohexane.

In summary, we prepared well-defined block copolymers with β-dicarbonyl ligating segments via the chemical modification of suitable precursor polymers that are the acetoacetylation of hydroxylated polymers and, with some limitation, the Claisen acylation of poly(*tert*-butyl methacrylate). Initial studies indicate that amphiphilic diblock copolymers of this type form complexes with metal salts to yield sterically stabilized colloidal hybrid materials. In future studies, the chemical structure and properties of polymer−metal complexes, their phase behavior in organic (→**A-2**) and aqueous (→**B-2**) media, and their use to prepare nanostructured hybrid materials shall be investigated.

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References and Notes

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(13) Depending on the analyte, SEC analyses with simultaneous UV and DRI detection were performed in THF, $CHCl_3$ (25 °C), or 0.5 wt % LiBr in DMA (70 °C) as the eluent at a flow rate of 1.0 mL/min. The column sets employed were 300 × 8 mm, 5 μm MZ-SD*plus*: 10^3, 10^5, 10^6 Å (THF, $CHCl_3$) and 300 × 8 mm, 10 μm PSS-GRAM: 30, 30, 100, 3000 Å (DMA).

Poly(*n*-butyl methacrylate), poly(*tert*-butyl methacrylate), poly(1,2-butadiene), and poly(ethylene oxide) calibration curves were used to evaluate molecular weights and molecular weight distributions.

(14) ^{1}H and ^{13}C NMR spectra of polymer samples were recorded at 25 °C in $CDCl_3$ with a Bruker DPX-400 spectrometer operating at 400.1 and 100.6 MHz, respectively. NMR signals were referenced to that of the solvent at $\delta = 7.24$ (^{1}H) and 77.0 ppm (^{13}C). Signals were assigned with the aid of literature data reported elsewhere and the *gNMR V4.1.0* software package (Cherwell Scientific Publishing).

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(20) Infrared spectra of solid samples were recorded at room temperature with a BioRad 6000 FT-IR spectrometer equipped with a single reflection diamond ATR.

(21) DLS measurements were carried out at 20 °C with a spectrometer consisting of an argon laser ($\lambda = 488$ nm, 500 mW; Coherent Innova 300), a self-constructed goniometer, a single-photon detector (ALV SO−SIPD), and a multiple-tau digital correlator (ALV 5000/FAST). From the measured time-correlation functions, intensity-weighted particle size distributions were calculated according to: Schnablegger, H.; Glatter, O. *Appl. Opt.* **1991**, *30*, 4889.

(22) AUC sedimentation−velocity runs were performed with a Beckman model XL-I equipped with UV/vis absorption and Rayleigh interference optics. Experiments were carried out at 25 °C with a rotor speed of 20 000 rpm. Raw data were evaluated with the *sedfit7* software (Peter Schuck; http://www.cauma.uthscsa.edu) to obtain diffusion-corrected sedimentation coefficient distributions.

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