

## Reaction behaviour of monomeric $\beta$ -ketoesters

### 1. Synthesis and polymerization of complexes of 2-acetoacetoxyethyl methacrylate

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#### Summary

Complexes of various metal salts and 2-acetoacetoxyethyl methacrylate (AAEMA) were synthesized and characterized by elemental analyses, IR and  $^1\text{H}$  NMR spectroscopy. The prepared complexes are radically polymerizable. The polymer complexes can be hydrolyzed under acidic conditions yielding poly(AAEMA).

#### Introduction

Polymerizable  $\beta$ -diketones like methacrylacetone possess a complexing affinity for metals and have thus received interest for use as primers for metal coatings or as starting compounds for polymer-supported catalysts [1-3]. Also, the chelation as a means of crosslinking emulsion polymers based of 2-acetoacetoxyethyl methacrylate was investigated [4]. Recently, the polymerization of some  $\alpha,\beta$ -ethylenically unsaturated  $\beta$ -ketoesters has been described [5-7]. In the case of ethyl  $\alpha$ -(acetoacetoxymethyl)acrylate, its copper(II) chelate was prepared and polymerized [8].

Biocompatible cements on the basis of metal oxides and organic chelating agents, like zinc oxide-eugenol or calcium oxide-salicylate systems, are used in dentistry as underfilling materials for protection of dental pulp [9]. Reports of investigations of  $\beta$ -dicarbonyl compounds as complexing component in dental cements are only few and concern only combinations of zinc oxide and acetylacetone or ethyl acetoacetate (EAA), which were ineffective [10,11]. In this paper the synthesis and polymerization of metal complexes of AAEMA are presented.

#### Experimental

##### Materials

AAEMA (Lonza) was used in a purity of about 96% and contained 2-hydroxyethyl methacrylate (HEMA, about 3.0%) and methacrylic acid (about 0.5%).  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaCO}_3$ ,  $\text{Ca}(\text{CH}_3\text{COO})_2$ ,  $\text{BaO}$ ,  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ,

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$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Fluka) and analytical grade tribasic Calciumphosphate ( $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ , Sigma) were used without further purification.

Dimethylformamide (DMF), and 2,2-azobisisobutyronitrile (AIBN) were purified as described previously [12]. Methyl ethyl ketone (MEK) was dried by refluxing over  $\text{P}_2\text{O}_5$  and distilled before use.

## Synthesis

### Monomers

Acetoacetylated poly(ethylene glycol)-200-monomethacrylate (PEG-200-AAMA) or 4-vinylbenzyl acetoacetate (VBAA) were prepared by reaction of diketene with poly(ethylene glycol)-200-monomethacrylate (PEG-200-MA, Poly-science) or 4-vinylbenzyl alcohol in the presence of 1,4-diazabicyclo[2.2.2]-octane according to W. Connely et al. [13].

AAEMA:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 1.95 (s, =C-CH<sub>3</sub>, =C(OH)-CH<sub>3</sub>), 2.27 (s, -CO-CH<sub>3</sub>), 3.49 (s, -CO-CH<sub>2</sub>-CO-), 4.40 (4H, s, -CH<sub>2</sub>-CH<sub>2</sub>-), 5.05 (s, -CH=C(OH)-), 5.68 (1H, s) and 6.13 (1H, s, CH<sub>2</sub>=); from the  $^1\text{H}$  NMR spectra results the enol-content is about 10%; IR (film,  $\text{cm}^{-1}$ ): 1740 (C=O), 1720 (C=O), 1637 (C=C).

PEG-200-AAMA:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 1.94 (3H, s, =C-CH<sub>3</sub>), 2.27 (3H, s, -CO-CH<sub>3</sub>), 3.48 (2H, s, -CO-CH<sub>2</sub>-CO-), 3.65-3.72 (16H, m, -CH<sub>2</sub>-O-CH<sub>2</sub>-), 4.28 (4H, t, -CO-O-CH<sub>2</sub>-), 5.58 (1H, s) and 6.13 (1H, s, =CH<sub>2</sub>); IR (film,  $\text{cm}^{-1}$ ): 1744 (C=O), 1717 (C=O), 1637 (C=C).

VBAA:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 1.95 (s, =C(OH)-CH<sub>3</sub>), 2.24 (s, -CO-CH<sub>3</sub>), 3.48 (s, -CO-CH<sub>2</sub>-CO-), 5.03 (s, -CH=C(OH)-), 5.16 (2H, s, -O-CH<sub>2</sub>-Ar), 5.27 (1H, d) and 5.76 (1H, d, CH<sub>2</sub>=), 6.71 (1H, dd, Ar-CH=), 7.18-7.43 (4H, m, Ar-H), from the  $^1\text{H}$  NMR spectra results the enol-content is about 8%; IR (film,  $\text{cm}^{-1}$ ): 1745 (C=O), 1719 (C=O), 1646 (arom. C=C), 1630 (C=C).

### Calcium-Complexes

10 ml of an ethanol solution containing 40 mmol AAEMA were added to a suspension of  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$  or tribasic Calciumphosphate or solution ( $\text{CaCl}_2$  or  $\text{Ca}(\text{CH}_3\text{COO})_2$ ) of 20 mmol calcium compound in 70 ml water/ethanol (1:1) at room temperature. In the case of calcium chloride, carbonate, acetate or phosphate 10 ml of 2.0 molar aqueous ammonia were added. After stirring for 2 h, the formed precipitates were filtered off, washed with water and cold ethanol, and dried to constant weight in vacuo. Yield: 73% ( $\text{Ca}(\text{OH})_2$ ), 31% ( $\text{CaCl}_2$ ) and 29% ( $\text{Ca}(\text{CH}_3\text{COO})_2$ ). The reaction of  $\text{Ca}(\text{OH})_2$  with EAA (Fluka, yield: 69%) or PEG-200-AAMA was carried out in the same manner. Furthermore, the Ca-AAEMA complex ( $\text{Ca}(\text{AAEMA})_2$ ) was prepared from metallic calcium (Fluka) and AAEMA in 94% yield analogous to the synthesis of calcium acetoacetate described in [14].  $\text{Ca}(\text{AAEMA})_2$  is well soluble in DMF or dimethylsulfoxide, but a recrystallization from these solvents failed.

$\text{Ca}(\text{AAEMA})_2$ : m.p.: 189-191 °C;  $\text{CaC}_{20}\text{H}_{26}\text{O}_{10}$  (466.5): found: C: 50.26 (calculated: 51.50), H: 5.66 (5.62); residue of ignition: 12.74% (calc.: 12.02% CaO);  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ,  $\delta$  (ppm)): 1.72 (3H, s, CH<sub>3</sub>-C(O<sup>-</sup>)=), 1.90 (3H, s, CH<sub>3</sub>-C=), 4.03-4.33 (4H, m, -CH<sub>2</sub>-CH<sub>2</sub>-), 4.53 (1H, s, =CH-), 5.70 (1H, s) and 6.07 (1H, s, CH<sub>2</sub>=); IR (KBr,  $\text{cm}^{-1}$ ): 1719 (C=O), 1646 (C=O), 1530 (C=C).  $\text{Ca}(\text{EAA})_2$ : Residue of ignition: 18.80% (19.13% CaO);  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ,  $\delta$

(ppm): 1.22 (3H,t,-CH<sub>2</sub>-CH<sub>3</sub>), 1.71 (3H,s,CH<sub>3</sub>-C(O<sup>-</sup>)=), 3.92 (2H,q,-CH<sub>2</sub>-CH<sub>3</sub>-), 4.49 (1H,s,=CH-); IR (KBr, cm<sup>-1</sup>): 1642 (C=O), 1518 (C=C).

#### *Other complexes*

The reaction of AAEMA with copper(II) acetate or barium oxide were carried out analogous to calcium hydroxide and with NiCl<sub>2</sub> or CoCl<sub>2</sub> to CaCl<sub>2</sub>, respectively. The copper(II) and nickel(II) complexes were recrystallized from ethanol, whereas the cobalt(II) complex showed some decomposition.

Cu(AAEMA)<sub>2</sub>: Yield: 83%; m.p.: 141-142 °C; CuC<sub>20</sub>H<sub>26</sub>O<sub>10</sub> (490.0): C: 48.83 (49.03), H: 5.38 (5.35); Residue of ignition: 16.26 (16.24 CuO); IR (KBr, cm<sup>-1</sup>): 1721 (C=O), 1599 (C=O), 1527 (C=C).

Ba(AAEMA)<sub>2</sub>: Yield: 48%; Residue of ignition: 27.91 (27.20 BaO); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ (ppm)): 1.66 (3H,s, CH<sub>3</sub>-C(O<sup>-</sup>)=), 1.91 (3H,s,CH<sub>3</sub>-C=), 4.23-4.38 (4H,m,-CH<sub>2</sub>-CH<sub>2</sub>-), 4.48 (1H,s, =CH-), 5.79 (1H,s) und 6.14 (1H,s, CH<sub>2</sub>=); IR (KBr, cm<sup>-1</sup>): 1729 (C=O), 1642 (C=O), 1513 (C=C).

Ni(AAEMA)<sub>2</sub>: Yield: 75%; m.p.: 109-110 °C; NiC<sub>20</sub>H<sub>26</sub>O<sub>10</sub> (485.1): C: 48.18 (49.52), H: 5.47 (5.40); Residue of ignition: 15.97 (15.40 NiO); IR (KBr, cm<sup>-1</sup>): 1720 (C=O), 1629 (C=O), 1525 (C=C).

Co(AAEMA)<sub>2</sub>: Yield: 73%; m.p.: 74-76 °C (decomp.); CoC<sub>20</sub>H<sub>26</sub>O<sub>10</sub> (485.4): C: 46.73 (49.49), H: 5.36 (5.40); Residue of ignition: 14.27 (15.55 CoO); IR (KBr, cm<sup>-1</sup>): 1722 (C=O), 1626 (C=O), 1526 (C=C).

#### Polymerization

The polymerization reactions were carried out in sealed glass tubes containing a given amount of AIBN dissolved in DMF. Subsequently, the monomer or complexes were introduced. The tubes were degassed through three freeze-thaw cycles (liquid nitrogen) before they were placed in a constant-temperature bath (60 °C). Polymerizations were terminated by the addition of excess methanol. The monomer conversion was calculated from the gravimetrically determined yields of the dried polymers. The polymer were reprecipitated and dried under vacuo to constant weight. In case of polymeric β-ketoester MEK/ether was used as solvent/nonsolvent. The polymeric AAEMA-metal complexes were only washed with DMF and subsequent with methanol.

Poly[AAEMA]: C: 56.20 (56.01), H: 6.72 (6.59); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ (ppm)): 4.28 (4H,-CH<sub>2</sub>-CH<sub>2</sub>-), 3.69 (2H,-CO-CH<sub>2</sub>-CO-), 2.24 (3H,-CO-CH<sub>3</sub>), 1.85 (2H,-CH<sub>2</sub>-), 0.92 (3H,-C(CH<sub>3</sub>)-); IR (KBr, cm<sup>-1</sup>): 1730 (C=O);

Poly[PEG-200-AAMA]: IR (KBr, cm<sup>-1</sup>): 1728 (C=O).

Poly[AAST]: <sup>1</sup>H NMR (acetone-d<sub>6</sub>, δ (ppm)): 1.18-2.00 (3H,m,-CH<sub>2</sub>-CHAr), 2.19 (3H,s,CH<sub>3</sub>-CO-), 3.56 (2H,s,-CO-CH<sub>2</sub>-CO-), 5.14 (2H,s,-O-CH<sub>2</sub>-Ar), 6.32-7.40 (4H,m,Ar-H); IR (KBr, cm<sup>-1</sup>): 1739 (C=O), 1718 (C=O) 1646 (arom. C=C).

Poly[Ca(AAEMA)<sub>2</sub>]: IR (KBr, cm<sup>-1</sup>): 1726 (C=O), 1645 (C=O), 1515 (C=C).

Poly[Cu(AAEMA)<sub>2</sub>]: C: 49.91 (49.03), H: 5.81 (5.35); IR (KBr, cm<sup>-1</sup>): 1731 (C=O), 1599 (C=O), 1517 (C=C).

Poly[Ni(AAEMA)<sub>2</sub>]: IR (KBr, cm<sup>-1</sup>): 1733 (C=O), 1626 (C=O), 1511 (C=C).

Poly[Co(AAEMA)<sub>2</sub>]: IR (KBr, cm<sup>-1</sup>): 1728 (C=O), 1628 (C=O), 1515 (C=C).

Hydrolysis of polymerized complexes were carried out by suspension of poly[Cu(AAEMA)<sub>2</sub>] in THF and addition of concentrated hydrochloric acid. After 2 h stirring the resulting polymer solution was precipitated in excess methanol and the polymer was further purified by reprecipitation from dioxane/methanol.

Hydrolyzed Poly[Cu(AAEMA)<sub>2</sub>]:  $M_n = 10400$  g/mol); C: 55.80 [56.01 as P(AAEMA)], H: 6.49 (6.59); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ (ppm)): 4.27 (4H, -CH<sub>2</sub>-CH<sub>2</sub>-), 3.69 (2H, -CO-CH<sub>2</sub>-CO-), 2.25 (3H, -CO-CH<sub>3</sub>), 1.86 (2H, -CH<sub>2</sub>-), 0.92 ppm (3H, -C(CH<sub>3</sub>)-); IR (KBr, cm<sup>-1</sup>): 1727 cm<sup>-1</sup> (C=O).

### Measurements

<sup>1</sup>H NMR measurements were recorded on an EM 390 (Perkin-Elmer, 90 MHz) using hexamethyldisilane (HMDS) as the standard and CDCl<sub>3</sub> or dimethylsulfoxide-d<sub>6</sub> as a solvent. An FT-IR spectrometer 1600 (Perkin-Elmer) was used to record IR spectra. The number-average molecular weights of polymers were determined by GPC using an isocratic pump IsoChrom (Spectra-Physics) and THF as eluent, an detector RI-4 (Varian) and columns calibrated with poly(methyl methacrylate) standards. Magnetic measurements were performed by using a magnetic balance Mark II (Johnson Matthey).

### Results and Discussion

The choice of a suitable β-ketoester monomer as complexing agent for various metal compounds was made on basis of their radical polymerization behaviour. The results given in Table 1 demonstrate a clearly lower monomer conversion of VBAA in comparison with that of both AAEMA and PEG-200-AAMA. During the polymerization of PEG-200-AAMA gelation occurred after some minutes and thus the obtained polymers were insoluble. Since PEG-200-MA, the starting compound of synthesis of PEG-200-AAMA, shows similar behaviour, it can be proposed that reason of gelation is the presence of traces of dimethacrylate. On the basis of these results only AAEMA was used as complexing agent.

Complexes of β-dicarbonyl compounds are usually prepared by the reaction of metal salts, oxides, hydroxides or carbonates in aqueous or organic solution [15,16]. Due to the low water solubility of AAEMA, the complex formation was carried out in a water/ethanol mixture (1/1) as reaction medium.

Table 1 Polymerization of monomeric β-ketoesters (2.0 mol/l) in MEK in the presence of AIBN (0.05 mol/l)

Monomer	Time (h)	Conversion (%)	$M_n \times 10^3$ (g/mol)
AAEMA	0.5	28.0	88.8
	1.0	53.3	100.8
	2.0	75.6	-
VBAA	0.5	6.1	-
	1.0	12.5	15.6
PEG-200-AAMA	1.0	80.8	-

Basic compounds, such as Ca(OH)<sub>2</sub>, Ca(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> or BaO, and copper(II) acetate reacted directly with AAEMA with complex formation. In contrast, other

metal compounds formed a complex with AAEMA only in the presence of aqueous ammonia as base. The reactivity of zinc compounds with poly(AAEMA) is similar to that of copper(II) or nickel(II) compounds [4]. Thus it was surprising, that complex formation of AAEMA with zinc acetate failed. Also with the pure soluble tribasic calcium phosphate all attempts to prepare a AAEMA-complex were not successful. The reaction of  $\text{Ca(OH)}_2$  with PEG-200-AAMA occurred in the same manner as that with AAEMA. With the usual procedure it was not possible to isolate the PEG-200-AAMA complex because it is soluble both in polar and nonpolar solvents. This suggests that calcium ions can be solubilized in nonpolar medium by the reaction with PEG-200-AAMA. Complexation also took place by addition of AAEMA to pure  $\text{Ca(OH)}_2$ , and the setting of the formed cement was complete after only few seconds.

Table 2 Polymerization of  $\text{Cu(AAEMA)}_2$  (0.25 mol/l) in the presence of AIBN (0.02 mol/l) in DMF at 60 °C

Time (min.)	Conversion (%)
10	31.2
20	61.9
30	75.5
60	84.6
120	92.1
30	17.2 <sup>1)</sup>

1)  $[\text{AAEMA}] = 0.25 \text{ mol/l}$

The synthesized AAEMA-complexes were characterized by  $^1\text{H}$  NMR and IR spectroscopy and partially by elemental analysis. The DMF soluble complexes  $[\text{Ca(AAEMA)}_2, \text{Ca(EAA)}_2 \text{ or } \text{Ba(AAEMA)}_2]$  showed the expected signals of protons of enolate  $\text{C}=\text{C}$  bond or of methyl group linked to this bond at 4.5 or 1.7 ppm. These shift values are in accordance with those of calcium acetylacetonate at 5.10 or 1.71 measured in  $\text{DMSO-d}_6$  [17]. In contrast to the above, the  $^1\text{H}$  NMR signals of prepared transition metal AAEMA-complexes are clearly broad, which is typical with paramagnetic compounds [18]. Based on magnetic susceptibility measurements of the copper(II) or nickel(II) AAEMA-complex the magnetic moments were calculated to be 1.65 or 3.24 Bohr magnetons, respectively corresponding to one or two unpaired electrons. The IR spectra of AAEMA-complexes show two additional strong absorption bands compared to the AAEMA spectrum between 1599-1642 and 1513-1530  $\text{cm}^{-1}$ . The first signal can be assigned to chelated carbonyl stretching vibrations, while the other band to the  $\text{C}=\text{C}$  stretching vibrations of the endolic double bond [19-23].

The radical polymerization of AAEMA-complexes were carried out in DMF in the presence of AIBN. During the polymerization of the copper (II) complex the precipitation of polymerized complex started after 2 minutes under the condi-

tions which are shown in Table 2. As a result of high viscosity at the beginning of polymerization, monomer conversion after 30 minutes was about 75.5%, whereas with AAEMA only 17.2% conversion was realized. The successful polymerization was confirmed by the fact, that the acidic hydrolysis of the crude product yielded a polymer. For example the polymeric complex formed after 1h (Tab. 2) yielded after hydrolysis with aqueous HCl a polymer with a number-average molecular weight of 10400 g/mol and the  $^1\text{H}$  NMR and IR spectra, and elemental analysis are in agreement with that of poly(AAEMA).

Analogous to  $\text{Cu}(\text{AAEMA})_2$  also the other AAEMA-complexes were radically polymerizable (Tab. 3). In contrast to the transition metal AAEMA-complexes, the solubility of  $\text{Ca}(\text{AAEMA})_2$  was poor and only 0.1 molar solution of it in DMF could be prepared. The polymerizations were accompanied by precipitation of polymeric complexes. The lower monomer conversion of the cobalt or nickel complexes in comparison to the calcium or copper complexes was unexpected. These may be caused by the participation of the Co- or Ni-complex in the chain termination reaction of polymerization [23,24].

Table 3 Polymerization of various AAEMA-complexes (0.1 mol/l) in the presence of AIBN (10 mmol/l)

Metal(II) complex	Conversion (%) <sup>1)</sup>
copper	84.8
calcium	88.3
nickel	28.8
cobalt	43.7

1) Polymerization time: 20 h

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