

## Controlled synthesis of homopolymers and block copolymers based on 2-(acetoacetoxy)ethyl methacrylate via RAFT radical polymerisation

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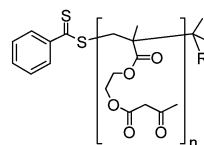
**Reversible addition–fragmentation chain transfer (RAFT) radical polymerisation enables to synthesise well-defined homopolymers and block copolymers based on 2-(acetoacetoxy)ethyl methacrylate, which are capable to strongly coordinate to metals and metal ions.**

Coordination compounds play an extraordinary role in diverse areas like supramolecular chemistry,<sup>1</sup> chemistry of living matter and biominerals, catalysis, hydrometallurgy or waste-water treatment.<sup>2</sup> In recent decades, polymer science has strongly been entering the field of inorganic–organic hybrid materials, aiming to combine potential applications of metal compounds with special properties of block copolymers, namely the formation of nanometer-scale structured materials, the electrosteric stabilisation of colloids, and good mechanical performance.<sup>3,4</sup>

We are in particular interested in block copolymers carrying  $\beta$ -dicarbonyl moieties, which are known to act as strong bidentate ligands, capable of coordinating a wide range of metal ions with different geometries and oxidation states.<sup>5</sup> The monomer of choice is 2-(acetoacetoxy)ethyl methacrylate (AEMA), which is a commercially available product.<sup>†</sup> Up to the present, only the free radical (co-)polymerisations of AEMA, producing polydisperse homopolymers (*cf.* the SEC trace C in Fig. 2) and random copolymers, have been reported.<sup>2</sup>

The first example of an AEMA block copolymer with a narrow molecular weight distribution (MWD) (apparent polydispersity index, PDI < 1.1) was synthesised by us *via* a chemical modification route, *i.e.* the azeotropic esterification of a poly(2-hydroxyethyl methacrylate) segment with *tert*-butyl acetoacetate in a benzene–water mixture.<sup>6</sup> This procedure can be applied to prepare well-defined copolymers, but fails to produce AEMA homopolymers, which is due to its insolubility in the reaction medium.

To overcome this limitation, among others, we considered to use a technique of controlled radical polymerisation—an overview of available procedures is given in ref. 7. For our purpose, reversible addition–fragmentation chain transfer (RAFT) radical polymerisation appeared to be the method of choice: it promotes a well-controlled polymerisation of methacrylate monomers and does not involve any kind of a metal ion complex catalyst, as found in atom transfer radical polymerisation (ATRP), that might interfere with the  $\beta$ -dicarbonyl group of AEMA. Following a standard recipe described in the literature,<sup>8</sup> RAFT radical polymerisation of AEMA was performed in the presence of either 2-cyano- or 2-phenyl-prop-2-yl dithiobenzoate (CPDB or PPDB, respectively) as the chain transfer agent (CTA) and 2,2'-azobis(isobutyronitrile) (AIBN) as the radical source in ethyl acetate (EA) at 60 °C. First experiments indicate that the polymerisation follows a first-order kinetics with respect to AEMA. The products were characterised by means of NMR and size exclusion chromatography (SEC).<sup>‡</sup> <sup>1</sup>H NMR confirmed the expected chemical structure of poly(AEMA) as depicted in Fig. 1. The number-average molecular weights ( $M_n$ ) of polymers were found to increase linearly with the conversion of AEMA, but were usually ~70% higher (NMR) than calculated from the ratio  $[AEMA]_0/[CTA]_0 \times \text{conversion}$ . Evidently, a considerable

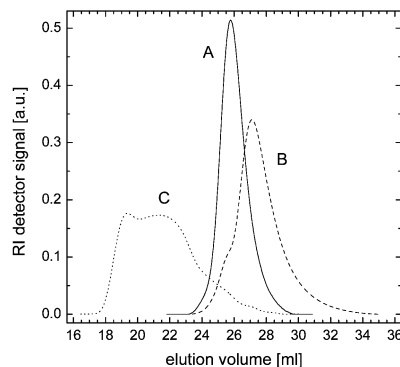


**Fig. 1** Chemical structure of poly(AEMA) (keto tautomer)<sup>6</sup> (R = CN, C<sub>6</sub>H<sub>5</sub>), produced by RAFT radical polymerisation.

fraction of CTA molecules seems not to be active in the RAFT process. SEC shows that the polymer samples have a monomodal and narrow MWD (PDI < 1.2) (*cf.* SEC trace A in Fig. 2). These results suggest that RAFT promotes a controlled radical polymerisation of AEMA.

We also investigated the ATRP of AEMA using *tert*-butyl  $\alpha$ -bromoisobutyrate ( $\alpha$ BiB) as the initiator and CuBr/4,4'-dinonyl-2,2'-bipyridine (dNbpy) as the catalyst complex in methyl ethyl ketone (MEK) at 90 °C.<sup>9</sup> Here, a product with a bimodal and fairly broad MWD (SEC trace B in Fig. 2, PDI ~ 1.5) was obtained. It should be noted that in the early stages of polymerisation the colour of the reaction mixture turned from red–brown to yellow. This points to a structural change of the catalyst complex, perhaps the dNbpy ligand being exchanged by the growing multidentate AEMA chains. With the tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>TREN) ligand,<sup>10</sup> however, we obtained an insoluble polymer gel. We assume that Me<sub>6</sub>TREN as a base is sufficiently strong to abstract CH-acidic protons of AEMA, thus promoting an aldol-type cross-linking of the polymer chains.

Having well-defined samples of poly(AEMA) in our hands, we were able to determine some of its physical properties. Poly(AEMA) was found to dissolve in chloroform, tetrahydrofuran, ethyl acetate or dimethyl sulfoxide, but is insoluble in cyclohexane, benzene, methanol or water. Its specific density is 1.263<sub>2</sub> g ml<sup>-1</sup>, as measured for a sample with a molecular weight of 6.6 kg mol<sup>-1</sup> (PDI = 1.16). For this sample and a



**Fig. 2** SEC chromatograms of poly(AEMA) obtained by RAFT (A), atom transfer (B) and free radical polymerisation (C). *Experimental conditions:* A:  $[AEMA]_0 = 5.2$  M,  $[CPDB]_0 = 0.271$  M,  $[AIBN]_0 = 36.0$  mM, solvent: EA, temperature: 60 °C, reaction time: 18 h. B:  $[AEMA]_0 = 2.1$  M,  $[\alpha\text{BiB}]_0 = 10.5$  mM,  $[\text{CuBr}]_0 = 7.4$  mM,  $[\text{CuBr}_2]_0 = 0.4$  mM,  $[\text{dNbpy}]_0 = 14.7$  mM, MEK, 90 °C, 80 min; C:  $[AEMA]_0 = 2.1$  M,  $[AIBN]_0 = 10.0$  mM, EA, 60 °C, 20 h.

poly(AEMA) with  $M_n = 22.7 \text{ kg mol}^{-1}$  (PDI = 1.13), a glass transition point was observed by differential scanning calorimetry (DSC) occurring at  $+3.0 \text{ }^\circ\text{C}$  ( $\Delta C_p = 0.269 \text{ J g}^{-1} \text{ K}^{-1}$ ) and  $+3.4 \text{ }^\circ\text{C}$  ( $\Delta C_p = 0.306 \text{ J g}^{-1} \text{ K}^{-1}$ ), respectively. Poly(AEMA) is thermally stable up to  $\sim 200 \text{ }^\circ\text{C}$  (thermogravimetric analysis (TGA)).<sup>¶</sup> \*\*

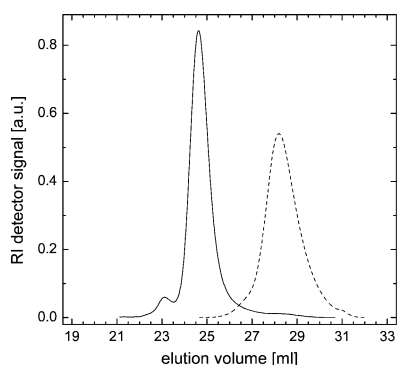
As mentioned above, it is our main goal to synthesise linear amphiphilic block copolymers with a poly(AEMA) segment. RAFT radical polymerisation is known as a versatile method which allows to prepare a large number of polymers with complex architectures like block, star, or graft copolymers.<sup>11</sup> Table 1 shows a list of AEMA block copolymers synthesised by us; as second monomers we used methyl methacrylate (MMA), *n*-butyl (meth)acrylate (BMA, BA), or *N*-isopropylacrylamide (NiPAM). The block structure of copolymers was confirmed by <sup>1</sup>H NMR and SEC analysis. All samples were found to exhibit a fairly narrow MWD with a PDI < 1.3 (SEC). Exemplarily, the SEC trace of poly(AEMA)-*b*-poly(BMA) (Table 1, #3) is shown in Fig. 3. As indicated by SEC, the samples contain up to 10 wt% of homopolymer residuals ( $\sim 3 \text{ wt}\%$  in the case of sample #3) and a fraction of presumably recombined polymer chains (*cf.* Fig. 3, peak arising at  $\sim 23 \text{ ml}$ ). However, even though the quality of copolymers should be satisfactory for most applications, we are working to further optimise polymerisation conditions.

We prepared the poly(AEMA) first block segment in a separate run and used it as a 'macro-CTA' (*cf.* Fig. 1) for the polymerisation of the second monomer. It is also possible to

**Table 1** Block copolymers based on AEMA prepared by RAFT radical polymerisation in EA (#5: dioxane) at  $60 \text{ }^\circ\text{C}$ , reaction time: 12–20 h

Sample <sup>a</sup>	$M_n^c$ (kg mol <sup>-1</sup> )	$w_{\text{AEMA}}^{bc}$	PDI <sup>d</sup>	Yield <sup>e</sup> (%)
poly(AEMA)- <i>b</i> -poly(MMA)	12.9	0.73	1.20	38
poly(MMA)- <i>b</i> -poly(AEMA)	15.1	0.47	1.12	95
poly(AEMA)- <i>b</i> -poly(BMA)	34.8	0.19	1.15	84
poly(AEMA)- <i>b</i> -poly(BA)	14.9	0.63	1.22	49
poly(AEMA)- <i>b</i> -poly(NiPAM)	12.3	0.56	1.17	56

<sup>a</sup> See text for abbreviations. <sup>b</sup> Weight fraction of AEMA in the copolymer. <sup>c</sup> Determined by <sup>1</sup>H NMR. <sup>d</sup> SEC. <sup>e</sup> Gravimetric analysis.



**Fig. 3** SEC chromatogram of poly(AEMA)-*b*-poly(BMA) (solid line) (Table 1, #3) and of the corresponding poly(AEMA) precursor (dashed line) ( $M_n = 6.6 \text{ kg mol}^{-1}$ , PDI = 1.16).

perform a sequential polymerisation of comonomers and to reverse the sequence of monomer addition; this was exemplarily shown for the system AEMA/MMA (entries #1, 2 in Table 1). However, the poly(AEMA) macro-CTA seems to be more effective in the RAFT process than the low-molecular weight CPDB (see above). This apparent molar mass-dependence of the efficiency of CTAs is currently being investigated by us.

In the future, we aim to extend the palette of available block copolymers and to screen application potentials for nanocasting<sup>3,12</sup> and biomineralisation processes.<sup>4</sup> Also, we are using micellar or vesicular aggregates<sup>3</sup> as 'nano containers' to solubilise metal ions in media, in which otherwise they were totally insoluble—first results have already been communicated.<sup>6</sup> Systematic studies on the aggregation behaviour of poly(BMA)-*b*-poly(AEMA) and its complexes with different metal ions ( $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pd}^{2+}$ ) in hydrocarbon solvents will be reported in a forthcoming publication.

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## Notes and references

† Sigma–Aldrich, product #36,076-7.

‡ <sup>1</sup>H NMR spectra were recorded at  $25 \text{ }^\circ\text{C}$  in  $\text{CDCl}_3$  with a Bruker DPX-400 spectrometer operating at 400.1 MHz.

§ SEC with simultaneous UV and RI detection were performed at  $25 \text{ }^\circ\text{C}$  using THF as the eluent at a flow rate of  $1.0 \text{ ml min}^{-1}$ . The column set consisted of three  $300 \times 8 \text{ mm}$  MZ-SDplus (spherical polystyrene particles with an average diameter of  $5 \mu\text{m}$ ) columns with pore sizes of  $10^3$ ,  $10^5$  and  $10^6 \text{ \AA}$ . Chromatograms were evaluated using a poly(MMA) calibration curve.

¶ Density measurements were performed on a density meter DMA 5000 (Anton Paar) at  $25 \text{ }^\circ\text{C}$ . The specific density of the bulk polymer was extrapolated from the density data measured for EA and a  $0.9 \text{ wt}\%$  solution of the polymer in EA.

|| DSC was measured on a Netzsch DSC 200 at a heating/cooling rate of  $10 \text{ K min}^{-1}$ . The glass transition temperature ( $T_g$ ) was determined from the inclination point of the second heating curve.

\*\* TGA was performed on a Netzsch TG 209 at a scanning rate of  $20 \text{ K min}^{-1}$ .

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