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An in-depth analytical approach to the mechanism of the RAFT process in acrylate free radical polymerizations via coupled size exclusion chromatography–electrospray ionization mass spectrometry (SEC–ESI-MS)

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Abstract

Coupled size exclusion chromatography (SEC)–electrospray ionization mass spectrometry (ESI-MS) was applied to carefully map the product spectrum of a series of acrylate free radical polymerizations mediated via the reversible addition fragmentation chain transfer (RAFT) process. The product stream of a significantly rate retarded RAFT system (i.e. *n*-butyl acrylate (BA)/cumyl dithiobenzoate (CDB)) was compared with the less rate retarded RAFT polymerizations of BA mediated by cumyl phenyl dithioacetate (CPDA) and methyl acrylate (MA)/CPDA. In each case excellent agreement between the theoretical and experimental masses, as well as the simulated isotopic peak distributions, of polymeric species in the product stream was observed. Although conventional disproportionation and combination bimolecular termination products were clearly identified within the product spectra, the presence of irreversibly terminated RAFT intermediates, i.e. 3-armed star polymers, was not observed. The mass spectroscopic results are compared to modeling estimations (carried out via the PREDICI® program package) of the concentration ratios of 3-armed stars vs. conventional termination products. It is demonstrated that the occurrence of conventional termination products should be accompanied by a significant product stream associated with 3-armed star polymer material if cross termination was operational—at least under the current reaction conditions. The absence of three armed star polymer products in the polymers stream suggests that irreversible cross termination reactions may be of minor importance in the present systems.

Keywords: Reversible addition fragmentation chain transfer (RAFT) polymerization; Mechanism and kinetics; Electrospray ionization mass spectrometry (ESI-MS)

1. Introduction

Controlled/living free radical polymerization is one of the most rapidly developing fields of polymer science. All living techniques—including nitroxide mediated polymerisation (NMP) [1], atom transfer free radical polymerisation (ATRP) [2], and reversible addition fragmentation chain transfer polymerisation (RAFT) [3]—aim to control the molecular weight and polydispersity of the resulting polymers. RAFT is a very versatile method with respect to the monomers that can be successfully polymerized and the temperature range in which the corresponding polymerizations can be carried out. In addition, RAFT polymerization enables the formation of a large variety of macromolecular architectures such as block copolymers [4], star shaped molecules [5] and comb structures [6]. Applications for RAFT also include generating novel structures and materials for use in bioengineering and nanotechnology. Copolymers made via the RAFT process have been used both to stabilize transition metal nanoparticles [7] and develop nano- and micro-porous materials [6,8,9]. The

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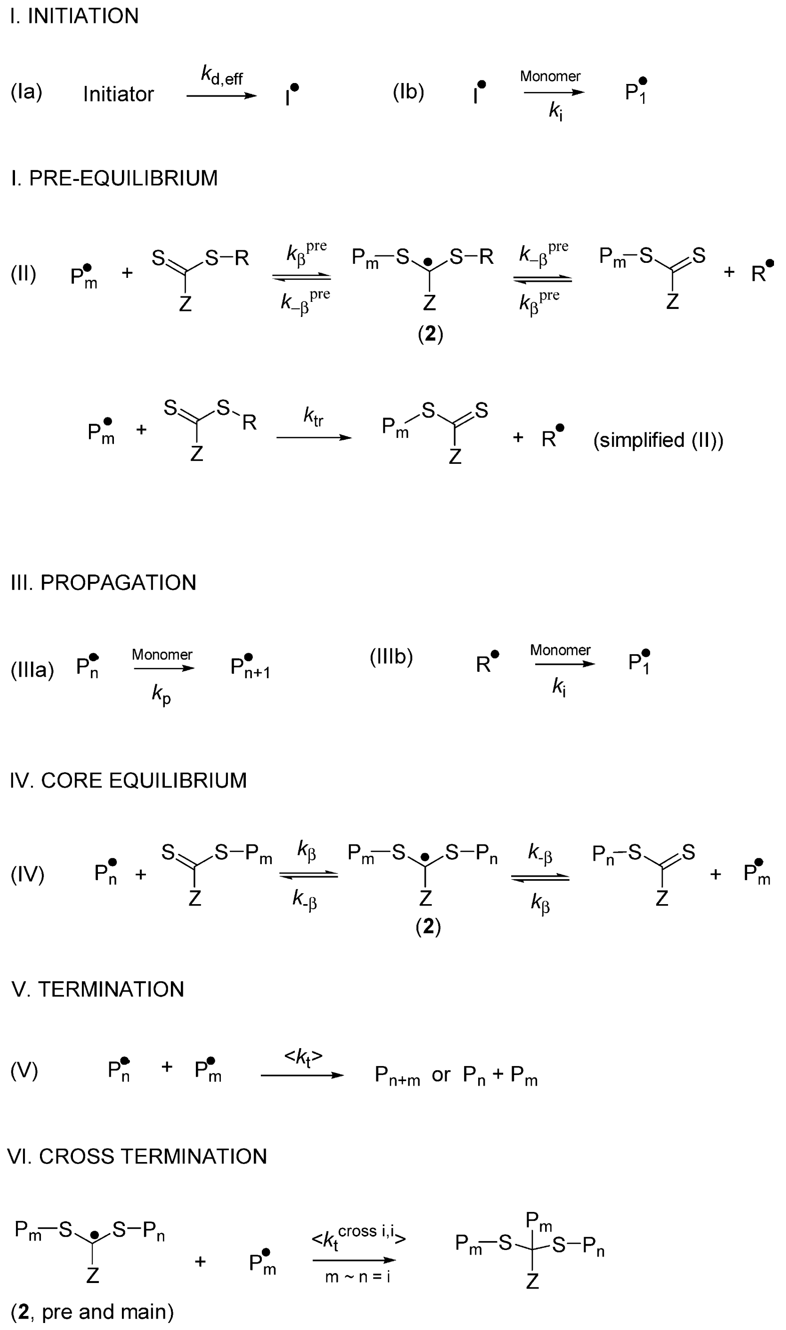


Scheme 1. Basic mechanism of the reversible addition fragmentation chain transfer (RAFT) process.

CAMD group designed biocompatible nano-containers for delivery applications via RAFT mediated polymerizations [10]. The basic underpinning mechanism of the RAFT process is shown in Scheme 1.

The reaction sequence depicted in Scheme 1—alongside the associated rate coefficients—also servers as the basis for modelling the RAFT process with the aim of estimating the theoretically expected product spectrum for various rate coefficient combinations (i.e. k_β^{pre} and $k_{-\beta}^{\mathrm{pre}}$, k_β and $k_{-\beta}$ as well as $\langle k_t^{\mathrm{cross}}\rangle$). The pre-equilibrium may be simplified by considering it as a non-reversible transfer reaction [simplified (II)] in which the leaving group, R, is released as an initiating free radical. Thus, the transfer rate coefficient, $k_{\mathrm{tr\ RAFT}}$, can be expressed as a composite of the k_β^{pre} and $k_{-\beta}^{\mathrm{pre}}$ rate coefficients [11]. Not shown in Scheme 1 are termination reactions between free polymeric radicals and initiator derived radicals, $\mathrm{I}^\cdot$, or initial RAFT agent derived radicals, $\mathrm{R}^\cdot$.

Despite the versatility and extensive use of RAFT mediated polymerizations, the mechanism of this process is still subject to a lively scientific debate [12–15]. Especially in situations where the RAFT process is employed as a kinetic tool to map out chain length dependent termination rate coefficients, [16,17] information about its mechanism is crucial for the data evaluation. The current discussion is focused on the explanation for rate retardation phenomena, which have been observed for some monomer/RAFT agent systems including styrene/cumyl dithiobenzoate (CDB). Significant evidence has been put forward for a relatively long lifetime of these species, i.e. a slow fragmentation rate coefficient/large equilibrium constant [18–21] leading to a radical sink. Other researchers argue that the rate retardation effects are caused by cross termination reactions (see reaction step (VI) in Scheme 1) between the intermediate radical species and other (propagating) radicals, accompanied by a relatively small (main and/or pre) equilibrium constant [22,23].

For a better understanding of these mechanistic details of the RAFT process, great effort has been directed into obtaining detailed information about the intermediate radicals [22–25]. However, only limited research has been directed into finding possible cross termination products within the polymeric material [12,26,27]. In this respect it should be noted that Tonge and co-workers [28] identified the products of coupling reactions involving the RAFT intermediate radical in polymerizing systems. However, these authors were careful to stress that these products were only observed in extremely low concentrations and under very forceful reaction conditions (i.e. very high initial RAFT agent concentrations) that bear little relation to actual polymerization systems. It has been pointed out that the concentration of these species may be low and, therefore, an identification using conventional molecular weight analysis tools, such as size exclusion chromatography (SEC), would be rather difficult [23].

Identifying possible products of all reaction pathways in a RAFT process requires highly sensitive experimental techniques such as mass spectrometry. The potential of mass spectrometric analysis of synthetic polymers has been discussed in numerous publications, including review articles [29–33]. The two main mass spectrometry techniques for polymers are matrix assisted laser desorption and ionization—time of flight mass spectrometry (MALDI-TOF) [34] and electrospray ionization mass spectrometry (ESI-MS) [35]. Whereas the accessible mass range for MALDI-TOF-MS is significantly larger ($m/z \cong 100{,}000$ amu) than for ESI-MS ($m/z < 4000$ amu), ESI-MS is a very soft ionization technique and may allow for polymer sample ionization with very limited fragmentation.

ESI-MS (in combination with on-line pre-separation of the polymer sample in a low molecular weight SEC) has been successfully applied in a recent study by the CAMD group on the cumyl dithiobenzoate (CDB) mediated RAFT polymerization of methyl acrylate [12]. These researchers could identify the products corresponding to the polymeric RAFT agent as well as disproportionation and recombination termination products, but no evidence of products associated with termination of intermediate radical species such as 3- or 4-armed polymer stars was found. Although there is some ambiguity associated with the disproportionation products of the intermediate radical species, the CAMD group identified a peak in close vicinity to the theoretical expected mass of the intermediate radical (species (**2**) in Scheme 1). These initial findings may suggest that the intermediate radical species is stable enough to be present in the SEC–ESI-MS spectrum. However, this notion could not be confirmed by Venkatesh et al.—albeit under different polymerization and mass spectroscopic conditions—who found no evidence of intermediate macroRAFT radicals in a recent MALDI-TOF-MS study of a RAFT acrylate system [26]. While the same authors did confirm the earlier CAMD findings that no 3-armed star polymers can be identified in the RAFT product stream [12,26], they have also demonstrated that 3-armed star butyl acrylate polymers made under non-RAFT conditions are stable during MALDI-TOF analysis.

The aim of the present study is to further investigate the mechanistic details of the RAFT process, particularly the potential side reactions of the intermediate radical species. In here we follow the methodology used in Ref. [12] and analyze the polymeric material of RAFT mediated polymerizations by means of ESI-MS coupled with SEC. The approach taken is twofold: (i) polymerizations mediated with a RAFT agent that stabilizes the intermediate species (i.e. CDB) will be compared with polymerizations using cumyl phenyl dithioacetate (CPDA), a RAFT agent with a non-stabilizing Z-group. (ii) Polymerizations of *n*-butyl acrylate (BA) will be simulated using the program package PREDICI® for several combinations of the rate coefficients governing the pre- and main-equilibria as well as for different values of the coefficient for the (potential) cross termination reaction of the intermediate species, $\langle k_t^{\mathrm{cross}} \rangle$. The aim of these simulations is to predict the concentrations of termination products of the intermediate species in comparison to polymeric material generated by recombination of two propagating macroradicals. The modeling of RAFT mediated polymerizations using PREDICI® has been thoroughly described in earlier publications [19,36–39]. Details of the implementation of the RAFT process into this program package will not be reiterated in the present study.

2. Experimental

2.1. Polymer preparation

n-Butyl acrylate (BA, Aldrich 99%) and methyl acrylate (MA, Aldrich 99%) were purified by passing over basic alumina and thoroughly deoxygenated by purging with nitrogen gas. Cumyl dithiobenzoate (CDB) was synthesized using the method of Oae et al. [40] employing *n*-hexane as the solvent. Cumyl phenyl dithioacetate (CPDA) was prepared using the method given in Ref. [41]. Mixtures of RAFT agent ($c^0_{\mathrm{RAFT}} = 1.0 \times 10^{-2}$ mol L^{-1}), monomer and 2,2′-azobisisobutyronitrile (AIBN, Aldrich, 99%, recrystallized twice from ethanol, $c^0_{\mathrm{AIBN}} = 3.5 \times 10^{-3}$ mol L^{-1}) or azobis(cyclohexane–carbonitrile) (ACHCN, Aldrich, 98%, recrystallized twice from ethanol, $c^0_{\mathrm{ACHCN}} = 4.1 \times 10^{-1}$ mol L^{-1}) as the initiator were heated at 80 °C for times varying between 6 and 15 min. The resulting polymers were isolated by evaporating off the residual monomer.

2.2. Coupled size exclusion chromatography–mass spectrometry

SEC–ESI-MS experiments were carried out using a Thermo Electron LCQ Deca ion trap mass spectrometer (Thermo Electron, San Jose, CA, USA) coupled with an HPLC pump including solvent mixing unit and autosampler (Thermo Electron SCM1000, P4000 and AS3000), two low molecular weight high resolution size exclusion chromatography columns (Phenomenex Phenogel 50 and 100 Å, bead size 5 µm, column temperature 25 °C) and a UV/vis detector set to the absorption maximum of the dithiobenzoate/dithioacetate end groups (Thermo Electron UV2000). The flow rate of the system was 0.35 mL min^{-1}, the injection sample concentration was close to 5 mg mL^{-1} and the injection volume into the SEC system was 5.0 µL. Thus, prior to mass spectrometric analysis, the polymer is fractionated via the SEC system. The ESI-MS spectrometer is equipped with an atmospheric pressure ionization source operated in nebulizer assisted electrospray mode. The instrument was calibrated with caffeine, MRFA, and Ultramark 1621 (all from Aldrich) in the mass range of 195–1822 amu. All spectra were acquired in positive ion mode over a range of m/z 500–2000 with a spray voltage of 5 kV, a capillary voltage of 26 V and a capillary temperature of 295 °C. Nitrogen was used as sheath gas (flow: 50% of max) while helium was used as auxiliary gas (flow: 10% of max). The eluent was a 6:4 v/v mixture of THF/methanol with sodium acetate used as the doping salt ($c = 0.25$ mM). Simulated isotopic pattern generation was done using the Xcalibur program, included with the thermo electron ESI-MS. The theoretical molecular weight over charge ratios, m/z (always assuming $z = 1$) are calculated using the exact molecular mass of the predominant isotope within the structure.

2.3. Simulations

All simulations have been carried out using the program package PREDICI®, version 5.36.4a, on a Pentium IV (HT), 2.6 GHz IBM compatible computer.

3. Results and discussion

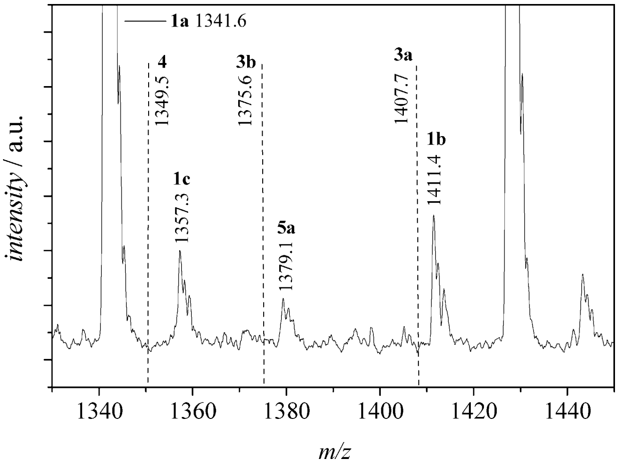
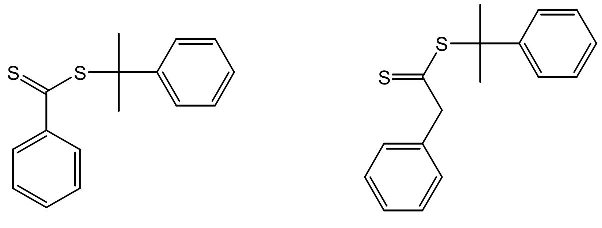


Fig. 1. ESI-MS spectrum of polymeric material from the MA/CPDA system generated at 80 °C using ACHCN as the thermally decaying initiator. The dashed lines give the potential m/z values for species (**3a**), (**3b**) and (**4**).

Polymerizations of methyl acrylate with cumyl dithiobenzoate as the RAFT agent have been investigated by Ah Toy et al. in great detail [12]. As mentioned above, these authors found no evidence for termination products of the intermediate species such as 3- or 4-armed stars, but a peak in the close vicinity of the intermediate radical had been observed. The (possible) occurrence of stabilized intermediate species (**2**) (Scheme 1) may be envisaged when using RAFT agents with a stabilizing Z-group, such as CDB (see Scheme 2). The change to a non-stabilizing RAFT agent such as cumyl phenyl dithioacetate (CPDA)—carrying a benzyl Z-group—should result in no signals corresponding to (**2**). Recently, the CAMD group and Coote have demonstrated that the notion of long lived intermediate radicals can be consistent with both experimental rate data (albeit via a model dependent analysis) and (model independent) ab initio quantum mechanical predictions [19].

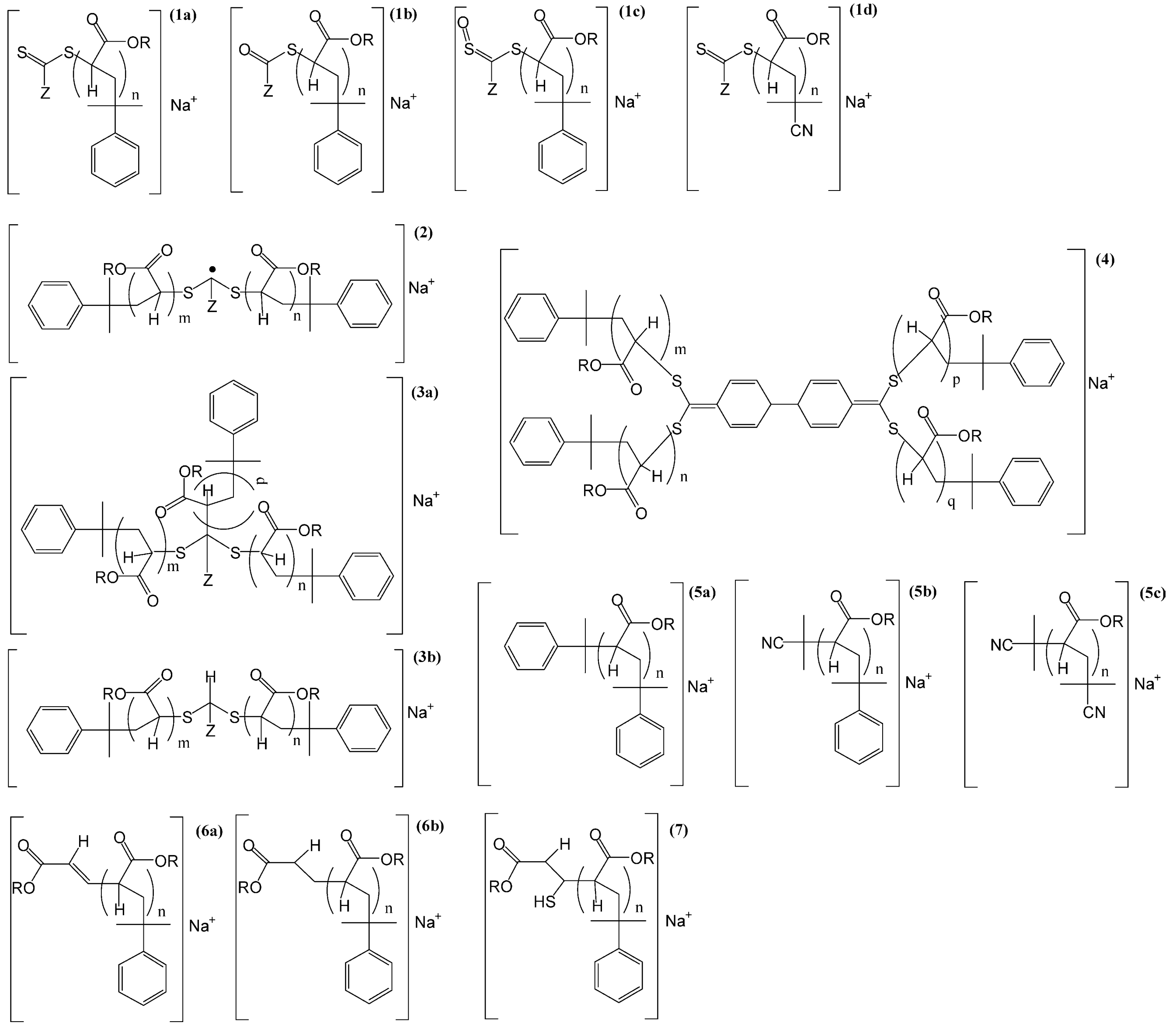
Fig. 1 depicts the ESI-MS spectrum of the polymeric material obtained from a CPDA mediated polymerization of methyl acrylate (MA) at 80 °C. An overview of possible reaction products for RAFT mediated polymerizations is shown in Scheme 3. It should be noted that the polymeric material presented in Fig. 1 was obtained from a polymerization initiated by azobis(cyclohexane–carbonitrile) (ACHCN) to avoid peak overlap for certain products [12].

Inspection of Fig. 1 indicates the presence of products associated with the basic RAFT mechanism as well as



CDB CPDA

Scheme 2. Structural representation of the RAFT agents cumyl dithiobenzoate (CDB) and cumyl phenyl dithioacetate (CPDA) employed in the present study.



Scheme 3. Overview of the possible ions generated by electrospray ionization of the polymeric material from the RAFT mediated polymerizations. The structures shown are valid for AIBN initiated polymerizations.

oxidation [42] and termination products. Peak (**1a**) corresponds to a macroradical initiated by a cumyl radical fragment and capped by a RAFT end group, whereas the peaks (**1b**) and (**1c**) may be assigned to oxidation products of (**1a**) (Scheme 3). The product stream also contained a significant concentration of the combination product (**5a**), which may overlap with the thiol (**7**) (see also the discussion of the pBA spectra below). In agreement with the presumption made above, a peak corresponding to the intermediate radical (**2**) could not be identified in the spectrum. It may be concluded that reducing the stability of a (potential) intermediate radical leads to a loss of their corresponding signal in the ESI-MS spectrum. No indication of three (**3a**) or four armed stars (**4**) can be discerned in Fig. 1. This confirms the observations made in Ref. [12] for the MA/CDB system, where also no peaks corresponding to these species have been identified.

To further investigate the possible occurrence of stabilized intermediate radicals and termination products of these species, we studied polymerizations of butyl acrylate (BA) mediated with CDB and CPDA as the RAFT agent and AIBN as thermally decaying initiator. The lower part of Fig. 2 shows the ESI-MS spectrum of the polymeric material obtained from the BA/CDB polymerization. The upper part of Fig. 2 gives the simulated isotopic patterns for the ions as a further confirmation of their assignments.

As in Fig. 1, peak (**1a**) corresponds to a macroradical with a RAFT end group, where the peaks (**1b**) and (**1c**) originate from oxidation products of (**1a**). Peak (**1d**) can be

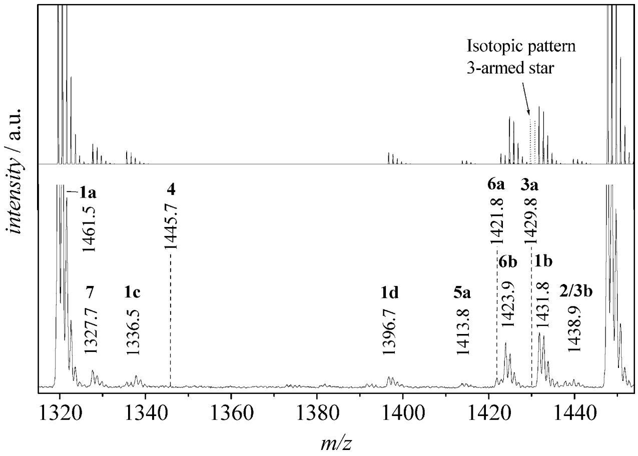


Fig. 2. ESI-MS spectrum of polymeric material from the BA/CDB system generated at 80 °C using AIBN as the thermally decaying initiator (lower part) as well the simulated isotopic pattern (upper part) including the potential pattern for the three armed star, species (**3a**).

assigned to a macroradical initiated by an initiator fragment and capped by a RAFT end group. The sample also contains small amounts of the combination product (**5a**) as well as larger concentrations of the disproportionation products (**6a**) and (**6b**). Chains terminated by a thiol functionality (**7**), recently observed by Llauro et al. [43], are also present in this RAFT system. The ESI-MS spectrum shows no evidence of any termination products of the intermediate radical, i.e. 3-armed star polymers (**3a**), as indicated by the missing isotopic peak patterned associated with (**3a**) in the experimental spectrum in the lower part of Fig. 2. In addition, no traces of species (**4**) can be identified in all the spectra (as indicated by the associated dashed lines). Some care, however, should be exercised when judging the presence or absence of (**4**), since there is the possibility that this more labile species may undergo fragmentation during the ionization process. In addition, it should be noted that the absence of a peak in the ESI-MS spectrum is not necessarily a proof for the absence of the corresponding species in the polymeric material, as the occurrence of peaks also requires a sufficient degree of ionization of the polymer chain. However, since ionization is mainly taking place through the acrylic polymer backbone, it is very likely that all chains—at least in the mass range under consideration—have similar ionization potentials. A peak in close vicinity of the expected mass of the intermediate radical (or the hydrogen terminated species) can also be identified in the spectrum, viz. species (**2**) or (**3b**). Such observations have also been made by other researchers earlier [44]. As mentioned above, the same observation has been made for the MA/CDB system [12]. The occurrence of these species has been correlated with the use of a RAFT agent with a stabilizing Z-group. To further confirm this assumption, the polymeric material generated in butyl acrylate polymerizations mediated by a non-stabilizing RAFT agent, CPDA, were subjected to ESI-MS analysis. The ESI-MS spectrum of the polymer obtained from the BA/CPDA system is shown in Fig. 3, alongside the isotopic pattern simulation of the assigned peaks.

In addition to the main product (**1a**), the oxidation products (**1b**) and (**1c**), the chain with an initiator end group (**1d**) as well as polymer from combination (**5a**, **5b**) and disproportionation reactions (**6b**) can be identified. It should be noted that some of the intensities of the peaks of the above products are very low (i.e. (**5a**, **5b**)) and some caution has to be exercised in these peak allocations. The spectrum again shows significant amounts of the thiol species (**7**). The main observations from Fig. 3 are the absence of peaks corresponding to the 3-armed star (**3a**) and the intermediate radical species (**2**). The results obtained so far may be thus summarized as follows: the polymerizations mediated by a RAFT agent with a stabilizing Z-group (CDB) yield polymeric material with a peak in close vicinity to the expected mass for the intermediate radical. As discussed above, CDB mediated polymerizations exhibit strong rate retardation phenomena [12,13,18,19,22,23]. Although the peak which may be attributed to the intermediate radical is weak and there may be other possible products with similar masses, the data presented for the BA/CDB system together with the results for MA/CDB [12] give some indication that rate retardation phenomena is related to intermediate species with a significant lifetime in either the pre- or main equilibrium, i.e. a slow fragmentation rate coefficient. Replacing the stabilizing RAFT agent with a non-stabilizing (CPDA) causes the disappearance of the corresponding peak in methyl acrylate and butyl acrylate polymerizations. Significantly less severe rate retardation has been reported for any CPDA mediated polymerizations [45]. As it is very unlikely that termination reactions of intermediate radicals occur in CDB systems but not in CPDA mediated polymerizations, the reason for these rate retardation phenomena for CBD systems are likely to be associated—at least in part—with the stabilization of the intermediate

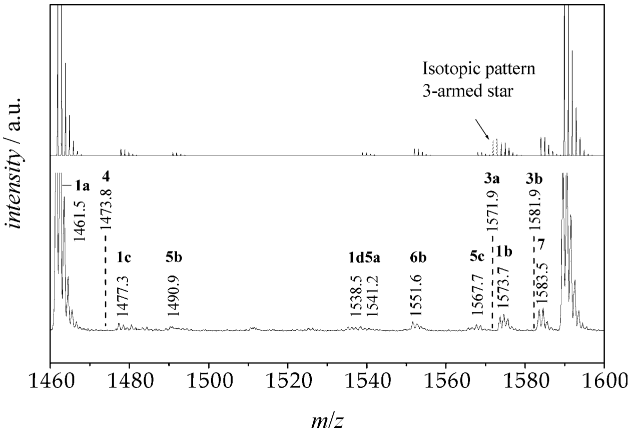


Fig. 3. ESI-MS spectrum of polymeric material from the BA/CPDA system generated at 80 °C using AIBN as the thermally decaying initiator (lower part) as well as the simulated isotopic pattern (upper part) including the potential pattern for the three armed star, species (**3a**).

radicals. In addition, for none of the systems under investigations any evidence of termination products of the intermediate species (3- and 4-armed star polymer) could be found.

It should be mentioned that an alternative explanation for a product close to the mass (i.e. the *m*/*z* ratio) of the RAFT intermediate radical, (**2**), in the spectrum may be the subsequent inclusion of a disproportionation product as part of the main polymer chain. Although the RAFT process reduces the amount of termination reactions in a free radical polymerization system significantly, termination via disproportionation may still occur to some extent, even in acrylate systems [46]. The vinyl functionality of the disproportionation product may enable it to react again during the polymerization process as a macromonomer. In the BA/CDB system (based on a chain having 8 monomer units) the theoretical *m*/*z* of (**3b**) is 1439.8 amu, whereas the main polymer chain with a disproportionation product incorporated as a macromonomer has an *m*/*z* of 1437.8 amu. In a previous mass spectroscopic investigation by the CAMD group into the MA/CDB system [12], a difference between the theoretical *m*/*z* of (**3b**) and an actual unidentified peak in the product spectrum was close to 2 amu. The incorporation of a macromonomer into a cumyl and dithiobenzoate capped polymer chain (i.e. an analogue to (**1a**)) gives also a reasonable agreement with the unidentified peak. In the BA/CDB system the presence of both disproportionation products is evident (see compounds (**6a**) and (**6b**) in Fig. 2). However, the abundance of (**6a**)—the vinyl functionalized product—is significantly less than (**6b**). The difference in signal strength may be attributed to the further polymerization of the (**6a**) moiety. This line of reasoning can also be extended to the possible generation of polymer with two disproportionation products incorporated in the polymer chain, resulting in a mass close to the 3-armed termination product. However, the low concentration of the disproportionation products makes such a reaction relatively unlikely. The absence of a signal in the region of the spectrum corresponding to the 3-armed star—even with another possible pathway for the formation of such a product available—gives evidence that cross termination is probably not an extensively frequented reaction pathway. Although the presence or absence of the RAFT intermediate radical in the spectra is difficult to ascertain, the absence of any 3- (and 4-) armed star polymer is evident. Table 1 collates a comparison of theoretical and expected *m*/*z* for all assigned ESI-MS peaks of the current study. Inspection of Table 1 shows the good agreement of the theoretical and experimental masses. In all cases the mass difference was less than 1 amu.

It may be argued that the amount of the 3-armed star polymers in the product stream strongly depends on the reaction conditions and on the kinetic rate coefficients governing the pre-and main-equilibria as well as the (possible) cross termination reaction. We, therefore, simulated CDB mediated butyl acrylate polymerizations (conditions chosen to be identical to the experiments) and to determine which combinations of rate coefficients should yield significant concentrations of 3-armed star polymers. The simulations have been carried out using the program package PREDICI® with a basic set of kinetic coefficients as summarized in Table 2. To avoid further complication, the values for the pre- and main-equilibrium constants were assumed to be identical—an assumption which has recently been shown to be of approximate validity [19]. Starting from the values depicted in Table 1, polymerizations were modeled under variation of (i) the rate coefficient for the termination reaction of intermediate species, $\langle k_{\mathrm{t}}^{\mathrm{cross}}\rangle$, (ii) the fragmentation rate coefficients ($k_{-\beta}^{\mathrm{pre}} = k_{-\beta}$) and (iii) the coefficients for the addition reaction between free macroradicals and (polymeric) RAFT agent, $k_{\beta}^{\mathrm{pre}} = k_{\beta}$. In each simulation, the expected concentration of 3-armed star polymers was compared to the sum of dead polymer chains, i.e. the combination and disproportionation products (**5a**–**c**)

Table 1
Experimental and theoretical *m*/*z* values for the ions detected in MA/CPDA, BA/CDB and BA/CPDA polymerizations

Species	MA-CPDA		BA-CPDA		BA-CDB	
	Theoretical mass	Experimental mass	Theoretical mass	Experimental mass	Theoretical mass	Experimental mass
1a	1341.6	1341.6	1461.8	1461.5	1319.7	1319.7
1b	1411.6	1411.4	1573.9	1573.7	1431.8	1431.8
1c	1357.6	1357.3	1477.8	1477.3	1335.7	1336.5
1d	1416.6	–	1538.8	1538.5	1396.7	1396.7
3a	1407.6	–	1571.9	–	1429.8	–
2	1374.6	–	1580.9	–	1438.8	?
3b	1375.6	–	1581.9	–	1439.8	?
4	1349.5	–	1473.8	–	1445.7	–
5a	1379.7	*1379.1*	1542.0	1541.2	1413.9	1413.8
5b	1368.7	–	1490.9	1490.9	1362.9	–
5c	1403.7	–	1568.0	1567.7	1311.8	–
6a	1431.7	–	1550.0	–	1421.9	1421.8
6b	1433.7	–	1552.0	1551.6	1423.9	1423.9
7	1379.6	*1379.1*	1584.0	1583.5	1327.8	1327.7

Italicized values indicate peaks in the close vicinity of other peaks (potential peak overlap).

Table 2
Basic set of rate coefficients (BA, 80 C) employed in the PREDICI® simulations of the present study

f	k_d/s^{-1a}	k_i	k_p [49]	$\langle k_t\rangle$	$\langle k_t^{\mathrm{cross}}\rangle$	$k_\beta^{\mathrm{pre}} = k_\beta$	$k_{-\beta}^{\mathrm{pre}} = k_{-\beta}$/s^{-1}
0.7	1.1×10^{-4}	48,000	48,000	3×10^8	1.5×10^8	1×10^7	1×10^4

All rate coefficients are given in L mol^{-1} s^{-1} unless otherwise indicated.

[a] The initiator decomposition rate coefficient, k_d, of AIBN was determined via on-line UV/vis spectrometry in butyl acetate at 80 °C.

and (**6a–b**); these species are referred to as 'pBA'. As the pBA moieties were clearly identified in significant amounts in the experimentally obtained polymeric material from the CDB/BA system (Fig. 2) it is expected—if the cross termination product is generated in similar abundance—it also must be visible in the product spectrum. The ratio of the corresponding concentrations was plotted vs. the overall degree of polymerization, P_n, for $8 \leq P_n \leq 30$, i.e. the currently accessible ESI-MS mass range in our experiments. It must be mentioned that the below analysis is based on a cumulative calculation, i.e. all generated polymeric product (whether star or conventional) is continuously accumulated. However, below we will also give an example for a non-cumulative ratio calculation. Fig. 4 shows the outcome for the variation of $\langle k_t^{\mathrm{cross}}\rangle$ with all other coefficients taken from Table 2.

As can be seen from Fig. 4, $\langle k_t^{\mathrm{cross}}\rangle$ was varied between 3×10^8 L mol^{-1} s^{-1}, which is the value associated with the rate coefficient for conventional termination between two macroradicals $\langle k_t\rangle$ (Table 2) and 1×10^5 L mol^{-1} s^{-1}. Very small values of $\langle k_t^{\mathrm{cross}}\rangle$ do not need to be considered as in these cases the importance of the cross termination reaction are negligible, not altering the kinetics or product spectrum of the polymerization process. As expected, the (relative) concentration of the 3-armed star polymers increases with larger values for $\langle k_t^{\mathrm{cross}}\rangle$. For $\langle k_t^{\mathrm{cross}}\rangle = 1\times10^7$ L mol^{-1} s^{-1}, the amount of these species reaches ≅30% of the dead polymer, which is significantly higher than the estimated lowest concentration detectable in the ESI-MS spectrum (10% of the dead polymer, see the intensities of the peaks (**5a–c**) and (**6a–b**) in Fig. 2). As we cannot find any evidence of 3-armed star polymers in the product stream, we argue that $\langle k_t^{\mathrm{cross}}\rangle$ must be smaller than 1×10^7 L mol^{-1} s^{-1}. Fukuda and co-workers recently suggested a potential value for $\langle k_t^{\mathrm{cross}}\rangle$ as being half the size of $\langle k_t\rangle$ [47]. This is not in agreement with the observations made in this study, as for a value of $\langle k_t^{\mathrm{cross}}\rangle = 1.5\times10^8$ L mol^{-1} s^{-1} the quantity of 3-armed star polymer would exceed the concentration of conventional dead polymer.

One may argue against the value chosen for the fragmentation rate coefficient, $k_{-\beta}^{\mathrm{pre}} = k_{-\beta}$. In a next step we, therefore, varied this coefficients between 1×10^3 and 1×10^6 s^{-1} under the assumption of a $\langle k_t^{\mathrm{cross}}\rangle$ as suggested in Ref. [47] and all other coefficients taken from Table 2. The outcome of the simulations is shown in Fig. 5.

As can be seen from Fig. 5 for $k_{-\beta}^{\mathrm{pre}} = k_{-\beta}$ equal or smaller 1×10^4 s^{-1}, the concentration of 3-armed star polymer is expected to be larger than the concentration of conventional termination products. Fig. 5 also indicates that for $k_{-\beta}^{\mathrm{pre}} = k_{-\beta}$ significantly larger than 1×10^5 s^{-1} the concentration of 3-armed star polymer is below the detection limit of the ESI-MS spectrometer. It can be anticipated that the fragmentation rate coefficient in acrylate systems should be lower than in, for example, styrene polymerizations, since acryl radicals display a significantly higher reactivity (or lower stability).

The last set of simulations was carried out for different values for $k_\beta^{\mathrm{pre}} = k_\beta$, the coefficients describing the addition

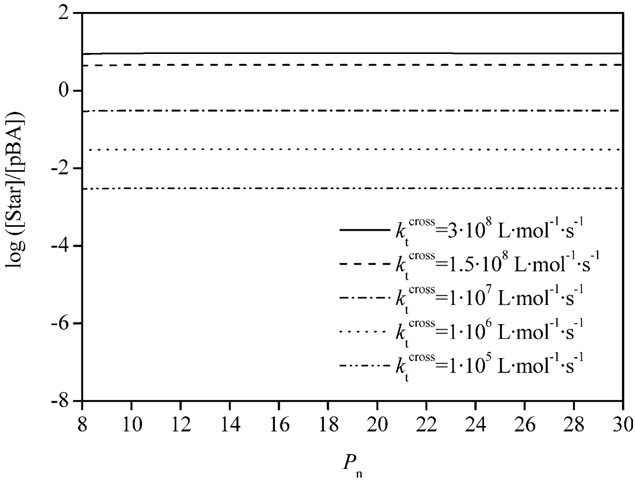


Fig. 4. Simulated ratio of the concentrations of the (potential) 3-armed star species (**3a**) and dead polymer (**5a**, **5b**, **5c**, **6a**, **6b**) for several values of $\langle k_t^{\mathrm{cross}}\rangle$. All other coefficients are taken from Table 2.

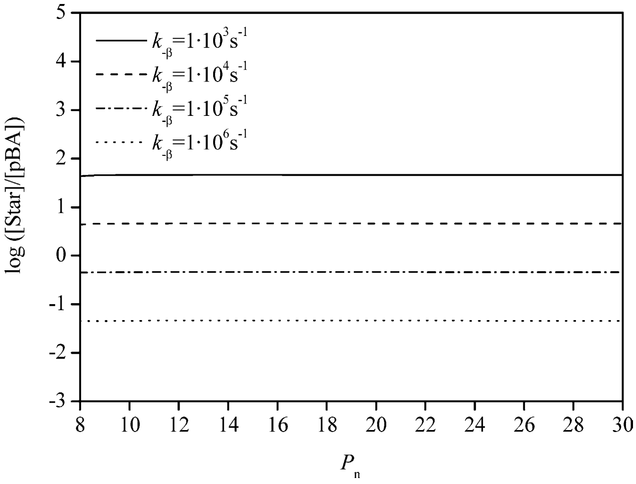


Fig. 5. Simulated ratio of the concentrations of the (potential) 3-armed star species (**3a**) and dead polymer (**5a**, **5b**, **5c**, **6a**, **6b**) for several values of $k_{-\beta} = k_{-\beta}^{\mathrm{pre}}$. All other coefficients are taken from Table 2.

reaction between propagating macroradicals and the (polymeric) RAFT agent. The results for the variation between 1×10^5 and 1×10^8 L mol^{-1} s^{-1}, with all other coefficients according to Table 2, are depicted in Fig. 6.

In the degree of polymerization region considered, there is a significant influence of the addition rate coefficient on the ratio of 3-armed star and conventionally terminated products (Fig. 6). For $k_\beta^{\text{pre}} = k_\beta = 1\times10^7$ or 1×10^8 L mol^{-1} s^{-1} the expected amounts of 3-armed star polymers exceed the concentrations of the conventional termination products, whereas values of 1×10^5 or 1×10^6 L mol^{-1} s^{-1} for the addition rate coefficient yield smaller quantities of star shaped species. However, the simulated molecular weight distributions with the smaller $k_\beta^{\text{pre}} = k_\beta$ feature a strong hybrid behavior [48] between conventional and living free-radical polymerizations, i.e. a rapid rise (within the first few 100 μs) of the molecular weight in the very beginning of the polymerization (to $M_n \cong 1\times10^4$ g mol^{-1} for $k_\beta^{\text{pre}} = k_\beta = 1\times10^6$ L mol^{-1} s^{-1}) followed by a linear increase up to high monomer to polymer conversions. This behavior results in cases when the addition rate coefficient k_β^{pre} (or k_β) is not significantly larger than the propagation rate coefficient, k_p. As the k_p of butyl acrylate at 80 °C may be estimated to be close to 48,000 L mol^{-1} s^{-1} [49], a very high value of the addition rate coefficient is required to avoid any hybrid behavior. The experimentally obtained polymeric material (after several minutes of reaction, see experimental section) for the BA/CDB system (Fig. 2) showed peaks in the mass spectrum close to $m/z = 1400$ amu. It can, therefore, be argued that the addition rate coefficient is at least higher than 1×10^6 L mol^{-1} s^{-1} for the BA/CDB at 80 °C system and is likely to be close to 1×10^7 L mol^{-1} s^{-1}.

As mentioned above, the simulations presented so far are cumulative and do not give the instantaneous ratios of conventional dead polymer to 3-armed star product at a specific chain length. Recently, a set of rate coefficients has been suggested for the CDB/methyl acrylate mediated polymerization at 80 °C and measured concentrations of the intermediate (combined pre- and main-equilibrium) and propagating radicals [50]. At an initial CDB concentration of 2.5×10^{-2} mol L^{-1} and an AIBN concentration of 1.0×10^{-2} mol L^{-1}, an intermediate radical concentration of close to 1.5×10^{-6} mol L^{-1} (for the entire polymerization process) was reported alongside a propagating radical concentration of approximately 1×10^{-8} mol L^{-1}. The rate coefficient of conventional termination was reported to be close to 3×10^8 L mol^{-1} s^{-1}, with cross termination assumed to be 4.5×10^7 L mol^{-1} s^{-1}. With these numbers, it is relatively simple to estimate the rate of formation of conventional dead polymeric material and star polymer. The rate of formation of pMA reads $R^{\text{pMA}} = k_t[P_n][P_n] = 3.0\times10^{-8}$ mol L^{-1} s^{-1}, whereas the rate of star polymer formation is $R^{\text{star}} = k_t^{\text{cross}}[P_n][\text{intermediate radical}] = 6.75\times10^{-7}$ mol L^{-1} s^{-1}. Thus, star polymer is formed (at any given chain length) 22.5 times faster than the conventional dead polymer. It would, therefore, be expected that the concentration of star polymer exceeds that of dead polymer by a factor of close to 22.5. This is clearly not observed in the above discussed mass spectra, where the dead polymeric product is clearly visible, but no trace of three armed star polymer can be discerned.

Under these conditions, a significant concentration of 3-armed star polymers should be expected. The absence of any evidence for these species in the mass spectra suggests that the model which takes into account (possible) cross termination reactions involving the intermediate radical species is not suited—at least in its present form—to describe the experimental mass spectroscopic data. On the other hand, slow fragmentation alone as the cause for rate retardation can be in discrepancy with the measured ESR concentrations. To address these outstanding mechanistic dilemmas, an IUPAC task force has been established to critically evaluate the currently available mechanistic and kinetic data.

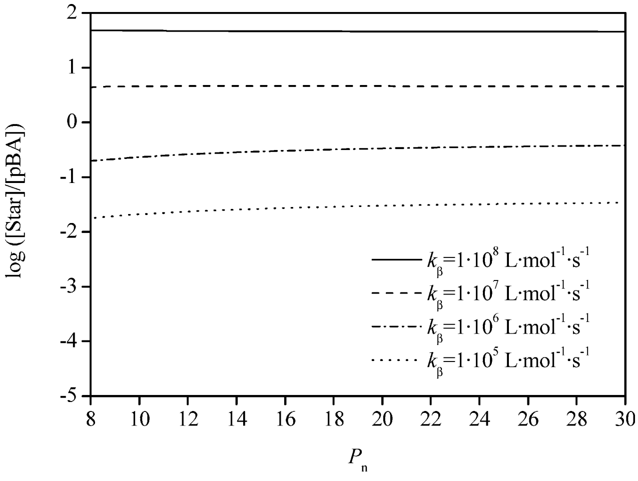


Fig. 6. Simulated ratio of the concentrations of the (potential) 3-armed star species (**3a**) and dead polymer (**5a**, **5b**, **5c**, **6a**, **6b**) for several values of $k_\beta = k_\beta^{\text{pre}}$. All other coefficients are taken from Table 2.

4. Conclusions

In the present paper we have applied high resolution coupled size exclusion chromatography—electrospray ionization mass spectrometry (SEC–ESI-MS) to study the mechanism of RAFT mediated acrylate free radical polymerizations. We employed a stabilizing (CDB) and a non-stabilizing (CPDA) RAFT agent. In addition to the products corresponding to the polymeric RAFT agent, oxidation products as well as combination and disproportionation products, a peak in the close vicinity to the intermediate radical was identified for the CDB mediated polymerizations but not for systems containing CPDA as the RAFT agent. These findings indicate that the intermediate species may indeed be relatively stabilized (or long lived) for some RAFT agent/monomer combinations, in agreement with recent findings in styrene/CDB systems. For none of the systems under investigation in the present study any evidence for termination products of the intermediate radicals such as 3-armed stars could be identified. Simulations using the program package PREDICI® indicate that the cross termination model can only explain the absence of these species with either a very low rate coefficient for the cross termination reaction, a very fast fragmentation of the intermediate species (which is rather unlikely in acrylate systems due to the increased stability of the intermediate radicals compared to styrene polymerizations) or a rather slow addition of the propagating macroradical (which is ruled out by the very limited hybrid behavior observed in the present study) to the (polymeric) RAFT agent.

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