DOI: 10.1002/masy.200950121

Characterization of Z-RAFT Star Polymerization of Butyl acrylate by Size-Exclusion Chromatography

Daniel Boschmann,[1] *Rob Edam,*[2,3] *Peter J. Schoenmakers,*[2] *Philipp Vana**[1]

Summary: Z-RAFT star polymerization of butyl acrylate using multifunctional trithiocarbonate-type RAFT agents carrying methyl propionate as the leaving group were used to form star polymers having 3, 4, and 6 arms. The polymerizations showed well controlled behavior up to high monomer conversions. By using a mixture of mono- and multifunctional RAFT agents, arm and star polymer were obtained simultaneously within a single RAFT polymerization, which enabled the evaluation of the apparent arm numbers. The desired topology of the star polymers was found being present already from the early phase of polymerization on. The apparent arm number slightly increases at very high monomer conversions in accordance to earlier reported star coupling reactions. Correction factors for conventionally calibrated SEC showed excellent agreement with data for polystyrene stars, indicating that the contraction of the hydrodynamic volume in comparison to linear polymer is only dependent on the polymer topology. The evaluation of absolute molar masses of star polymers was however limited by the accuracy of the conventional calibration.

Keywords: branched; reversible addition-fragmentation chain transfer (RAFT); size-exclusion chromatography: star polymers; Z-RAFT star polymerization

Introduction

Complex macromolecular architectures from controlled radical polymerization are only accessible after rational design of controlling agents and diligent optimization of process conditions. This requires a fundamental understanding of the underlying reaction mechanisms. Among the array of possible polymer topologies, star polymers are attracting particular attention, because of their extraordinary rheological characteristics arising from their spatial shape,[1] which are exploited, e.g., in oils and lubricants for automotives,[1,2] in adhesives,[3] and for flocculation.[4] Star polymers are also becoming increasingly important in life sciences, where they find applications for drug release[5] and serve as unimolecular polymeric micelles.[6] When targeting very well-defined star polymers via Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization[7–11] – which is arguably one of the most versatile techniques for controlling radical polymerization – a multifunctional star-shaped RAFT agent needs to be used, in which the stabilizing group (Z-group) constitutes the core.[12–17] This Z-RAFT star polymerization (see Scheme 1) suppresses star coupling reactions as well as side-production of living linear material, which both are unavoidable mechanistic features when linking the RAFT agent via its leaving group (R-group) to the core.[16,18–23] For a detailed description of the mechanistic underpinnings of core-first RAFT star polymerizations, the reader is referred to ref. [13]

Our interest in Z-RAFT star polymerization is driven by our efforts to construct

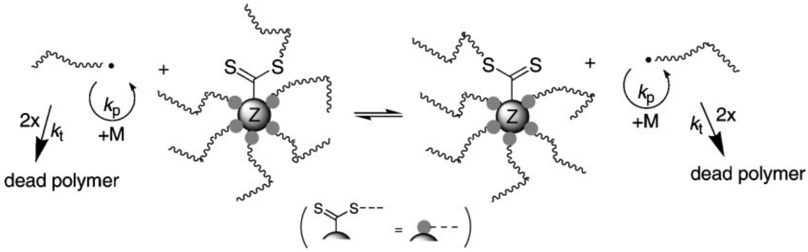
---

[1] Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany
Fax: +49 551 393144;
E-mail: pvana@uni-goettingen.de

[2] Polymer-Analysis Group, Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV, Amsterdam, The Netherlands

[3] Dutch Polymer Institute, P.O. Box 902, 5600 AX Eindhoven, The Netherlands

WILEY InterScience®



Scheme 1.
Main equilibrium of Z-RAFT star polymerization.

well-defined unimolecular nano-carriers, based on star polymers as templates.[24] Z-RAFT star polymerization was consequently studied in detail by the Göttingen group: By using star polymerizations of several acrylates (methyl acrylate, butyl acrylate, and dodecyl acrylate), well-defined six-arm star polymers with molecular weights of more than 1 million Da could be generated.[13] At higher monomer conversions, however, an unexpected high molecular weight component occurred, which was identified as a star-star couple containing two living cores. Such species is not in accordance to the basic mechanism (see Scheme 1), but could be assigned to intermolecular chain transfer to polymer, which becomes significant in acrylate polymerization at high monomer conversions. The amount of star-star couples, which is an indication for the extent of long-chain branching, was quantified and modeled via kinetic simulations, by which the rate coefficient of intermolecular transfer to polymer could be obtained directly for the first time.[13]

In order to arrive at star polymeric material with improved homogeneity, the impact of high pressure on Z-RAFT star polymerization was explored up to 2.5 kbar,[25] which was found as being beneficial for controlling molecular weight. This is due to an increased kinetic chain length which reduces the amount of dead polymeric material and suppresses the amount of small living material originating from the continuous initiation process.[26]

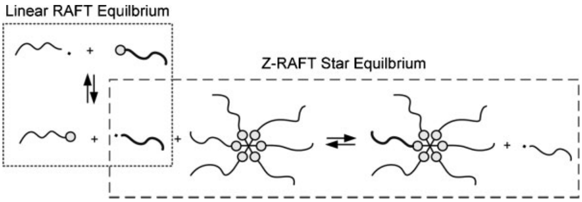
In Z-RAFT star polymerization, the growing radical is located at the end of a linear chain (i.e., the arm) and the equilibrating reaction happens at a central unit, where the thiocarbonylthio-moieties are located throughout the entire process. Consequently, this controlling reaction is increasingly shielded with proceeding polymerization by the neighboring polymer segments. It is, however, experimentally found that Z-RAFT star polymerization is well controlled up to very high monomer conversions.[13,25] We consequently started to question frequently reported arguments about the detrimental shielding of growing arms, which was accused to increasingly hamper the RAFT process.[14,15,27–29] In order to quantify the shielding effect of growing arms, simulations of chain pairs that mimic the steric situation occurring in the main equilibrium were performed.[30,31] Shielding effects were estimated by exact enumeration of star/chain samples prepared by Monte Carlo techniques. The contact probability between the center of star polymer and the end of a linear chain were found to decrease with increasing chain lengths, which indeed indicates a progressive steric congestion. It was, however, found that by slightly expanding the core – which accounts for actual chemical structures being used in Z-RAFT star polymerization – steric crowding can substantially be relieved. From the shielding factors, it could be estimated that the addition reaction in Z-RAFT star polymerization is roughly ten times slower than in linear RAFT polymerization. Such a decrease is *not* sufficient to completely impede the overall RAFT process, as has been shown in earlier kinetic simulation studies.[32] To what extent, however, this drop in the addition rate is affecting polydispersity and molecular weight evolution waits to be studied.

In further work, arm-growth initiation in 6-armed Z-RAFT star polymerization of styrene-d_8 was followed via the disappearance of ^{1}H-NMR signals of the leaving group at their original position.[24] These measurements revealed a dramatic impact of the leaving group on star polymer topology. Phenylethyl as the leaving group induced formation of completely initialized stars already after 8% of monomer conversion. Benzyl as leaving group, however, drastically slows down arm-growth initiation, resulting in fully initialized star polymers only after ca. 60% of monomer conversion. Below that value, star-polystyrene of the expected topology cannot be generated with benzyl as the leaving group. This situation has also become apparent from kinetic modeling of the pre-equilibrium in Z-RAFT star polymerization by Monte Carlo methods.[33]

Recently, we developed a new method for characterizing star polymers from Z-RAFT star polymerization using conventionally calibrated size-exclusion chromatography (SEC),[25] in which the fact is exploited that the arms are occurring as free linear chains during propagation. It is hence possible to let the arms of the star participate in two individual RAFT equilibriums (see Scheme 2) when using a cocktail of conventional and star-shaped RAFT agents.

Because of the dynamic equilibrium between all dormant species, i.e., between arms and stars, it is guaranteed that the arms have identical chain lengths no matter if they occur within the star or outside. Since the SEC is calibrated against linear standards, a determination of the average molecular weight of the linear arm polymer is feasible. The absolute molecular weights of star polymeric material can subsequently be calculated via the known number of arms. Comparison of the apparent and the expected molecular weight of polystyrene stars revealed that 3-arm star polymer appears as having only approx. 2.5 arms, that 4-arm stars seem to have only approx. 3 arms and that 6-arm stars appear to have approx. 4.[25] This indicates the contraction of star polymer coils in solution in comparison to linear chains.[34] Application of this method in Z-RAFT star polymerization of styrene revealed that when using trithiocarbonate-type RAFT agents with phenylethyl as the leaving group, a rapid chain-transfer of the initial RAFT step occurs and well-defined star polymers which perfectly match the theoretical predictions were formed. However, when using benzyl as the leaving group, a pronounced impact of monomer conversion on the number of arms was observed. These findings are consistent with our results from studies into arm-growth initiation via NMR.[24]

In the present communication the new method for characterizing Z-RAFT star polymers via usage of RAFT agent cocktails is expanded to acrylate polymerization,



Scheme 2.
The interdigitated equilibriums of simultaneously proceeding linear and Z-RAFT star polymerization. Thiocarbonylthio-moieties are indicated by circles. One of the arm polymer – which is arbitrarily chosen and is not differing in nature to the other arms – is indicated by a thicker line in order to illustrate its participation in both equilibriums.

which in comparison to the already studied styrene exhibits an increased complexity with respect to side reactions. On the example of butyl acrylate polymerization the impact of such side reactions will be evaluated and the strengths and limitations of the new technique will be explored.

Experimental Part

Chemicals

Dipentaerythritol-hexakis(3-mercaptopropionate) was obtained from Wako Chemicals and used without further purification. The initiator 2,2′-azobis(isobutyronitrile) (AIBN, Aldrich) and *tert*-amyl peroxy acetate (TAPA, 97%, AKZO) were used as received. Butyl acrylate ($\geq$99.0%, Fluka) was purified by passing through a column filled with inhibitor remover for hydrochinone (Aldrich). Column-chromatographic purification of the RAFT agent was performed using silica gel (Merck, Kieselgel 60) and technical grade *n*-pentane, ethyl acetate and CH_2Cl_2. Tetrahydrofuran, used as the eluent for SEC (THF, Carl Roth, stabilized with 2,6-di-*tert*-butyl-4-methylphenol) was used as received for all experiments using conventional calibration. For the triple-detection SEC measurements, unstabilized HPLC-grade THF from Biosolve (Valkenswaard, The Netherlands) was filtered over a 20 nm ceramic filter (Anodisk 47 from Whatman, Maidstone, England) and continuously purged with helium 5.0 (99,999%, Praxair, Vlaardingen, The Netherlands). All other chemicals were purchased from Aldrich and used without further purification.

Instrumentation

Molecular weight distributions were primarily determined by size-exclusion chromatography (SEC) using a JASCO (Tokyo, Japan) AS-2055-plus autosampler, a Waters 515 HPLC pump (Milford, MA, USA), three PSS-SDV columns (Mainz, Germany) with nominal 5 μm particle size and pore sizes of 10^5, 10^3 and 10^2 Å, a Waters 2410 refractive index-detector, and THF at 35 °C as the eluent at a flow rate of $1.0\ \mathrm{mL \cdot min^{-1}}$. 50 μL of polymer solution with a concentration of approximately 3 mg/mL were injected. This SEC setup was calibrated with polystyrene standards of narrow polydispersity ($M_p = 410$ to $2\,000\,000\ \mathrm{g \cdot mol^{-1}}$) from PSS. Mark-Houwink parameters for linear polystyrene ($K = 1.41 \times 10^{-2}\ \mathrm{mL \cdot g^{-1}}$ and $a = 0.700$)[35] and linear poly(BA) ($K = 1.22 \times 10^{-2}\ \mathrm{mL \cdot g^{-1}}$, $a = 0.700$)[36] were employed to recalculate the molecular weight distributions according to the principle of universal calibration.

The triple-detector SEC setup comprised a SIL9a autosampler, LC20Advp micropump and SCL10a system controller all from Shimadzu (Kyoto, Japan). Various columns with mixed-bed particles were used (Resipore 3 μm, Minimix-C 5 μm and Minimix-B 10 μm, 250x4.6 mm each). All of these were obtained from Polymer Laboratories (Church Stretton, UK). The separation was performed at a flow rate of 400 μL/min and 50 μL of sample was injected. The sample solution was prepared by dissolving the polymer at a concentration of approximately 1.5 mg/mL in THF with 250 ppm butyl-hydroxylated toluene (Acros, 99%) to prevent degradation by radicals. The triple-detection array was assembled in-house (University of Amsterdam) and comprised an LD600 90° light scattering detector (Viscotek, Houston, TX, USA), an on-line viscometry detector (Viscochip, Polymer Laboratories) and a differential refractive-index detector (RID10a, Shimadzu). The data were acquired using a PL-datastream A/D converter (Polymer Laboratories) and processed using PL-Cirrus v3.0 software (Polymer Laboratories).

Electrospray-ionization mass spectrometry (ESI-MS) experiments were carried out using a Finnigan LCQ ion trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA). For further details regarding the ESI-MS setup see ref.[37]. NMR spectroscopy was performed using a Varian Mercury 200 and a Varian Unity 300 NMR spectrometer.

RAFT Agent Synthesis

Methyl-2-(hexylsulfanylcarbonothioylsulfanyl) propanoate, **1**. To a solution of 1-hexanethiol (1.00 g, 8.46 mmol) in 50 mL, chloroform triethylamine (1.41 mL, 1.03 g, 10.2 mmol, 1.2 eq) was added. After stirring the reaction mixture for one hour at room temperature, 5 ml of CS_2 and 2-bromo-methylpropionate 1.13 mL, 1.69 g, 10.1 mmol, 1.2 eq) were added slowly. The mixture was stirred for 15 h and the reaction was then quenched by adding 50 mL of 10% hydrochloric acid. The organic phase was separated and washed twice with 50 mL of water and dried over Na_2SO_4. Solvent and traces of educts were removed in vacuum. 2.91 g (86%) of **1** were received as a yellow liquid. ^{1}H-NMR (300 MHz; $CDCl_3$) δ (ppm): 0.88 (t, $J=7.4$ Hz, 3 H, $C\underline{H}_3$), 1.35 (m, 6 H, $C\underline{H}_2$), 1.59 (d, $J=7.4$ Hz, 3 H, $C\underline{H}_3$), 1.67 (p, $J=7.4$ Hz, 2 H, $C\underline{H}_2$), 3.35 (t, $J=7.3$ Hz, 2 H, $C\underline{H}_2$), 3.74 (s, 3 H, $C\underline{H}_3$), 4.83 (q, $J=7.4$ Hz, 1 H, $C\underline{H}$). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm): 13.95 ($\underline{C}H_3$), 16.90 ($\underline{C}H_3$), 22.43 ($\underline{C}H_2$), 27.80 ($\underline{C}H_2$), 28.53 ($\underline{C}H_2$), 31.21 ($\underline{C}H_2$), 37.24 ($\underline{C}H_2$), 47.67 ($\underline{C}H_3$), 52.84 ($\underline{C}H$), 171.64 ($\underline{C}$=O), 221.99 $\underline{C}$=S). Mass spectrometry: *m/z* 907.0 ($M+Na^+$).

Trimethylolpropane-tris-(3-(S-methyl-2-propanoatotrithiocarbonyl)propanoate), **2**. To a solution of trimethylolpropane-*tris*-(3-mercaptopropionate) (1.00 mL, 1.21 g, 3.04 mmol) in 50 mL chloroform triethylamine (1.52 mL, 1.11 g, 10.9 mmol, 3.6 eq) was added. After stirring the reaction mixture for one hour at room temperature 5 mL of CS_2 and 2-bromo-methylpropionate (1.22 mL, 1.83 g, 10.9 mmol, 3.6 eq) were added slowly. The mixture was stirred for 15 h and the reaction was then quenched by adding 50 mL of 10% hydrochloric acid. The organic phase was separated and washed twice with 50 mL of water and dried over Na_2SO_4. Solvent and traces of non reacted starting materials were removed in vacuum. 2.69 g (99%) of **2** were received as a yellow liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 0.88 (t, $J=7.6$ Hz, 3 H, $C\underline{H}_3$), 1.43 (q, $J=7.6$ Hz, 2 H, $C\underline{H}_2$), 1.59 (d, $J=7.4$ Hz, 9 H, $C\underline{H}_3$), 2.79 (t, $J=7.0$ Hz, 6 H, $C\underline{H}_2$), 3.59 (t, $J=7.0$ Hz, 6 H, $C\underline{H}_2$), 3.75 (s, 9 H, $C\underline{H}_3$), 4.03 (t, $J=7.0$ Hz, 6 H, $C\underline{H}_2$), 4.79 (q, $J=7.4$ Hz, 3 H, $C\underline{H}$). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm): 7.34 ($\underline{C}H_3$), 16.87 ($\underline{C}H_3$), 22.91 ($\underline{C}H_2$), 31.35 ($\underline{C}(CH_2)_4$, 32.91 ($\underline{C}H_2$), 40.71 ($\underline{C}H_2$), 47.95 ($\underline{C}H_2$), 52.91 ($\underline{C}H_3$), 64.01 ($\underline{C}H_2$), 170.89 ($\underline{C}$=O), 171.40 ($\underline{C}$=O), 221.14 ($\underline{C}$=S). Mass spectrometry: *m/z* 897.07($M+H^+$), 914.10 ($M+NH_4^+$).

Pentaerythritol-tetrakis-(3-(S-methyl-2-propanoatotrithiocarbonyl)propanoate), **3**. To a solution of pentaerythritol-*tetrakis*-(3-mercaptopropionate) (0.71 mL, 1.44 g, 5.00 mmol) in 100 mL chloroform triethylamine (5.53 mL, 4.04 g, 40.0 mmol, 8 eq) was added. After stirring the reaction mixture for one hour at room temperature 10 mL of CS_2 and 2-bromo-methylpropionate (3.28 mL, 6.68 g, 40.0 mmol, 8 eq) were added slowly. The mixture was stirred for 15 h and afterwards the reaction was quenched by adding 100 mL of 10% hydrochloric acid. The organic phase was separated and washed twice with 100 mL of water and dried over Na_2SO_4. Solvent was removed in vacuum and the crude product was purified on silica with pentane/ethyl acetate 3:1 (*Rf* = 0.28) as eluent. 1.80 g (18%) of **3** were received as yellow oil. ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm): 1.60 (d, $J=7.4$ Hz, 12 H, $C\underline{H}_3$), 2.78 (t, $J=7.0$ Hz, 8 H, $C\underline{H}_2$), 3.60 (t, $J=7.0$ Hz, 8 H, $C\underline{H}_2$), 3.75 (s, 12 H, $C\underline{H}_3$), 4.13 (s, 8 H, $C\underline{H}_2$), 4.82 (q, $J=7.4$ Hz, 4 H, $C\underline{H}$). ^{13}C-NMR (50 MHz, $CDCl_3$) δ (ppm): 16.87 ($\underline{C}H_3$), 31.24 ($\underline{C}(CH_2)_4$, 32.85 ($\underline{C}H_2$), 42.02 ($\underline{C}H_2$), 47.99 ($\underline{C}H_2$), 52.94 ($\underline{C}H_3$), 62.25 ($\underline{C}H_2$), 170.7 ($\underline{C}$=O), 171.39 ($\underline{C}$=O), 221.08 ($\underline{C}$=S). Mass spectrometry: *m/z* 1158.9 ($M+Na^+$).

Dipentaerythritol-hexakis-(3-(S-methyl-2-propanoatotrithiocarbonyl)propanoate), **4**. was prepared as described earlier.[13]

Polymerizations

Butyl acrylate was degassed via three freeze-pump-thaw cycles, transferred along with RAFT agent and initiator into an argon-filled glove box (oxygen content below 1.5 ppm), where stock solutions of 10 mL monomer, initiator (AIBN), and

RAFT agent or RAFT agent mixtures were prepared. Ten samples of each stock solution were filled into individual glass vials and sealed with Teflon/rubber septa. The vials were subsequently inserted into a block heater, thermostated at 60 ± 0.1 °C. The samples were removed after preset time intervals and the reactions were stopped by cooling the solutions in an ice bath. The reaction times were up to 5 h. Monomer to polymer conversions were determined gravimetrically.

Arm Cleavage

20 mg of star polymer and 20 mg of radical initiator (either AIBN or TAPA) was dissolved in 5 mL of toluene. The solution was degassed by nitrogen gas for 10 min. and subsequently heated to 60 °C in the case of AIBN and 140 °C in the case of TAPA. The reaction times were chosen to be two half-life times of the respective initiator. Samples were then filtered and the solvent was evaporated in vacuum.

Results and Discussion

Multifunctional trithiocarbonates as RAFT agents (see Chart 1) were chosen for the present study into Z-RAFT star polymerization of butyl acrylate. Trithiocarbonates are becoming more and more popular as RAFT agents, as they are easily prepared and because they do not show any potentially perturbing rate retardation effects, which are frequently observed with more reactive RAFT agents such as dithiobenzoates.[38] Mayadunne *et al.*[19] were the first who introduced pentaerythritol-based multifunctional trithiocarbonates as Z-RAFT star agents. The synthesis protocols for this class of star-shaped RAFT agents were later on modified by us[13,24,25] and others,[39] giving access to bi-, tri-, tetra- and hexa-functional mediating agents. The synthesis allows for an facile modification of the R-group. Consequently, a methyl acrylate type leaving group was chosen for the present study (see Chart 1). This R-group generates a monomeric methyl acrylate radical, which is structurally similar to growing butyl acrylate radicals. It is hence anticipated that this R-group provides a fast passing of the pre-equilibrium, which leads to a homogenous initiation of arm-growth. This was found as being crucial for guaranteeing a low level of topological defects.[25]

The Z-RAFT star polymerizations of butyl acrylate (BA) in bulk at 60 °C using 3-armed (**2**), 4-armed (**3**), and 6-armed (**4**) RAFT agents exhibited very well controlled behavior up to very high monomer conversion. This is exemplified on **3**-mediated 4-arm star polymerization of BA (see Figure 1). Polydispersity indices, *PDI*, are exhibiting minimal values of 1.11 at a monomer conversion (*X*) of 25% when using RAFT agent concentrations of 1.3 $\text{mmol} \cdot \text{L}^{-1}$, which refers to 5.5 $\text{mmol} \cdot \text{L}^{-1}$ of trithiocarbonate moieties. Due to less pronounced steric shielding, it comes as no surprise that the presented 4-arm star polymerization proceeds under slightly better control than the already earlier presented 6-arm star polymerization of BA using **4** as the controlling agent,[13] in which a minimal *PDI* of 1.17 has been observed with very similar trithiocarbonate-moiety concentrations. The slight negative curvature of the $\overline{M}_\text{n}$ vs. *X* traces – which are expected to be linear for ideal living processes – comes from the continuous initiation process that constantly produces additional chains, manifested in an increase of dead polymer.[40] Since it is clear that the hydrodynamic volume of star polymer is differing from those of the linear standards, which were used for evaluating the molar masses presented in Figure 1 (see below), we abstain from presenting theoretical molecular weights in this figure.

In order to arrive at true molecular weights of Z-RAFT star polymer using SEC that is conventionally calibrated against linear polymer standards, it seems at a first glance rational to deconstruct the final star polymer, by which the individual arms can be yielded as linear chains. This approach seems to be especially suited for Z-RAFT star polymerization, in which the

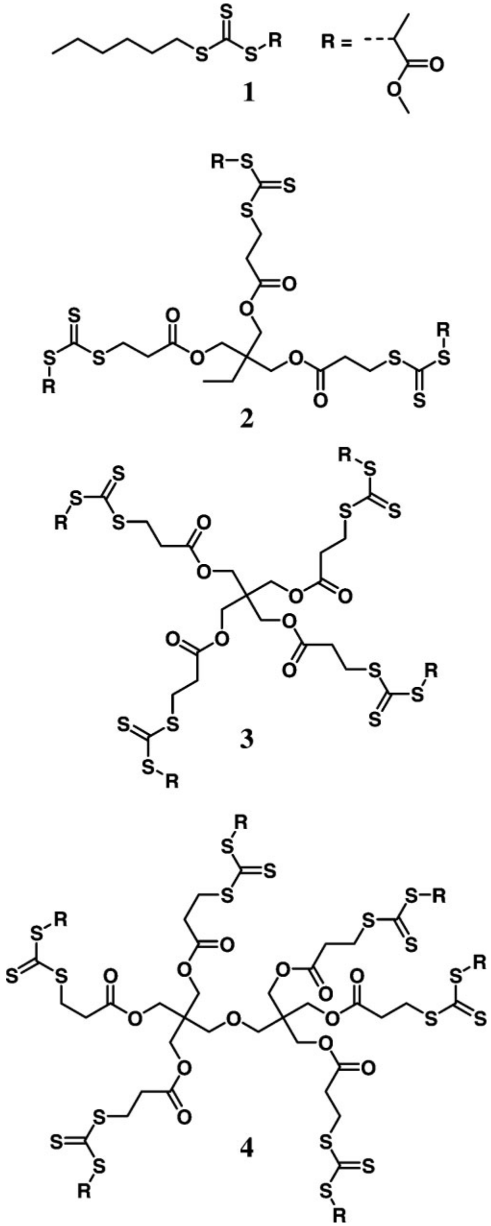


Chart 1.
Mono-, tri-, tetra-, and hexafunctional RAFT agents used in this study.

arm polymer is linked to the central core via a relatively weak dithioester bond that may easily be cleaved. Consequently, arm cleavage experiments of Z-RAFT star polymer were reported either using nucleophilic substitution with amines[16] or via a single RAFT step using an excess of small initiator-derived radicals.[13,41,42] The first method yields thiol end-groups, which are prone to oxidization, whereby disulfide-linkages are generated that couple two polymer chains.[43] This distorts the resulting chain-length distributions and complicates the exact evaluation of the molecular

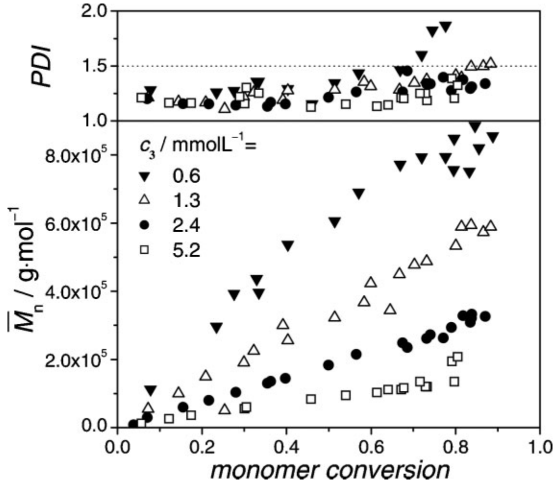


Figure 1.
Polydispersity index, *PDI*, and number average molecular weight, $\overline{M}_n$, vs. monomer conversion in **3**-mediated butyl acrylate bulk polymerization (4-arm Z-RAFT star polymerization) with various RAFT agent concentrations at 60 °C using AIBN ($c_{AIBN} = 2$ mmol · L^{-1}) as the initiator.

weight of the arm polymer. The second method using small radicals is thus generally preferred. It was, however, found that the reactivity of the used radical has an important impact on the cleavage experiments. 2,2′-Azobis(isobutyronitrile) (AIBN)-derived cyanoisopropyl radicals were, e.g., found as being suitable for cleaving dithioester-moieites from polystyrene,[41] but as not being reactive enough for cleaving xanthate-moieties from poly(vinyl acetate). In the latter case, however, the more reactive *tert*-amyl peroxy acetate (TAPA)-derived ethyl radicals[44] showed transfer constants that were sufficient to effectively cleave the terminal RAFT-groups.[45] In order to evaluate the suitability of different types of radicals for the cleavage reaction of RAFT-group carrying polyacrylates, we treated the BA star polymers generated in this work both with AIBN and with TAPA. The chain length distributions of an original star polymer and those of the respectively obtained arm polymer are depicted in Figure 2 on the example of a four arm star. The dead polymer originating from the termination of two growing macroradicals (arms) is visible as a hump at the low molecular weight side of the star polymer.

It can be clearly seen that both initiators are capable of cutting off the individual arms. The radical type, however, has a small, but significant impact on the molecular weight of the obtained arm polymer. Inspection of Table 1 reveals that the obtained number average molecular weights of arm polymer differ by around 30 kDa, which is about 20%, depending on

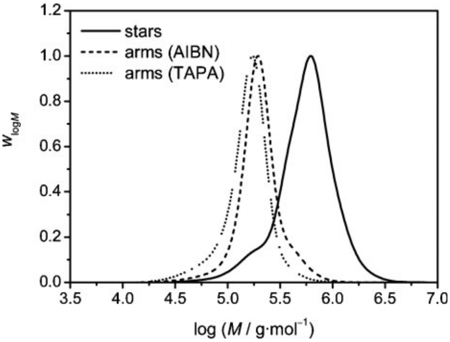


Figure 2.
SEC-distributions of poly(butyl acrylate) produced in **3**-mediated ($c_3 = 1.3$ mmol · L^{-1}) butyl acrylate bulk polymerization (4-arm Z-RAFT star polymerization) at 60 °C using AIBN ($c_{AIBN} = 1.8$ mmol · L^{-1}) as the initiator. The full line indicates the original star polymer, the dashed and dotted lines indicate the arm polymer after cleavage with AIBN and TAPA, respectively.

Table 1.
Number average molecular weight, $\overline{M}_n$, peak molecular weight, M_p, and polydispersity index, *PDI*, both for 4-arm poly(butyl acrylate) and linear arm polymer after star cleavage, and ratio between star and arm number average molecular weight.

	4-arm polyBA star [a)]	polyBA arms after cleavage by AIBN	polyBA arms after cleavage by TAPA
$\overline{M}_n$/kg · mol^{-1}	438	160	133
M_p/kg · mol^{-1}	624	194	172
PDI	1.51	1.28	1.29
$\overline{M}_{n,star}/\overline{M}_{n,arm}$		2.7	3.3

[a)] apparent molecular weight data from conventionally calibrated SEC.

what initiator has been used. The situation improves, when the peak molecular weights are compared, which are less affected by side products. The difference decreases to 11%, but is still significant. Since it is not clear, whether incomplete star cleavage or degrading side reactions are responsible for the differences, it cannot decided, which of the differing results are more significant. The impact of the observed uncertainties on the evaluated apparent number of arms can be seen by inspection of the ratio of the number average molecular weight of the star polymer and that of the arm polymer (see Table 1, last row). Assuming that 4-arm star polymer is indeed present, this factor reflects the contraction of star polymer in solution in comparison to linear polymer. The values are in rough agreement with what has been found for polystyrene star polymers, where apparent arm numbers of 3.05 were found for 4-arm stars.[25] When aiming at detailed values of apparent arm numbers, it is however clear that potentially incomplete arm cleavage and unknown side reactions are an obstacle. It is for this reason, why the application of the recently developed method of preparing arm and star polymer simultaneously during the Z-RAFT star polymerization seems favorable.

We consequently performed 3-, 4 and 6-arm star polymerizations using a cocktail of monofunctional RAFT agent, **1**, and multifunctional RAFT agent, **2**, **3**, and **4**, respectively. In such a RAFT polymerization, two RAFT equilibriums are established, which are interlinked via the growing macroradicals, *i.e.* the individual arms (see Scheme 2). Because of the controlled nature of RAFT polymerization, all macroradicals in the system have approximately the same chain length and during the polymerization either add to a linear polymeric RAFT agent (linear RAFT equilibrium) or to a living star polymer (Z-RAFT star equilibrium). This situation implies that linear polymer and arm polymer within the star have identical average molecular weights, as they are constantly exchanged via the RAFT equilibriums. Molecular-weight distributions of polymer formed in the presence of such a RAFT agent cocktail are characteristically bimodal.[25] Both the linear polymer (arms) and the star polymer increase steadily in molecular weight with monomer conversion. Since the trithiocarbonate-group concentration was chosen to be identical for both RAFT agents, the weight fraction of both types of polymer is identical, which allows for optimal peak separation. The molecular weight of the linear arm polymer can be determined via conventionally calibrated SEC using polystyrene standards and applying literature values of Mark-Houwink coefficients of polystyrene and polyBA. The molecular weight of the simultaneously formed star polymer can be evaluated by multiplying the molecular weight of the arm polymer by the number of arms of the respective star. Both the arm and star polymers are relatively narrowly distributed. Thus, the number average molecular weights are in good approximation represented by the peak molecular weight, M_p. This means that by dividing the peak molecular weight of the star polymer,

$M_{\mathrm{p,star}}$, by the peak molecular weight of the linear arm polymer, $M_{\mathrm{p,arm}}$, the apparent number of arms, as shown in Figure 3 for 3-arm, 4-arm, and 6-arm poly(butyl acrylate) stars, can be deduced.

It can be seen that the apparent number of arms is approximately constant over a wide range of monomer conversion, which indicates that the chosen R-group enables a quick arm growth initiation and that star polymers of the desired topology are present from the early phase of polymerization on. Inappropriate R-groups, such as benzyl in styrene polymerization,[25] would effect only slow arm growth initiation and the apparent number of arms would consequently increase pronouncedly up to intermediate monomer conversions. Closer inspection of Figure 3 shows that the apparent arm numbers slightly increase, especially at monomer conversion above 60%. It was found in earlier studies that transfer to polymer in BA polymerization, which becomes prominent above around 60% of monomer conversion, leads to star-star couples.[13] Star couples constitute entities with an increased number of arms. The accumulation of coupled material is evidently reflected in the slight increase of the apparent number of arms. It is for this reason, why the data were averaged for monomer conversion values below 60% only (average lines in Figure 3). The resulting values are 2.48 for 3-arm stars, 2.98 for 4-arm stars and 3.98 for 6-arm stars, which are in excellent agreement with data obtained for polystyrene stars (2.58; 3.05; 3.94).[25] This convincing match underpins the following conclusion: (i) the desired topology, i.e., 3-, 4- and 6-arm stars, have been formed in the studied Z-RAFT star polymerization of BA using methyl propionate as the leaving R-group, and (ii) the contraction of the hydrodynamic volume of stars in comparison to linear polymer chains is independent of the chemical structure of the polymer, but depends on the topology only, which is also predicted by theory.[46–48]

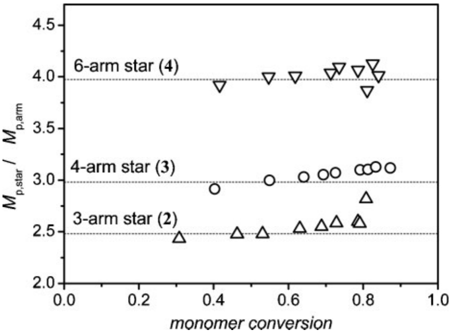


Figure 3.

Ratio of peak molecular weights of star polymer and peak molecular weights of linear arm polymer ($M_{\mathrm{p,star}}$/$M_{\mathrm{p,arm}}$), as obtained by conventionally calibrated SEC *vs.* monomer conversion for butyl acrylate bulk polymerizations at 60 °C using AIBN ($c_{\mathrm{AIBN}} = 2\ \mathrm{mmol \cdot L^{-1}}$) as the initiator and mixtures of **1** and **2** (3-arm star polymerization), **1** and **3** (4-arm star polymerization), and **1** and **4** (6-arm star polymerization). The overall trithiocarbonate-group concentration was around 38 $\mathrm{mmol \cdot L^{-1}}$ for all samples with approximately half the number of RAFT groups belonging to multifunctional RAFT agents. Horizontal lines indicate mean values for data below 60% of monomer conversion.

In a recent publication we demonstrated that data such as depicted in Figure 3 can be used to obtain a correction factor, *K*, by which it becomes possible to determine with high precision absolute molecular weights of star polymer by SEC that is conventionally calibrated against linear standards.[25] *K* is simply calculated by dividing the expected number of arms by the apparent number of arms. In Figure 4, the molecular weight data from conventional calibration before (open circles) and after (closed circles) correction with *K* is depicted on the example of 6-arm stars together with the theoretical molecular weights of star polymers, $\overline{M}_{\mathrm{n}}^{\mathrm{theo}}$ (dashed line), which were calculated using Eq. (1).

$$\overline{M}_{\mathrm{n}}^{\mathrm{theo}} = \frac{X \cdot c_{\mathrm{M}}^{0} \cdot M_{\mathrm{monomer}}}{c_{\mathrm{RAFT}}^{0} + c_{\mathrm{I}}^{0} \cdot d \cdot f \cdot (1 - e^{-k_{\mathrm{d}} \cdot t})} + M_{\mathrm{RAFT}} \tag{1}$$

with the monomer to polymer conversion, *X*, the initial monomer concentration, c_{M}^{0}, the initial RAFT agent concentration, c_{RAFT}^{0}, the initial initiator concentration, c_{I}^{0}, the molecular weights of monomer,

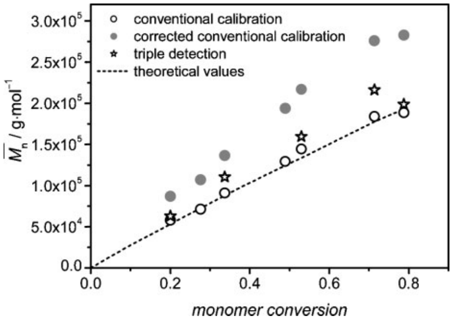


Figure 4.
Number average molecular weight, $\overline{M}_n$, of six-arm star poly(butyl acrylate) vs. monomer conversion, obtained via conventional SEC calibration and via triple-detection. The poly(butyl acrylate) samples were prepared via bulk polymerization at 60 °C in the presence of 1.7 mmol/L AIBN and 3.5 mmol/L **4**.

M_{monomer}, and of RAFT agent, M_{RAFT}, with d being the number of chains that are generated in the termination process ($d \approx 1$ for BA), with the initiator decomposition rate coefficient, k_d ($k_d = 1.10 \times 10^{-5}\ \mathrm{s}^{-1}$ for AIBN[49]), and the initiator efficiency $f = 0.72$.[50]

It can be clearly seen that the corrected values are significantly larger than the expected theoretical molecular weights, which is in contrast to what has been found for Z-RAFT star polymerizations of styrene, where a perfect match of predicted and corrected data from conventional calibration was found.[25] In order to get further insight into this unexpected behavior, we performed triple-detection (refractive index detection coupled with viscometric detection and light scattering detection) after SEC separation, which yields absolute molecular weights, independent of the hydrodynamic volume of the respective species (stars in Figure 4). The true molecular weights are very close to the theoretical values, indicating that the Z-RAFT star polymerization was performed under very well controlled conditions. Small deviations between absolute and theoretical molecular weights may well be due to uncertainties of the kinetic parameters that enter Eq. (1). The efficiency of AIBN, for instance, is only available for styrene solution and may be slightly different in BA solution. The fact that the data of apparent arm numbers found above are excellently matching the results of polystyrene stars implies that the relation between the molar mass of arm and star polymer is evaluated correctly. Inspection of Figure 4, however, clearly shows that the absolute level of the data from conventional calibration is incorrect. This finding strongly suggests that the evaluation of molecular weight via conventional calibration using Mark-Houwink coefficients for polystyrene and BA is beset with a systematic error. It is well known that small uncertainties in Mark-Houwink coefficients – which are difficult to evaluate with high precision – have a great impact on the obtained molecular weight. The Mark-Houwink coefficients available for linear polybutylacrylate in the literature ($K = 1.22 \times 10^{-2}\ \mathrm{mL \cdot g^{-1}}$ and $a = 0.700$ [36]; $K = 7.4 \times 10^{-3}\ \mathrm{mL \cdot g^{-1}}$ and $a = 0.750$ [51]; $K = 8.57 \times 10^{-3}\ \mathrm{mL \cdot g^{-1}}$ and $a = 0.865$ [52]; $K = 1.18 \times 10^{-2}\ \mathrm{mL \cdot g^{-1}}$ and $a = 0.716$ [53]) have a significant scatter and lead to molecular weights that differ by around a factor of two.[36] The much smaller discrepancy of around 20% observed in the present communication, in which the data set of Beuermann et al.[36] has been used, may thus well be explained by the uncertainty of these values. It is clear that the proposed method of obtaining absolute molecular weights of star polymer using a conventionally calibrated SEC is limited by the accuracy of this calibration. In the present case, the uncertainty of the calibration is as big as the deviation of the hydrodynamic volume of 6-arm stars from that of linear polymer. This limiting accuracy could for instance be increased by using dedicated polymer standards, that is, narrowly distributed poly(butyl acrylate) standards for the present study. It is, however, gratifying to note that the determination of contraction factors of star polymers and the evaluation of apparent arm numbers by the proposed method is not significantly affected by the found uncertainty.

Conclusion

Z-RAFT star polymerizations of butyl acrylate using multifunctional trithiocarbonate-type RAFT agents carrying methyl propionate as the leaving group lead to the formation of to star polymers having 3, 4, and 6 arms. The reactions show well controlled behavior up to high monomer conversions. Cleavage of the formed star polymers using radical delivering agents yields arm polymer which is dependent in molecular weight on the type of employed radicals. Star cleavage is thus not an appropriate tool for diligently characterizing Z-RAFT star polymer. When using a mixture of mono- and multifunctional RAFT agents, however, arm and star polymer of great homogeneity are obtained simultaneously within a single RAFT polymerization. Thereby evaluated apparent arm numbers indicate that the desired topology of the star polymer is present already at the early stage of star polymerization, which implies that methyl propionate is an effective leaving group for trithiocarbonate-mediated BA polymerization. In accordance to earlier reported star coupling reactions, the apparent arm number slightly increases at very high monomer conversions. The obtained correction factors for conventionally calibrated SEC showed excellent agreement with data for polystyrene stars, which underpins the fact that the contraction of the hydrodynamic volume is not dependent on the chemical nature of the polymer, but on the topology only. Using the correction factors for obtaining absolute molar masses of star polymers from conventionally calibrated SEC is however limited by the accuracy of the calibration. Employing polystyrene standards in conjunction with Mark-Houwink coefficients of polystyrene and polyBA was found as being not accurate enough to obtain precise molar masses of star polymer.

Acknowledgements: Financial support by the *Deutsche Forschungsgemeinschaft* within the frame of the European Graduate School "Microstructural Control in Free-Radical Polymerization" and for project VA226/3 is gratefully acknowledged. P.V. acknowledges receipt of a Heisenberg-Professorship (DFG). D.B. and P.V. are indebted to M. Buback (University of Göttingen) for continuous support of this work. R.E. would like to thank the Dutch Polymer Institute for funding project No. 509 Cobra (comprehensive characterization of branched polymers).

[1] J. H. Lee, J. M. Goldberg, L. J. Fetters, L. A. Archer, *Macromolecules* **2006**, *39*, 6677.
[2] T. C. B. McLeish, *Chem. Eng. Res. Des.* **2000**, *78*, 12.
[3] N. Hadjichristidis, S. Pispas, M. Pitsikalis, H. Iatrou, C. Vlahos, in: *Branched Polymers I*, Vol. *142*, **1999**, 71.
[4] J. S. Li, P. R. Modak, H. N. Xiao, *Colloids Surf., A* **2006**, *289*, 172.
[5] L. Y. Qiu, Y. H. Bae, *Pharm. Res.* **2006**, *23*, 1.
[6] D. Kul, L. M. Van Renterghem, M. A. R. Meier, S. Strandman, H. Tenhu, S. S. Yilmaz, U. S. Schubert, F. E. Du Prez, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 650.
[7] J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, *31*, 5559.
[8] C. Barner-Kowollik, T. P. Davis, J. P. A. Heuts, M. H. Stenzel, P. Vana, M. Whittaker, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 365.
[9] G. Moad, E. Rizzardo, S. H. Thang, *Aust. J. Chem.* **2005**, *58*, 379.
[10] S. Perrier, P. Takolpuckdee, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5347.
[11] G. Moad, E. Rizzardo, S. H. Thang, *Aust. J. Chem.* **2006**, *59*, 669.
[12] D. Boschmann, P. Vana, *Polym. Bull. (Heidelberg, Ger.)* **2005**, *53*, 231.
[13] D. Boschmann, P. Vana, *Macromolecules* **2007**, *40*, 2683.
[14] M. H. Stenzel, T. P. Davis, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4498.
[15] V. Darcos, A. Dureault, D. Taton, Y. Gnanou, P. Marchand, A. M. Caminade, J. P. Majoral, M. Destarac, F. Leising, *Chem. Commun. (Cambridge, U. K.)* **2004**, 2110.
[16] J. Bernard, A. Favier, L. Zhang, A. Nilasaroya, T. P. Davis, C. Barner-Kowollik, M. H. Stenzel, *Macromolecules* **2005**, *38*, 5475.
[17] X. J. Hao, E. Malmstrom, T. P. Davis, M. H. Stenzel, C. Barner-Kowollik, *Aust. J. Chem.* **2005**, *58*, 483.
[18] M. Stenzel-Rosenbaum, T. P. Davis, V. Chen, A. G. Fane, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2777.
[19] R. T. A. Mayadunne, J. Jeffery, G. Moad, E. Rizzardo, *Macromolecules* **2003**, *36*, 1505.
[20] C. Y. Hong, Y. Z. You, J. Liu, C. Y. Pan, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6379.

[21] H. Chaffey-Millar, M. H. Stenzel, T. P. Davis, M. L. Coote, C. Barner-Kowollik, *Macromolecules* **2006**, *39*, 6406.

[22] G. C. Zhou, J. B. He, Harruna, II, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4225.

[23] O. Liu, Y. Chen, *Macromol. Chem. Phys.* **2007**, *208*, 2455.

[24] D. Boschmann, M. Mänz, A.-C. Pöppler, N. Sörensen, P. Vana, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 7280–7286.

[25] D. Boschmann, R. Edam, P. J. Schoenmakers, P. Vana, *Polymer* **2008**, accepted.

[26] T. Arita, M. Buback, O. Janssen, P. Vana, *Macromol. Rapid Commun.* **2004**, *25*, 1376.

[27] M. Jesberger, L. Barner, M. H. Stenzel, E. Malmstrom, T. P. Davis, C. Barner-Kowollik, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3847.

[28] C. Barner-Kowollik, T. P. Davis, M. H. Stenzel, *Aust. J. Chem.* **2006**, *59*, 719.

[29] A. Dureault, D. Taton, M. Destarac, F. Leising, Y. Gnanou, *Macromolecules* **2004**, *37*, 5513.

[30] M. G. Frohlich, P. Vana, G. Zifferer, *J. Chem. Phys.* **2007**, *127*.

[31] M. G. Frohlich, P. Vana, G. Zifferer, *Macromol. Theory Simul.* **2007**, *16*, 610.

[32] P. Vana, T. P. Davis, C. Barner-Kowollik, *Macromol. Theory Simul.* **2002**, *11*, 823.

[33] M. Drache, D. Boschmann, P. Vana, **2008**, in preperation.

[34] W. Burchard, *Adv. Polym. Sci.* **1999**, *143*, 113.

[35] C. Strazielle, H. Benoit, O. Vogl, *Eur. Polym. J.* **1978**, *14*, 331.

[36] S. Beuermann, D. A. Paquet, J. H. McMinn, R. A. Hutchinson, *Macromolecules* **1996**, *29*, 4206.

[37] M. Buback, H. Frauendorf, P. Vana, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4266.

[38] C. Barner-Kowollik, M. Buback, B. Charleux, M. L. Coote, M. Drache, T. Fukuda, A. Goto, B. Klumperman, A. B. Lowe, J. B. Mcleary, G. Moad, M. J. Monteiro, R. D. Sanderson, M. P. Tonge, P. Vana, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5809.

[39] G. Johnston-Hall, M. J. Monteiro, *Macromolecules* **2008**, *41*, 727.

[40] T. Arita, M. Buback, P. Vana, *Macromolecules* **2005**, *38*, 7935.

[41] D. H. Nguyen, P. Vana, *Polym. Adv. Technol.* **2006**, *17*, 625.

[42] S. Perrier, P. Takolpuckdee, C. A. Mars, *Macromolecules* **2005**, *38*, 6770.

[43] M. R. Whittaker, Y. K. Goh, H. Gemici, T. M. Legge, S. Perrier, M. J. Monteiro, *Macromolecules* **2006**, *39*, 9028.

[44] M. Buback, H. Frauendorf, F. Günzler, P. Vana, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2453.

[45] D. H. Nguyen, M. R. Wood, Y. Zhao, S. Perrier, P. Vana, *Macromolecules* **2008**, submitted.

[46] J. F. Douglas, J. Roovers, K. F. Freed, *Macromolecules* **1990**, *23*, 4168.

[47] K. Shida, K. Ohno, Y. Kawazoe, Y. Nakamura, *Polymer* **2004**, *45*, 1729.

[48] A. Takano, M. Okada, T. Nose, *Polymer* **1992**, *33*, 783.

[49] Initiators for High Polymers, AKZO Nobel Chemicals, **2006**.

[50] M. Buback, B. Huckestein, F. D. Kuchta, G. T. Russell, E. Schmid, *Macromol. Chem. Phys.* **1994**, *195*, 2117.

[51] E. Penzel, N. Goetz, *Angew. Makromol. Chem.* **1990**, *178*, 191.

[52] T. P. Davis, K. F. Odriscoll, M. C. Piton, M. A. Winnik, *Polym. Int.* **1991**, *24*, 65.

[53] L. Couvreur, G. Piteau, P. Castignolles, M. Tonge, B. Coutin, B. Charleux, J. P. Vairon, *Macromol. Symp.* **2001**, *174*, 197.