Polymer Bulletin 53, 231–242 (2005)
DOI 10.1007/s00289-005-0338-9

Polymer Bulletin

Poly(vinyl acetate) and Poly(vinyl propionate) Star Polymers via Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization

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Received: 4 November 2004 / Revised version: 21 December 2004 / Accepted: 4 January 2005

Summary

Poly(vinyl acetate) and poly(vinyl propionate) star polymers with four arms were produced via reversible addition fragmentation chain transfer (RAFT) polymerization, employing a tetra-functional xanthate as the RAFT agent, in which the stabilizing groups are linked to the core. These novel star-like RAFT agents induced living/controlled behavior in both the vinyl acetate polymerization at 60 °C and in the vinyl propionate polymerization at 90 °C, respectively, leading to star polymers with minimum polydispersities of 1.2 and maximum apparent number average molecular weights of about 50,000 $g \cdot mol^{-1}$. The microstructure of the star polymers was confirmed by electrospray ionization mass spectrometry.

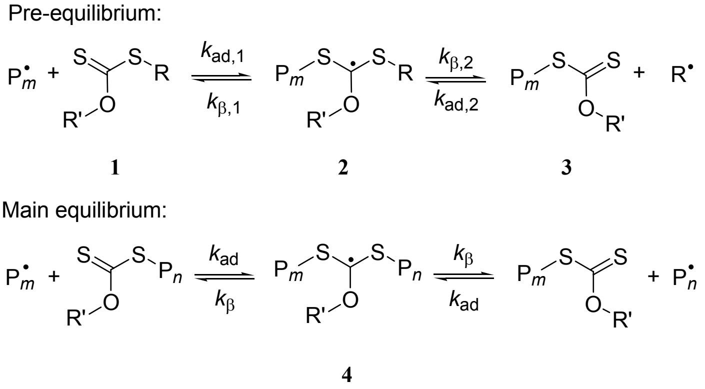
Introduction

The advent of living/controlled radical polymerization techniques has revolutionized the field of radical polymerization, because they allow for the generation of polymeric materials with narrowly distributed and controlled molecular weights as well as complex macromolecular architectures – such as block, comb, and star polymers – with relative ease. The most prominent of these techniques are the nitroxide-mediated polymerization (NMP) [1,2], the atom transfer radical polymerization (ATRP) [3-5], and the reversible addition fragmentation chain transfer (RAFT) polymerization [6,7]. RAFT has proven to be extremely versatile with respect to monomer type and reaction condition and therefore developed into a leading technique for the controlled formation of polymeric materials with novel macromolecular microstructures.

Star polymers, i.e., macromolecules with one distinct central branching point and several polymeric arms, are attracting attention since decades, because they exhibit interesting characteristics: (*i*) They show both a decreased zero-shear viscosity and a decreased steady-state compliance in comparison to linear polymer with the same molecular weight [8], (*ii*) they exhibit an increased end-group functionality [9], and (*iii*) they are important model compounds, due to their well-defined branching. The introduction of controlled/living radical polymerization methods has opened up a multitude of monomer families to the controlled synthesis of such star-shaped polymers, which were mostly generated via ionic polymerization techniques earlier, hence being limited to certain monomer types. The last years have thus witnessed a renaissance of star polymers and a multitude of new star polymeric materials have been synthesized [10].

Vinyl esters (e.g., vinyl acetate (VAc) and vinyl propionate (VPr)) are typical examples for monomers that are not easily polymerized in a controlled manner, mainly because of the extremely high reactivity of the corresponding propagating radical. However, living/controlled radical polymerization of vinyl esters seems rewarding for two reasons: (*i*) The resulting poly(vinyl esters) are precursors for poly(vinyl alcohol), which is of importance for biomedical applications. (*ii*) Vinyl acetate is known to almost perfectly copolymerize with ethylene [11], demonstrating some similarity between these two polymerizing systems. The efforts in controlling vinyl ester polymerizations and simultaneously designing novel macromolecular microstructures may thus be rewarding for attaining the goal of performing controlled/living radical olefin polymerization via RAFT, which is an ongoing task in our laboratory.

Although some progress in controlling vinyl acetate polymerization via ATRP using an iron-complex has been made [12], the RAFT process has proven to be the method of choice for successfully mediating VAc polymerization: Alkyl iodides [13], dithiocarbamates [14], and especially xanthates [15,16] have been found to effectively control vinyl ester polymerizations. When using xanthates as mediating agents [17,18], in which the stabilizing Z-groups are –OR′, an enhanced electron density on the central carbon effectively decreases the stability of the intermediate RAFT radicals **2** and **4** (see Scheme 1), hence, counterbalancing the instability of the growing vinyl ester radicals. Additionally, the addition rates of the propagating radicals toward **1** and **3** are decreased, due to a resonance stabilization that lowers the double-bond character of the S=C-bond in **1** and **3**.

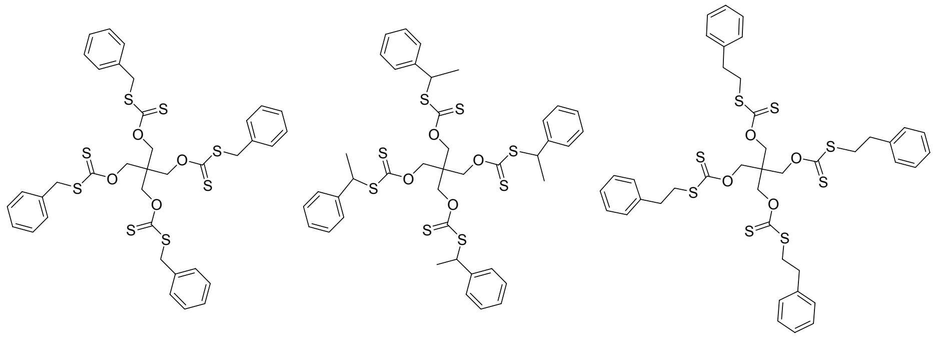


Scheme 1. Basic reaction steps of the RAFT process employing xanthates as mediating agents

Very recently, Stenzel *et al.* [19] have utilized the capability of xanthates to effectively control vinyl acetate polymerization for the production of three- and four-arm poly(vinyl alcohol) star polymers. These authors designed a multi-functional xanthate based RAFT agent, in which the central core of the star-like molecule constitutes the leaving R-group (see Scheme 1). Such an approach induces two undesirable effects: (*i*) Star-star-coupling reactions occur, due to the fact that the growing radical is located on the star polymer molecule, and (*ii*) additional linear polymer is formed along with the star polymer, because the dithioester group separates from the star polymer molecule during the RAFT equilibrium reaction (see Scheme 1). These complications in star polymer formation via RAFT have been extensively described by Stenzel *et al.* [20,21] and Mayadunne *et al.* [22].

As a consequence, we chose a different approach and designed novel xanthate based multi-functional RAFT agents (see Scheme 2), in which the central core constitutes the stabilizing Z-group. Employing such compounds leads to a RAFT equilibrium, in which the propagating radicals, i.e., the star polymer arms, separate from the central core molecule. That is, no radical functionality is located on the actual star polymer at any time, preventing star-star coupling reactions. In addition, the dithioester moiety remains at the central core, disabling controlled polymer formation in the surrounding bulk phase.

The objectives of the present communication are the design and synthesis of novel tetra-functional xanthate based RAFT agents, in which the core is the stabilizing Z-group, as well as exploring the capacity of these compounds as controlling agents for the star polymer formation in vinyl ester polymerizations.



5 **6** **7**

Scheme 2. Star-shaped xanthates used as RAFT agent

Experimental

Materials

Dimethyl formamide (DMF, Fluka) was refluxed 8 h over calcium hydride and subsequently distilled prior to use. Column chromatographic purification was performed using silica gel (Merck, Kieselgel 60) and technical grade *n*-pentane, diethyl ether, and toluene, respectively, which were distilled before usage. Vinyl acetate (VAc, Aldrich, ≥ 99.0 %) and vinyl propionate (VPr, Aldrich, ≥ 98.0 %) were purified by passing through a column filled with basic Al_2O_3. The initiator 2,2′-azobis(*iso*-butyronitrile) (AIBN, Merck) and 1,1′-azobis(cyclohexane-1-carbonitrile) (ACCN, Aldrich) was used as received; the purity was more than 98 % as verified by ^{1}H-NMR analysis. Tetrahydrofuran used as the eluent in size-exclusion chromatography (THF, Carl Roth, Rotipuran, stabilized with 2,6-di-*tert*-butyl-4-methylphenol) was used as received. All other chemicals were purchased from Aldrich and used without further purification.

Instruments

^{1}H-NMR analyses were performed on a Varian VXR 200 in $CDCl_3$. Mass spectrometry data were collected on a Finnigan LCQ ion trap mass spectrometer equipped with an atmospheric pressure ionization source and operated in the nebulizer-assisted electrospray mode. Molecular weight distributions were determined by means of size-exclusion chromatography using a Waters 712 WISP autosampler, a Waters 515 HPLC pump, PSS-SDV columns with nominal 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. The SEC set-up was calibrated against polystyrene standards of narrow polydispersity from Polymer Standards Service. Mark-Houwink parameters for poly(VAc) in THF ($K = 2.24\cdot10^{-2}$ mL·g^{-1}, $a = 0.674$ K) [23] provided access to absolute molecular weight distributions according to the principles of universal calibration [24].

Synthesis of tetrakis(benzyl-sulfanyl-carbothioyl-oxymethyl)methane **5**

0.25 g (1.8 mmol) of pentaerythritol **8** is dissolved in 50 mL of dry DMF and subsequently added to a suspension of 0.44 g (18 mmol) sodium hydride (60 % in paraffin) in 75 mL of dry DMF at room temperature. After stirring for 4 h, the mixture was cooled to 0 °C and 1.8 mL (30 mmol) of carbon disulfide was added dropwise. The ice-bath was then removed and after stirring the reaction mixture for 12 h at room temperature, 1.3 mL (11 mmol) of benzyl bromide was added dropwise. After subsequent stirring for 20 h at ambient temperature, the reaction was quenched via addition of a few drops methanol. The reaction mixture was poured on ice, extracted with diethyl ether (3 × 50 mL), washed with water (1 × 100 mL) and dried over sodium sulfate. After evaporation of the solvent under reduced pressure the crude product was purified via column chromatography on silica gel (toluene; *Rf* = 0.92, and pentane:diethyl ether = 10:1, *Rf* = 0.60). The product **5** was obtained as yellow crystals (0.50 g, 0.62 mmol, 35 %).

^{1}H-NMR ($CDCl_3$) δ (ppm): 4.38 (s, 8H, 4 × $C\underline{H}_2$), 4.68 (s, 8H, 3 × $C\underline{H}_2$), 7.3–7.4 (m, 20H, 4 × $C_6\underline{H}_5$).

^{13}C-NMR ($CDCl_3$) δ (ppm): 40.90 ($\underline{C}H_2Ph$), 43.78 ($\underline{C}(CH_2OR)_4$), 70.75 ($C(\underline{C}H_2OR)_4$), 128.20, 128.72, 128.98, 129.00, 134.80 ($\underline{C}_{arom}$), 213.35 ($\underline{C}$=S).

Accurate mass: 822.9 amu (theoretical mass for $C_{37}H_{36}O_4S_8$ / Na^+ = 823.03 amu).

Synthesis of tetrakis((1-phenyl-ethyl)-sulfanyl-carbothioyl-oxymethyl)methane **6**

The synthesis procedure of **6** is identical to that of **5**, except that instead of benzyl bromide 3.0 mL (22 mmol) of (1-bromoethyl)benzene was added. The crude product was purified via column chromatography on silica gel (toluene; *Rf* = 0.96, and pentane:diethyl ether = 10:1, *Rf* = 0.60). The product **6** was obtained as pale yellow liquid (0.30 g, 0.35 mmol, 9.5 %).

^{1}H-NMR ($CDCl_3$) δ (ppm): 1.60 (d, J = 6.3 Hz, 12H, 4 × $C\underline{H}_3$), 4.32–4.52 (m, 8H, 4 × $C\underline{H}_2O$), 4.8 (q, J = 6.3 Hz, 4H, 4 × $C\underline{H}$), 7.25–7.40 (m, 20H, 4 × $C_6\underline{H}_5$).

^{13}C-NMR ($CDCl_3$) δ (ppm): 21.89 ($\underline{C}H_3$), 43.28 ($\underline{C}(CH_2OR)_4$), 49.75 ($\underline{C}H$), 70.40 ($C(\underline{C}H_2OR)_4$), 128.19, 128.67, 129.00, 141.15, 141.88 ($\underline{C}_{arom}$), 212.58 ($\underline{C}$=S).

Elementary analysis: C 58.50 %, H 5.34 % (theoretical: C 57.44 %, H 5.17 %).

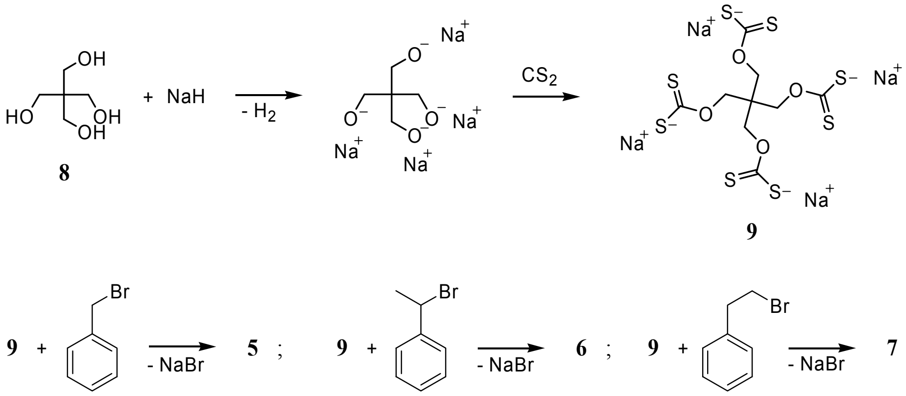
Synthesis of tetrakis((2-phenyl-ethyl)-sulfanyl-carbothioyl-oxymethyl)methane **7**

The synthesis procedure of **7** is identical to that of **5**, except that instead of benzyl bromide 3.0 mL (22 mmol) of (2-bromoethyl)benzene was added. The crude product was purified via column chromatography on silica gel (toluene; $Rf = 0.91$, and pentane:diethyl ether = 10:1, $Rf = 0.41$). The product **7** was obtained as pale yellow liquid (0.64 g, 0.75 mmol, 20 %).

^{1}H–NMR ($CDCl_3$) δ (ppm): 2.99 (dd, $J = 6.4$, 9.0 Hz, 8H, 3 × $C\underline{H}_2Ph$), 3.39 (dd, $J = 6.4$, 9.0 Hz 8H, 3 × $C\underline{H}_2S$), 4.79 (s, 8H, 3 × $C\underline{H}_2$), 7.22–7.33 (m, 20H, 4 × $C_6\underline{H}_5$).

^{13}C–NMR ($CDCl_3$) δ (ppm): 34.36 ($\underline{C}H_2Ph$), 37.55 ($\underline{C}H_2S$), 43.88 ($\underline{C}(CH_2OR)_4$), 70.73 ($C(\underline{C}H_2OR)_4$), 126.68, 128.57, 128.59, 139.41 ($\underline{C}_{arom}$), 214.24 ($\underline{C}$=S).

Elementary analysis: C 58.61 %, H 5.49 % (theoretical: C 57.44 %, H 5.17 %)



Scheme 3. Synthetic approach to star-shaped RAFT agent

Polymerizations

Stock solutions of monomer (25 mL VAc and VPr, respectively), initiator (AIBN and ACCN, respectively) with initial concentrations between $3\cdot10^{-4}$ and $1\cdot10^{-3}$ mol·L^{-1}, and tetra-functional RAFT agent **5**, **6** and **7**, respectively, with initial concentrations between $6\cdot10^{-4}$ and $3\cdot10^{-3}$ mol·L^{-1}, were prepared and thoroughly degassed via three freeze-pump-thaw cycles. Five samples of each stock solution were transferred inside a glove-box to individual glass vials and sealed with Teflon/rubber septa. The vials were subsequently inserted into a block heater thermostated at 60 ± 0.1 °C and 90 ± 0.1 °C, respectively. Samples were removed after predetermined time intervals and reactions were stopped by cooling the solutions in liquid nitrogen. The polymeric product was isolated by evaporating off the residual monomer. Monomer conversions were determined gravimetrically.

Results and Discussion

We performed bulk polymerizations of VAc at 60 °C, initiated by $3\cdot10^{-4}$ mol·L^{-1} AIBN, and with different concentrations of star RAFT agent **5**. The experimental results, listed in Table 1, indicate that **5** induces living/controlled characteristics in the VAc polymerization: (*i*) The number average molecular weight, M_n, increases steadily with monomer conversion, and (*ii*) the polydispersity index, $PDI = M_w/M_n$, reaches values below 1.5, depending on monomer conversion and RAFT agent concentration. The minimum *PDI* values of approximately 1.2 are observed at high RAFT agent concentrations. Maximum M_n values of approximately 50,000 g·mol^{-1} could be reached in a controlled manner. It should be noted that relatively low RAFT agent concentrations have been employed, because of the multifunctional nature of the star RAFT agent, which quadruplicates the concentration of active dithioester groups, and in order to target high molecular weight material. Additionally, it was an objective of the present work to probe the lower limit of RAFT agent concentration at which successful mediation can be sustained. It goes without saying that improved control may be achieved by using largely increased RAFT agent concentration, however, concomitantly reducing the average molecular weight.

Table 1. Selected experimental data of VAc bulk polymerization at 60 °C using **5** as the mediating agent and $3\cdot10^{-4}$ mol·L^{-1} AIBN as the initiator.

[**5**] / mol·L^{-1}	*time* / h	*monomer conversion* (%)	M_n / g·mol^{-1}	*PDI*
$5.94\cdot10^{-4}$	2	0.5	6767	1.52
	4	2.1	23720	1.36
	6	5.3	41116	1.47
	8	17.1	57170	1.92
	10	18.0	62368	1.86
$1.25\cdot10^{-3}$	2	0.3	1010	1.90
	4	0.5	1707	2.17
	6	1.0	5815	1.42
	8	1.7	10206	1.33
	10	4.8	26968	1.24
$2.54\cdot10^{-3}$	2	0.4	1198	1.33
	4	0.6	2109	1.50
	6	1.0	3735	1.33
	8	2.2	10139	1.28
	10	10.5	40327	1.18

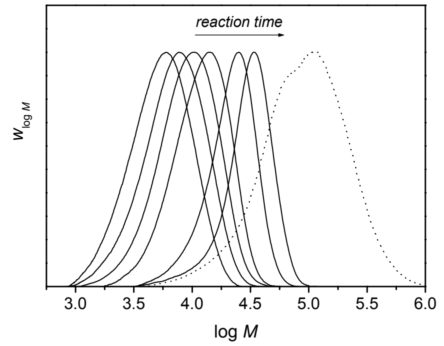


Figure 1. Evolution of normalized chain-length distribution (SEC-curves) with time (6, 7, 8, 9, 10, 11 (full lines) and 17 h (dotted line)) for a VAc bulk polymerization at 60 °C, mediated by $2.5\cdot10^{-3}$ mol·L^{-1} of **5** and using $3\cdot10^{-4}$ mol·L^{-1} AIBN as the initiator.

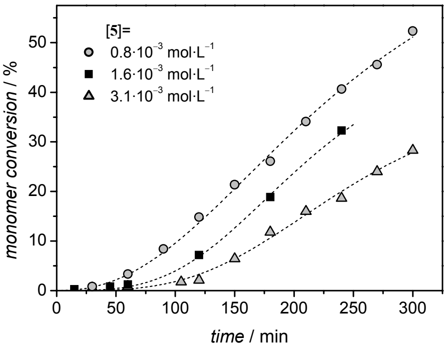


Figure 2. Monomer conversion vs. time profiles for VPr bulk polymerization at 90 °C, mediated by **5** and using $5\cdot10^{-4}$ mol·L^{-1} ACCN as the initiator. Dashed lines are guiding lines.

The evolution of the full molecular weight distribution with reaction time is depicted in Figure 1. It can be seen that the molecular weight of the produced polymer is increasing progressively with time, signifying the controlled nature of the polymerization. In addition, the unimodal distributions at lower conversions (full lines in Figure 1) indicate that termination reactions, including star-star coupling, are not playing a prominent role in that conversion regime. The increasing amount of polymeric material at the low molecular weight slope of the main peak is a common feature in RAFT and relates to the conventional termination reaction between two propagating radicals.

Closer inspection of the M_n vs. monomer conversion data (see Figure 3a) reveals an almost linear dependence in the low conversion regime (< 5 %), according to the theory of living polymerization. However, when higher monomer conversions are reached, the M_n vs. monomer conversion traces exhibit deviations from linearity (see Figure 3b), especially when low RAFT agent concentrations are used. When employing, e.g., $0.6 \cdot 10^{-3}$ mol·L^{-1} of **5** the increase in molecular weight with monomer conversion is significantly reduced after approximately 5 % of monomer conversion and 40,000 g·mol^{-1} of molecular weight, respectively. This flattening, however, is less pronounced in the case of RAFT agent concentrations being higher.

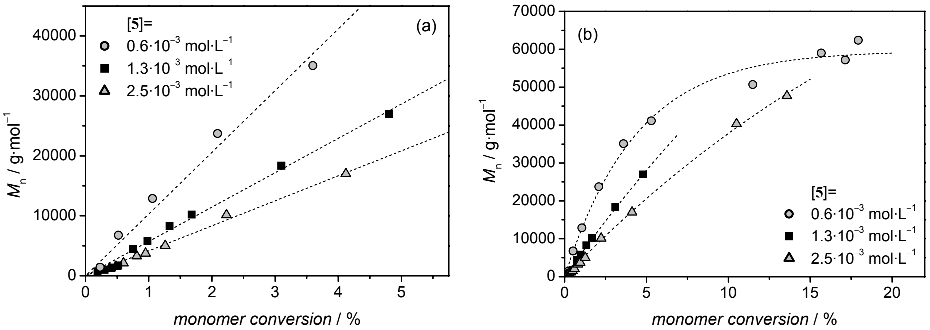


Figure 3. Number average molecular weight vs. monomer conversion for (a) the low and (b) the full experimental conversion regime of VAc polymerizations at 60 °C, mediated by **5**, and with $3 \cdot 10^{-4}$ mol·L^{-1} AIBN as the initiator. Dashed lines are guiding lines.

This effect may be understood by the star-like nature of the generated polymer: On the one hand, the increasing lengths of the polymeric chains constituting the arms of the star polymer provide an effective shielding, which progressively prevents the incoming propagating radical from reacting with the dithioester moiety that sits inside the star polymer molecule adjacent to the core. Thus, the control of the polymerization eventually weakens with increasing monomer conversion, as is also evident from concomitantly increased *PDI* values and full chain length distributions indicating presence of uncontrolled polymer (see Figure 1, dotted line). Such an effect is inherent when using RAFT agents, in which the core is the Z-group, however, it is somewhat relieved when employing high RAFT agent concentrations (see Figure 3b). On the other hand, the imperfect calibration of the SEC set-up, which is calibrated against linear polymer standards, reduces the apparent molecular weight of the star polymers, due to a reduced hydrodynamic volume. It should be noted that this effect renders detailed comparison of theoretical and experimental molecular masses at this stage problematic, although good agreement can be found in the very low conversion regime. Detailed determination of the star polymer molecular weight via absolute methods is underway and will be presented in a forthcoming study.

The boiling point of VAc (*bp* = 72 °C) is a natural upper limit for the VAc polymerization at ambient pressure conditions. In order to explore the influence of elevated temperature on the controlling ability of **5** in vinyl ester polymerization, we performed bulk polymerizations of VPr, the next homologue member of the vinyl ester family, at 90 °C, initiated by $5 \cdot 10^{-4}$ mol·L^{-1} ACCN, and with different concentrations of **5**. The results, tabulated in Table 2, indicate a somewhat decreased quality of control in this system, as obvious from higher *PDI* values.

Table 2. Selected experimental data of VPr bulk polymerization at 90 °C, using **5** as the mediating agent and $5 \cdot 10^{-4}$ mol·L^{-1} ACCN as the initiator.

[**5**] / mol·L^{-1}	*time* / min	*monomer conversion* (%)	M_n / g·mol^{-1}	*PDI*
$7.9 \cdot 10^{-4}$	60	3.3	11447	1.74
	120	14.8	14039	2.10
	180	26.1	15194	2.05
	240	34.1	18843	2.06
	300	52.3	20098	2.32
$1.6 \cdot 10^{-3}$	30	0.5	1266	1.95
	60	1.2	4791	1.41
	120	7.2	11560	1.77
	180	18.9	14031	2.07
	240	32.3	15090	2.28
$3.1 \cdot 10^{-3}$	60	0.8	1451	1.57
	120	2.1	5107	1.31
	180	11.8	10201	1.54
	240	18.6	14687	1.84
	300	28.3	19556	1.89

Increasing M_n values with monomer conversion, however, imply a controlled nature of the polymerization (see Figure 4a and 4b). As in the case of **5**-mediated VAc polymerization, a close-to-linear dependence of M_n vs. monomer conversion can be observed for very low conversions (< 2.5 %), again followed by a flattening of the M_n vs. monomer conversion trace with progressive polymerization. The diminution of control occurs at already 5 % monomer conversion, when using $0.8 \cdot 10^{-3}$ mol·L^{-1} of **5** as the RAFT agent. The molecular weight control, however, stays to some extent in operation up to 30 % conversion, when employing $3.1 \cdot 10^{-3}$ mol·L^{-1} of **5** – as evident from Figure 4b – leading to polymeric material that even exceeds the molecular weight from experiments using lower concentrations of **5**.

It should be noted that in all polymerizations reported a pronounced inhibition effect, that is, a considerable time period in the initial polymerization phase with only very small polymerization activity, has been observed. This effect, exemplarily shown in Figure 2, has been detailed earlier [16,25] and can be attributed to a RAFT pre-equilibrium being kinetically significantly different to the RAFT main equilibrium. After the inhibition period has passed, the polymerization proceeds with polymerization rates, which are slightly dependent on the initial RAFT agent concentration, i.e., rate retardation is operative. Detailed discussion, however, of such effects is beyond the scope of the present communication.

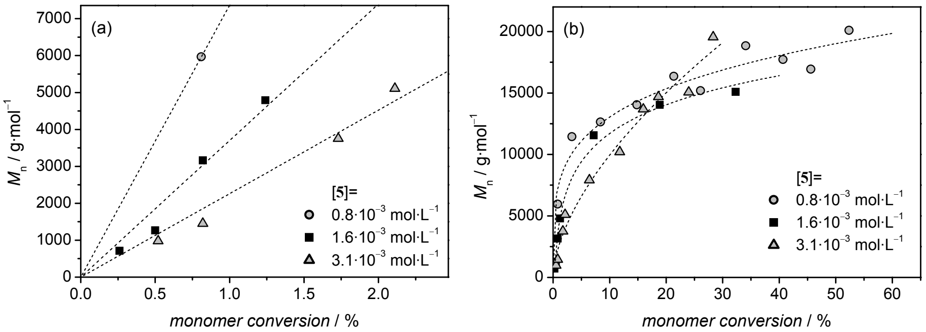


Figure 4. Number average molecular weight vs. monomer conversion for (a) the low and (b) the full experimental conversion regime of VPr polymerizations at 90 °C, mediated by **5**, and with 5·10^{-4} mol·L^{-1} ACCN as the initiator. Dashed lines are guiding lines.

To further explore the influence of the leaving R-group on the control that is exerted on vinyl ester polymerization, we employed **6** as the RAFT agent, in which the R-group benzyl is replaced by 1-phenyl ethyl. Secondary leaving groups – forming more stable radicals – are generally considered inducing a higher RAFT agent activity, due to an increased fragmentation rate of the first intermediate RAFT radical. We therefore performed VAc polymerizations at 60 °C using **6** as the RAFT agent. Interestingly, total inhibition up to ten hours of reaction time with no polymer production was observed. This might be explained by a decreased reinitiation ability of the more stable 1-phenyl ethyl radical toward the relatively unreactive VAc monomer, leading to enhanced termination by those primary leaving group radicals. Polymerizations of VPr at 90 °C, however, using **6** as the RAFT agent displayed features of controlled/living polymerization (see Table 3). These data indicate slightly enhanced control, as evident from *PDI* values, when comparing to the controlled VPr polymerizations using **5**. The M_n vs. monomer conversion traces (see Figure 5a and b) show very similar behavior to the **5**/VPr system, with good control in the initial conversion regime, succeeded by gradual loss of living behavior.

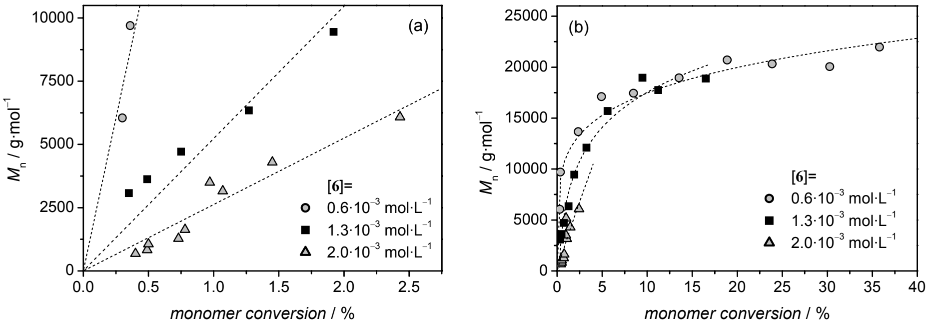


Figure 5a. Number average molecular weight vs. monomer conversion for (a) the low and (b) the full experimental conversion regime of VPr polymerizations at 90 °C, mediated by **6**, and with 5·10^{-4} mol·L^{-1} ACCN as the initiator. Dashed lines are guiding lines.

Destabilization of the expelled leaving group radical, as realized by a 2-phenyl ethyl leaving R-group in **7**, did not induce any control in both the VAc polymerization at

60 °C and the VPr polymerization at 90 °C. It may be envisaged that the primary leaving group yields a good reinitiating radical for vinyl esters. However, the ability of such radical to leave the intermediate RAFT radical is considerably reduced, which is obviously fatal for the overall RAFT process.

Table 3. Selected experimental data of VPr bulk polymerization at 90 °C using **6** as the mediating agent and $5\cdot10^{-4}$ mol·L^{-1} ACCN as the initiator.

[**6**] / mol·L^{-1}	*time* / min	*monomer conversion* (%)	M_n / g·mol^{-1}	*PDI*
$6.2\cdot10^{-4}$	60	0.4	9698	1.66
	120	4.9	17099	1.73
	180	13.5	18945	1.84
	240	23.9	20315	1.92
	300	35.8	21965	1.99
$1.3\cdot10^{-3}$	60	0.5	3620	1.42
	120	1.3	6344	1.57
	180	3.3	12090	1.62
	240	9.5	18957	1.65
	300	16.5	18881	1.88
$2.0\cdot10^{-3}$	60	0.5	827	1.59
	120	0.7	1277	1.91
	180	1.1	3158	1.32
	240	1.4	4296	1.46
	300	2.4	6079	1.52

In order to probe, if star polymer was indeed produced, we performed electrospray ionization (ESI) mass spectrometry (MS), which has been proven to be an excellent tool for the detailed characterization of polymeric microstructures [26,27]. This is especially true for polymeric materials originating from RAFT polymerizations with its relatively weakly bonded dithioester groups that may easily fragment [28]. Figure 6 depicts the ESI-MS spectrum of polymer from VAc polymerization mediated by **5**. The absolute mass of the main peaks, which are separated by the mass of one VAc monomer unit, i.e. 86.04 amu, can unambiguously be assigned to star polymer, consisting of the core moiety of **5** with its four Z-groups, various amounts of VAc monomeric units, and four leaving groups, i.e., benzyl, as terminal groups. The theoretical mass for the isotopic peak with maximum intensity of star-shaped 12-mer, for instance, ionized via attachment of Na^+ is *m*/*z* 1856.5, which is in excellent agreement with the experimentally determined value of *m*/*z* 1856.2. The relatively low signal-to-noise ratio is connected to the fact that the peak molecular weight of the sample studied already exceeded the upper mass limit of the experimental setup. Additional minor peaks could consequently not been assigned.

An increased spectral quality can be observed in Figure 7, in which the ESI-MS spectrum of polymer from RAFT polymerizations of VPr with **5** is depicted. A regular series of major peaks, accompanied by a sequence of minor peaks, can be observed. Each series is separated by 105.05 amu, corresponding to the molecular mass of VPr. The larger peaks can be attributed to VPr star polymer (e.g., 4-mer, with an NH_4^+ attached, which was added deliberately to increase ionization, theoretical *m*/*z* 1218.3, experimental *m*/*z* 1218.3), the smaller peaks are due to the same oligomeric species, in which *one* VPr unit has been hydrolyzed to yield a $(-CH_2-CHOH-)$ group (theoretical *m*/*z* 1162.3; experimental *m*/*z* 1162.3). It cannot be decided at the moment, if this fractional hydrolysis of star poly(VPr) occurs during the polymerization or because of the addition of ammonium acetate prior to the ESI-MS measurement. These studies are currently underway in our laboratory. It should be noted that deliberate hydrolysis of poly(VAc) star polymers generated via the Z-group approach may well lead to destruction of the star molecule, due to hydrolysis of the dithioester-bond.

It should be noted that the MS measurements do not allow for discrimination of star polymer species with different arm lengths. The fact, however, that the controlling dithioester groups are located next to the core renders the possibility of preferential growth of individual arms, leading to pseudo-linear polymer, extremely unlikely.

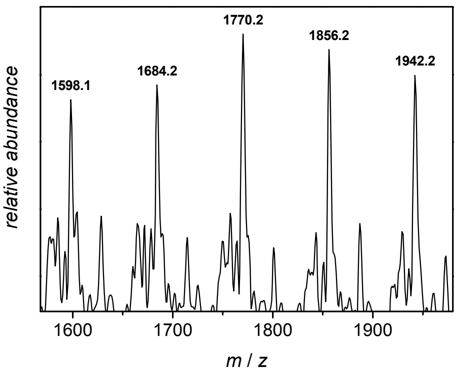


Figure 6. ESI-MS spectrum of star poly(VAc), generated via RAFT polymerization of VAc, mediated by $2.5\cdot10^{-3}$ mol·L^{-1} of **5** at 60 °C. For peak assignment see text.

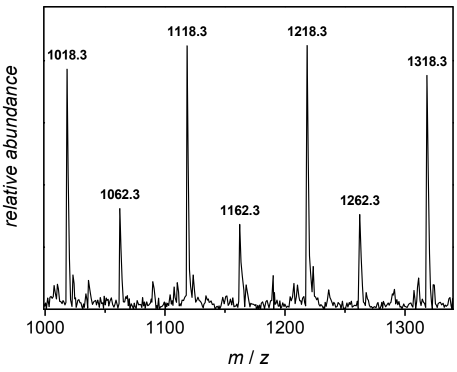


Figure 7. ESI-MS spectrum of star poly(VPr), generated via RAFT polymerization of VPr, mediated by $3.1\cdot10^{-3}$ mol·L^{-1} of **5** at 90 °C. For peak assignment see text.

Conclusion

Employment of *tetrakis*(benzyl-sulfanyl-carbothioyl-oxymethyl)methane as multi-functional xanthate based RAFT agent induced molecular weight control in both vinyl acetate polymerization at 60 °C and vinyl proprionate polymerization at 90 °C, respectively. In addition, *tetrakis*((1-phenyl-ethyl)-sulfanyl-carbothioyl-oxymethyl)-methane was successfully used as star RAFT agent in VPr polymerization at 90 °C. The generated polymers displayed increasing number average molecular weights with monomer conversion and relatively narrow polydispersities, depending on the concentration of the initial RAFT agent. Full molecular weight distributions indicated that termination reactions, including star-star coupling, are negligible. An increasing shielding effect of the growing polymeric arms, which hampers the addition reaction of the propagating radical to the dithioester groups next to the core, led to gradual reduction of control. The star-like architecture of the produced polymer was verified by electrospray ionization mass spectrometry.

Acknowledgements. The authors thank Michael Buback for stimulating discussions. Financial support by the *Deutsche Forschungsgemeinschaft* is gratefully acknowledged.

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