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Reversible addition fragmentation chain transfer polymerization of 3-[tris(trimethylsilyloxy) silyl] propyl methacrylate

Sureyya Saricilar[a,c], Robert Knott[b,c], Christopher Barner-Kowollik[a,*], Thomas P. Davis[a], Johan P.A. Heuts[a]

[a]*Centre for Advanced Macromolecular Design, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia*
[b]*Australian Nuclear Science and Technology Organization, PMB 1 Menai, NSW 2234, Australia*
[c]*Cooperative Research Center for Polymers, 32 Business Park Drive, Notting Hill, Vic. 3168, Australia*

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Abstract

Reversible addition fragmentation chain transfer (RAFT) bulk polymerizations of 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate (TRIS) have been carried out at 60 °C, employing cumyl dithiobenzoate (CDB) and 2-cyanoprop-2-yl dithiobenzoate (CPDB) as mediating agents at concentrations ranging from 5.0×10^{-3} to 2.0×10^{-2} mol l^{-1}. The monomer conversion vs. time evolution was followed via dilatometry and ^{1}H NMR spectroscopy. The CDB mediated polymerization displays RAFT agent concentration dependent inhibition and rate retardation phenomena, whereas the CPDB mediated polymerization process is less susceptible to rate retardation and inhibition effects. The different behavior of CDB and CPDB in TRIS polymerization is most likely due to the increased stability of the intermediate macroRAFT radicals in the CDB mediated process. The generated RAFT polymers were analyzed via size exclusion chromatography indicating linear macromolecular growth with respect to monomer conversion and low polydispersities (PDI < 1.15) up to high monomer to polymer conversion ($>90\%$).

Keywords: Living radical polymerization; Reversible addition fragmentation chain transfer (RAFT); Polymerization kinetics

1. Introduction

3-[Tris(trimethylsilyloxy)silyl] propyl methacrylate (Scheme 1, TRIS (**1a**)), is an important monomer in contact lens manufacture due to its high Si–O content, which imparts high oxygen permeability to the lenses. The application of TRIS has always been in co- and terpolymeric-formulations with monomers containing hydroxyl or amino or/and fluorine groups such as 2-hydroxyethyl methacrylate, *N*-vinyl-2-pyrrolidone, *N*,*N*-dimethyl acrylamide, ethylene glycols and fluorine containing silicone monomers [1–3]. Because anionic polymerization methods are not applicable to such monomers, living free radical polymerization is an attractive alternative to achieve controlled macromolecular growth and narrow polydispersity polymers. The main advantages of free radical chemistry are the undemanding conditions required for polymerization and the large number of monomers that can be polymerized. A minor disadvantage of this method comes from a substantial gel effect in some systems (Norrish–Trommsdorff effect) that causes a sudden increase in the rate of polymerization at elevated monomer conversions and may impede the formation of polymers adequate for lens formation [4]. The application of living free radical polymerization has opened the possibility of generating complex macromolecular architectures in undemanding reaction conditions [5–9].

Among the most prominent living free radical polymerization techniques are atom transfer radical polymerization (ATRP) [5], nitroxide mediated polymerisation (NMP) [6] and reversible addition fragmentation chain transfer polymerization (RAFT) [7–10]. The use of ATRP and NMP in the synthesis of block copolymers and other structures of complex architecture has been limited by the fact that both processes are not compatible with all

* Corresponding author. Tel.: +61-2-9385-4331; fax: +61-2-9385-6250.
E-mail address: camd@unsw.edu.au (C. Barner-Kowollik).

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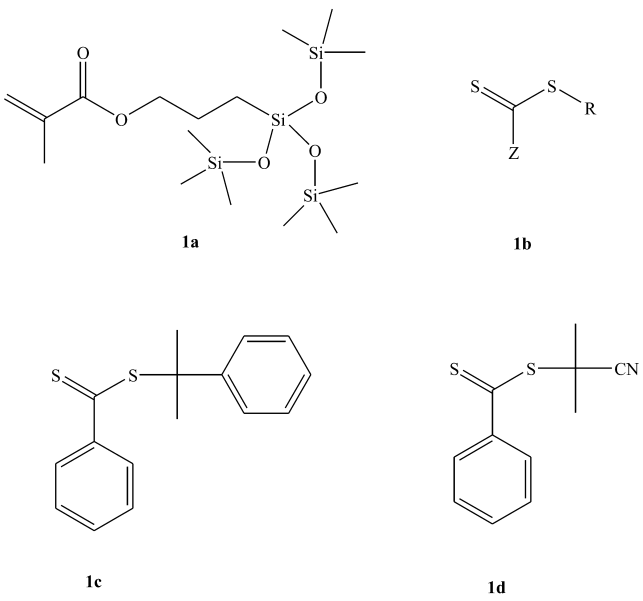
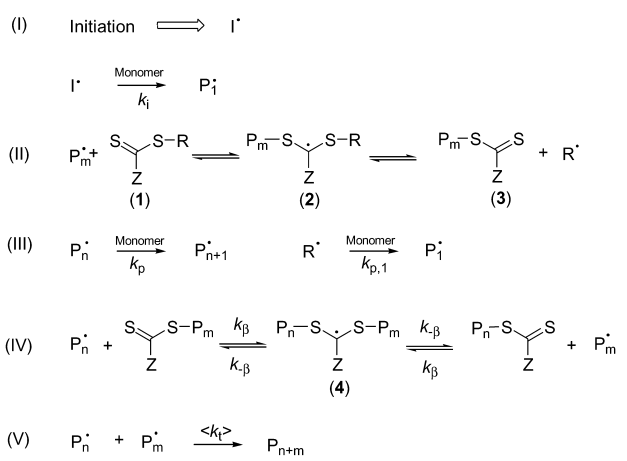


Scheme 1. Generic structure of TRIS (1a) and dithiobenzoate-type RAFT agents (**1b**), cumyl dithiobenzoate (CDB) (**1c**) and 2-cyanoprop-2-yl dithiobenzoate (i.e. cyanoisopropyl dithiobenzoate (CPDB) (**1d**)).

monomers or reaction conditions. The RAFT technique is probably the most versatile of the above as it exhibits a high degree of compatibility with a wide range of functional monomers and is tolerant to water and oxygen present in the system, while giving excellent access to complex architectures ranging from block to star polymers [11–13].

The currently accepted RAFT mechanism is depicted in Scheme 2. The process involves a series of reversible addition–fragmentation steps in addition to the conventional free radical polymerization steps. Initiation (I) is followed by a pre-equilibrium (II) in which the transfer agent (**1**) reacts with the growing polymer chains resulting in an intermediate radical species (i.e. a macroRAFT radical (**2**)), which may fragment either back to the starting materials (**1**) or release the leaving group R to generate a macroRAFT agent (**3**). This step will only be effective in the early stages of the polymerization. After a specific period of time



Scheme 2. Basic mechanism of the RAFT process.

depending on the rate of chain transfer to the initial RAFT agent and molar ratio of the RAFT agent to propagating radical all initial RAFT agents will be consumed. The leaving group R may subsequently react with the monomer to form a new propagating radical in the re-initiation step (III) with a short chain propagation rate coefficient, $k_{p,1}$. Reaction step (IV) constitutes the core step of the RAFT process. An equilibrium establishes between the active propagating radicals, macroRAFT radicals (**4**) and the polymeric RAFT agent in such a manner that there is an equal probability of growth for all chains, resulting in a narrow molecular weight distribution. The efficient transfer between propagating radicals and polymeric RAFT agent is necessary to maintain control of the polymerization. The last step involves bimolecular termination reactions (combination and disproportionation), which always occurs to some extent, but can be proportionally decreased by increasing the concentration of the RAFT agents. Spectroscopic techniques (NMR, UV/VIS) have provided some evidence [9] for the mechanism shown in Scheme 1 and additional ESR studies have shown the presence of intermediate macroRAFT radicals (**4**) [14]. Furthermore, the stability of the intermediate macroRAFT radical (**2**) formed in the pre-equilibrium has been investigated in recent studies [15–16]. It has been shown that structural adjustment (i.e. by changing the Z group) is required to decrease the stability of the intermediate macroRAFT radical (**4**). However, a straight isolation of the intermediate RAFT radical in the pre-equilibrium and core steps of the RAFT polymerization has yet to be achieved.

The effectiveness of the RAFT agents in terms of their transfer ability and control of molecular weight and polydispersities strongly depends on the nature of the Z and R groups (Scheme 1, (**1b**)). Highly effective RAFT agents are thiocarbonylthio compounds, where R is a free radical leaving group that is capable of reinitiating polymerization activity and Z is a group that modifies the reactivity of the carbon sulphur double bond on the one hand and the stability of the intermediate macroRAFT radical on the other [10,17,18]. The effect of various Z and R-group combinations on the polymerization kinetics of a range of monomers has recently been reviewed [19,20]. In a recent study, we provided evidence that the R group also affects the stability of the intermediate macroRAFT radicals (**2**) [21]. In an ideal RAFT system, the chain transfer and equilibration process should be fast and favour the parallel growth of the polymer chains without influencing the rate of polymerization. However, it has been reported for some RAFT agent mediated polymerization that the rate of polymerization decreases significantly when increasing the RAFT agent concentrations [21–25]. The origin of the inhibition and retardation effects in RAFT polymerizations is currently undergoing debate in the scientific community [23,31].

In earlier work from this laboratory, it was shown that hydrogels made from a hydrophilic polymer backbone

substituted with long perfluoro side chains can display very high oxygen permeability [4]. It was surmised that a phase separated structure allowed oxygen transmission by two pathways. As with conventional hydrogel materials, the water provides one route via dissolved oxygen. The second route was suggested to be via a co-continuous fluorine-rich polymeric phase. It is well known that high oxygen permeability can be attained by utilizing either fluoro- or siloxanyl-groups in polymer design. Optimizing oxygen permeability without losing transparency, mechanical integrity and surface hydrophilicity requires controlled phase separation via careful macromolecular design. Therefore, in this work, we describe our initial work into controlling the polymerization of TRIS. In future work, we will describe block copolymer formation, phase separated materials and the relationship between morphology and oxygen permeability.

2. Experimental

2.1. Materials

3-[Tris(trimethylsilyloxy) silyl] propyl methacrylate ($c^{\text{bulk}}_{\text{TRIS}} = 2.17\ \text{mol l}^{-1}$ (at 25 °C), 422.81 g mol^{-1}, TRIS, Aldrich, 98%) was passed through a column of activated basic alumina (Acros, 50–200 μm) in order to remove the inhibitor hydroquinone monomethyl ether (MEHQ). 2,2′-Azobisisobutyronitrile (AIBN, Aldrich, 99%) was recrystallized twice from methanol prior to use. The two RAFT agents employed in this study, i.e. cumyl dithiobenzoate (CDB) and 2-cyanoprop-2-yl dithiobenzoate (i.e. cyanoisopropyl dithiobenzoate, CPDB) were synthesized according to the procedures described in Ref. [8]. The purity of the RAFT agent was greater than 98% (as assessed via ^{1}H- and ^{13}C NMR spectroscopy). Analytical grade tetrahydrofurane (THF, Spectrosol, 99.99%) was used for the size exclusion chromatography (SEC) measurements without further purification.

2.2. General polymerisation procedure

Stock solutions for TRIS bulk polymerizations were prepared with initial RAFT agent concentrations ranging from 5.0×10^{-3} to 2.0×10^{-2} mol l^{-1} and AIBN concentrations close to 3.5×10^{-3} mol l^{-1}. The stock solutions were placed in a 50 ml tube, specially modified for use with standard Schlenk equipment, and deoxygenated via three freeze–pump–thaw cycles. Six samples of each stock solution were transferred to individual ampoules by a gas tight syringe. The sealed ampoules were deoxygenated again by nitrogen purging for approximately 10 min after the sample transfer. The reaction ampoules were then placed in a thermostated water bath at a constant temperature (60 °C), and ampoules were removed after pre-set reaction times. The polymerization was stopped by placing the solutions into an ice bath. The polymer was isolated from the reaction mixtures by precipitation in a large excess of methanol. The polymers were subsequently dried under reduced pressure at 50 °C. The conversions were determined via both ^{1}H NMR analysis and gravimetry.

2.3. Dilatometry

The mixtures of monomer (TRIS), AIBN and RAFT agent were degassed by three freeze–pump–thaw cycles on a high vacuum line. Subsequently, a reactor especially designed for dilatometry was charged with the degassed reaction mixture using a gas tight syringe. The monomer conversion was traced using a contraction factor, γ, according to $\gamma = (1/d_{\text{TRIS}}) - (1/d_{\text{poly(TRIS)}}) = 0.1143$ ml × g^{-1} at 60 °C. Here, $d_{\text{TRIS}} = 0.8892$ g ml^{-1} and $d_{\text{poly(TRIS)}} = 0.9898$ g ml^{-1} are the densities of TRIS and polymeric TRIS of sufficiently high molecular weight (i.e. $M_n > 100,000$ g mol^{-1}), respectively. In the case where polymeric RAFT agent (polyTRIS dithiobenzoate) was used, the density of the initial reaction mixture was close to 0.9402 g ml^{-1}. The contraction factor, γ, for this experiment—obtained by using the same polymer density as used in the conventional system—is close to 0.0533 ml g^{-1}. The densities of monomer and polymer were measured using both densitometry and the density bottle method.

2.4. NMR spectroscopy

Characterization of the reaction mixtures (to monitor the progress of the reaction) and the final polymer was carried out via ^{1}H NMR spectroscopy, using a Bruker DPX 300 MHz NMR spectrometer with a pulse angle of 45°. Deuterated chloroform, $CDCl_3$ (Aldrich, 99.8%) was used as solvent. Pure TRIS monomer (Fig. 1) gives the following ^{1}H NMR spectrum (300 MHz, $CDCl_3$, $CDCl_3 = 7.26$ ppm) δ: 6.10, 5.54 (dd, 2H, CH_2=), 4.10 (t, 2H, CH_2–O), 1.91 (s, 3H, C–CH_3), 1.62 (q, 2H, CH_2–C), 0.50 (t, 2H, CH_2–Si), 0.10 (s, 27H, 3 × Si–$(CH_3)_3$).

As an independent check of the dilatometric results, off-line ^{1}H NMR spectroscopy has been used to assess monomer to polymer conversions by two methods. (i) One of the vinyl signals (denoted **a** in Fig. 1) is set into relation to the non-changing signal of the methysiloxy groups (denoted **f** in Fig. 1) according to Eq. (1). (ii) The triplet signal at approximately 4.1 ppm (**c** in Fig. 1) resonates at a significantly higher field in the polymer (close to 3.8 ppm, denoted c^{p} in Eq. (2)). The procedure based on Eq. (2) yields the monomer to polymer conversion. It should be noted that both methods yielded identical results within the present study.

$$\text{Conversion} = 1 - \frac{\text{Integral}[a]}{\text{Integral}[f]} \times 27 \quad (1)$$

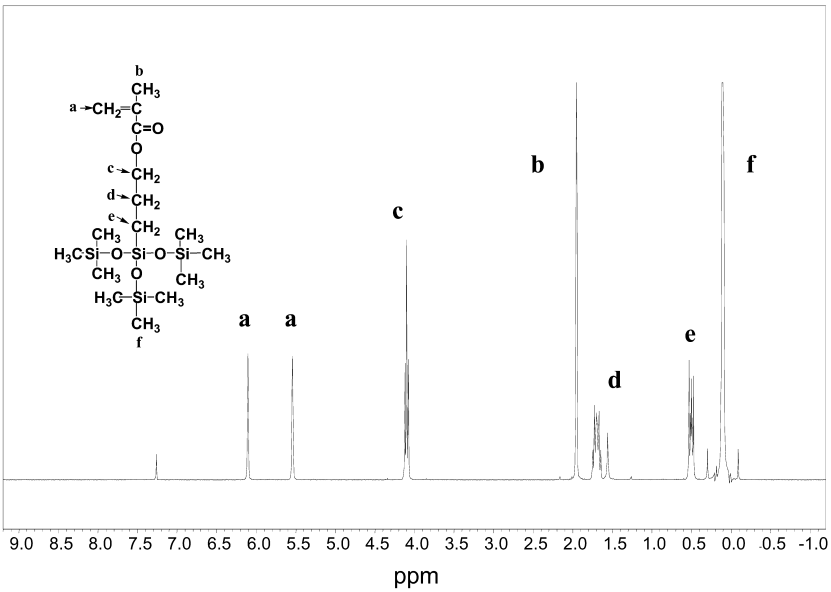


Fig. 1. Typical ^{1}H NMR spectrum of TRIS in bulk used to asses overall monomer conversions (see text for details).

$$\text{Conversion} = 1 - \frac{\text{Integral}[c]}{\text{Integral}[c^{\text{p}}] + \text{Integral}\,[c]} \qquad (2)$$

2.5. Molecular weight characterisation

Molecular weight distributions were determined via a SEC system consisting of a Shimadzu LC-10 AT VP pump, a SIL-10AD VP auto-injector, a RID-10A differential refractive index detector and a column set consisting of three linear PL columns (10^5, 10^4 and 10^3 Å). The analysis was carried out at 40 °C in tetrahydrofurane as the eluent at a flow rate of 1.0 ml min^{-1}. The system was calibrated using narrow poly(methyl methacrylate) standards ranging from 500 to 10^6 g mol^{-1}. The resulting molecular weight distributions were subsequently re-calibrated using the universal calibration equation with the Mark–Houwink parameters for poly(TRIS) ($K = 1.67 \times 10^{-5}$ dl g^{-1} and $a = 0.74$) [32]. The Mark–Houwink parameters for poly (methyl methacrylate) to effect the universal calibration read $K = 12.8 \times 10^{-5}$ dl g^{-1} and $a = 0.69$.

3. Results and discussion

The kinetic coefficients, i.e. the propagation and termination rate coefficient, governing the free radical polymerization of TRIS have been investigated intensively in previous studies [32–34]. The activation energy, E_A, for the propagation reaction determined for the bulk polymerization of TRIS is significantly less than that obtained for the lower alkyl methacrylates and is similar to that reported for dodecyl methacrylate [32]. The requirements for a RAFT agent to be an effective mediator of the polymerization are that the rate of addition of the propagating radicals to the RAFT agent—governed by the rate coefficient k_β (Scheme 2) must be fast relative to the rate of propagation. In addition, the leaving group must be capable of reinitiating macromolecular growth. The electronic and possibly steric nature of the Z and R-groups as well as that of the propagating radical thus determine the effectiveness of the RAFT process. The free radical polymerization of TRIS involves relatively bulky propagating radicals that are stabilized by intra-molecular interaction of the long alkyl chain. Previous studies indicate that efficient RAFT polymerization of bulky monomers require RAFT agents with effectively reinitiating R groups as well as a stabilizing group Z that enhances the rate of addition of propagating radicals to the carbon sulfur double bond. The effectiveness of cumyl dithiobenzoate (CDB) as RAFT agent in the free radical polymerization of MMA has been demonstrated in previous studies [7,35]. A phenyl Z-group in conjunction with both a cumyl and cyanoisopropyl R-group were selected for the present study (Scheme 1, (**1c**), (**1d**)).

Initially, the cumyl dithiobenzoate mediated polymerization of TRIS was carried out in bulk at 60 °C using AIBN as the initiator and with three different initial CDB agents concentrations ranging from 5.0×10^{-3} to 2.0×10^{-2} mol l^{-1}. An additional polymerization was conducted in the absence of CDB, but otherwise identical reaction conditions. Monomer conversion vs. time profiles were obtained for a series of polymerizations via dilatometry along with parallel experiments using ^{1}H NMR spectroscopy and gravimetry for conversion measurement. Excellent agreement between the three types of experiments can be observed by inspection of Fig. 2a ($c^0_{\text{CDB}} = 1.0 \times 10^{-2}$ mol l^{-1}).

The corresponding number average molecular weights, M_n, along with the associated polydispersities for CDB

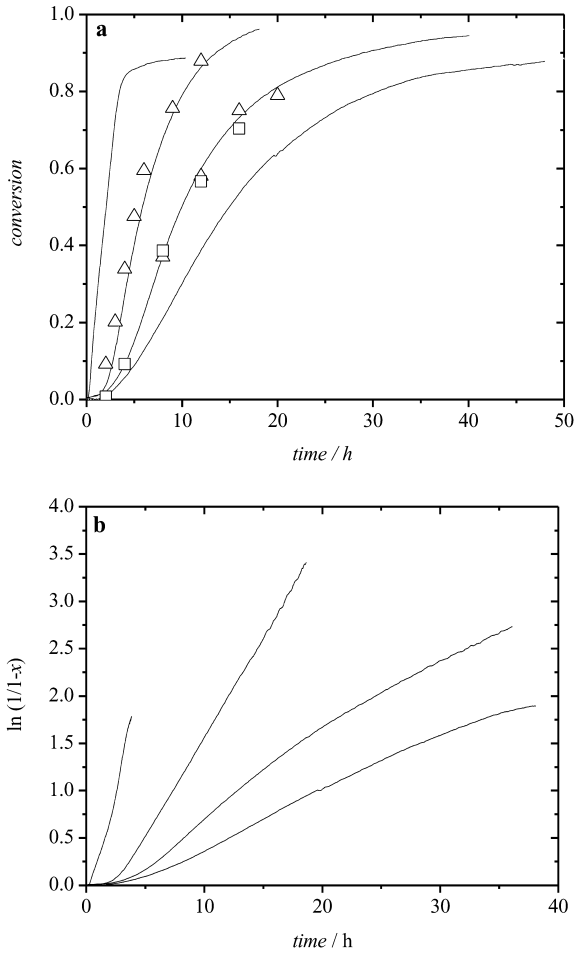


Fig. 2. (a) Monomer conversion vs. time evolution in the (bulk) cumyl dithiobenzoate (CDB) mediated free radical polymerization of TRIS at 60 °C monitored via on-line dilatometry, off-line ^{1}H NMR spectroscopy (□) and gravimetry (△) at varying initial CDB concentrations ranging from $c^0_{CBD} = 0$, 5.0×10^{-3}, 1.0×10^{-2} to 2.0×10^{-2} mol l^{-1}, respectively. The initial AIBN concentrations was close to 3.5×10^{-3} mol l^{-1} in all cases. (b) Pseudo-first-order plots generated from the dilatometry data given in (a).

concentrations of 5.0×10^{-3} and 1.0×10^{-2} mol l^{-1} are collated in Table 1. Close inspection of Fig. 2a indicates that during the early stage of the RAFT polymerization there is a significant inhibition period that increases with higher initial RAFT agent (i.e. cumyl dithiobenzoate) concentrations. In the case of the highest RAFT agent concentration the reaction takes up to 2 h at 60 °C before polymer formation is observed. A slight inhibition period (≈12 min) is also observed for the control system (i.e. no CDB present in the reaction mixture) that may be attributed to traces of molecular oxygen in the monomer. As TRIS is specifically utilized to impart high oxygen permeability to biomaterials, it is possible that due to the very high oxygen equilibrium concentration of the monomer, dissolved O_2 is not completely removed by nitrogen bubbling or routine freeze–pump–thaw procedures [4]. It is well known that molecular oxygen may act as an inhibitor, forming relatively poor initiating peroxy-type radicals, which may react with themselves or propagating radicals by combination and disproportionation to form inactive products.

It can be inferred from Fig. 2a that the polymerization takes longer to reach the steady state propagating radical concentration with increasing initial CBD concentrations. Fig. 2a also shows that there is a strong reduction in the rate of polymerization when the initial CDB concentration in the reaction mixture is increased. Such rate retardation phenomena have already been reported for some monomer/RAFT agent combinations and have been extensively discussed in the literature [8,21–30]. However, the molecular weight increases linearly with conversion and the PDI is below 1.2 for all CDB concentrations and monomer conversions. The inhibition period and the rate retardation have therefore no effect on the molecular weight control, but dramatically influence the kinetics of polymerization. The conversion vs. time data measured via dilatometry shown in Fig. 2a can be alternatively plotted in a first order plot (Fig. 2b). Inspection of Fig. 2b indicates that after an initial inhibition period—as discussed above—the plots are approximately linear, which may be indicative

Table 1
Number average molecular weights, M_n, and polydispersities, PDI, obtained in the free radical (bulk) polymerization of TRIS at 60 °C using cumyl dithiobenzoate (CDB) and cyanoisopropyl dithiobenzoate (CPDB) as RAFT agents. The initiator (AIBN) concentration was close to 3.5×10^{-3} mol l^{-1} in all cases

RAFT agent concentration										
[CDB] = 5.0×10^{-3} mol l^{-1}				[CDB] = 1.0×10^{-2} mol l^{-1}				[CPDB] = 1.0×10^{-2} mol l^{-1}			
Time[a] (h)	M_n	M_n^{theo}	PDI	Time[a] (h)	M_n	M_n^{theo}	PDI	Time[a] (h)	M_n	M_n^{theo}	PDI
2 (9.2)	17,000	16,846	1.19	4 (9.9)	11,000	9084	1.10	1 (7.0)	8500	6423	1.22
3 (20)	31,400	37,004	1.13	8 (37)	25,000	34,499	1.09	2 (29)	21,000	26,608	1.09
4 (37)	48,300	67,529	1.10	12 (58)	32,700	53,491	1.11	3 (44)	33,200	40,371	1.06
5 (48)	63,400	87,274	1.08	16 (75)	44,100	68,814	1.04	4 (56)	35,100	51,381	1.06
6 (60)	73,200	109,129	1.06	20 (80)	45,900	73,402	1.04	6 (69)	49,200	63,309	1.06
9 (76)	99,500	139,463	1.14	24 (85)	49,500	77,989	1.03	8 (79)	54,400	72,485	1.04
12 (92)	121,400	168,824	1.15	48 (90)	57,000	82,577	1.08	12 (96)	62,000	88,082	1.06

[a] The monomer to polymer conversions (dilatometry) are given in brackets.

of the fact that the polymerization proceeds under steady state conditions up to high monomer conversions [36]. The observed inhibition and retardation effects can be caused by a variety of factors. In a previous publication, we have presented evidence that inhibition in CDB mediated acrylate bulk polymerizations is likely caused by relatively stable intermediate radical species (**2**) [21]. Alternatively, it has been suggested that inhibition periods may also be caused by selecting leaving groups which are not efficient in re-initiating macromolecular growth in correlation with their individual radical stabilities [30]. Rate retardation phenomena may also be caused by stable intermediate RAFT radicals and a bulk of evidence has been put forward to support this claim [15,28,25,36]. In addition, irreversible and reversible termination processes of the intermediate RAFT radicals (**4**) may also contribute to a reduction in the propagating free radical concentration, thus inducing rate retardation effects [27,23]. It is difficult to assess from data on the CDB mediated polymerization of TRIS alone, which of the above mechanism is operative in this case. For this reason, the CPDB mediated polymerization system was included in the experimental design (see below).

The generated polymer was also analyzed via SEC. Polymer synthesized under conditions of a low initial CDB concentration shows a bimodal SEC distribution particularly at high conversions—as shown in Fig. 3a and b.

The CDB concentration in this case was close to 5.0×10^{-3} mol l^{-1}. The SEC chromatograms (Fig. 3a) of the generated polymers exhibited symmetrical peaks which are extremely narrow (PDI = 1.06 at 59% monomer conversion). However, at 76% conversion and above, a small second peak appears on the high molecular weight side of distributions and the PDI increases to above 1.10. The second peak is relatively small and its peak molecular weight is double that of the main peak, suggesting that it may be formed via the combination of propagating radicals, although it was reported previously that the disproportionation reactions predominate over combination for methacrylates type systems [37]. An additional possibility that may account for the formation of the high (double) molecular weight shoulder is termination via disproportionation of the intermediate macroRAFT radical (species (**4**) in Scheme 2). The likely possibility of species (**4**) being relatively stable [21,28,24,25,29] would make such reaction a consequence of slow fragmentation. A similar bimodal distribution is not seen at higher initial concentrations of CDB (1.0×10^{-2} mol l^{-1} and over) even at very high monomer conversions (Fig. 3b).

In a subsequent set of experiments, cyanoisopropyl dithiobenzoate (CPDB) was employed to mediate the (bulk) polymerization of TRIS. Fig. 4a compares the monomer conversion vs. time evolution of CDB, CPDB and polyTRIS dithiobenzoate (PTRISDB, $M_n = 29,800$ g mol^{-1}, PDI = 1.09) mediated TRIS polymerizations. All mediating agents have been employed at a (RAFT end group) concentration of 1.0×10^{-2} mol l^{-1}.

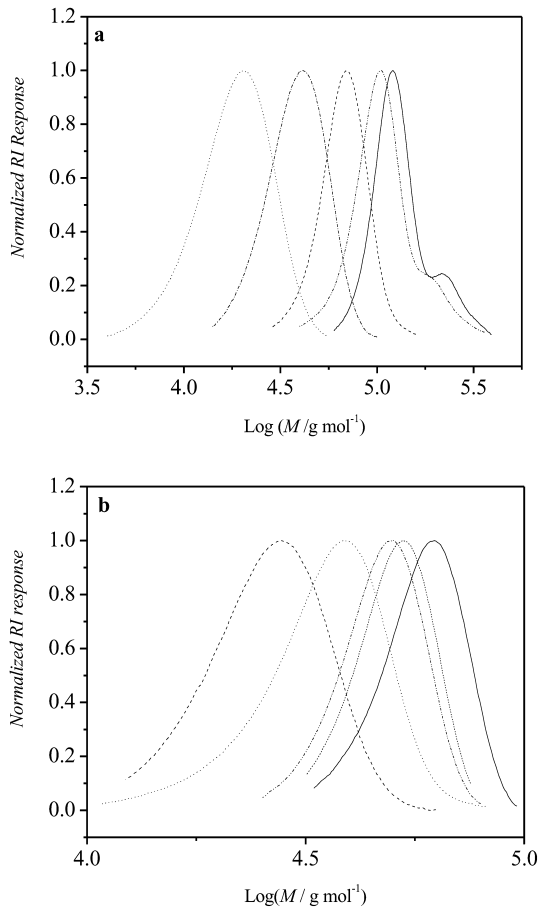


Fig. 3. Evolution of the molecular weight distribution for a cumyl dithiobenzoate (CDB) mediated TRIS (bulk) free radical polymerization at 60 °C using AIBN as initiator ($c^0_{AIBN} = 3.5 \times 10^3$ mol l^{-1}). (a) $c^0_{CDB} = 5.0 \times 10^{-3}$ mol l^{-1}, samples taken after 2, 3, 4, 9 and 12 h, (b) $c^0_{CDB} = 1.0 \times 10^{-2}$ mol l^{-1}, samples taken after 8, 12, 20, 24 and 48 h.

Inspection of Fig. 4a clearly indicates that CPDB induces far less rate retardation *and* a shorter inhibition time than CDB. A still somewhat smaller retardation and almost no inhibition is induced when the polymeric RAFT agent is employed. Thus, a change in the leaving group has a profound effect on both the inhibition time and the magnitude of rate retardation induced. As mentioned above, possible causes for reduced inhibition phenomena include the possibility that the cyanoisopropyl leaving group is more effective in reinitiating polymerization activity than the cumyl group (reaction step (III) in Scheme 2). However, it can also be envisaged that the intermediate macroRAFT radical (species (**2**) in Scheme 2) is more stable in the cases when CDB is employed instead of CPDB. This notion is underpinned by recent findings on CDB and CPDB mediated acrylate (bulk) free radical polymerizations, which point out that indeed the cumyl radical is superior to the cyanoisopropyl radical in its reinitiating ability [21]. (The addition rate coefficient of a cumyl radical to an acrylate vinyl bond is estimated to be close to 430 l mol^{-1} s^{-1} at 23 °C, while the same coefficient reads 367 l mol^{-1} s^{-1} at 42 °C for the cyanoisopropyl radical)

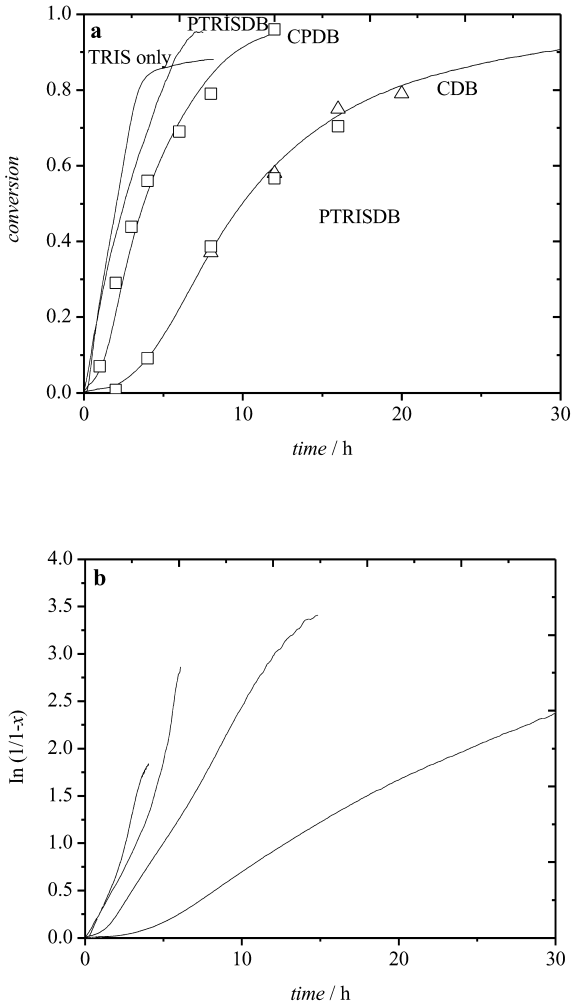


Fig. 4. (a) Comparison between the monomer conversion vs. time evolution for the TRIS (bulk) free radical polymerizations at 60 °C mediated by cumyl dithiobenzoate (CDB), cyanoisopropyl dithiobenzoate (CPDB) and polyTRIS dithiobenzoate (PTRISDB) monitored via on-line dilatometry, off-line ^{1}H NMR spectroscopy (□) and gravimetry (△). The RAFT agent concentration was close to 1.0×10^{-2} mol l^{-1} in each case. (b) Pseudo-first-order plots generated from the dilatometry data given in (a).

[38]. If slow or inefficient re-initiation is the cause for inhibition phenomena, then enhanced inhibition would be expected for the cyanoisopropyl carrying RAFT agent, i.e. CPDB. The polymeric RAFT agent may thus yield—at least in the context of this study—the least stable intermediate macroRAFT radical species (**2**). The rate retardation effect—which is observed to some extent for both CDB and CPDB (Fig. 4a and b) may also be caused by a relatively stable macroRAFT radical species (**4**). Recent quantum mechanical calculations also point to slow fragmentation of the intermediate macroRAFT radicals as the likely cause for inhibition and retardation phenomena [28]. Of course, additional reversible and irreversible termination process of these species with propagating macro radicals or—even more likely—with other intermediate radicals are also possible [39].

Fig. 5 shows the evolution of the number average molecular weight, M_n, with monomer conversion at 60 °C for two CDB (i.e. $c^0_{CDB} = 5.0 \times 10^{-3}$ and 1.0×10^{-2} mol l^{-1}) and one CPDB concentration (i.e. $c^0_{CPDB} = 1.0 \times 10^{-2}$ mol l^{-1}). In two ideal RAFT systems (i.e. both having an efficient chain transfer equilibrium), identical CDB and CPDB concentrations should yield identical molecular weight vs. conversion traces. The number average molecular weights expected theoretically (deduced via rationing the achieved monomer conversion times the fractional monomer conversion with the initial RAFT agent concentration) are higher than the experimentally found numbers. However, it should be pointed out that the measured molecular weights are associated with a considerable error of close to 30% due to the universal calibration procedure that was employed in the SEC analysis of the polymers. The polydispersity evolution with monomer conversion is in agreement with previous results for other RAFT systems, i.e. an initial decrease in the PDI is observed at low conversions, followed by an increase of this value towards higher monomer conversions [25]. It is noteworthy that the polydispersities of the generated polymers remain low (PDI < 1.2) even for extremely high monomer conversions. In an extension of the present study, it is envisaged to prepare block copolymers of TRIS with other monomers via the RAFT procedure.

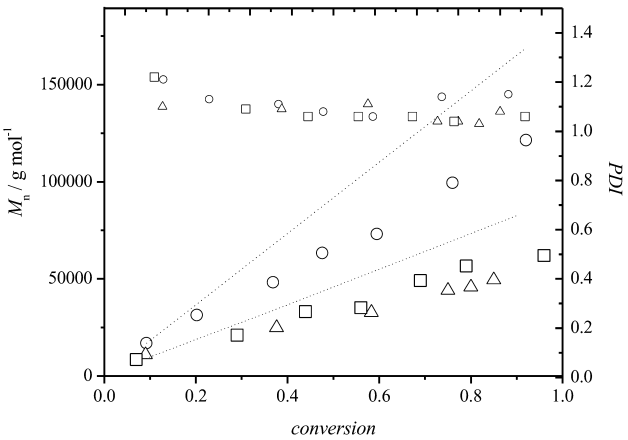


Fig. 5. Evolution of the number average molecular weight, M_n, and the polydispersity index, PDI, with monomer conversion in the bulk free radical polymerization of TRIS at 60 °C mediated by cumyl dithiobenzoate (CBD) at concentrations of $c^0_{CBD} = 5.0 \times 10^{-3}$ mol l^{-1} (○) and 1.0×10^{-2} mol l^{-1} (△) as well as cyanoisopropyl dithiobenzoate (CPDB) ($c^0_{CPDB} = 1.0 \times 10^{-2}$ mol l^{-1}) (□). The dotted lines give the theoretical number average molecular weights.

4. Conclusions

The present paper demonstrates that the RAFT bulk polymerizations of 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate (TRIS) can be successfully conducted at 60 °C when cumyl dithiobenzoate (CDB) and 2-(2-cyanopropyl) dithiobenzoate (CPDB) are used as mediating agents at concentrations ranging from 5.0×10^{-3} to

2.0×10^{-2} mol l^{-1}. The observed monomer conversion vs. time evolution indicates that CDB mediated polymerizations display strongly concentration dependent inhibition and rate retardation phenomena, whereas the CPDB mediated polymerization process is less susceptible to rate retardation and inhibition effects. The different behavior of CDB and CPDB in TRIS polymerization is—at least for the inhibition phenomenon—most likely due to an increased stability of intermediate macroRAFT radicals in the pre-equilibrium in the CDB mediated process. The generated RAFT polymers were analyzed via SEC indicating linear macromolecular growth with respect to monomer conversion and low polydispersities in all cases (PDI < 1.15) up to extremely high monomer conversions ($>90\%$).

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