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Retardation in RAFT Polymerization: Does Cross-Termination Occur with Short Radicals Only?

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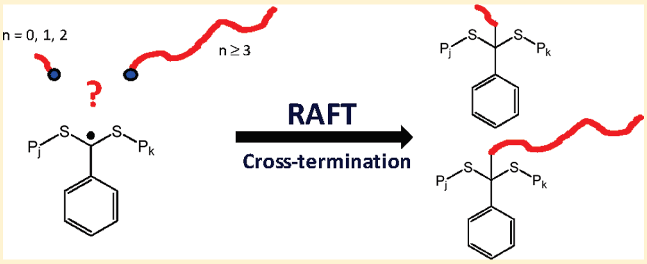
Supporting Information



ABSTRACT: The recently proposed model by Perrier and co-workers [J. Polym. Sci., Part A: Polym. Chem. 2009, 47, 3455] to account for retardation effects in dithiobenzoate-mediated reversible addition−fragmentation chain transfer (RAFT) polymerization of styrene has been tested experimentally. According to this model, retardation is caused by cross-termination of very short radicals only. Polymerizations were conducted employing a macroazoinitiator and a polymeric RAFT agent based on cumyl dithiobenzoate, thereby effectively eliminating all short radicals from the system. The results show, in basic agreement with the model, that there is very little, if any, retardation in dithiobenzoate-mediated RAFT polymerization of styrene in the absence of short radicals.

INTRODUCTION

Reversible addition−fragmentation chain transfer (RAFT) polymerization[1−5] is one of the most well-known techniques of controlled/living radical polymerization,[6] which has enormously expanded the scope of radical polymerization. It is now possible to synthesize polymer of narrow molecular weight distribution, block copolymers, and more complex architectures such as stars and polymer brushes as well as polymer particles[7,8] and other complex nanostructures[9] comprising well-defined polymer by free radical means.

Despite intensive research for many years, the exact mechanism of RAFT polymerization in the case of dithiobenzoate-based systems remains under debate.[10−13] The controversy is centered around the origin of the reduction in the polymerization rate that is observed in the presence of a dithiobenzoate RAFT agent relative to the corresponding conventional radical polymerization. Two main theories exist: (i) the cross-termination model[14] and (ii) the slow fragmentation model.[15,16] The cross-termination model results in fragmentation rate coefficients of the intermediate radical (the radical adduct generated on addition of a radical species to the RAFT moiety) of the order 10^5 s^{-1}, to be compared with the order of 10^{-2} s^{-1} for the slow fragmentation model.[12] The cross-termination model mainly finds support in fragmentation rate coefficients estimated by electron paramagnetic resonance (EPR) spectroscopy, employing (i) combined analysis of intermediate radical concentration and polymerization rate[17,18] and (ii) time-resolved EPR after pulsed laser initiation,[19] and model predictions of intermediate radical concentrations consistent with EPR data. The shortcoming of the cross-termination model is that three-armed stars (the cross-termination product) have to date not been detected under normal RAFT polymerization conditions.[20] However, cross-termination products have been detected in experiments designed to favor their formation and easy detection, demonstrating the feasibility of this reaction step.[21−25] The slow fragmentation model is mainly supported by the fact that three-armed stars have not been detected under normal RAFT polymerization conditions, by calculations based on *ab initio* molecular orbital theory,[16,26,27] by recent EPR results involving spin trapping,[28] and by the stability of the adduct radicals that can be inferred from thioketone-mediated radical polymerization.[29,30] The problem with the slow fragmentation model is that it predicts intermediate radical concentrations orders of magnitude higher than measured by EPR.[17,18,31,32]

It has also been proposed that an additional reaction step involving a propagating radical and the three-armed star cross-termination product should be considered.[33] In addition, so-called "radical storage" experiments, which reveal how radicals can be "stored" in the case of low molecular weight dithiobenzoates, remain to be rationalized.[34,35] To further complicate the situation, the purity of the RAFT agent (CDB) can significantly influence the polymerization rate.[36] The issues surrounding retardation in dithiobenzoate-mediated RAFT polymerization were thoroughly reviewed in 2006[12] and 2010.[37]

In an attempt to reconcile the discrepancies between the cross-termination model and the slow fragmentation model, Perrier and co-workers[38,39] recently proposed an alternative model, the essence of which is that cross-termination only occurs with short

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Table 1. Recipes for Conventional (No RAFT Agent) and RAFT Polymerizations of St in Bulk at 60 °C

	conventional	conventional	CDB	CDB	macroCDB	macroCDB
RAFT agent (M)			7.83×10^{-3}	7.83×10^{-3}	7.83×10^{-3}	7.83×10^{-3}
VPE-601 (M)	1.14×10^{-3}		1.14×10^{-3}		1.14×10^{-3}	
AIBN (M)		6.86×10^{-3}		6.86×10^{-3}		6.86×10^{-3}

radicals. The exact meaning of "short" radicals has been estimated to be radicals comprising an initiator fragment and two monomer units or shorter.[39] This model produces data that are largely consistent with experimental polymerization rates and intermediate radical concentrations as well as polymer structure (i.e., no detectable three-armed stars, since the third arm is very short).

The present paper describes RAFT polymerizations of styrene conducted specifically to test the model of Perrier and coworkers.[38,39] To this end, polymerizations have been carried out under conditions with no short radicals present in the system, which was achieved by employing a macroazoinitiator and polymeric dithiobenozate RAFT agent. The results show that in the absence of short radicals there is very little, if any, retardation in the dithiobenzoate-mediated polymerization of styrene.

■ EXPERIMENTAL SECTION

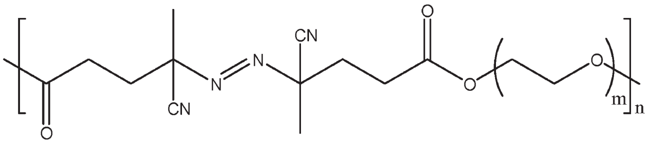
Materials. Styrene (St, 99%; Sigma-Aldrich) was purified by passing through an aluminum oxide column (Ajax) to remove the inhibitor. 2,2′-Azobis(isobutyronitrile) (AIBN; Aldrich) was purified by recrystallization twice in methanol. The macroazoinitiator (VPE-601; WAKO) and 1,1′-azobis(cyclohexane-1-carbonitrile) (ACN; Aldrich) were used as received. Cumyl dithiobenzoate (CDB) was synthesized as reported in the literature.[40−42]

Synthesis of Polystyrene MacroRAFT Agent (MacroCDB). CDB (9.8×10^{-2} g, 3.60×10^{-4} mol), St (3.0 g, 2.88×10^{-2} mol), and the initiator ACN (8.8×10^{-3} g, 3.60×10^{-5} mol) were charged into a glass vial containing a magnetic stirrer, which was subsequently capped with a rubber septum and further sealed with parafilm and copper wire. The mixture was left stirring at room temperature until complete dissolution of CDB and ACN. The final solution was bubbled with nitrogen for at least 40 min before it was immersed into a preset oil bath at 85 °C for 48 h. The St conversion was measured by ^{1}H NMR by comparing the aromatic protons of styrene and polystyrene at 6.2−9.0 ppm with the vinylic protons of St at 5.84 ppm. The crude mixture was precipitated in methanol and dried under vacuum overnight at room temperature to yield a pink powder. Conversion: 82%; M_n = 5400 g mol^{-1}; M_w/M_n = 1.10.

Polymerizations. Polymerizations of St were carried out at 60 °C with or without macroCDB/CDB RAFT agent initiated by either VPE-601 or AIBN (Table 1). In the case of St/CDB, CDB (1.28×10^{-2} g, 4.70×10^{-5} mol), St (6.0 g, 5.76×10^{-2} mol), and VPE-601 (2.40×10^{-1} g, 6.86×10^{-6} mol) or AIBN (6.8×10^{-3} g, 4.14×10^{-5} mol) were charged into a glass vial. After complete dissolution of all solids, the solution was separated equally into individual glass vials that were sealed with rubber septa. Parafilm and copper wires were used to ensure maximum seal between the septa and the glass vials. Nitrogen was bubbled through the sealed vials for at least 40 min before they were immersed into a preset oil bath at 60 °C. Individual vials were removed from the oil bath at different polymerization times and place in an ice bath, and conversions were measured using ^{1}H NMR as detailed above.

Gel Permeation Chromatography (GPC). Molecular weights and molecular weight distributions (MWDs) were measured by GPC using a Shimadzu modular system with tetrahydrofuran as eluent at 40 °C at a flow rate of 1.0 mL/min with injection volume of 100 μL. The GPC was equipped with a DGU-12A solvent degasser, a LC-10AT pump, a CTO-10A column oven, an ECR 7515-A refractive index detector, and a Polymer Laboratories 5.0 μm bead-size guard column (50 × 7.8 mm) followed by four 300 × 7.8 mm linear Phenogel columns. The system was calibrated against polystyrene standards ranging from 500 to 10^6 g mol^{-1}.

Scheme 1. Structure of VPE-601



Nuclear Magnetic Resonance (NMR). All NMR spectra were recorded using a Bruker DPX-300 spectrometer at a resonance frequency of 300.2 MHz for ^{1}H nuclei at 25 °C. Conversions of St were measured by adding five drops of crude mixture directly to deuterated chloroform as NMR solvent.

■ RESULTS AND DISCUSSION

Polymerizations with Macroazoinitiator. The main objective of the present work has been to investigate whether the presence of short radicals in the dithiobenzoate-based RAFT polymerization of St influences the extent of retardation caused by the RAFT agent. Polymerizations have been carried out using two different types of radical initiators, namely the low molecular weight initiator AIBN and the macroazoinitiator VPE-601 (Scheme 1). This macrozoinitiator has M_n = 35 000 g/mol and comprises on average six azo moieties per chain, and consequently complete initiator decomposition generates radicals of $M_n \approx 5000$ g/mol. Short radicals would also be generated by expulsion of the short radical associated with the pre-equilibrium in the case of a low molecular weight RAFT agent like cumyl dithiobenzoate (CDB).

Figure 1 shows conversion−time data for polymerization of St in bulk at 60 °C initiated by VPE-601 in the absence of RAFT agent, in the presence of a macroCDB agent based on polystyrene and CDB (M_n = 5400, M_w/M_n = 1.10), and in the presence of CDB. The data for the system without RAFT agent are very similar to the system with the macroCDB agent, but there is clear retardation for the CDB system. In order to more clearly expose how the polymerization rate (R_p; here defined as the rate of fractional conversion (min^{-1})) changes with conversion, the conversion−time data were carefully fitted with polynomials (see Supporting Information) followed by differentiation with respect to time to yield continuous values of R_p vs conversion (Figure 2). As also apparent from Figure 1, R_p is only marginally affected by the presence of the macroCDB agent, with minor retardation seen within the approximate conversion range of 10−35%. The slightly higher initial R_p value for the system with macroCDB agent is within experimental error (considering also errors associated with the extraction of R_p values from the

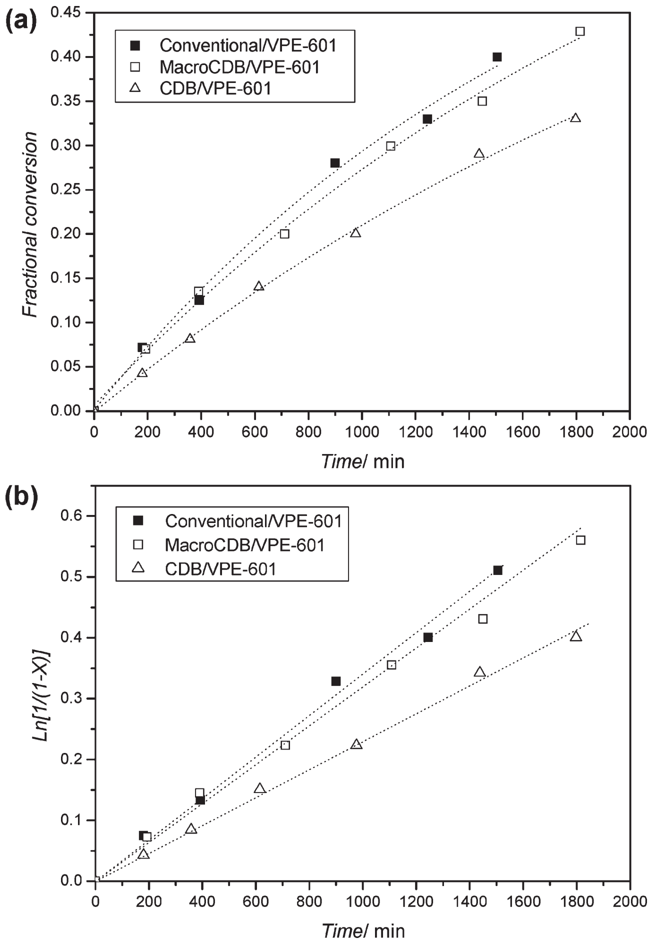


Figure 1. Conversion vs time data (a) and first-order plots (b) of bulk polymerizations of St at 60 °C with (■) VPE-601 (no RAFT agent), (□) VPE-601 and macroCDB, and (Δ) VPE-601 and CDB with [St]/[RAFT agent] = 1226 (except when RAFT agent not present). Lines in (a) are guides to the eye only and in (b) linear fits through the origin.

conversion−time data). R_p for CDB is considerably lower than both of the other systems up to ~20% conversion. Beyond conversion levels of ~35%, it appears that all three systems approach close to identical R_p values. There are thus two important messages from Figures 1 and 2: (i) Whatever the mechanistic origin, it is clear that by removal of all short radicals from the system, RAFT polymerization of St based on a dithiobenzoate RAFT agent proceeds with minimal, if any, retardation. (ii) The system St/CDB exhibits retardation at low conversion but approaches R_p of the corresponding conventional radical polymerization at intermediate conversion levels.

Once the initial low molecular weight RAFT agent CDB has been consumed, the CDB system initiated by the macroazoinitiator would no longer contain any short radicals. On the basis of the premise that the short radicals are the origin of retardation, one would therefore expect R_p at a given conversion to be similar to that of the system with the macroCDB agent (there would of course be minor differences due to chain-length effects on mainly k_t[43]). The rate of consumption of CDB relative to that of St can be estimated based on the apparent value of the transfer constant ($C_{tr,app}$), which for the system St/CDB/AIBN/60 °C has been reported as $C_{tr,app}$ = 50.[4,44] This apparent value accounts for regeneration of CDB by addition of expelled cumyl radicals to the

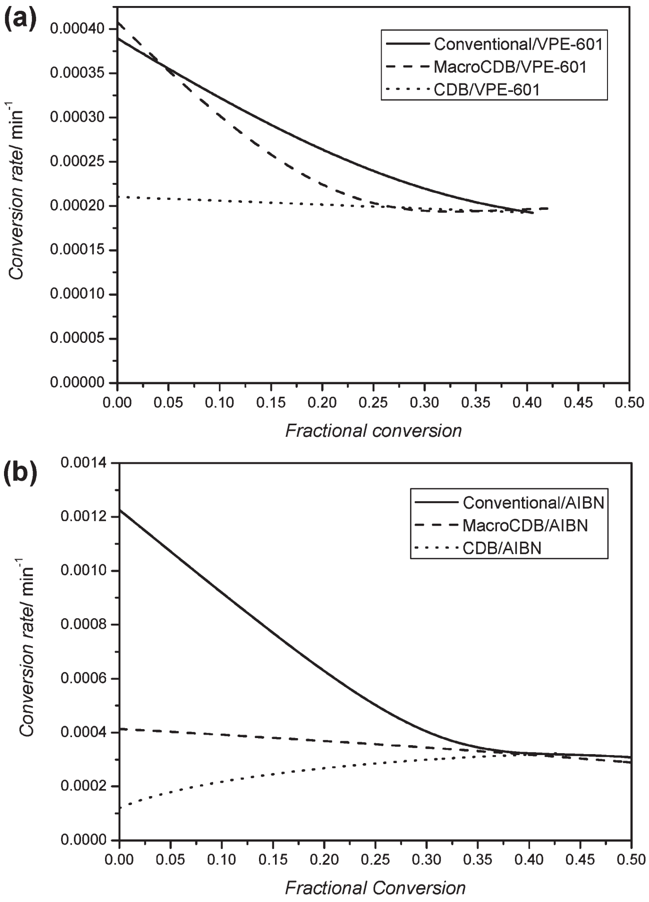


Figure 2. St conversion rates (min^{-1}) vs fractional conversion for the systems (a) VPE-601, macroCDB/VPE-601 and CDB/VPE-601 and (b) AIBN, macroCDB/AIBN and CDB/AIBN at [St]/[RAFT agent] = 1226 (except when RAFT agent not present).

polymeric dithiobenzoate RAFT agent generated in situ. The relative rates of consumption of St and CDB can be expressed as $\ln\{[St]_0/[St]\} = (1/C_{tr,app}) \ln\{[CDB]_0/[CDB]\}$, and it follows that 98% of CDB would be consumed at ~8% St conversion. Note also that in the model of Perrier et al.[45] short radicals are defined as initiator radicals as well as the oligomeric radicals generated after one and two monomer additions to the initiator radicals; i.e., short radicals would remain in the system some time after all CDB is consumed. Considering this as well as the errors associated with the estimate of $C_{tr,app}$ and the errors from estimation of R_p from the conversion−time data, it appears reasonable to tentatively ascribe the approach of R_p(St/CDB/macroazoinitiator) to that of R_p(St/macroCDB/macroazoinitiator) to the consumption of CDB and oligomeric RAFT agent. However, as discussed below, the apparent lack of retardation beyond intermediate conversion levels is also observed for the RAFT polymerizations (CDB and macroCDB) initiated by AIBN, in which cases short radicals are present throughout the polymerizations.

Polymerizations were also conducted for the system macroCDB/VPE-601 at different ratios [St]/[macroCDB], i.e., at different targeted polymer molecular weights. Figure 3a shows conversion−time data in the form of first-order plots for [St]/[macroCDB] = 800, 1226, and 2000 as well as the corresponding polymerization without RAFT agent. Within

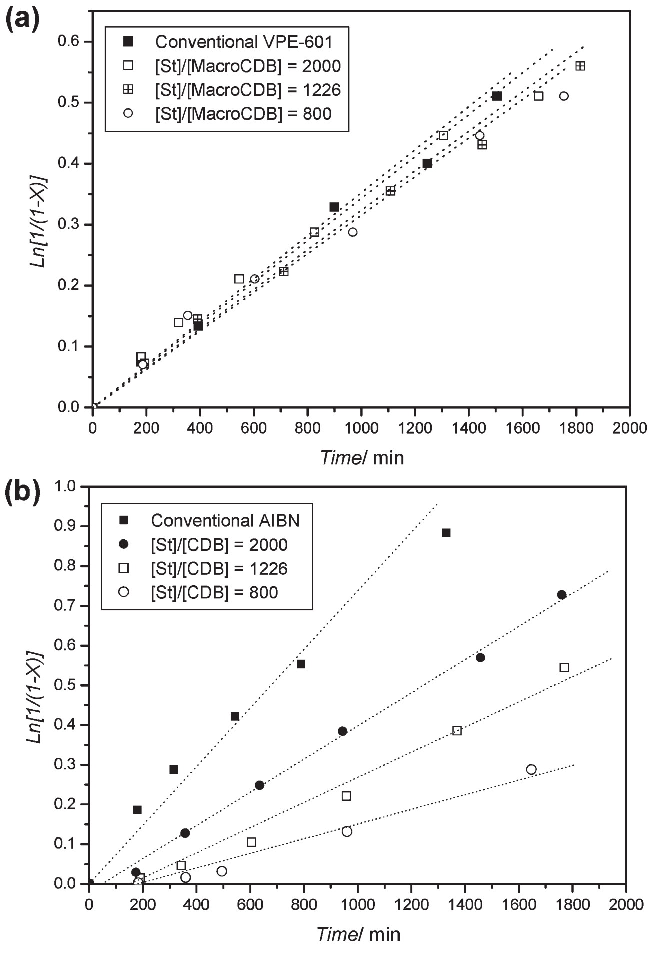


Figure 3. First-order plots of bulk polymerizations of St at 60 °C (a) initiated by VPE-601 with [St]/[RAFT agent] = 2000, 1226, and 800 (except when RAFT agent not present) and (b) initiated by AIBN with [St]/[RAFT agent] = 2000, 1226, and 800 (except when RAFT agent not present). Lines are linear fits through the origin.

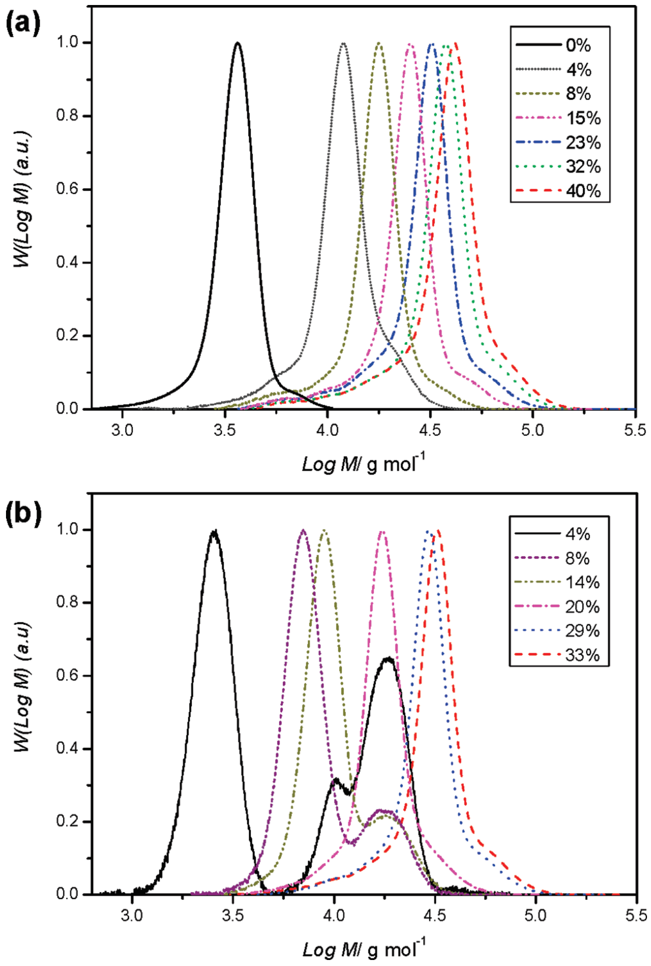


Figure 4. Molecular weight distributions of bulk polymerizations of St at 60 °C initiated by VPE-601 with [St]/[RAFT agent] = 1226 for (a) macroCDB and (b) CDB (conversions as indicated).

experimental error, the ratio [St]/[macroCDB] has no significant effect on the polymerization rate (fitting the first-order plots to straight lines going through the origin reveals no trend in slopes with respect to the ratio [St]/[macroCDB]).

In order to confirm that the polymerizations initiated by VPE-601 proceeded in a controlled/living manner, molecular weight analysis was performed. The MWDs shifted to higher molecular weights with increasing conversion as expected for both macroCDB and CDB (Figure 4). The presence of the polymeric initiator VPE-601 complicates the MWD analysis—in the case of CDB (no polymer initially present other than VPE-601), a bimodal peak corresponding to VPE-601 and partially decomposed VPE-601 appears around log M = 4−4.5. The peak due to VPE-601 is less visible when using macroCDB agent because polymer is then present initially also in the form of the macroCDB agent. The presence of undecomposed and partially decomposed VPE-601, both free-standing and as part of polymer with a RAFT end group (i.e., having reacted with RAFT moieties), causes the MWDs to be broader than when using a traditional low molecular weight initiator such as AIBN. This is reflected in the M_w/M_n values (Figure 5) that increase somewhat with conversion, although they remain below 1.25. The M_n values increase close to linearly with conversion. Because of the complexities introduced by the presence of VPE-601, it is of limited meaning to calculate theoretical M_n values.

Polymerizations with Low Molecular Weight Initiator. The polymerizations described above were also carried out for the low molecular weight initiator AIBN for comparison. The use of AIBN ensures that small radicals are present throughout the polymerization. Figure 6 shows conversion−time data for polymerization of St in bulk at 60 °C initiated by AIBN in the absence of RAFT agent, in the presence of the macroCDB agent, and in the presence of CDB. The corresponding plots of R_p vs conversion (obtained as above; see Supporting Information) are displayed in Figure 2. The following observations can be made: (i) In the approximate conversion range 0−40%, there is marked retardation (relative to the conventional radical polymerization) in the presence of the macroCDB agent and even stronger retardation with CDB. (ii) Above ~40% conversion (as far as data are available), all three systems exhibit very similar R_p.

Polymerizations were also performed for the system CDB/AIBN at different ratios [St]/[CDB] of 800, 1226, and 2000 as well as the corresponding polymerization without RAFT agent (Figure 3b). The extent of retardation strongly increases with increasing RAFT agent concentration.

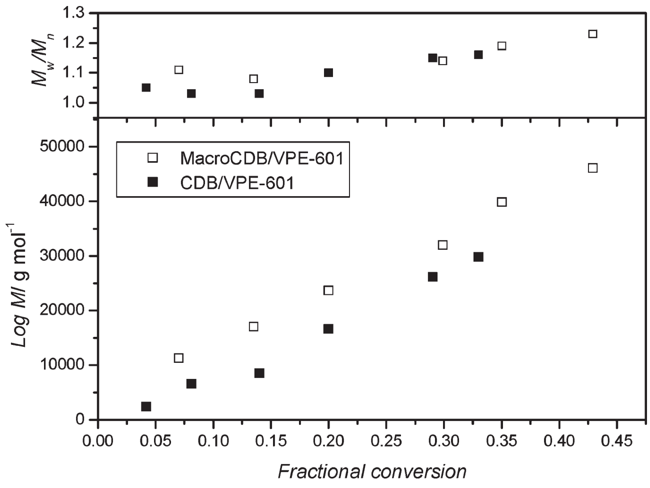


Figure 5. M_n and M_w/M_n vs conversion for bulk polymerizations of St at 60 °C initiated by VPE-601 with [St]/[RAFT agent] = 1226 for (□) macroCDB and (■) CBD.

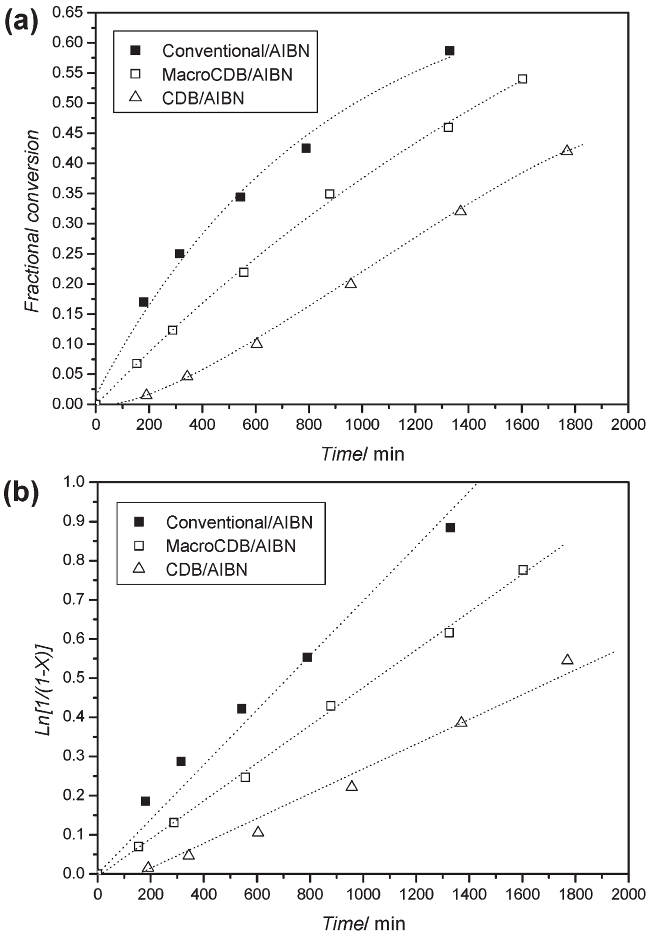


Figure 6. Conversion vs time data (a) and first-order plots (b) of bulk polymerizations of St at 60 °C with (■) AIBN (no RAFT agent), (□) AIBN/macroCDB, and (Δ) AIBN/CDB with [St]/[RAFT agent] = 1226 (except when RAFT agent not present). Lines in (a) are guides to the eye only and in (b) linear fits through the origin.

Compared to the polymerizations with macroazoinitiator, the qualitative trends are the same, except for one important difference: The system macroCDB/macroazoinitiator shows very little, if any, retardation (relative to the system without RAFT agent), whereas the system macroCDB/AIBN exhibits marked retardation.

Discussion. The experimental data presented above are largely consistent with the model of Perrier and co-workers.[38,39] In the absence of short radicals in the system, there is no significant retardation. This suggests that cross-termination involving intermediate radicals and long propagating radicals does not occur to any significant extent (at least not to the extent that it is a cause of retardation). This is consistent with the resulting 3-armed stars not having been detected under normal RAFT polymerization conditions.

According to quantum-chemical calculations by Coote and co-workers[46] for St/dithiobenzoate with a cyanoisopropyl end group (AIBN), the RAFT equilibrium constant ($K = k_{add}/k_f$, where k_{add} is the addition rate coefficient and k_f is the fragmentation rate coefficient) increases with increasing chain length of the attacking radical at least to the trimer stage. Considering that k_{add} decreases with increasing chain length (as in chain length dependence of the propagation rate coefficient (k_p)[47,48]), it is safe to say that k_f decreases with chain length. It could thus be argued that removal of short radicals from the system leads to an increase in K, and therefore less retardation, consistent with the observations in the present study.

The experimental data show that retardation (i.e., when short radicals are present in the system) does not appear to occur beyond a certain intermediate conversion level of ~40%, which cannot be explained based on the model of Perrier and co-workers.[38,39] This behavior has previously been observed by Barner-Kowollik and co-workers[37,49] for the CDB-mediated polymerization of St initiated by γ-radiation in the temperature range 30−70 °C. The quantum-chemical calculations by Coote and co-workers[46] for St/dithiobenzoate/AIBN show that the fragmentation rate coefficient k_f decreases with conversion (i.e., with chain length). Thus, one would expect more retardation with increasing conversion due to a more stable intermediate radical, contrary to the observed experimental trend. Moreover, retardation is not observed for the system macroCDB/AIBN beyond ~40% conversion (Figure 2) also when short radicals are present (AIBN generates short radicals throughout the polymerization). A possible explanation of the fact that no retardation is seen beyond a certain conversion may be that the intermediate radical is relatively stable, and this would mean that it would take considerable time to reach the steady state, which would manifest itself as retardation at lower conversions.[12,16] However, this explanation appears inconsistent with EPR data on intermediate radical concentrations,[17,18,31,32] which are considerably lower than what such a slow approach to a steady state would predict. It has been shown that in the presence of various dithiobenzoate RAFT agents the ketenimine side product generated on AIBN decomposition is further converted to a byproduct (of yet to be confirmed structure).[50] Such ketenimine consumption does not occur in the absence of RAFT agent, and as such the presence of RAFT agent would be expected to cause retardation as the ketenimine would otherwise revert back to cyanoisopropyl radicals. However, if this were an important cause of retardation in the present work, retardation would have been observed also beyond 35% conversion for the systems initiated by AIBN (Figure 2b). In concluding this section, it thus seems that further work is required to explain why retardation does not occur beyond a certain intermediate conversion level.

■ CONCLUSIONS

Retardation effects in dithiobenzoate-mediated RAFT polymerization of St have been investigated with respect to chain-length effects. The main objective has been to test the recently proposed model by Perrier and co-workers,[38,39] according to which retardation is caused by cross-termination of very short radicals only. Dithiobenzoate-mediated RAFT polymerizations of St were conducted in the absence of short radicals in the system, which was achieved by use of a macroCDB agent and a macroazoinitiator. The results have clearly shown that in the absence of short radicals there is very minor, if any, retardation in dithiobenzoate-mediated RAFT polymerization of St (relative to the system without RAFT agent).

The data have also revealed that in the RAFT systems with retardation (i.e., when short radicals are present, due to the use of AIBN and/or the low molecular weight RAFT agent cumyl dithiobenzoate) there is no significant retardation beyond ~40% St conversion. This behavior cannot be rationalized based on the model of Perrier et al., and the reasons remain unclear at present.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Polynomials fitted to the conversion−time data for estimation of polymerization rates vs conversion. This material is available free of charge via the Internet at http://pubs.acs.org.

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