A ^{1}H NMR Investigation of Reversible Addition−Fragmentation Chain Transfer Polymerization Kinetics and Mechanisms. Initialization with Different Initiating and Leaving Groups

J. B. McLeary,[†] F. M. Calitz,[†] J. M. McKenzie,[‡] M. P. Tonge,[*,†,§]
R. D. Sanderson,[†] and B. Klumperman[*,†,||]

Dutch Polymer Institute, UNESCO Centre for Macromolecules and Materials, Department of Chemistry and Polymer Science, and Nuclear Magnetic Resonance Laboratories, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa, and Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received November 10, 2004; Revised Manuscript Received February 2, 2005

ABSTRACT: In situ ^{1}H nuclear magnetic resonance spectroscopy was used to directly investigate the processes that occur during the early stages (the first few monomer addition steps) of azobis(isobutyronitrile)-initiated reversible addition−fragmentation chain transfer (RAFT) polymerizations of styrene in the presence of cumyl dithiobenzoate at 70 and 84 °C. The change in concentration of important dithiobenzoate species and monomer as a function of time was investigated. The predominant type of growing chain under the reaction conditions carries a cumyl end group. The initialization period (the period during which the initial RAFT agent is consumed) in the presence of cumyl dithiobenzoate in homogeneous media was significantly longer than for equivalent reactions using cyanoisopropyl dithiobenzoate as RAFT agent, and the rate of monomer conversion was correspondingly slower. Very strong fragmentation selectivity of the formed intermediate radicals (to form the tertiary propagating radical) was observed during the initialization period. The rate-determining step for the initialization process was the addition (propagation) of the initiator-derived and cumyl radicals to styrene, to form the corresponding single-monomer adducts. The greater length of this period with respect to the same reaction using cyanoisopropyl dithiobenzoate as RAFT agent is suggested to be a result of slower propagation due to a smaller addition rate coefficient of the cumyl radical (which was found to be the dominant propagation process during initialization) to styrene, than for the cyanoisopropyl radical, and to a higher average termination rate for the cumyl radicals than for the cyanoisopropyl radicals. The probable (small) difference in intermediate radical concentration is considered to be a less significant contributor to the length of the period.

Introduction

Nuclear magnetic resonance spectroscopy is one of the most powerful modern analytical tools available to molecular scientists. Of relevance here is that it can be a useful technique for the in situ investigation of the kinetics of free radical polymerization reactions. In previous studies we have demonstrated that NMR spectroscopy provides significant insight into the first stages of living (reversible addition−fragmentation chain transfer, RAFT) radical polymerization.[1,2]

Living free radical polymerization has revolutionized the architecture of polymers that can be prepared by free radical polymerization. The ability to chain extend polymers has made it possible to produce tapered gradients and pure block copolymers, providing materials that are of great interest in a wide variety of applications ranging from coatings to biomedical uses. A number of living radical polymerization techniques are currently under investigation, each with its own unique characteristics and specific advantages and/or disadvantages. Two of the most well-established techniques are stable free-radical-mediated polymerization (SFRP)[3,4] and atom transfer radical polymerization (ATRP),[5−8] which are reversible end-capping techniques.

The focus of the current study is the RAFT process,[9−14] another living radical polymerization technique that is extremely versatile and robust. It is compatible with almost all monomers and most conditions that are applicable to conventional free radical polymerization. The benefits of the RAFT process are obtained simply by the addition of the correct choice of RAFT agent to the polymerization mixture.

The RAFT process is a relatively new technique and has recently generated substantial controversy,[15,16] the focus of which is the determination of the precise RAFT mechanism. Being a new technique, there are still some anomalies in the process that at present are not well understood.

Dithioester RAFT agents have the form R−SCSZ, the two main features being the initial leaving group (R) and the “activating” group (Z). Both of these groups have a significant effect on the kinetics and degree of control of the RAFT process. In Scheme 1 the elementary reactions for the central exchange process of the RAFT mechanism are depicted. The relatively stable intermediate radical that is formed (for some RAFT agent/monomer combinations) by the addition process can fragment to release one of two radical species. These are the original incoming radical species ($P_m\cdot$, a propagating radical of degree of polymerization m), or the homolytic leaving group ($P_n\cdot$) that was previously a part of the RAFT agent. If this central exchange is the only process that controls the RAFT-mediated polymeriza-

---

[*] To whom correspondence should be addressed.

[†] UNESCO Centre for Macromolecules and Materials, Department of Chemistry and Polymer Science, University of Stellenbosch.

[‡] Nuclear Magnetic Resonance Laboratories, University of Stellenbosch.

[§] Current address: Key Centre for Polymer Colloids, School of Chemistry, F11, University of Sydney, NSW 2006, Australia.

[||] Eindhoven University of Technology.

10.1021/ma047696r CCC: $30.25

Scheme 1. Elementary Reversible Addition−Fragmentation Chain Transfer Process As Commonly Accepted in the Literature[9]

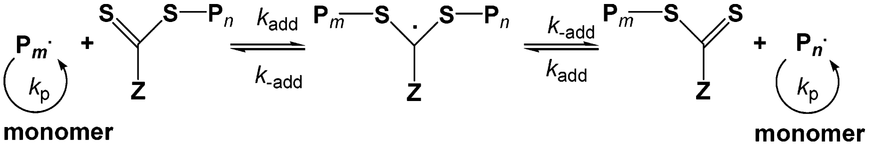


Table 1. Composition of Reaction Mixtures for in Situ NMR Spectroscopic Analysis[a]

	solvent		initiator		styrene		RAFT agent		monomer/RAFT agent ratio, $[M]_0/[R]_0$	RAFT agent/(initiator × 2) ratio, $[R]_0/2[I]_0$
sample	mass (g)	mol × 10^{-3}	mass (g)	mol × 10^{-5}	mass (g)	mol × 10^{-3}	mass (g)	mol × 10^{-4}		
1(CD)[b]	0.250	2.99	0.010	6.3	0.260	2.46	0.100	3.68	6.68	2.92
2(CD)[c]	0.250	2.99	0.010	6.3	0.260	2.46	0.100	3.68	6.68	2.92
3[b]	0.365	4.34	0.011	6.7	0.380	3.68	0	0	0	0
4[c]	0.300	3.56	0.010	6.1	0.380	3.68	0	0	0	0
5(AD)[b]	0.300	3.56	0.010	6.7	0.250	2.40	0.107	4.84	4.96	3.96
6(AD)[c]	0.300	3.56	0.010	6.1	0.240	2.31	0.100	4.52	5.10	3.70

[a] The solvent used was deuterated benzene (99.6%), and the initiator used was azobis(isobutyronitrile). The RAFT agent was cumyl dithiobenzoate (CD) or cyanoisopropyl dithiobenzoate (AD). [b] Reaction carried out at 70 °C. [c] Reaction carried out at 84 °C.

tion reaction, then the inhibition and retardation phenomena that occur in many RAFT-mediated polymerizations cannot easily be fully explained.[17−19]

Previously we reported experimental results that helped to further the understanding of the “inhibition” effect observed in certain RAFT-mediated polymerizations and defined the term “initialization”.[1,2] *Initialization* is the process by which the starting RAFT agent is consumed. The *initialization period* is the period in which the starting RAFT agent is consumed. The *initialization time* is the time required for the starting RAFT agent to be completely consumed (converted to other forms). In this paper, the cause and length of the initialization period for azobis(isobutyronitrile)-initiated, *cumyl* dithiobenzoate-mediated polymerization of styrene are investigated at two temperatures. In this case, the initiator-derived and leaving group radicals are different, which has a significant effect on the kinetics of the reaction when compared to the situation where the initiator-derived and leaving group radicals are the same.[1]

The rate of polymerization in a radical polymerization is a function of the radical concentration and type available for propagation, and depends on all radical generation and loss mechanisms. When different types of radicals are present (and thus often competing) in a system, understanding the rate-determining factors for polymerization becomes substantially more complex. We previously reported substantial selectivity during initialization when the only radicals in the system are the tertiary cyanoisopropyl radicals, derived from both initiator and RAFT agent, and secondary radicals derived from monomer addition reactions to the tertiary radical.[1] Very strong addition−fragmentation selectivities have also been observed in RAFT-mediated polymerization of methyl acrylate.[2] This type of selectivity is probably representative of the behavior of many such systems.

The current study addresses, in a manner similar to that of a previous study,[1] the early part of azobis(isobutyronitrile)-initiated styrene polymerization in the presence of the RAFT agent cumyl dithiobenzoate, at 70 and 84 °C, before complete consumption of the initial RAFT agent and the period immediately following initialization. In situ ^{1}H NMR spectroscopy was used to directly determine the variation in concentration of several species during the course of the reaction, with focus being on the early part of the reaction, i.e., the first monomer addition step(s). The effects of using dissimilar initiator and RAFT agent leaving groups on the rate of polymerization and length of the initialization period, and the implication on the RAFT mechanism, are investigated and compared to those of the case where these groups are the same.

Experimental Section

Chemicals. Styrene (Plascon Research Centre, University of Stellenbosch, estimated purity ~99% by ^{1}H NMR) was washed with 0.3 M KOH, and distilled under vacuum prior to use to remove inhibitor and polymer. Azobis(isobutyronitrile) (AIBN, Riedel De Haen) was recrystallized from AR grade methanol and found to be ~99% pure by ^{1}H NMR spectroscopy. Deuterated solvent (C_6D_6, 99.6%, 0.1% tetramethylsilane (TMS), Sigma-Aldrich) and pyrazine (99%, Sigma-Aldrich) were used as received.

Sample Preparation. The masses of the reactants used to make up the various samples are given in Table 1. The samples were transferred to NMR tubes. The tubes were flushed with ultra-high-purity nitrogen for 10 min. At this point a sealed glass insert containing the integration reference standard (pyrazine) was inserted, and the tubes were sealed. The use of the reference standard was solely for integration normalization purposes. A specific example of a reaction is as follows: A stock solution was prepared by weighing 0.250 g (2.99×10^{-3} mol) of C_6D_6, 0.010 g (6.3×10^{-5} mol) of azobis(isobutyronitrile), 0.260 g (2.46×10^{-3} mol) of styrene, and 0.100 g (3.68×10^{-4} mol) cumyl dithiobenzoate into a vial. This stock solution was then transferred into an NMR tube using a pipet and filled to a height of 5 cm. The tube was then flushed with nitrogen (10 min), and the integration reference was inserted. The tube was sealed and refrigerated prior to insertion.

Analysis. NMR spectra were collected on a 600 MHz Varian $^{\text{Unity}}$Inova spectrometer operating at 600 MHz. A 5 mm inverse detection PFG probe was used for the experiments, and the probe temperature was calibrated using an ethylene glycol sample in the manner suggested by the manufacturer using the method of Van Geet.[20] ^{1}H spectra were acquired with a 3 μs (40°) pulse width and a 4 s acquisition time. The chosen pulse angle allowed complete relaxation of all relevant peaks in the sample, the T_1 values of the system having been measured and taken into account. For the ^{1}H NMR kinetic experiments, samples were inserted into the magnet at 25 °C and the magnet was fully shimmed on the sample. A spectrum was collected at 25 °C to serve as a reference. The sample was then removed from the magnet, and the cavity of the magnet was raised to the required temperature (70 or 84 °C). Once

Table 2. ^{1}H NMR Spectroscopy Chemical Shifts of a Representation of Integrated Species Relevant to the Investigation of Initialization in the Cumyl Dithiobenzoate-Mediated Polymerization of Styrene[a]

δ (ppm), methyl protons of R groups	δ (ppm), ortho protons of corresponding dithiobenzoate ring	species
singlet, 0.93	N/A	AA
singlet, 1.18	N/A	CC
two peaks, 1.10, 1.08	N/A	AC
singlet, 1.45	doublet, 7.71	AD
singlet, 1.81	doublet, 7.81	CD
two peaks, 1.01, 0.87	doublet, 7.85	ASD
two peaks, 1.25, 1.20	doublet, 7.78	CSD
two peaks, 0.81, 0.65	doublet, 7.90	AS_2D[b]
two peaks, 0.89, 0.72	doublet, 7.79	
two peaks, 0.95, 1.02	doublet, 7.81	CS_2D[b]
two peaks, 1.02, 1.14	doublet (not identified)	

[a] Species AA is tetramethylsuccinonitrile, AD is cyanoisopropyl dithiobenzoate, and AS_nD are the styrene adducts of AD containing *n* styrene units. CD is cumyl dithiobenzoate, and CS_nD are the styrene adducts of CD containing *n* styrene units. [b] Note stereoisomers.

the magnet cavity had stabilized at the required temperature, the sample was reinserted and allowed to equilibrate for approximately 5 min. Additional shimming was then carried out to fully optimize the system, and the experiments were started approximately 10 min after the sample was inserted into the magnet, the exact time being noted.

Integration of spectra was carried out both manually and automatically to allow identification of species during formation. Automated integration was carried out using ACD Labs 7.0 ^{1}H NMR processor.

Synthesis of the RAFT Agent. The synthesis of cumyl dithiobenzoate was carried out according to the method of Le et al.[9] The RAFT agent was purified by successive liquid chromatography on silica and alumina using hexane as eluent. The product crystallized after vacuum removal of solvent and storage below −10 °C. The purity was estimated by ^{1}H NMR to be >95%. Impurities were identified during the integration process and found to be unreactive on the time scale of the reaction.

Results and Discussion

The NMR spectroscopic data that were obtained during the investigation provide instantaneous concentrations of detectable nonradical species in the RAFT-mediated reactions.

The concentrations and molar ratios of the reaction components in all reactions in this study are summarized in Table 1. A representative selection of peaks that were integrated for this study can be found in Table 2. Where two or more peaks are indicated, diastereotopic groups were present.

Figure 1 shows the chemical structures of the primary species of interest for this study. For convenience the following naming convention will be used. Species CD is the initial RAFT agent containing the dithiobenzoate species (D) and the initial cumyl leaving group (C), CSD is the dithiobenzoate species of the single styrene (S) adduct of a cumyl radical ($C^\bullet$), and CS_2D refers to the second styrene adducts of the cumyl radicals. The same naming convention applies for derivatives of the RAFT agent cyanoisopropyl dithiobenzoate (AD), with consecutive monomer adducts ASD, AS_2D, etc., with the cyanoisopropyl group replacing the cumyl group. A sample spectrum showing the most important peaks during initialization is shown in Figure 2. Although the styrene peaks in the spectra collected were large in comparison to the peaks of species containing RAFT groups, no dynamic range problems were experienced. As can be seen from Figure 2, a good signal-to-noise ratio was achieved, allowing for integration of the smaller peaks in the spectrum.

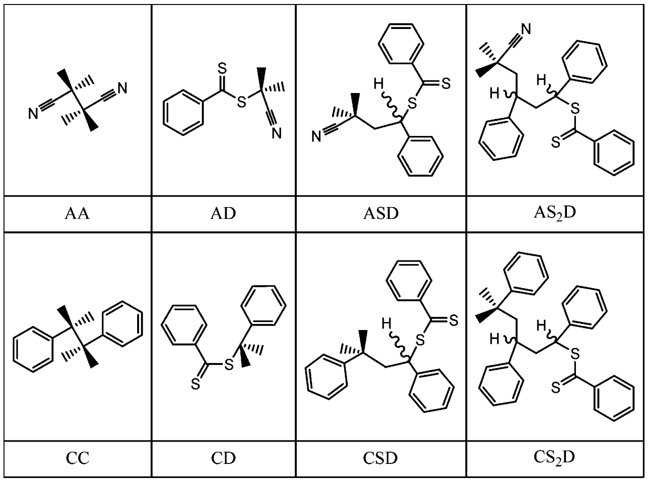


Figure 1. Predominant species of interest for the investigation of the early period of the free radical polymerization of styrene in the presence of cumyl dithiobenzoate, using azobis(isobutyronitrile) as an initiator.

The assignments of the ^{1}H NMR peaks were confirmed in a number of ways. Initially the ^{1}H NMR spectrum of each component in the reaction mixture was individually obtained to ensure the peaks belonging to each component were unambiguously assigned. Observation of azobis(isobutyronitrile) decomposition at 70 and 84 °C by ^{1}H NMR spectroscopy allowed for the assignment of the peak due to tetramethylsuccinonitrile (AA), which forms during this process. To assign peaks due to the combination of two cumyl radical species (CC) as well as the combination of cumyl and cyanoisopropyl radical species (AC), cumyl dithiobenzoate was reacted with azobis(isobutyronitrile) in the absence of monomer. The assignment of the AD, ASD, and AS_2D peaks has been made previously.[1]

The assignment of peaks due to species formed by addition of cumyl radicals to styrene was carried out in a fashion similar to that previously reported.[1] Once a cumyl dithiobenzoate-mediated reaction had begun, initiator-derived radicals allowed consumption of styrene to begin, CD was consumed to produce CSD (and a small amount of ASD and AD), and most AD formed was consumed to produce ASD, as previously observed.[1] The assignment of the CSD peaks was confirmed by comparing the rates of consumption of CD and styrene, and the corresponding formation of peaks assigned to CSD. Additionally, it was found that when all of the CD peaks (both methyl and *o*-phenyl protons) disappeared, the assigned CSD peaks reached a maximum, and the amount of monomer consumption according to the assigned styrene peaks was in good agreement with the amount required for complete consumption of the CD species. Thus, all assigned peaks showed good consistency in the time dependences of their intensities, and the rate of monomer consumption was internally verified. The assignments of the peaks for CS_2D were similarly made. Further verification of the peak assignments was carried out via various NMR spectroscopy techniques, at room temperature, on the samples after reaction. 2D NMR spectroscopic techniques were investigated, but the most information in regard to confirmation of the peak assignments was obtained by carrying

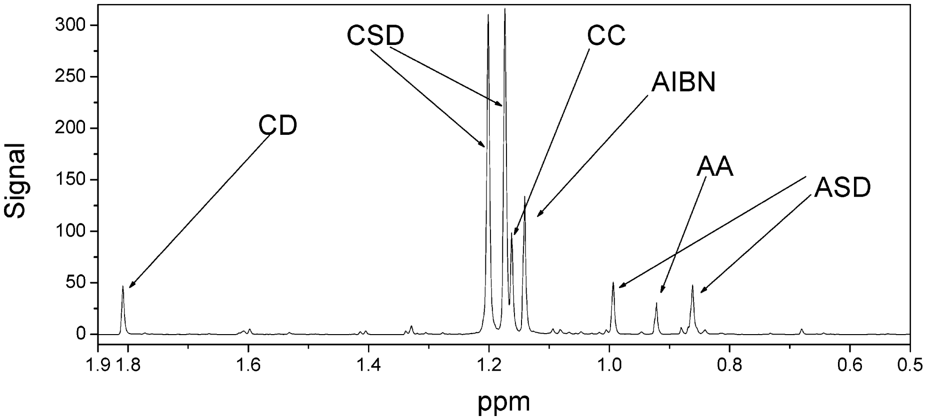


Figure 2. A typical ^{1}H NMR spectrum between 1.9 and 0.5 ppm during initialization, showing the peaks corresponding to several of the important species studied here. Cumyl dithiobenzoate (CD), cumyl styryl dithiobenzoate (CSD), cyanoisopropyl styryl dithiobenzoate (ASD), the geminate cumyl radical product (CC), tetramethylsuccinonitrile (AA), and azobis(isobutyronitrile) (AIBN) are labeled within the spectrum.

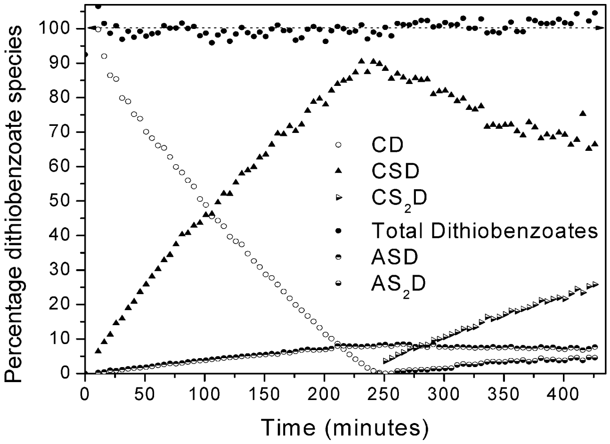


Figure 3. Relative concentrations of the methyl protons of dithiobenzoate species versus time in the in situ free radical polymerization of styrene in the presence of cumyl dithiobenzoate using azobis(isobutyronitrile) as an initiator at 70 °C. Table 1, reaction 1: 2.99×10^{-3} mol of C_6D_6, 6.30×10^{-5} mol of azobis(isobutyronitrile), 2.46×10^{-3} mol of styrene, 3.68×10^{-4} mol of cumyl dithiobenzoate.

out 1D TOCSY and 1D NOESY experiments. In this way it was possible to identify peaks belonging to a single species and confirm the peak assignments.

The use of cumyl dithiobenzoate, styrene monomer, and azobis(isobutyronitrile) as initiator results in a system in which two different tertiary radical species are present. The choice of styrene as monomer results in the vast majority of radicals formed from propagation reactions being secondary radicals.

In a previous study,[1] the radical reactivity for only one type of tertiary initiating radical (cyanoisopropyl) needed to be considered. When a system with two tertiary radical species (cyanoisopropyl and cumyl here) is considered, the polymerization becomes substantially more complex.

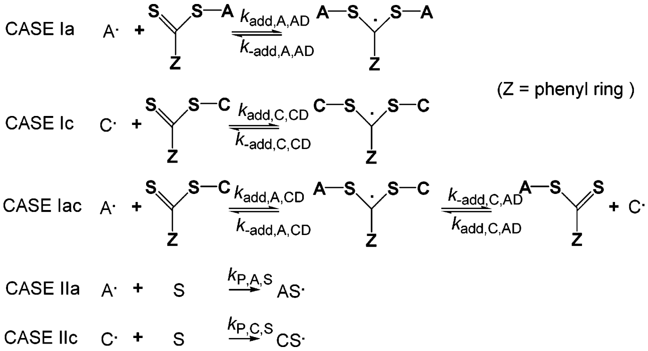
The first experimental system examined is the reaction of styrene, cumyl dithiobenzoate, and azobis(isobutyronitrile) at 70 °C (reaction 1, Table 1). Figure 3 shows the time dependence of the concentrations of dithiobenzoate species within the first 7 h of the reaction. Initially, a small but significant amount of AD is formed, due to addition of cyanoisopropyl radicals to CD, followed by fragmentation to produce cumyl radicals and AD. This is the only likely route given existing models for RAFT kinetics that can produce AD from CD at the beginning of the reaction (since almost no CSD exists at this stage). The exchange of end groups is addressed in a later section. Simultaneously, there is a decrease in the concentration of species CD, and a corresponding increase in the concentration of the species CSD and ASD as a single monomer unit is added. This trend continues until the cumyl dithiobenzoate and any cyanoisopropyl dithiobenzoate formed have been completely consumed (after about 240 min). At this point the concentrations of species CSD and ASD have reached a maximum. Once all of the cumyl dithiobenzoate has reacted, the second monomer additions to the radical species begin to increase in frequency (leading to the formation of species CS_2D and AS_2D). The implication of this behavior is that the formation of the CSD and ASD (i.e., addition of $A^\bullet$ and $C^\bullet$ to styrene to form $AS^\bullet$ and $CS^\bullet$) species or the consumption of the starting RAFT agent is the rate-determining step in the process. This behavior is the same as was previously described when the initiating and leaving groups were the same; that is, there is also extremely strong selectivity of the fragmentation of formed intermediate radicals during the initialization period to form the tertiary propagating radicals and the “propagated” form of the RAFT agent (i.e., ASD or CSD). This results in significantly different behavior of the system before and after the completion of initialization.

For clarity in the following discussion, termination reactions (with either propagating or intermediate radicals) are not shown, although they play a significant part in the reaction kinetics. Termination of intermediate radicals is not expected to be significant during initialization, due to the low intermediate radical concentration (as measured by ESR spectroscopy)[21] during most of the initialization period.

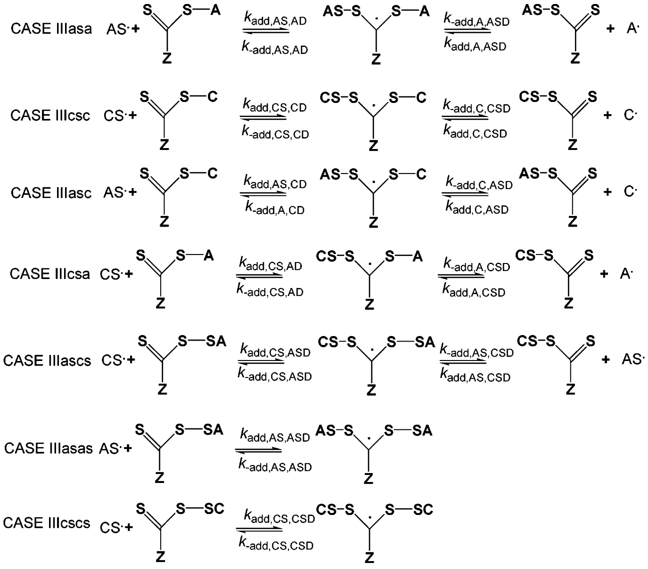
The reaction scheme, although similar to, is now substantially more intricate than the scheme reported previously.[1] Scheme 2 shows the types of reactions that are under consideration at the beginning of the reaction (i.e., prior to total consumption of the initial RAFT agent). Those reactions labeled with “c” and “a” are specific to cumyl or cyanoisopropyl radical species, respectively, and those labeled with “as” and “cs” refer to the single-monomer adducts of the cumyl and cyanoisopropyl radical species.

For convenience, the reaction scheme during initialization has been divided into two parts. The first part, as shown in Scheme 2, describes the main processes

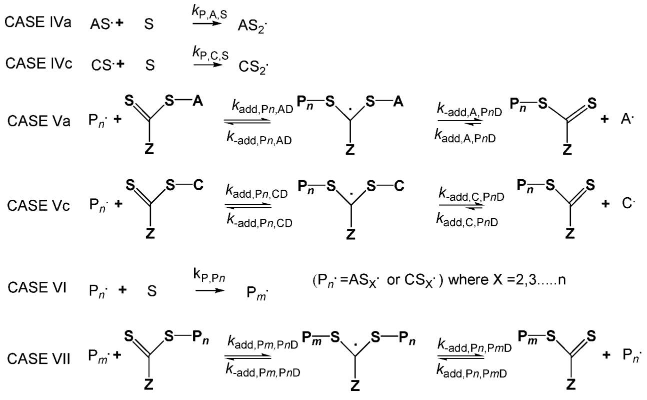
Scheme 2. Steps Involved in the Early Part of the Initialization Period (Involving Tertiary Radicals That Have Not Yet Propagated) of the Reversible Addition−Fragmentation Chain Transfer Reaction of Cumyl Dithiobenzoate, Styrene Monomer, and Azobis(isobutyronitrile) Initiator



Scheme 3. Additional Steps Involved in the Initialization Period (Including Radicals That Have Propagated Once) of the Reversible Addition−Fragmentation Chain Transfer Reaction of Cumyl Dithiobenzoate, Styrene Monomer, and Azobis(isobutyronitrile) Initiator



Scheme 4. Additional Steps Involved toward the End of the Initialization Period (Including Radicals That Have Propagated More Than Once) of the Reversible Addition−Fragmentation Chain Transfer Reaction of Cumyl Dithiobenzoate, Styrene Monomer, and Azobis(isobutyronitrile) Initiator



occurring at the start of the reaction, before significant propagation has occurred, and the second part (Scheme 3) the remaining reactions in the initialization period. The species involved in Scheme 2 include RAFT agents that have not added monomer units, propagating radicals that have not undergone propagation, and intermediate radicals formed from the reaction of the aforementioned species. Note that the reactions in Scheme 2 occur throughout the initialization period, until all of the initial RAFT agent has been consumed. The cyanoisopropyl radicals generated by initiator decomposition undergo one of three main reactions: (i) addition to a RAFT agent (case Ia or Iac), (ii) addition to monomer (propagation), to give radical species AS$^\bullet$ (case IIa), or (iii) termination. Cumyl radicals generated by fragmentation of the formed intermediate radical in case Iac will either undergo addition to a RAFT agent (case Ic or Iac) or addition to monomer (propagation) to produce CS$^\bullet$ (case IIc) or terminate.

The remaining significant reactions of propagating radicals (those that involve at least one species that has previously reacted with monomer) during the initialization period are shown in Scheme 3. The new reactions are as follows: the cyanoisopropyl and cumyl radicals can undergo two other reactions, namely, addition to either cyanoisopropylstyryl or cumylstyryl dithiobenzoate (shown on the right-hand side of either case IIIasa or case IIIcsa (for A$^\bullet$) or case IIIasc or case IIIcsc (for C$^\bullet$)) to form the corresponding intermediate radicals. Similarly, AS$^\bullet$ can add to a RAFT agent, i.e., cases IIIasa, IIIasc, IIIcsas, and IIIasas. CS$^\bullet$ can also add to a RAFT agent, i.e., cases IIIcsc, IIIcsa, IIIcsas, and IIIcscs. The formed intermediate radicals will predominantly fragment to give the shorter, tertiary radicals.

Note that, in this reaction, where the initiating and leaving radicals are different, there are now ten distinct types of intermediate radicals that can form during the initialization period, whereas there are only three such types of intermediates when the two radicals are the same. This can potentially significantly change the kinetics of the system, and makes accurate modeling of these kinetics extremely problematic, since there are then 32 potentially different rate coefficients (all of which are currently unknown) for the addition−fragmentation equilibria in the initialization period alone. However, as for the system previously described,[1] it appears that the most important factors determining the length of the initialization period are the propagation and/or termination rates of the cyanoisopropyl and cumyl radicals and the initial amount of RAFT agent and initiator present in the reaction.

Toward the end of the initialization process the reactions shown in Scheme 4 begin to dominate. AS$^\bullet$ and CS$^\bullet$ can propagate (cases IVa and IVc, respectively), or alternatively, AS$^\bullet$ and CS$^\bullet$ can add to any remaining RAFT agent (cases Va and Vc). It is expected that, after initialization, no C$^\bullet$ (seen as CD) will be present in the reaction mixture, since all of the initial CD has been consumed. Once significant amounts of CS$_n$D and AS$_n$D ($n \geq 2$) have formed, longer chain propagation can occur (case VI), and the system is probably at or approaching steady-state equilibrium. Once the chains have reached a sufficient degree of polymerization, the steady-state (main) addition−fragmentation equilibrium will be reached (case VII). A$^\bullet$ radicals formed by initiator decomposition throughout the reaction will be able to add to RAFT chains. However, being unable to displace the longer chains that are attached to RAFT agents (i.e.,

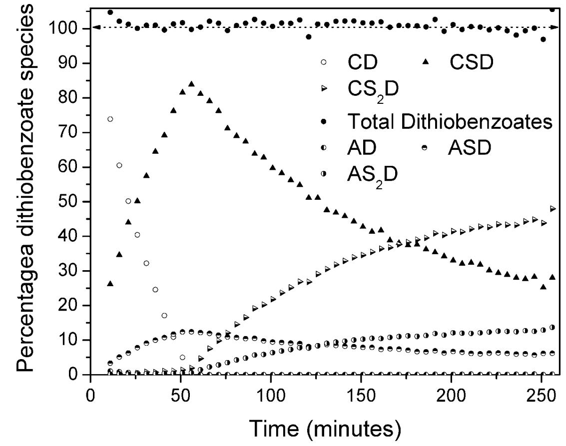


Figure 4. Relative concentrations of the methyl protons of the dithiobenzoate species versus time in the in situ free radical polymerization of styrene in the presence of cumyl dithiobenzoate using azobis(isobutyronitrile) as an initiator at 84 °C. Table 1, reaction 2: 2.99×10^{-3} mol of C_6D_6, 6.30×10^{-5} mol of azobis(isobutyronitrile), 2.46×10^{-3} mol of styrene, 3.68×10^{-4} mol of cumyl dithiobenzoate.

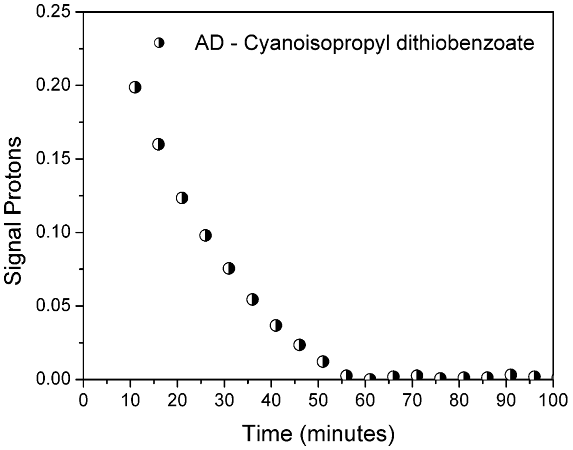


Figure 5. Concentration–time evolution of the AD species in reaction 2 (Table 1) at 84 °C: 2.99×10^{-3} mol of C_6D_6, 6.30×10^{-5} mol of azobis(isobutyronitrile), 2.46×10^{-3} mol of styrene, 3.68×10^{-4} mol of cumyl dithiobenzoate.

the right-hand side of case Va), the $A^\bullet$ radicals will instead terminate or propagate to a length at which they can effectively participate in the main addition–fragmentation equilibrium.

Effect of Temperature. The second reaction (reaction 2, Table 1) was a duplicate of reaction 1 (see Table 1) carried out at 84 °C for comparative purposes. The time dependences of the concentrations of important species are shown in Figure 4. The initialization period (about 50 min) was much shorter than that of reaction 1 (about 240 min). The radical flux from the initiator and the temperature dependence of the $A^\bullet$ and $C^\bullet$ propagation and/or termination reactions clearly play a very important role in the length of the initialization period. It is interesting to note that species AD, which is not an original component of the reaction mixture, reaches a maximum concentration prior to the commencement of spectral data collection at 8 min. This is shown in Figure 5. AD is formed by the addition of $A^\bullet$ to CD, and subsequent fragmentation of the formed intermediate radical to eject the $C^\bullet$ radical.

It has been shown that the initialization time is temperature dependent in the case of cyanoisopropyl dithiobenzoate.[1] This is again true for the case where cumyl dithiobenzoate is used as RAFT agent. This is because the same factors (propagation and/or termination of $A^\bullet$ and $C^\bullet$ radicals, and subsequent addition to a RAFT agent) govern the initialization behavior for both RAFT systems. In the initial cyanoisopropyl dithiobenzoate experiments, the initialization time was determined by the rate of addition of a single styrene unit (per RAFT agent) to the cyanoisopropyl radicals ($A^\bullet$) to form $AS^\bullet$, which then added to the initial RAFT agent. In the cumyl dithiobenzoate experiments, the duration of the initialization period is directly dependent on the rate of addition of a single styrene unit to the cumyl and (to a lesser extent) cyanoisopropyl radicals. The length of the initialization period is directly related to monomer conversion, and reasons for differences from the previously studied system will be discussed below.

Monomer Consumption. In RAFT polymerizations in which initiator-derived initiating radicals and initial leaving group radicals ($R^\bullet$) are different, the number of different *propagating* (and intermediate) radicals is increased. It should be noted that in the cumyl dithiobenzoate system there are two main types of propagating radical species present during the initialization period, i.e., $C^\bullet$ and $A^\bullet$. In this case the expression for the rate of monomer consumption in the initialization period becomes a composite term (the average "propagation" rate coefficient will be $\langle k_p \rangle = k_{p,A}[A^\bullet] + k_{p,C}[C^\bullet]$, where $k_{p,A}$ and $k_{p,C}$ are the addition rate coefficients of $A^\bullet$ and $C^\bullet$ radicals to monomer, respectively, assuming that there are no significant side reactions of these radicals) to take into account the fractions of the two types of radicals active in the system. This substantially increases the difficulty in resolving different influences on the propagating radical concentration.

Comparison between the amount of CC and AA termination products formed, which will be discussed below, suggests that the dominant propagating radical through most of the initialization period is $C^\bullet$, which mainly adds to styrene, as evident through the dominance of the CSD (over ASD) product during initialization. This has been confirmed by electron spin resonance (ESR) spectroscopy.[22]

The monomer consumption of the cumyl dithiobenzoate-mediated reactions (1 and 2), as seen in Figure 6, is faster during the initialization period (240 and 50 min) for both reactions than after this period has ended. A decrease in the rate of monomer consumption after the initialization period is seen for the reactions even after correction for initiator decomposition (not shown). However, the change in rate of monomer consumption at the end of initialization is not as clearly evident as was previously seen in the cyanoisopropyl dithiobenzoate-mediated reactions (Figure 6).[1] Since the length of the initialization period is much greater for the CD than for the AD system under similar reaction conditions, then the average termination rates are much higher in the current case (leading to a lower propagating radical concentration), the average propagation rate coefficient (dominated by $C^\bullet$) is lower in the current case, and/or a difference in partitioning of radicals between the intermediate and propagating form is present. The observed differences between the AD- and CD-mediated reactions and the change in monomer consumption rates at the end of the initialization period are consistent with a system not yet having reached steady-state equilibrium during initialization. Since the length of the initialization period is dependent on the rate of mono-

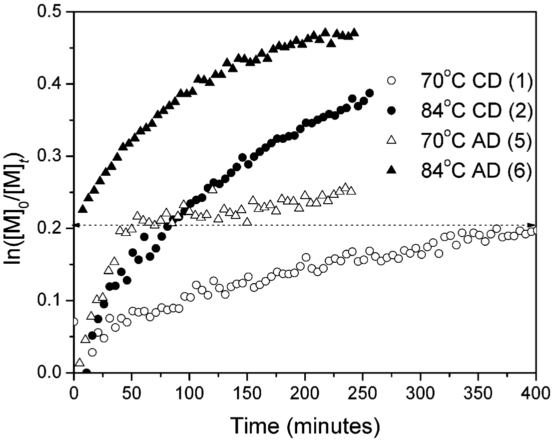


Figure 6. Semilogarithmic plot of fractional conversion versus time in the reactions of cumyl dithiobenzoate and cyanoisopropyl dithiobenzoate with azobis(isobutyronitrile) and styrene in deuterated benzene, respectively, at 84 and 70 °C. Table 1, reactions 1, 2 and 5, 6: (1) 2.99×10^{-3} mol of C_6D_6, 6.30×10^{-5} mol of azobis(isobutyronitrile), 2.46×10^{-3} mol of styrene, 3.68×10^{-4} mol of cumyl dithiobenzoate; (2): 2.99×10^{-3} mol of C_6D_6, 6.30×10^{-5} mol of azobis(isobutyronitrile), 2.46×10^{-3} mol of styrene, 3.68×10^{-4} mol of cumyl dithiobenzoate; (5) 3.56×10^{-3} mol of C_6D_6, 6.75×10^{-5} mol of azobis(isobutyronitrile), 2.40×10^{-3} mol of styrene, 4.84×10^{-4} mol of cyanoisopropyl dithiobenzoate; (6) 3.56×10^{-3} mol of C_6D_6, 6.1×10^{-5} mol of azobis(isobutyronitrile), 2.31×10^{-3} mol of styrene, 4.84×10^{-4} mol of cyanoisopropyl dithiobenzoate.

mer consumption under these conditions, the same reasons for the differences in monomer propagation rates apply to the lengths of the initialization periods.

A possible cause for the rate differences seen in the cumyl and cyanoisopropyl systems during initialization is a difference in partitioning of radicals between the intermediate and propagating forms, resulting in a lower propagating radical concentration and thus more retardation in polymerization rate occurring in the cumyl dithiobenzoate-mediated system. This would imply that there is a substantial concentration of intermediate radicals in the CD-mediated system, but not in the AD-mediated case. This could occur if the addition rate coefficients to the thiocarbonyl thio moiety (and/or the fragmentation rate coefficients of the formed intermediate radicals) of the cumyl and cyanoisopropyl radical species are substantially different.[12] However, ESR data[22] suggest that there is no significant difference in the intermediate radical concentrations during the initialization period for the AD and CD reactions, so although this cannot be completely ruled out as a contributing factor, higher intermediate radical concentrations are unlikely to be the cause of the rate difference. Note that, since low concentrations of intermediate radicals form in these cases, it is predicted that the rate of monomer consumption during initialization, and the length of the initialization period, should be similar to that of analogous reactions using non-retarding RAFT agents. This has indeed been observed.[2]

If the intermediate radical concentration is very low during initialization, then, as a first approximation, the total propagating radical concentration for both cyanoisopropyl and cumyl dithiobenzoate-mediated systems will be proportional to the square root of the rate coefficient of initiator decomposition, and inversely proportional to the square root of the average termination rate coefficients for the systems. The rate of initiator decomposition is identical for the reactions studied. Since the initial rates of monomer consumption (and the resulting initialization time) are about 3–5 times faster when AD is used as the initial RAFT agent, $\langle k_p \rangle / \langle k_t \rangle^{1/2}$ (where these rate coefficients are appropriately weighted averages for the propagation (addition, as described above) and termination of the $A^\bullet$ and $C^\bullet$ radicals for each case) must be larger by the same ratio for the AD case. It is not possible to distinguish between propagation and termination rate coefficients as a cause of the rate difference with the current experiments. Arguments for both cases are now discussed.

As (to a good approximation) only a single styrene unit adds to the cyanoisopropyl radicals for each RAFT species (and cumyl radicals for the cumyl dithiobenzoate case) during initialization, a lower $k_{p,C}$ (propagation rate coefficient of a cumyl radical) will contribute toward a longer initialization period for the cumyl dithiobenzoate case. It has been stated[13] that the value for $k_{p,A}$ (propagation rate coefficient of a cyanoisopropyl radical) (4040–4896 L mol^{-1} s^{-1} depending on the parameters used) is higher than that for $k_{p,C}$, (3800 L mol^{-1} s^{-1}) at 60 °C. The values given above were calculated by Chong et al.[13] using the Arrhenius parameters provided by Herberger et al.[23] and Walbiner et al.,[24] respectively. The value for $k_{p,C}$ was based on the averaged log A value of 7.5 for tertiary radicals and the activation energy provided by Fischer and Radom.[25] When the averaged log A value is used for the cyanoisopropyl with the values provided by Fischer and Radom,[25] the difference in rate coefficients is approximately 20%. It should be noted that the activation energy used in ref 13 for the cumyl radical is based on similar radicals (not the cumyl radical), and thus, the difference in k_p values might be slightly larger than that quoted here. The above difference between $k_{p,A}$ and $k_{p,C}$ alone is however unable to explain the difference in monomer consumption observed for the cyanoisopropyl and cumyl dithiobenzoate reactions. Thus, unless the $k_{p,C}$ value for our reaction is significantly different from the value calculated by Chong et al.[13] and from $k_{p,A}$, it is likely that there is a difference in total propagating radical concentrations between the two systems.

A difference in propagating radical concentrations for the two systems could be due to a difference in termination kinetics. This suggests that the rate coefficients for termination of cumyl radicals with themselves and/or cyanoisopropyl radicals are significantly higher than for the mutual termination of cyanoisopropyl radicals under the same conditions. This is contrary to expectations based on molecular size, since the cumyl radical is larger (and therefore expected to diffuse and terminate[26,27] more slowly) than the cyanoisopropyl radical. Terazima and co-workers have shown that the diffusion of radicals in solution is sometimes significantly slower than for their parent closed shell molecules,[28,29] and the same phenomenon was reported in the case of the cyanoisopropyl radical species ($D = 1.18 \times 10^9$ m^2 s^{-1} in benzene at 22 °C, estimated 70% of predicted value based on volume).[30] Although Fischer et al.[31] reported a $k_{t,C}$ value of 1.2×10^9 M^{-1} s^{-1}, in *tert*-butylbenzene at 297 K, Terazima indicates that the benzyl ($D = 4.1 \times 10^9$ m^2 s^{-1} in hexane,[32] also previously reported by Burkhart et al.[33] as $D = 4.1 \times 10^9$ m^2 s^{-1} in benzene) and 4-aminophenylthiyl radicals do not suffer from the slower rate of diffusion. This was attributed to the stable π electron resonance structure which resulted in less solvent interaction and a faster diffusion rate than those of their parent closed shell molecules.[32,34] It is consid-

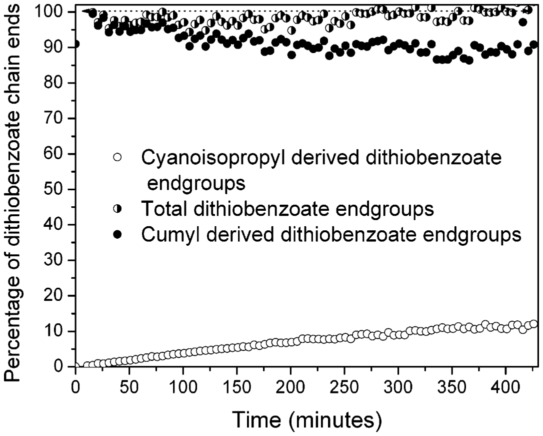


Figure 7. Percentage of cumulative integrated end groups of the dithiobenzoate species, in the polymerization of styrene, mediated by cumyl dithiobenzoate, using azobis(isobutyronitrile) as an initiator at 70 °C.

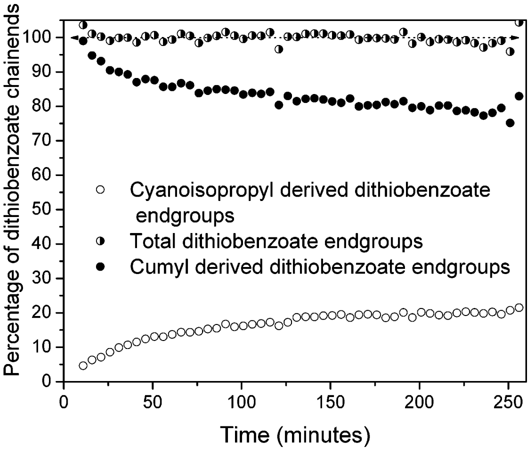


Figure 8. Percentage of cumulative integrated end groups of the dithiobenzoate species, in the polymerization of styrene, mediated by cumyl dithiobenzoate, using azobis(isobutyronitrile) as an initiator at 84 °C.

ered reasonable that the same behavior could potentially be observed in the case of the cumyl radical. Weiner reported that termination rate coefficients for the cumyl radical were ca. 8 times higher than for the cyanoisopropyl radical at room temperature in benzene.[35] This is the only study in which the termination rate coefficients of the cyanoisopropyl and cumyl radicals are directly compared by the same techniques. The estimation technique used is reported to lead to overestimation of the rate coefficients in the case of the cumyl radical; however, their value for the cyanoisopropyl radical is consistent with that of Terazima at 22 °C.[30] Unfortunately, there is a lack of consistency among experiments, temperatures, and reported termination rate coefficients for cumyl and cyanoisopropyl radicals throughout the available literature, so the large difference in termination rate coefficients reported by Weiner when compared to the value of Fischer needs further verification at the reaction temperature with consistent techniques. It is considered that the implied large difference in termination rate coefficients between systems is possible, but not certain. Such differences in termination kinetics (in addition to small differences in propagation kinetics) between the two types of radicals are capable of explaining the observed rate differences during initialization. Moreover, there is also the possibility that there are side reactions that produce undetectably (in these experiments) small amounts of side products that might have kinetic significance during the initialization process. However, it should be noted that there was no detectable loss of dithiobenzoate species throughout the entire duration of the reactions (as shown in Figures 7 and 8).

Radical Generation and Termination Products. The terminated species give insight into the reactions that govern the RAFT mechanism during the early stages of the polymerization process. These can be examined indirectly from the relative concentrations of all of the dithiobenzoate species with cumyl and cyanoisopropyl end groups and directly by the nature and amounts of the formed terminated species.

Figure 7 shows the time dependence of the relative concentrations of all dithiobenzoate species with cumyl (CD, CSD, CS_2D) and cyanoisopropyl (AD, ASD, AS_2D) end groups in reaction 1. There is a gradual displacement of cumyl end groups from the living polymer, with a corresponding equivalent increase in cyanoisopropyl end groups, and no observable overall loss of dithiobenzoate species. All of the dithiobenzoate species with cumyl end groups are present at the beginning of the reaction, resulting in an initial maximum concentration, followed by the observed decrease. Addition of cyanoisopropyl-ended radicals to cumyl-ended RAFT chains, followed by fragmentation of the formed intermediate radical to give cumyl or cumylstyryl radicals that are then terminated, is responsible for this change in end groups.

The number of living chains with a cyanoisopropyl end group increases with time due to two factors: (1) “transfer” is efficient; therefore, species CD will be displaced by any other radical in the system, allowing possible termination of expelled $C^\bullet$;[13] (2) there is a limited supply of cumyl groups, whereas $A^\bullet$ groups are continually supplied. Under such conditions, the total number of chains with cyanoisopropyl end groups *must* therefore increase. A constant concentration of chains with dithiobenzoate end groups throughout the reaction indicates that very little loss (below the detection limit of the NMR spectrometer) of this type of chain occurs (due to intermediate radical termination, formation of stable intermediates, or degradation) throughout the duration of the reaction.

Figure 8 shows the time dependence of the relative concentrations of all dithiobenzoate species with cumyl and cyanoisopropyl end groups within the first 3 h of reaction 2. As in the reaction at 70 °C, there is a gradual displacement of the cumyl end groups by cyanoisopropyl groups. The rate of increase of cyanoisopropyl end groups is at a maximum early in the reaction. This is because the number of radicals generated by azobis(isobutyronitrile) decomposition is highest early in the reaction, and the number of cumyl-ended chains (which will compete for cyanoisopropyl-ended radicals) is at a maximum at the beginning of the reaction. As all of the dithiobenzoate species with cumyl end groups are present at the beginning of the reaction, a maximum is expected at the beginning of the reaction and a gradual decrease in the concentration of the dithiobenzoate species with cumyl end groups, as some of the cumyl groups are involved in termination. This was observed. It is also interesting to note that the highest rate of decrease is during the earlier part of the reaction, i.e., during the initialization period. The high level of cumyl−cumyl (CC) termination seen during the initial-

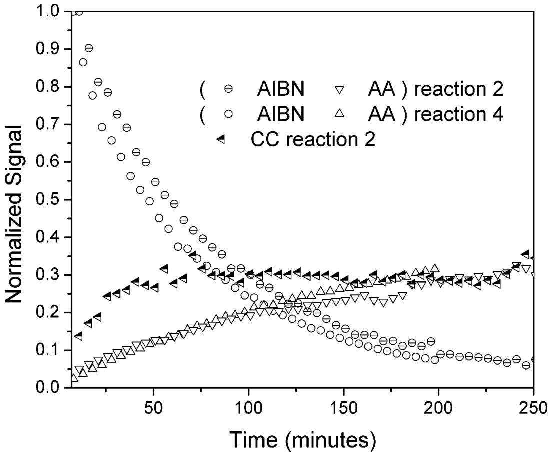


Figure 9. Concentration evolution of the termination products AA and CC formed in the reaction of styrene and azobis(isobutyronitrile) with (reaction 2) and without (reaction 4) cumyl dithiobenzoate in deuterated benzene at 84 °C.

ization period is also confirmation of this (Figure 8). The increased temperature in reaction 2 compared to reaction 1 increased the radical flux in the system, leading to a higher rate of displacement of cumyl end groups from the dithiobenzoate species. The net result was approximately 20% end group interchange by the end of the monitoring period in reaction 2 and 10−12% in reaction 1. The interchange of end groups is especially important for applications in which specific end groups are required.

There are significantly more (Figure 9) cumyl−cumyl (CC) termination products than products of other termination processes during the initialization period. Production of CC ceases at the end of the initialization period, since (by definition) there are no remaining cumyl leaving groups on RAFT chains. The amount of AA produced by termination is not significantly greater than for the control (conventional) reaction (reaction 4, Table 1) without the RAFT agent; i.e., there is little "excess" reaction between A$^\bullet$ radicals, which is quite different from the case when AD was used as RAFT agent.[1] This suggests that the AA termination product is predominantly a geminate recombination product as in the case of the control reaction. Other termination reactions occur (i.e., giving products AC and CSC), but due to their lack of symmetry in structure (leading to fine structure and broad peaks) and small concentrations, these termination products were too small to be integrated accurately and are therefore not shown in Figure 9. This suggests that the concentration of cumyl radicals is much higher than that of the cyanoisopropyl radicals, which is complementary to ESR results.[22] This is also consistent with the dominance of C$^\bullet$ propagation during initialization (seen as the predominant formation of CSD). This is due to displacement of cumyl radicals by AS$^\bullet$, CS$^\bullet$, and A$^\bullet$ radicals (A$^\bullet$ radicals are the next most common propagating species, since insignificant amounts of AS$_2$D and CS$_2$D are seen during initialization), although the concentration of the generated species AD is low relative to that of the CD species. The rate of monomer consumption (Figure 6) implies that the concentration of propagating species (primarily C$^\bullet$) is at a maximum at the start of the reaction; consequently, the rate of termination will also be at a maximum as indicated by the initial maximum rate of CC termination products forming during the early parts of the reaction, implying that the cumyl radical will be the most abundant radical during the early reaction.

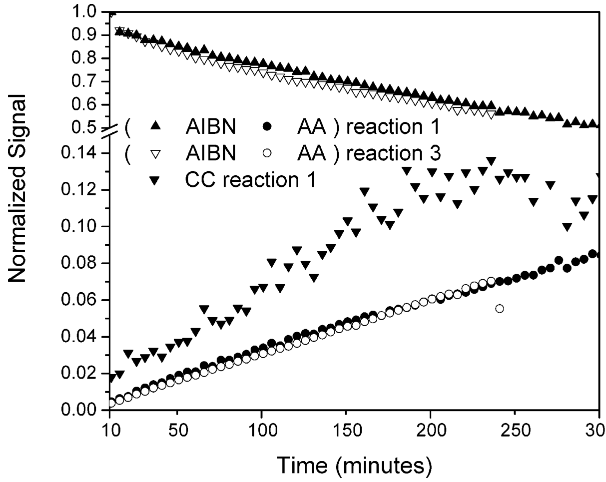


Figure 10. Concentration evolution of the termination products formed in the reaction of styrene and azobis(isobutyronitrile) with (reaction 1) and without (reaction 3) cumyl dithiobenzoate in deuterated benzene at 70 °C.

In Figure 10 the respective termination products for reaction 1 at 70 °C are shown. The very small amounts of termination at the lower temperature complicated analysis, but the same trends were observed as at the higher reaction temperatures. The CC termination product is dominant until the end of initialization, at which time the termination of the CC radicals ceases.

The increased concentrations of the respective termination products in the RAFT-mediated polymerizations during initialization are due to the unique process that is taking place, in which active chains are kept short. During the initialization period A$^\bullet$ or C$^\bullet$ will add to a monomer unit to form AS$^\bullet$ or CS$^\bullet$. When these species undergo efficient transfer, a short A$^\bullet$ or C$^\bullet$ will be expelled. The chain length dependence of the termination rate coefficients means that short species will have a higher rate of termination, and the overall termination rate will be higher than that in a control reaction in which the short chains are quickly converted into longer chains.[26,27] At the end of initialization, longer chain radicals can form in significant quantities, and thus the resulting average rate coefficient for termination is likely to decrease, leading to a possible increase in the propagating radical concentration (depending on other factors, such as the relative amounts of intermediate radicals). The longer initialization periods with CD as RAFT agent will result in less residual initiator at the end of initialization compared with that in the AD systems. Thus, propagating radical concentrations are expected to be lower at the end of initialization for CD-mediated reactions, compared to analogous AD reactions. The higher rate of radical loss through termination (Figure 11) implies that longer initialization periods will require significantly higher radical fluxes to allow reactions to reach conversions comparable to those of shorter initialization time reactions. This behavior might be a contributing factor to reported increased rate retardation during polymerizations where cumyl dithiobenzoate has been used as a RAFT agent.[36] The increased amount of short chain termination products during the first part of the initialization period (Figure 11) for the CD case is consistent with a higher overall rate of termination during this period, as suggested earlier.

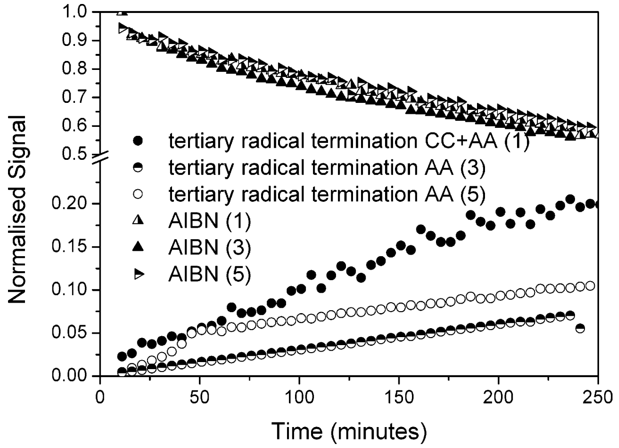


Figure 11. Sum of the concentration evolutions of the termination products AA and CC formed in the reaction of styrene and azobis(isobutyronitrile) without a mediating agent (reaction 3, Table 1), with cumyl dithiobenzoate (reaction 1, Table 1), and with cyanoisopropyl dithiobenzoate (reaction 5, Table 1) at 70 °C.

Beyond Initialization. In the case of an initiator that provides radicals that are unable to displace initial R groups from the initial RAFT agent, the process of initialization will be begun by the propagation of the initiator-derived radicals prior to exchange. This process may result in an initialization period that is less dependent on the initial R group and more dependent on the initiator fragment than the system studied here.

The propagated radicals are often better (as is the case here) able to displace the initial R groups. In the reactions presented in this study of cumyl dithiobenzoate with azobis(isobutyronitrile) as initiator, the relative abilities of the radicals are such that some displacement of the cumyl group (by the cyanoisopropyl radical) can occur before the first propagation step, as has been seen by the formation of the AD species in reactions 1 and 2. The amount of AD produced was however very small with respect to those of ASD and CSD and had no significant effect on the types of chains or kinetics.

However, the use of radical initiator or R group species that are less likely to fragment from the intermediate radical species than the species presented here should be carefully monitored. The initialization period as discussed here is not subject to retardation behavior as reported in the literature.[17,18,37−40] If the initial radical species in the system are such that the intermediate radical concentration begins to increase immediately, retardation will occur and the pseudo-zero-order behavior with respect to the initial RAFT agent concentration is unlikely to hold. The rate-determining processes will then also differ substantially.

Conclusions

In this study, in situ ^{1}H NMR spectroscopy has provided novel insight into the mechanism of the first interval of polymerization that could be observed in the studied systems (the initialization period) of the RAFT process. It was shown that when two efficient radicals were used as initiator and leaving groups, respectively, the addition−fragmentation process was extremely selective during this period, and because of this, significant quantities of RAFT adducts of degrees of polymerization greater than 1 were formed only after complete conversion of the initial RAFT agent to its monomeric adducts. The critical process in the initialization of these RAFT-mediated polymerizations was the formation of the single-monomer adduct dithiobenzoate species, and by implication, the propagation of the leaving and initiator-derived radical groups.

The observed behavior during initialization is suggested to be dependent on the relative reactivities and radical stabilities, and therefore the related addition and fragmentation rate coefficients of the tertiary radical species (and the formed intermediate radicals) in the systems and their monomer adducts. The possibility of termination rate differences between cyanoisopropyl and cumyl radicals based on diffusion differences is also considered as a contributing factor. The potential (small) difference in intermediate radical concentration is considered to play a negligible role.

The selectivity of the addition−fragmentation process during initialization was a result of a bias toward fragmentation to form the cumyl radical, which was responsible for the majority of the monomer consumption (and thus formation of the critical CSD group) and termination reactions. The dominance of this propagating radical was due to efficient transfer from initiator-derived radicals, the relatively high initial concentration of CD, and the fragmentation selectivity. The dominance of the cumyl radical during the initialization period resulted in significantly slower monomer consumption (and a correspondingly increased initialization time) during this period than for the previous[1] analogous AD-mediated reaction. The poorest leaving group was the styryl (i.e., AS$^\bullet$ and CS$^\bullet$) radical. As a result of the selectivity, the initialization period shows behavior different from that during the main RAFT equilibrium.

The dominance of cumyl-ended propagating radicals in this system leads to significant differences in the length of the initialization period with respect to that of the analogous AD-mediated system, and possibly until all chains in the system are “long”. The relative amounts of cumyl-ended growing chains decreased throughout the duration of the reaction (due to termination of cumyl-ended chains, and the continuous supply of cyanoisopropyl radicals that eventually form growing chains). This process was more significant at the higher temperature studied, presumably due to the relatively higher rate of generation of cyanoisopropyl radicals and resulting termination of cumyl-ended chains.

The general behavior here is likely to be applicable to many efficient RAFT systems (that show the strong addition−fragmentation selectivity observed here) where multiple radical species are present and should not be considered as solely an explanation of the cumyl dithiobenzoate system. Indeed, the general observations here are similar to those seen when the initiating and leaving groups are the same,[1,2] as expected when the same general mechanisms dominate.

At some time after initialization, the “long chain” values of addition, propagation, termination, and fragmentation rate coefficients will be achieved, at which point the system will reach steady-state equilibrium. This might require each chain to add two or more monomer units.

Acknowledgment. We acknowledge the financial assistance of the National Research Foundation of South Africa and the Dutch Polymer Institute. The NMR facilities of the Central Analytical Facility at the University of Stellenbosch are acknowledged for the

extensive machine time and expertise required for conducting the experiments.

References and Notes

(1) McLeary, J. B.; Calitz, F. M.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Macromolecules* **2004**, *37*, 2383−2394.

(2) McLeary, J. B.; Mckenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Chem. Commun.* **2004**, 1950−1951.

(3) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.

(4) Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909−914.

(5) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721−1723.

(6) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070−1072.

(7) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.

(8) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615.

(9) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Appl., 1998, WO 98/01478.

(10) Barner-Kowollik, C.; Quinn, J. F.; Nguyen, T. L. U.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2001**, *34*, 7849−7857.

(11) Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A.; Stenzel, M. H.; Vana, P.; Whittaker, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 365−375.

(12) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273−2282.

(13) Chong, Y. K. B.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−2272.

(14) Coote, M. L.; Radom, L. *J. Am. Chem. Soc.* **2003**, *125*, 1490−1491.

(15) Barner-Kowollik, C.; Coote, M. L.; Davis, T. P.; Radom, L.; Vana, P. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2828−2832.

(16) Wang, A. R.; Zhu, S.; Kwak, Y.; Goto, A.; Fukuda, T.; Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2833−2839.

(17) Monteiro, M. J.; de Brouwer, H. *Macromolecules* **2000**, *34*, 349−352.

(18) Kwak, Y.; Goto, A.; Tsujii, Y.; Murata, Y.; Komatsu, K.; Fukuda, T. *Macromolecules* **2002**, *35*, 3026−3029.

(19) Barner-Kowollik, C.; Quinn, J. F.; Morsley, D. R.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1353−1365.

(20) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227−2229.

(21) Calitz, F. M.; McLeary, J. B.; McKenzie, J. M.; Tonge, M. P.; Klumperman, B.; Sanderson, R. D. *Macromolecules* **2003**, *36*, 9687−9690.

(22) Calitz, F. M.; Tonge, M. P.; Sanderson, R. D. Manuscript in preparation.

(23) Herberger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1993**, *25*, 249−263.

(24) Walbiner, M.; Wu, J. Q.; Fischer, H. *Helv. Chim. Acta* **1995**, *78*, 910−924.

(25) Fischer, H.; Radom, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1340−1371.

(26) Heuts, J. P. A.; Davis, T. P.; Russell, G. T. *Macromolecules* **1999**, *32*, 6019−6030.

(27) Buback, M.; Egorovc, M.; Gilbert, R. G.; Kaminsky, V.; Olaj, O. F.; Russell, G. T.; Vana, P. *Macromol. Chem. Phys.* **2002**, *203*, 2570−2582.

(28) Terazima, M.; Okamoto, K.; Hirota, N. *J. Phys. Chem.* **1993**, *97*, 13387−13393.

(29) Terazima, M.; Hirota, N. *J. Chem. Phys.* **1993**, *98*, 6257−6262.

(30) Terazima, M.; Nogami, Y.; Tominaga, T. *Chem. Phys. Lett.* **2000**, *332*, 503−507.

(31) Sobek, J.; Martschke, R.; Fischer, H. *J. Am. Chem. Soc.* **2001**, *123*, 2849−2857.

(32) Okamoto, K.; Hirota, N.; Terazima, M. *J. Phys. Chem.* **1997**, *101*, 5269−5277.

(33) Burkhart, R. D. *J. Am. Chem. Soc.* **1968**, *90*, 273−277.

(34) Ukai, A.; Hirota, N.; Terazima, M. *Chem. Phys. Lett.* **2000**, *319*, 427−433.

(35) Weiner, S. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1969**, *91*, 986−990.

(36) Moad, G.; Chiefari, J.; Chong, B. Y.; Krstina, J.; Mayadunne, R. T.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993−1001.

(37) Kwak, Y.; Goto, A.; Fukuda, T. *Macromolecules* **2004**, *37*, 1219−1225.

(38) Perrier, S.; Barner-Kowollik, C.; Quinn, J. F.; Vana, P.; Davis, T. P. *Macromolecules* **2002**, *35*, 8300−8306.

(39) Souaille, M.; Fischer, H. *Macromolecules* **2002**, *35*, 248−261.

(40) Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromol. Theory Simul.* **2002**, *11*, 823−835.

MA047696R