Novel Approach to Tailoring Molecular Weight Distribution and Structure with a Difunctional RAFT Agent

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ABSTRACT: This work has demonstrated that for the first time a single RAFT agent (i.e., difunctional) can be used in conjunction with a radical initiator to obtain a desired M_n and PDI with controlled rates of polymerization. Simulations were used not only to verify the model but also to provide us with a predictive tool to generate other MWDs. It was also shown that all the MWDs prepared in this work could be translated to higher molecular weights through chain extension experiments with little or no compromise in the control of end group functionality. The ratio of monofunctional to difunctional $S{=}C(CH_2Ph)S-$ end groups, XPX and XP (where $X = S{=}C(CH_2Ph)S-$), can be controlled by simply changing the concentration of initiator, AIBN. Importantly, the amount of dead polymer is extremely low and fulfils the criterion as suggested by Szwarc (*Nature* 1956) that to meet "living" requirements nonfunctional polymeric species formed by side reactions in the process should be undetectable by analytical techniques. In addition, this novel methodology will allow the synthesis of AB, ABA, and statistical multiblock copolymers with predetermined ratios to be produced in a one-pot reaction.

Introduction

Living radical polymerization (LRP) has provided a tool to produce polymer chains of near uniform chain length. Polymers produced via this technique has opened an exciting realm of specialty applications, ranging from molecular computers[1,2] to miniature medical devices capable of entering individual cells to carry out a variety of functions.[3] However, it would be of commercial interest to synthesize polymers: (1) of a desired molecular weight distribution (MWD) with only "one" living agent and (2) with well-defined functionality on the polymer chains ends.

In the case of reversible addition−fragmentation chain transfer (RAFT) polymerization, it has been shown that controlled distributions can be synthesized using a variety of RAFT agents (CTAs).[4−7] The number-average molecular weight is controlled by the concentration ratio of monomer to RAFT agent, and the polydispersity (PDI) is controlled by selecting the appropriate activating Z and leaving R groups on the CTA, and in particular its chain transfer constant ($C_{tr} = k_{tr}/k_p$, for the reaction of polymeric radicals toward the $S{=}C(Z)S-$ moiety).[6−9] The greater the activating power (i.e., greater value of C_{tr}) of the Z group (and assuming $R^\bullet$ has a high reactivity toward monomer) the narrower the molecular weight distribution. Therefore, to obtain a desired MWD, one must choose from a variety of CTAs. It has been shown through modeling and experiment that using a CTA with a low C_{tr} constant (Xanthates[10]) can produce any PDI ranging from 1 to 2 through a monomer feed technique.[6,11] The control relies on maintaining a low and constant monomer concentration in the reaction vessel, but it is experimentally not viable as extremely long reaction times are required to produce near uniform polymer chains.

We report here an easy methodology to produce a desired MWD of polystyrene by using only one difunctional CTA. The interesting aspect of this work is that the MWD and ratio of mono- to difunctional end groups can be controlled by altering the ratio of radical initiator to CTA. This ratio of chain-end functionality becomes important in the preparation of recycled polymer. At the time of writing this paper, Patton et al.[12] published their work on a facile synthesis to thiol-functionalized α,ω-telechelic polymers using a difunctional RAFT agent similar to that used in this work.

Experimental Section

Chemicals. Styrene (STY, 99% pure, Aldrich) was passed through a column of basic alumina (activity I) to remove inhibitor. 2,2-azobis (isobutyronitrile) (AIBN, 98% pure, Fluka) was recrystallized twice from methanol prior to use. 1,3-diisopropenylbenzene (Aldrich, 97%), tetrahydrofuran (HPLC, LAB−SCAN, 99.8%), toluene (HPLC, LAB−SCAN, 99.8%), *n*-hexane (AR, UNIVAR), and diethyl ether (AR, Univar) were obtained at the highest purity available and used as received unless otherwise stated. Phenyldithioacetic acid (PDA) was prepared according to the literature.[19]

Synthesis of CTA, 1,3-Bis(2-(thiobenzylthio)prop-2-yl)benzene (BTBTPB). 1,3-Bis(2-thiobenzylthio)prop-2-yl)benzene (BTPTPB) was prepared based on the literature procedure.[4] Phenyldithioacetic acid (PDA) (8.7 g, 51.7 mmol) was reacted with 1,3-diisopropenylbenzene (3.67 g, 23.2 mmol), with a small amount of acid catalyst (toluene-*p*-sulfonic acid) in carbon tetrachloride (100 mL). The mixture was then refluxed in an oil bath at 65 °C for 63 h. The mixture was collected via rotary evaporation and purified by column chromatography on alumina oxide (using a mixture of 95% of *n*-hexane and 5% of diethyl ether.) An orange oil product was collected via the rotary evaporation of the solvent. (∼3.45 g, 7 mmol, 30%). The purity of the compound was verified from NMR and elemental analysis was better than 99%. ^{1}H NMR ($CDCl_3$): $\delta = 1.8$ s (12H), $\delta = 4.2$ s (4H), $\delta = 7.3$ m (13H), $\delta = 7.5$ s (1H).^{13}C NMR ($CDCl_3$): 28.1, 56.3, 59.2, 124.8, 127.1, 128.9, 137.2, 142.8, and 238.2.

Solution Polymerization of Styrene in the Presence of BTBTPB at 60 °C. A typical polymerization is as follows: styrene (2.90 g, 5.56 M), AIBN (2.06 mg, 2.50×10^{-3} M), BTPTPB (61.70 mg, 2.49×10^{-3} M), and toluene (1.79×10^{-3} L) were added to an ampule. Four ampules made by this stock solution were deoxygenated by three freeze−thaw−pump cycles, sealed, and placed in a heating block at 60 °C. The ampules were removed from the oil bath at predetermined times. The sample was dried

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Table 1. Experimental Conditions, Molecular Weight, and Conversion Data for the Polymerizations of Styrene in the Presence of 1,3-Bis(2-thiobenzylthio)prop-2-yl)benzene (BTBTPB) and Toluene and Initiated with 2,2-Azobis(isobutyronitrile) (AIBN) at 60 °C, Where the Styrene and Toluene Concentrations Used Are 5.56 and 3.38 M, Respectively

expt	[BTPTPB] (mol/L)	[AIBN] (mol/L)	time (s)	x	M_n(theory) (eq 1)	M_n	PDI
1a	2.52×10^{-2}	2.49×10^{-3}	18 120	0.031	1208.68	936	1.07
1b			36 000	0.064	1947.71	1874	1.12
1c			54 600	0.941	2607.69	3177	1.12
1d			72 840	0.124	3262.56	4569	1.12
1e			90 000	0.162	4092.29	4830	1.15
2a	2.50×10^{-2}	1.26×10^{-2}	18 120	0.083	2120.07	2903	1.27
2b			36 000	0.133	3510.34	4506	1.24
2c			54 600	0.238	5233.58	6705	1.23
2d			72 840	0.253	5832.30	8172	1.28
2e			90 000	0.313	6657.73	9752	1.29
3a	2.51×10^{-2}	5.05×10^{-2}	18 120	0.164	3667.87	4600	1.44
3b			36 000	0.283	5334.90	7557	1.50
3c			54 600	0.404	6758.61	9557	1.65
3d			72 840	0.466	7211.65	11 246	1.66
3e			90 000	0.609	8790.09	11 577	1.79
4a	2.49×10^{-2}	2.49×10^{-1}	6000	0.132	2791.52	2968	1.34
4b			10 020	0.205	3580.46	4307	1.54
4c			18 420	0.319	4266.29	5858	1.84
4d			26 040	0.416	4673.54	6791	2.00
4e			36 000	0.523	4932.14	7324	2.10
4f			51 180	0.634	4984.99	7765	2.21
4g			72 840	0.754	4877.90	8210	2.25
5a	3.85×10^{-3}	4.02×10^{-4}	36 000	0.037	5943.57	6777	1.25
5b			54 000	0.069	10586.92	12 334	1.19
5c			72 600	0.088	13290.27	12 599	1.20
5d			90 000	0.105	15691.64	15 346	1.18
5e			108 600	0.125	18601.68	18 707	1.21
5f			127 020	0.150	22148.01	23 336	1.17
6a	3.81×10^{-3}	1.54×10^{-3}	36 000	0.079	11613.76	12 562	1.15
6b			55 200	0.121	17082.45	18 082	1.20
6c			73 200	0.159	21855.20	23 499	1.20
6d			90 000	0.193	26018.01	26 857	1.21
6e			108 000	0.230	30485.30	33 437	1.29
6f			127 020	0.265	34625.12	35 152	1.28
7a	3.83×10^{-3}	3.51×10^{-3}	36 000	0.136	18169.17	20 390	1.42
7b			54 000	0.202	25438.81	28 088	1.47
7c			72 600	0.250	30061.49	33 594	1.53
7d			90 000	0.300	34923.14	38 478	1.58
7e			108 600	0.359	40540.67	41 660	1.61
7f			127 020	0.390	43394.78	43 232	1.60

Table 2. Chain Extension Results from the Polymerization of Styrene (5.47 M), Toluene (3.48 M) in the Presence of Dormant Starting Polymer Made from Different Amounts of 2,2-Azobis(isobutyronitrile) (AIBN) (See Table 1) at 60 °C

expt	[starting polymer] (mol/L)[a]	[AIBN] (mol/L)	time (s)	x	M_n(theory) (eq 1)	M_n SEC	PDI SEC
8	2.26×10^{-2} (4015, 1.18)	2.5×10^{-3}	14 400	0.345	12 293	15 464	1.26
9	2.21×10^{-2} (10686, 1.39)	2.5×10^{-3}	14 400	0.575	24 783	22 823	1.54
10	2.24×10^{-2} (10518, 1.78)	2.5×10^{-3}	14 400	0.761	28 934	27 771	1.73
11	2.19×10^{-2} (8485, 2.25)	2.48×10^{-3}	14 400	0.919	31 016	22 432	1.83
12	1.15×10^{-3} (23336, 1.17)	1.30×10^{-4}	21 780	0.212	107 442	112 507	1.73
13	1.20×10^{-3} (35152, 1.28)	1.27×10^{-4}	21 780	0.208	141 240	101 066	1.61
14	1.30×10^{-3} (43232, 1.60)	1.22×10^{-4}	21 780	0.158	143 808	120 127	1.93

[a] Note: values in parentheses are M_n and PDI, respectively.

and conversion determined gravimetrically. The molecular weight distribution was measured by size exclusion chromatography (SEC). All other experiments were carried out in the same way but with the addition of varying amounts of AIBN to BTPTPB (see Table 1).

Chain Extension of the Polymer Formed from STY/BTBTPB with Styrene at 60 °C. To test the living character of the polymer made above, a chain extension experiment was carried out using the dormant polymers from experiments 1e, 2e, 3e, 4h, 5f, 6f, and 7f in Table 1. For example, polymer 1e ($M_n = 4015$ PDI = 1.18) was added to a solution of STY (5 0.47 M, 3.39×10^{-3} L), toluene (1.98×10^{-3} L) and AIBN (2.50×10^{-3} M). The mixture was placed in a glass ampule and deoxygenated by three freeze−thaw−pump cycles, sealed, and placed in an oil bath at 60 °C for 40 h. All other experiments were carried out with a similar procedure (see Table 2).

Size Exclusion Chromatography. Size exclusion chromatography (SEC) measurements were performed using a Waters Alliance 2690 Separations Module equipped with an autosampler, column heater, differential refractive index detector, and a Photodiode Array (PDA) connected in series. For polystyrene analysis, HPLC grade tetrahydrofuran was used as eluent at a flow rate of 1 mL min^{-1}. The columns consisted of three 7.8 × 300 mm Waters Styragel GPC columns connected in series, comprising 2 linear UltraStyragel and one Styragel HR3 columns. Polystyrene standards ranging from 2e+06 to 517 g mol^{-1} were used for calibration.

Scheme 1. Reaction Scheme for the Free Radical Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization Using a Difunctional CTA[a]

Initiation

$$I_2 \rightarrow 2R\cdot \qquad k_d$$
$$R + M \rightarrow P_1\cdot \qquad k_p$$
$$Pn\cdot + M \rightarrow P_{n+1}\cdot \qquad k_p$$
$$XP_n\cdot + M \rightarrow Xp_{n+1}\cdot \qquad k_p$$
$$\cdot P_{n\cdot} + M \rightarrow \cdot P_{n+1}\cdot \qquad 2k_p$$

Conventional RAFT Equilibrium

$$P_nX + P_m\cdot \rightarrow P_n\cdot + P_mX \qquad k_{tr}$$

Difunctional RAFT Pre-equilibrium

$$P_n\cdot + XRX \rightarrow P_nX + XP_1\cdot \qquad 2k_{tr}$$

Transfer Steps

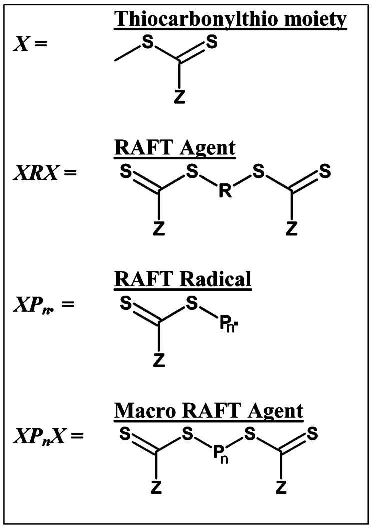
$$XP_n\cdot + P_m\cdot \rightarrow \cdot P_n\cdot + P_nX \qquad k_{tr}$$
$$XP_n\cdot + P_m\cdot \rightarrow P_{n+m}X + \qquad k_{tc}$$
$$XP_n\cdot + XP_m\cdot \rightarrow XP_nX + \cdot P_m\cdot \qquad k_{tr}$$
$$XP_n\cdot + XP_m\cdot \rightarrow XP_{n+m}X + \qquad k_{tc}$$
$$XP_n\cdot + \cdot P_m\cdot \rightarrow \cdot P_n\cdot + XP_m\cdot \qquad 2k_{tr}$$
$$XP_n\cdot + \cdot P_m\cdot \rightarrow XP_{n+m}\cdot + \qquad 2k_{tc}$$
$$XP_n\cdot + P_mX \rightarrow XP_nX + P_m\cdot \qquad k_{tr}$$

Difunctional RAFT Main-equilibrium

$$XP_nX + P_m\cdot \rightarrow XP_n\cdot + P_mX \qquad 2k_{tr}$$
$$XP_nX + XP_m\cdot \rightarrow XP_n\cdot + XP_m \qquad 2k_{tr}$$
$$XP_nX + \cdot P_m\cdot \rightarrow XP_n\cdot + XP_m\cdot \qquad 4k_{tr}$$
$$\cdot P_{n\cdot} + P_mX \rightarrow XP_n\cdot + \cdot P_m\cdot \qquad 2k_{tr}$$
$$\cdot P_{n\cdot} + \cdot P_m\cdot \rightarrow \cdot P_{n+m}\cdot \qquad 4k_{tc}$$

Termination

$$P_{n\cdot} + P_m\cdot \rightarrow D_{n+m} \qquad k_{tc}$$
$$P_{n\cdot} + P_m\cdot \rightarrow D_n + D_m \qquad k_{td}$$
$$P_{n\cdot} + \cdot P_m\cdot \rightarrow P_{n+m}\cdot \qquad 2k_{tc}$$



[a] This scheme was used in the simulations. XRX is the starting CTA, XP_n and XP_nX are the monofunctional and difunctional polymeric dormant species, respectively.

Nuclear Magnetic Resonance (NMR). NMR spectroscopy was carried out using a Bruker Avance DRX 500 spectrometer operating at 500.13 MHz for protons and equipped with a 5 mm triple resonance *z*-gradient probe.

Results and Discussion

Kinetic Modeling of the Difunctional RAFT Agent. Kinetic modeling was used to understand the factors and parameters that control the rate of polymerization, molecular weight distribution, amount of dead polymer (i.e., polymer without S═C(Z)-S− chain-end functionality), and the ratio of mono- to difunctional end groups attached to the polymer for the polymerization of styrene in the presence of a difunctional CTA. Simulations were performed on an IBM-compatible 1.6 GHz, 512MB RAM Pentium 4. The model was developed based on the method of moments,[13,14] and the evaluation of the stiffly coupled differential equations was carried out using MATLAB 7.1. The mechanism is given in Scheme 1, and the model was simplified from the complex addition−fragmentation to the degenerative chain transfer model. This was used as it is computationally faster to solve the differential equations and is accurate assuming that there are no side reactions (e.g., intermediate radical termination,[15] impurities,[16] etc.) in the RAFT-mediated polymerization. For the RAFT agent used in this study there are no observations of retardation or inhibition in rate. Therefore, simulations based on degenerative chain transfer will provide an excellent agreement with the RAFT-based model. This has been tested for a monofunctional RAFT agent and there is no difference, when retardation or inhibition are absent, between using the RAFT and degenerative chain transfer models. The parameters used in the model exclude poor leaving group reactions. A more detailed description of the modeling using a difunctional CTA is given in ref 17.

Simulations were carried out for the polymerization of styrene in the presence of a difunctional CTA and solvent at 60 °C and initiated with varying amounts of 2,2-azobis(isobutyronitrile) (AIBN). Figure 1A shows that the rate of polymerization increased with the increased ratio of initiator to CTA from 1:1 to 1:10. The polymerization stopped after 4×10^5 s due to the consumption of AIBN. The number-average molecular weight (M_n) increased relatively linear with conversion for all three experiments, suggesting that even at high amounts of AIBN there is little effect on the number of polymer chains produced (Figure 1B). The simulations showed that the polydispersity index (PDI) increased from approximately 1.2 at 10% conversion to 1.7 at 75% at the highest AIBN ratio (curve a; Figure 1C). A decrease in the ratio of AIBN to CTA resulted in a lowering of the PDI from 1.3 (ratio of 1:2.5) to below 1.1 (at a ratio of 1:10). This shows that in principle we can control the MWD with the use of a single difunctional RAFT agent. The simulations also show (Figure 1D) that by using a difunctional CTA, the amount of dead polymer is extremely low in comparison to when a monofunctional CTA is used. The amount of dead polymer at a [AIBN] to [CTA] ratio of 1:1 is only 3%, and decreased to 8×10^{-3} % at a ratio of 1:10, which is well below any analytical detection technique. It should be noted that there is still a high amount of radical−radical termination primarily through the most abundant radicals, $XP^\bullet$, which are approximately 2 orders of magnitude greater than $P^\bullet$. Therefore, although the termination rate is high the major products formed through this process are XPX (the sum of XP_nX from $n = 1$ to ∞) and XP (the sum of XP_n from $n = 1$ to ∞). The ratio of XPX to XP allows us to control the amount of monofunctional and difunctional polymer chain end groups, and as will be discussed in detail in a future publication provides a unique method to control the MWD through oxidation of the thiol end groups. This ratio can be controlled by the ratio of AIBN used

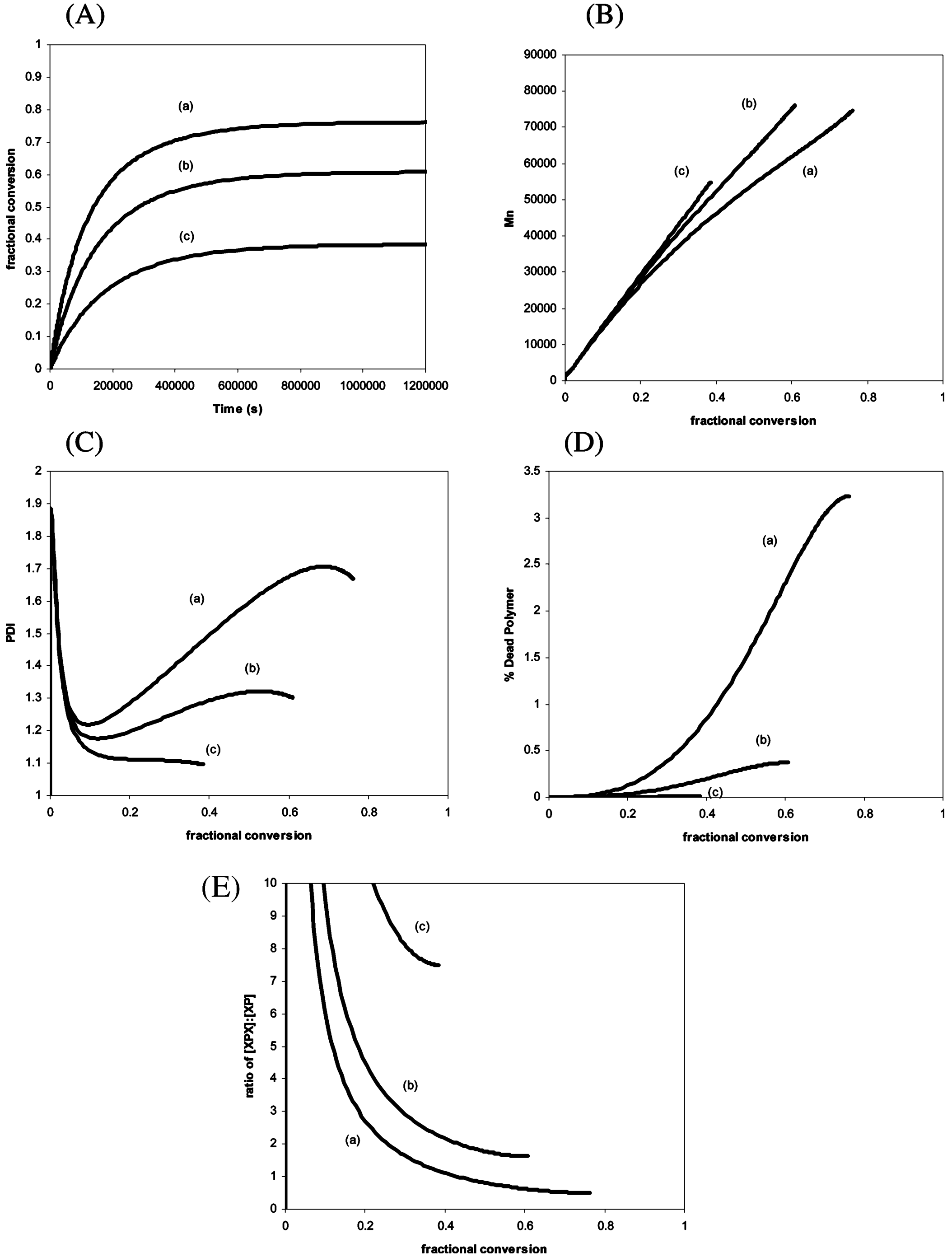


Figure 1. Simulations used to examine the effect of initiator concentration on the reaction rate and MWD's of styrene at $[M]_0:[XRX]_0 = 5.56/3.83 \times 10^{-3}$: (A) conversion vs time, (B) M_n vs conversion, (C) PDI vs conversion, (D) dead polymer vs conversion, and (E) ratio of di- to monofunctional S═C(Z)S− end groups. The $[I]_0:[XRX]_0$ ratios are given in parentheses, for curves a (1:1), b (1:2.5), and c (1:10). Kinetic parameters used in the simulation were $k_p = 340$ L mol^{-1} s^{-1}, $k_d = 9.443 \times 10^{-6}$ s^{-1}, and $k_t = 1 \times 10^8$ L mol^{-1} s^{-1}.

in the polymerization, and can be easily quantified using eq 4.

$$[XPX] = [XRX]_0 - \frac{1}{2}[PX] \tag{1}$$

$$\frac{[PX]}{[PX] + [XPX]} = \frac{[PX]}{[XRX]_0 + \frac{1}{2}[PX]} \tag{2}$$

$$[PX] = 2f([I]_0 - [I]_t) \tag{3}$$

$$\frac{[PX]}{[PX] + [XPX]} = \left(\frac{1}{2} + \frac{[XRX]_0}{2f([I]_0 - [I]_t)}\right)^{-1} \tag{4}$$

where t is time of reaction in seconds, $[I]_0$ is initial initiator concentration, $[I]_t$ is initiator concentration at *t*, and *f* is the initiator efficiency. Equation 4 shows that the ratio is controlled by the amount of AIBN decomposed. Obviously, should the monomer have a very high propagation rate constant, k_p, then the influence of AIBN decomposition on the MWD will be much smaller. Another method to increase the relative amount of PX would be to used a faster decomposing initiator.

Equation 4 is derived by the mass balance of eq 2, and incorporating this into eq 3 (which provides the ratio of PX to XPX). The amount of PX is equal to the formation of radical that propagate to form polymer and is given by eq 3. Substituting eqs 1 and 3 into 2 gives eq 4, allowing prediction of the relative

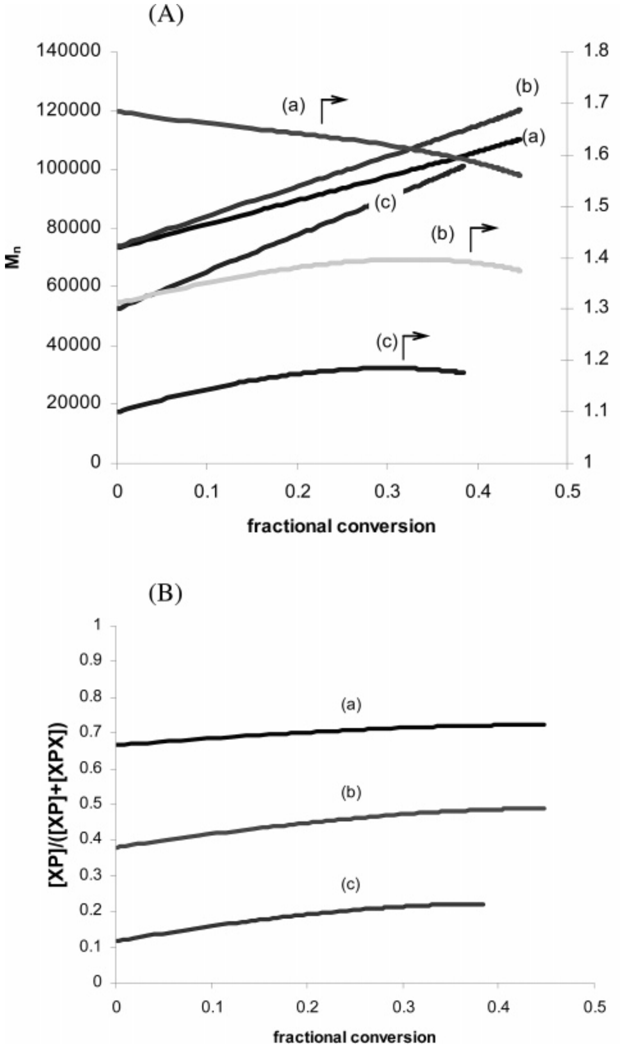
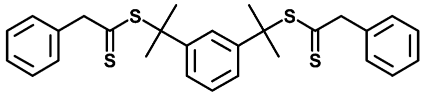


Figure 2. Simulations used to examine the effect of chain extension polymerization of styrene with premade polymer from Figure 1 after 160 h, initiated with 2,2-azobis(isobutyronitrile) (AIBN; 10:1 [AIBN]:{[XP] + [XPX]}) at 60 °C: (A) M_n and PDI vs conversion; (B) fraction of XP vs conversion. The chain extecsion polymerizations were carried out using the following starting polymers: curve a, $M_n = 73\,195$ and PDI = 1.69; curve b, $M_n = 73\,712$ and PDI = 1.31; curve c, $M_n = 52\,546$ and PDI = 1.10. Kinetic parameters used in the simulation were $k_p = 340$ L mol^{-1} s^{-1}, $k_d = 9.443 \times 10^{-6}$ s^{-1}, and $k_t = 1 \times 10^8$ L mol^{-1} s^{-1}.

proportions of [PX] and [XPX] for difunctional RAFT agents with a high transfer constants ($C_{tr} > 100$), and is proportional to the amount of initiator decomposed in the reaction. The validity of these equations is based on the criterion that termination events between XP. and P. are small. At early times this is the case, but the equation shows a slight overestimation of the true value of [PX] (<10% at the highest AIBN concentration) at very long reaction times. The ratio of XPX to XP in Figure 1E can be fit using eq 4.

As the majority of chains (>97%) consist of XPX or XP, the MWD can be translated to higher molecular weights through chain extension polymerizations by maintaining the initiator concentration much lower than the sum of XPX and XP concentrations (at a ratio of 1:10; [AIBN]:[XPX + XP]). Simulations were carried out on the chain extension polymerizations with styrene of the polymers (from Figure 1 after 160 h) initiated with AIBN in solvent at 60 °C. Figure 2 shows the simulations that are stopped after 160 h. The chain extension for the three starting polymers all show that the M_n increased linearly up to a conversion of 40% (a time where all the AIBN is consumed) as shown in Figure 2A. The PDI increased from 1.1 to 1.2 for the polymer with the narrowest MWD, and decreased from 1.7 to 1.55 for the starting polymer with broadest MWD. These simulations show that the MWD can be translated easily to a higher molecular weight even for the slow propagating styrene monomer. Should these polymers be extended with a fast propagating monomer the PDI should remain relatively constant (data no shown). Figure 2B shows that the fraction of XP increased slightly with conversion, demonstrating that the concentration of end group functionality was maintained as compared to the starting polymer.



1,3-bis-(2-(thiobenzylthio)prop-2-yl)benzene (BTBTPB)

Figure 3. Chemical structure of the difunctional CTA used in this work.

The aim of this work is to determine whether experimental data fits with simulation to show that a single difunctional RAFT agent can be used to obtain a desired M_n and PDI. Additionally, does this facile method for controlling the MWD also translate to control of the amount of chain-end S═C(Z)S functionality (i.e., ratio of mono- to difunctionality). The simulations in Figure 1E showed that the amount of monofunctionality increased with the ratio of AIBN. The ratio of dormant species XP to XPX is important as these dithoester end groups can easily be converted to thiols through a mild aminolysis. The oxidation of these polymers will also provide a unique method to control the MWD,[12,18] and more importantly can be reduced back to the starting polymer, that is a polymer system that can be recycled. This will be discussed in more detail in a future publication.

Polymerizations of Difunctional CTA with Styrene. The choice of CTA was based on the ability of the Z group on the difunctional CTA to eliminate or reduce the kinetic effects of inhibition and retardation,[19] which is primarily found when Z is a phenyl group. On the basis of these considerations, we synthesized the CTA shown in Figure 3, where Z is CH_2Ph.

The first set of styrene polymerizations were carried out in toluene at 60 °C using a CTA concentration of 2.5×10^{-2} M, and varying the concentration of AIBN from 2.5×10^{-3} to 2.5×10^{-1} M (experiments 1−4). The conversion data shows that at the lowest concentration of AIBN (experiment 1, Table 1) conversion reached only 16%. An increased amount of AIBN resulted in a faster rate of polymerization, which is as expected. The effect of the AIBN concentration on M_n as a function of conversion can be determined analytically using eq 5.[6]

$$M_n = \frac{[M]_o x}{[XRX] + af([I]_0 - [I]_x)}\mathrm{mw} \qquad (5)$$

where $[M]_0$ is the initial monomer concentration, x is the fractional monomer conversion to polymer, [XRX] is the initial difunctional RAFT agent concentration, a is the mode of termination (a equals 1 for termination by combination), $[I]_0$ is initial initiator concentration, $[I]_x$ is initiator concentration at x, mw is the molecular weight of the monomer unit, and f is the initiator efficiency. This equation is useful as it takes into account the higher AIBN concentrations used in the experiments, and is based on the assumption that the XRX is consumed within the first few percent conversion.

It can be seen that as the initiator concentration is increased, the M_n curves away from linearity. This is due to the greater

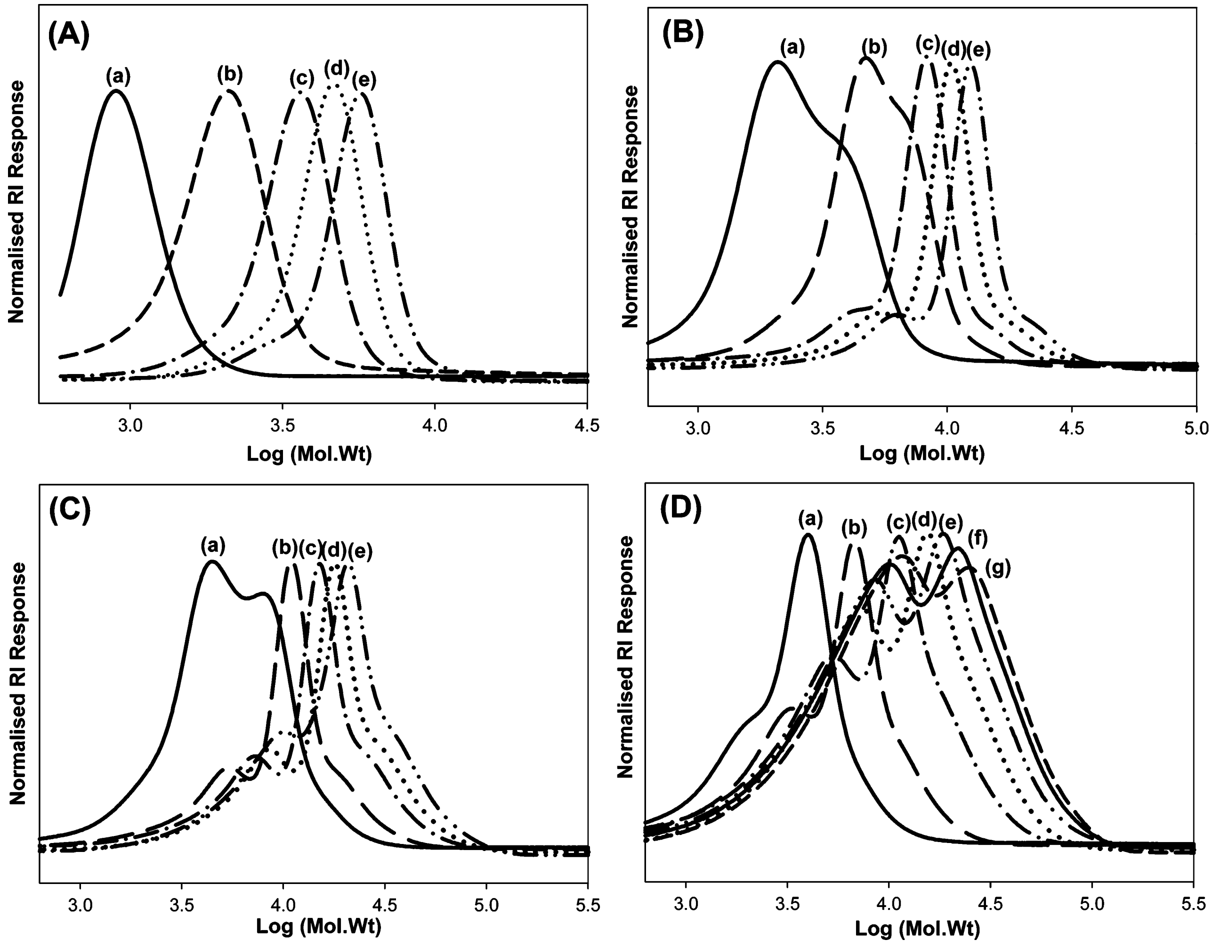


Figure 4. Size exclusion chromatograms for the RAFT-mediated polymerization of styrene in toluene using BTBTPB at 60 °C over a wide conversion range. (A) 2.52×10^{-2} M BTBTPB and 2.49×10^{-2} M AIBN (experiment 1, Table 1); (B) 2.50×10^{-2} M BTBTPB and 1.26×10^{-2} M AIBN (experiment 2, Table 1); (C) 2.51×10^{-2} M BTBTPB and 5.02×10^{-2} M AIBN (experiment 3, Table 1); (D) 2.49×10^{-2} M BTBTPB and 2.49×10^{-1} M AIBN (experiment 4, Table 1).

number of chains formed from AIBN. It seems that the theoretical values, in general, are lower than that found experimentally, especially at higher conversions. We believe this discrepancy is due to the limitations of the SEC to quantitatively describe the MWD below molecular weights of 5000 for our SEC system. At higher molecular weights the agreement between eq 1 and experiment is excellent (see M_n data for experiments 5−7), and as such it is more probable that the M_n (theory) value is a more accurate value to use in our case below 5000. It is clearly shown that as the concentration of AIBN is increased, the PDI also increased with conversion for these experiments. At the highest AIBN concentration (experiment 4), the PDI increased from 1.34 (at 13% conversion, experiment 4a) to 2.25 at 75% conversion (experiment 4g). At the lowest AIBN concentration (experiment 1), the PDI was found to be 1.07 at 3% conversion and increased slightly to 1.15 at 16% conversion. These data show that a wide range of MWDs are achievable at molecular weights below 10000 by using a single difunctional CTA.

To gain a better appreciation of the change in the MWD as a function of conversion for experiments 1 to 4, the SEC chromatograms are given in Figure 4. At the lowest AIBN concentration (experiment 1) the MWD shifts to higher molecular weights as a function of conversion, suggesting that most polymers consist of α,ω-dithioester telechelic polymer chains (i.e., polymer chains with a RAFT moiety on either end). At a greater starting AIBN concentration a bimodal distribution starts to appear (Figure 4B, curve a, experiment 2a) in which the lower molecular weight peak has a greater intensity than the higher molecular weight peak. After 16% conversion (experiment 2e) this was reversed, where the low molecular weight peak has much smaller intensity than the high molecular weight peak. The chromatograms at the highest conversions for each experiment (experiments 2e, 3e, and 4g, the order of increasing AIBN concentration) showed that this first low molecular weight peak increased with the increased starting AIBN concentration, and is consistent with polymeric species with only one RAFT moiety attached to the chain end (XP), and the second higher molecular weight peak is associated with the difunctional dormant polymer (XPX). Simulations confirm that the monofunctional dormant chains have a lower M_n than the difunctional chains. The reason for this is that the difunctional dormant chains have a C_{tr} that is twice that of a monofunctional dormant chain, and monomer thus incorporates twice as fast to the difunctional than to the monofunctional dormant chains.

Further experiments were carried out to determine the effect of this methodology at higher molecular weights between 15000 and 45000 (experiments 5−7 in Table 1), in which the CTA concentration was kept close to 3.8×10^{-3} M. It can be seen that as the AIBN concentration is increased the rate of polymerization is also increased. As stated above the M_n experimental values are very close to that of theory. The PDI values also show the trend that as the AIBN concentration is increased the PDI increased with conversion. The SEC chromatograms (Figure 5) also showed that at a ratio of [CTA]:[AIBN] greater than 10:1 a biomodal distribution appeared,

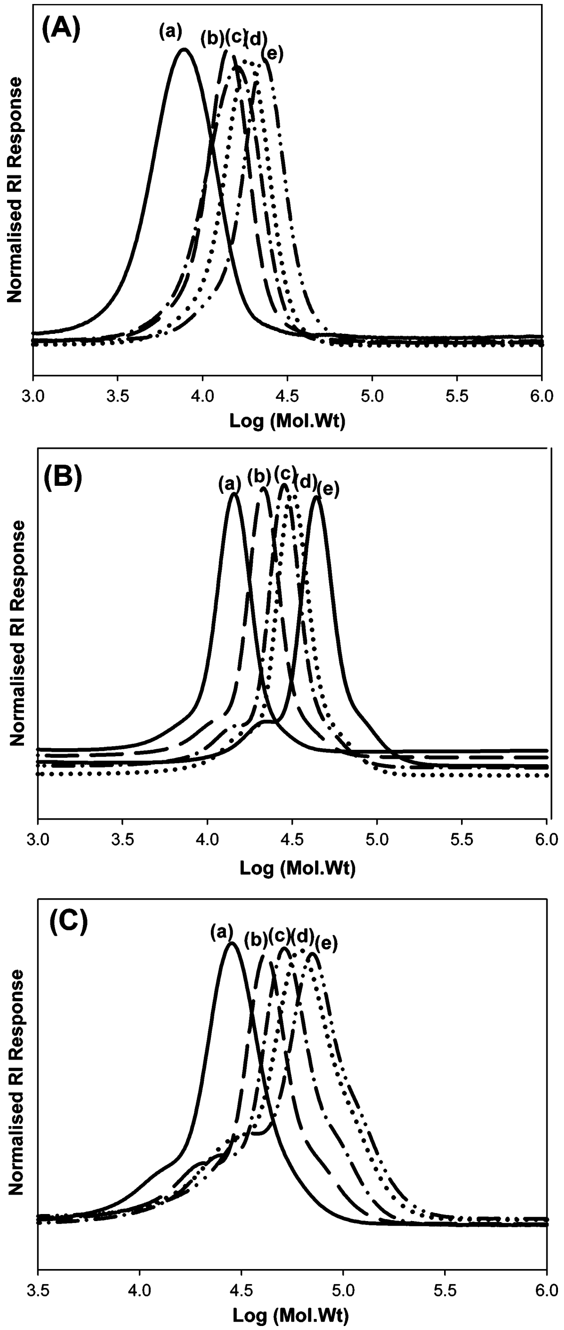


Figure 5. Size exclusion chromatograms for the RAFT-mediated polymerization of STY in toluene using the CTA, BTBTPB, at 60 °C over a wide conversion range. (A) 3.85×10^{-3} M TPTPB and 4.02×10^{-4} M AIBN (experiment 5, Table 1), (B) 3.81×10^{-3} M BTPTPB and 1.54×10^{-3} M AIBN (experiment 6, Table 1), and (C) 3.83×10^{-3} M BTPTPB and 3.51×10^{-3} M AIBN (experiment 7, Table 1).

supporting the conclusion that the first peak is monofunctional and the second peak the difunctional dormant polymer.

The interesting part of this work is that the molecular weight can be controlled by increasing the AIBN concentration, but more particular, the rate to form a broad and well-defined MWD can be greatly accelerated by this technique (experiments 4 and 7). For example, the use of monofunctional xanthates to give a PDI of 2 for polystyrene would take a similar time as for the CTA used in this work to give a PDI of 1 (experiments 1 and 4) due to the low concentration of AIBN required to minimize the amount of dead polymer.

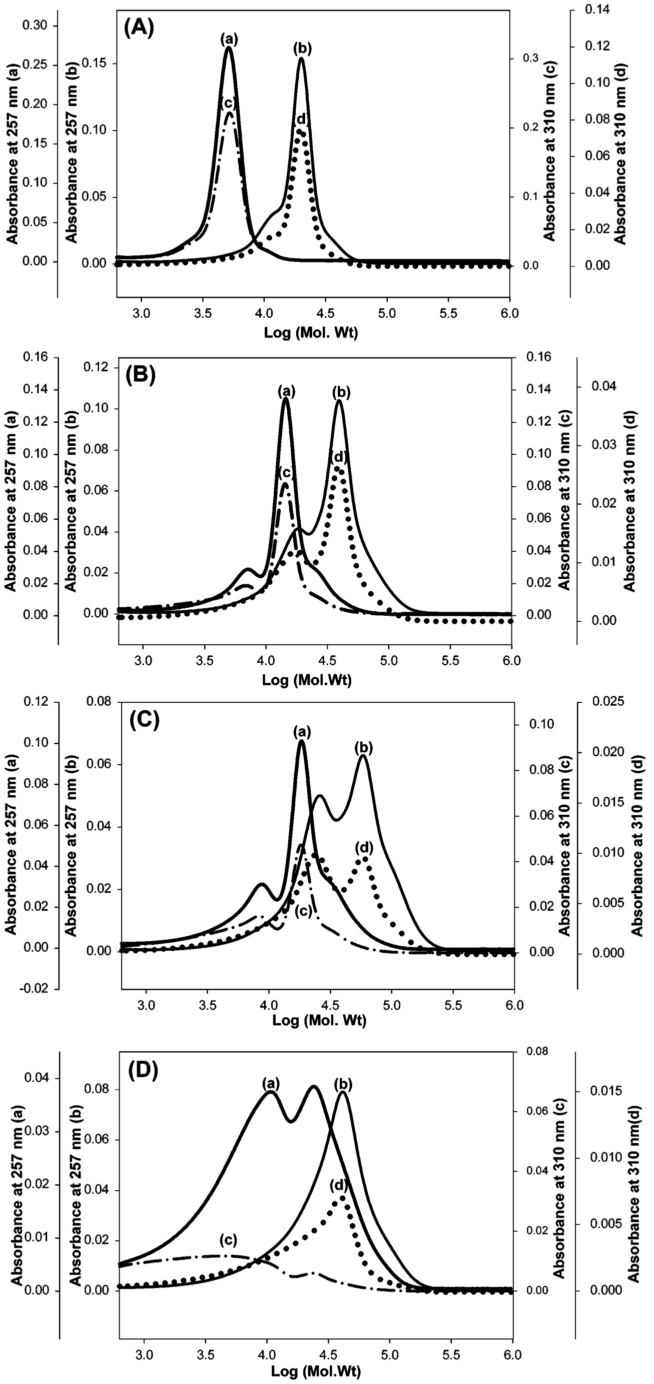


Figure 6. Size exclusion chromatograms of polystyrene prepared from the chain extension polymerization of starting polymers made from varying ratios of AIBN: BTBTPB (experiments 1−4, Table 1) with styrene and initiated with AIBN at 60 °C. Dual UV detection was carried out to determine the molecular weight distributions with attached $S{=}C(CH_2Ph)S$ groups (310 nm) and phenyl groups (257 nm). Starting polymers: (A) $M_n = 4015$, PDI = 1.18, (B) $M_n = 10686$, PDI = 1.39, (C) $M_n = 10518$, PDI = 1.78, and (D) $M_n = 8452$, PDI = 2.25. Curves: (a) chromatogram of starting polymer at 257 nm, (b) chromatogram of polystyrene after chain extension measured at 257 nm, (c) chromatogram of starting polymer at 310 nm, and (d) chromatogram of polystyrene after chain extension at 310 nm.

The simulations showed that the amount of dead polymer was below 3% for the difunctional CTA used in this work. To test this and to determine whether most the chains had attached at least one RAFT moiety we carried out chain extension polymerization of the dormant species from experiments 1e, 2e, 3e, 4g, 5f, 6f, and 7f with styrene (Table 2). It should be noted that a new batch of polymer was made and as such the M_n and PDI values (in parentheses, Table 2) of the starting

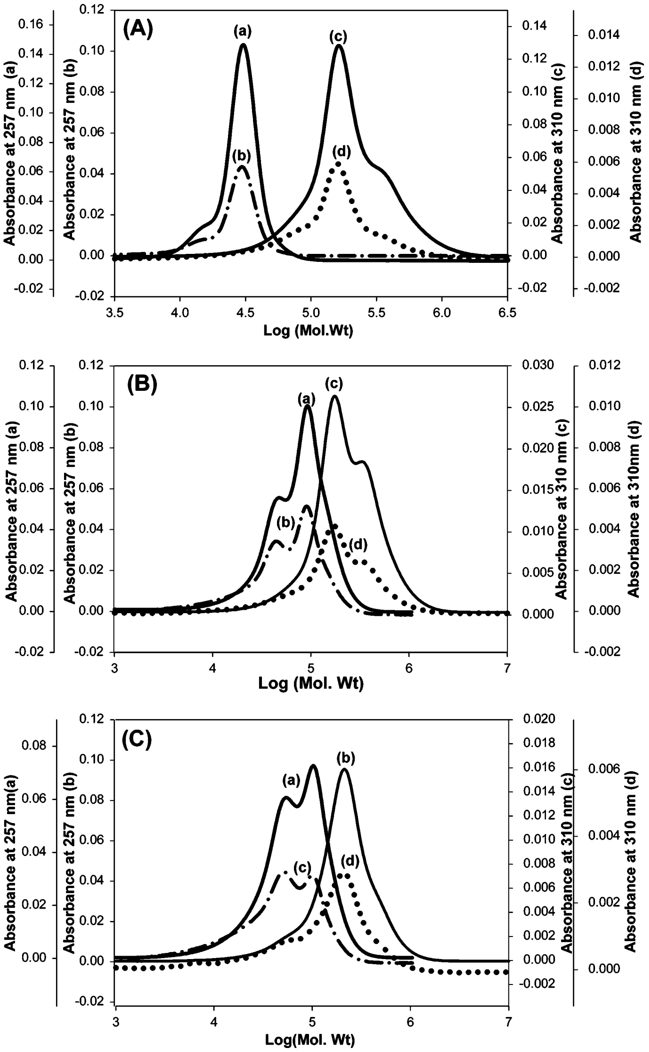


Figure 7. Size exclusion chromatograms of polystyrene prepared from the chain extension polymerization of starting polymers made from varying ratios of AIBN: BTBTPB (Expts 5−7, Table 1) with styrene and initiated with AIBN at 60 °C. A duel UV detection was carried out to determine the molecular weight distributions with attached S=C(CH$_2$Ph)S groups (310 nm) and phenyl groups (257 nm). Starting polymers: (A) M_n = 23336, PDI = 1.17, (B) M_n = 35152, PDI = 1.28, and (C) M_n = 43332, PDI = 1.60. Curves: (a) chromatogram of starting polymer at 257 nm, (b) chromatogram of polystyrene after chain extension measured at 257 nm, (c) chromatogram of starting polymer at 310 nm, and (d) chromatogram of polystyrene after chain extension at 310 nm.

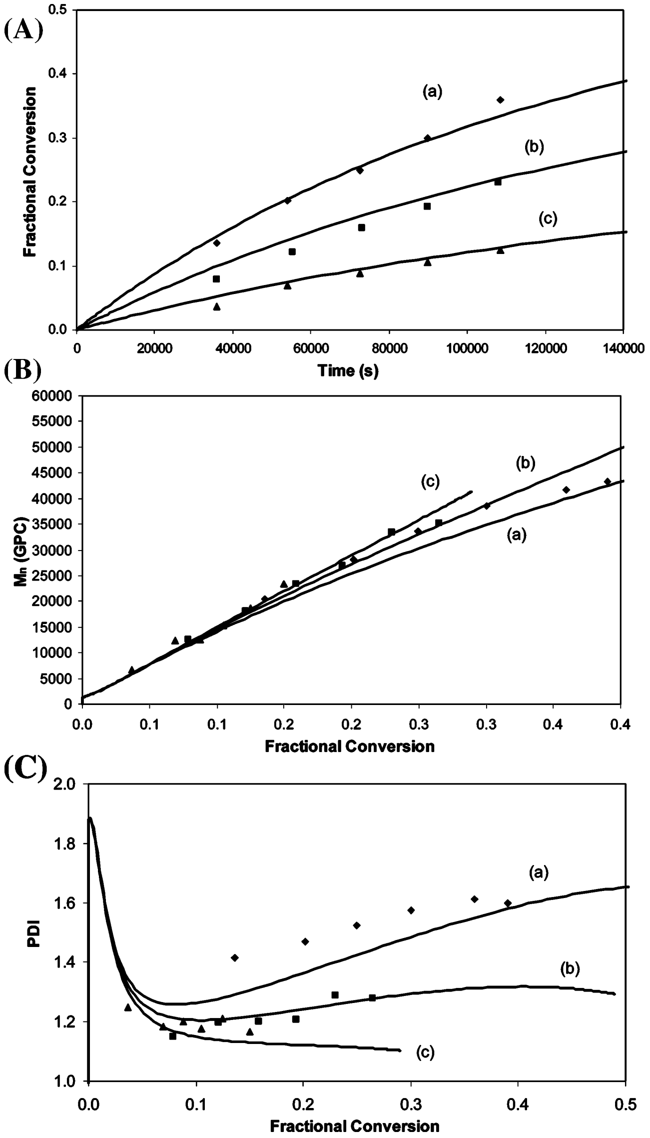


Figure 8. Comparison between simulation and experimental data for the RAFT-mediated polymerization of STY in toluene using the CTA, BTBTPB, at 60 °C. Key: (A) conversion vs time, (B) M_n vs conversion, and (C) PDI vs conversion. Lines represent simulated data and points represent experimental data points. The [AIBN]:[CTA] ratios for curves (a) 1:1, (b) 1:2.5, and (c) 1:10. Kinetic parameters used in the simulation were: k_p = 340 L mol^{-1} s^{-1}, k_d = 9.443 × 10^{-6} s^{-1}, and k_t = 2 × 10^8 L mol^{-1} s^{-1}.

dormant chains are in some cases slightly different to the values given in Table 1. It can be seen that the M_n values increased from their starting values, consistent with chain extension. In addition, there is a reasonable agreement between M_n theory and experiment. Figure 6 shows the SEC chromatograms of starting polymer and after chain extension (experiments 8 to 11 in Figure 6A−D, respectively). Curves a and c represent the starting polymer at 257 and 310 nm, respectively, in which the wavelength at 257 corresponds to chains with phenyl groups attached and the wavelength at 310 nm corresponds to chains that have an attached S=C(Z)S moiety. In Figure 6A, the starting material has nearly all chains with a RAFT moiety, and after chain extension (curves b and d) the starting MWD is shifted to a higher molecular weight while still retaining a very high percentage of S=C(Z)S end groups. Parts B and C of Figure 6 show that the starting polymer made at higher AIBN concentrations the starting bimodal distribution is translated to a higher molecular weight without loss of end group functionality. Even for starting polymer made from extreme levels of AIBN ([CTA]:[AIBN] = 1:10, Figure 6D), the functionality is retained after chain extension. Figure 7 shows the SEC chromatograms for the chain extension reactions using higher molecular weight starting polymer. The trend is similar as found in the low molecular weight starting polymer experiments, where there is a translation of the full molecular weight distribution to a higher molecular weight again with little loss of chain end functionality. These results show that once a polymer distribution is formed via the difunctional CTA, it can be translated to a higher molecular weight through a chain extension. This also opens the possibility to form block copolymers with varying amounts of AB and BAB in each system, and would allow variation and control of the mechanical properties.

Comparison with Simulations. An important aspect is not only to control but also to be able to predict the rate of polymerization and MWD. The fit of experimental with that of simulated results for conversion vs time, M_n vs conversion and

PDI vs conversion are given in Figure 8. The agreement between simulation and experiment for conversion vs time is excellent for the three different concentrations of AIBN, using a k_t value of 2×10^8 L mol^{-1} s^{-1} (see Figure 8A). The real test of the model is being able to fit both M_n and PDI as a function of conversion. Parts B and C of Figure 8 showed the fit of simulation to experimental data is again excellent for M_n and PDI profiles, respectively. This showed through a simple computer simulation model, accurate predictions of the MWD evolution and rate can be obtained. It also supports that our novel methodology allows with a single RAFT difunctional agent the wide range of MWDs to be prepared with control of the end group functionality.

Conclusion

This work has demonstrated that for the first time a single RAFT agent (i.e., difunctional) can be used to obtain a desired M_n and PDI with controlled rates of polymerization. Simulations were used not only to verify the model, but to provide us with a simple predictive tool to generate other MWDs. It was also shown that all the MWDs prepared in this work could be translated to higher molecular weights through chain extension experiments with little or no compromise in the control of end group functionality. The ratio of end groups, XPX and XP, can be controlled by simply changing the concentration of AIBN. This ratio is important as these dithoester end groups can easily be converted to thiols through a mild aminolysis. The oxidation of these polymers will also provide a unique method to control the MWD,[12,18] and more importantly can be reduced back to the starting polymer. This will be discussed in more detail in a future publication. The other main attribute of this methodology is that at ratios of AIBN to RAFT concentrations studied here the amount of dead polymer is well below any analytical detection limit, which is close to what Szwarc suggested as ideal living polymerization.[20]

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