Synthesis and Evaluation of New Dicarboxylic Acid Functional Trithiocarbonates: RAFT Synthesis of Telechelic Poly(*n*-butyl acrylate)s

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ABSTRACT: We report herein the synthesis of three new diacid functional trithiocarbonates (TTCs) in which the substitution pattern about the TTC functionality is varied and compare their effectiveness alongside examples of previously reported trithiocarbonates as mediating agents in the RAFT polymerization of *n*-butyl acrylate. For direct comparative purposes we show that at an initial TTC concentration: initial AIBN concentration ($[TTC]_0$:$[AIBN]_0$) of 20 2-(2-carboxyethylsulfanylthiocarbonylsulfanyl)propionic acid (**TTC5)** and 2-(2-carboxyethylsulfanylthiocarbonylsulfanyl)-2-methylpropionic acid (**TTC6**) perform as well as 3-benzylsulfanylthiocarbonylsulfanylpropionic acid (**TTC3**) with respect to kinetics and molecular weight control. In contrast, 2-(1-carboxy-1-methylethylsulfanylthiocarbonylsulfanyl)-2-methylpropionic acid (**TTC1**)-mediated homopolymerization deviates from "ideal" behavior due, we speculate, to steric crowding of the central TTC core. Additionally, 3-(2-carboxyethylsulfanylthiocarbonylsulfanyl)-propionic acid (**TTC4**) fails to confer any control on the homopolymerization of nBA with the polymerization exhibiting complex characteristics, as evidenced in the resulting molecular weight distribution, which may be indicative of hybrid behavior. Subsequently, we examine the effect of $[TTC]_0$:$[AIBN]_0$ for **TTC5** and **TTC6** and show that lower ratios result in faster polymerizations, consistent with previous reports. Finally, we demonstrate the ability to form block copolymers with high reinitiating efficiency. These new TTCs thus offer access to the direct synthesis of AB diblock dicarboxylic acid telechelic (co)polymers.

Introduction

The ability to synthesize functional (co)polymers in a controlled manner, i.e., with predetermined molecular weights, composition, and chain end functionality, has become increasingly important in recent years as the demand for materials in specialty applications grows. Fortunately, today the polymer chemist has many tools available to achieve these goals. Of particular note is the discovery and development of the controlled/living free radical polymerization techniques. For example, stable free radical polymerization (SFRP),[1] best exemplified by nitroxide-mediated systems (NMP),[2−5] atom transfer radical polymerization (ATRP),[6,7] reversible addition−fragmentation chain transfer (RAFT) polymerization,[8−11] tellurium-mediated radical polymerization (TERP),[12−15] and quinone transfer radical polymerization (QTRP),[16] are all versatile techniques for the preparation of well-defined polymers in a controlled fashion, although both TERP and QTRP have not yet been widely evaluated. Of these techniques, RAFT is arguably the most versatile, at least with respect to monomer choice. For example, monomers that have historically proven difficult to control via SFRP or ATRP can be readily polymerized in a controlled fashion via RAFT. Pertinent examples include the facile polymerization of both charged[17−20] and neutral[20−23] (meth)-acrylamido monomers as well as "problematic" species such as vinyl esters.[24]

The key to accomplishing successful RAFT polymerizations is appropriate choice of RAFT mediating agent, commonly referred to as the RAFT chain transfer agent (CTA) or, more simply, RAFT agent. An advantage of RAFT is the wide range of CTAs that can be readily prepared, thus facilitating the fine-tuning of a given polymerization system. Indeed, many research groups have, and continue to, report the preparation and evaluation of new RAFT agents. All RAFT agents are thiocarbonylthio compounds derived from dithioesters,[9,25] dithiocarbamates,[9,25−28] xanthates,[9,25] or trithiocarbonates.[9,25,29,30] While the acronym RAFT encompasses all systems in which the above thiocarbonylthio compounds are employed as mediating agents, the acronym MADIX (macromolecular design via the interchange of xanthate) is also used for those polymerizations that specifically employ xanthates. These thiocarbonylthio compounds differ only in the nature of the so-called Z and R groups. As a result of these structural differences, not all RAFT agents are effective mediators for all monomers. However, some general classes are more "universally" applicable than others. For example, the dithioesters are probably the most widely employed/versatile RAFT agents, whereas the xanthates do not typically work well for "common" monomer families but have, for example, proven to be particularly effective for the vinyl ester family including vinyl acetate[31] and the sugar derivative 6-*O*-vinyladipoyl-D-glucopyranose.[24] The trithiocarbonates (TTCs) represent one of the least studied of the RAFT agent family but have been attracting an increasing amount of attention recently. This is due, in part, to their ease of synthesis and purification. This is a distinct advantage when compared to the synthesis of many other RAFT agents. TTCs have proven to be especially useful for the controlled polymerization of styrenic, acrylate, and acrylamido monomer derivatives and in some instances under extremely facile conditions. For example, Lima and co-workers[32] recently reported the use of trithiocarbonate-based RAFT agents for the synthesis of a range of telechelic poly(*n*-butyl acrylate)s employing previously reported RAFT CTAs.

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As part of our continuing studies on RAFT polymerization, we have synthesized a series of new functional TTCs for the polymerization of functional acrylic monomers. We report herein the design and synthesis of three new dicarboxylic acid functional TTCs in which we have systematically varied the substitution about the TTC functionality. We have evaluated these new TTCs alongside previously reported literature examples in the polymerization of the model acrylic monomer *n*-butyl acrylate (nBA). We show that some of these species are indeed highly effective for this particular monomer, although, as expected, the overall degree of control is affected subtly by CTA structure, i.e., the nature of the Z and R groups.

Experimental Part

Reagents were purchased from Aldrich Chemical Co. at the highest possible purity and used as received unless stated otherwise. *n*-Butyl acrylate (nBA) was passed over a column of basic alumina to remove inhibitor and stored in a refrigerator at 0 °C until needed. 2,2′-Azobis(isobutyronitrile) was recrystallized from methanol and stored in a refrigerator prior to use. 2-(1-Carboxy-1-methylethylsulfanylthiocarbonylsulfanyl)-2-methylpropionic acid (**TTC1**) and 3-benzylsulfanylthiocarbonylsulfanylpropionic acid (**TTC3**) were prepared according to literature procedures.[33,34]

Synthesis of 3-(2-Carboxyethylsulfanylthiocarbonylsulfanyl)propionic Acid (**TTC4**). 3-Mercaptopropionic acid (10.6 g, 0.1 mol), distilled/deionized water (100 mL), and 50 wt % NaOH solution (16.0 g, 0.2 mol) were added to a 250 mL round-bottomed flask equipped with a magnetic stir bar. This mixture was stirred for 30 min prior to the dropwise addition of carbon disulfide (6.0 mL, 0.1 mol). The resulting yellow solution was stirred overnight. 3-Bromopropionic acid (15.3 g, 0.1 mol) was added dropwise to the yellow solution, and the mixture was stirred overnight. The reaction mixture was acidified by the addition of concentrated hydrochloric acid, and the resulting precipitate was collected using a Bucher funnel and flask. The product was washed with deionized water and then dried in vacuo overnight. Yield: ca. 90%. ^{1}H NMR (d_6-DMSO) δ (ppm): 2.65 (t, −C**H**$_2$−COOH), 3.51 (t, −S−C**H**$_2$), 12.5 (s, −COO**H**). ^{13}C NMR (d_6-DMSO) δ (ppm): 32.3 (−**C**H$_2$−COOH), 33.0 (−S−**C**H$_2$−), 173.0 (**C**=O), 224.9 (**C**=S). CHSO elemental microanalysis. Theoretical: C, 33.06%; H, 3.96%; O, 25.16%; S, 37.82%. Found: C, 33.16%; H, 3.67%; O, 25.68%; S, 37.49%. Mp: 110.2 °C.

Synthesis of 2-(2-Carboxyethylsulfanylthiocarbonylsulfanyl)propionic Acid (**TTC5**). The target compound was prepared in the same manner as **TTC4**, except 2-bromopropionic acid was used in place of 3-bromopropionic acid. Yield: ca. 90%. ^{1}H NMR (d_6-DMSO) δ (ppm): 1.55 (d, C**H**$_3$−CH), 2.74 (t, −C**H**$_2$−COOH), 3.59 (t, −C**H**$_2$−S−), 4.77 (quar, −S−C**H**−CH$_3$(COOH)). ^{13}C NMR (d_6-DMSO) δ (ppm): 17.4 (**C**H$_3$−CH), 32.5 (**C**H$_2$−COOH), 32.9 (-**C**H$_2$−S−), 48.9 (−**C**H−COOH), 172.2 (**C**OOH−CH−), 173.1 (**C**OOH−CH$_2$−), 222.9 (**C**=S). CHSO elemental microanalysis. Theoretical: C, 33.06%; H, 3.96%; O, 25.16%; S, 37.82%. Found: C, 33.18%; H, 3.75%; O, 25.72%; S, 37.35%. Mp: 126.0 °C.

Synthesis of 2-(2-Carboxyethylsulfanylthiocarbonylsulfanyl)-2-methylpropionic Acid (**TTC6**). 3-Mercaptopropionic acid (10.6 g, 0.1 mol), distilled/deionized water (100 mL), and 50 wt % NaOH solution (16.0 g, 0.2 mol) were added to a round-bottom flask equipped with a magnetic stir bar. The solution was stirred for 30 min prior to the dropwise addition of carbon disulfide (6.0 mL, 0.1 mol). The resulting yellow solution was stirred at room temperature overnight. Chloroform (29.9 g, 0.25 mol) and acetone (16.8 g, 0.3 mol) were then added followed by the dropwise addition of 50 wt % NaOH solution (60.0 g, 0.75 mol). Also, a small "pinch" of tetrabutylammonium hydrogen sulfate (TBAHS) was added to aid in phase transfer. The mixture was stirred at room temperature overnight. The mixture was acidified with concentrated hydrochloric acid, and the resulting precipitate was isolated by filtration with a Buchner funnel and flask. The precipitated was washed with distilled/deionized water. The product was then dried in vacuo overnight. TTC6 was subsequently recrystallized from acetone. Yield: ca. 40%. ^{1}H NMR (d_6-DMSO) δ (ppm): 1.59 (s, C(C**H**$_3$)$_2$), 2.62 (t, −C**H**$_2$−COOH), 3.43 (t, −C**H**$_2$−S), 12.7 (s, −COO**H**). ^{13}C NMR (d_6-DMSO) δ (ppm): 25.5 (−C(**C**H$_3$)$_2$, 32.0 (−**C**H$_2$−S), 35.0 (COOH−**C**H$_2$−), 57.1 (−S−**C**(CH$_3$)$_2$COOH), 173.0 (**C**=O), 173.6 (**C**=O), 222.1 (**C**=S). CHSO elemental microanalysis. Theoretical: C, 35.80%; H, 4.51%; O, 23.85%; S, 35.84%. Found: C, 36.52%; H, 4.54%; O, 25.82%; S, 33.12%. Mp: 179.5 °C.

Homopolymerization of *n*-Butyl Acrylate under Bulk Conditions. Below is a typical procedure for the homopolymerization of *n*-butyl acrylate under bulk conditions at 70 °C employing **TTC5** as the RAFT agent:

n-Butyl acrylate (12.8 g, 0.1 mol), **TTC5** (108 mg, 0.427 mmol), and AIBN (∼4.0 mg, 2.1 × 10^{-2} mmol) were added to a 50 mL round-bottom flask equipped with a magnetic stir bar. The mixture was stirred for at least 30 min to ensure complete dissolution of **TTC5** and AIBN in the monomer. Aliquots (2.0 mL) were transferred to 10 different vials (10.0 mL capacity), which were then sealed with rubber septa. Each vial was purged with nitrogen for 15 min. The vials were then immersed in a preheated oil bath at 70 °C. Vials were removed at various time intervals, and polymerization was halted by immediate exposure to air and cooling with liquid nitrogen. The samples were analyzed using a combination of size exclusion chromatography (SEC) and NMR spectroscopy.

Block Copolymerization. Below is a typical procedure for the block copolymerization of *n*BA under bulk conditions at 70 °C employing a poly(*n*-butyl acrylate) macro-CTA derived from **TTC5**:

n-Butyl acrylate (6.4 g, 0.05 mol), macro-CTA (1.85 g, 7.12 × 10^{-2} mmol), and AIBN (∼1.0 mg) were added to a 50.0 mL round-bottomed flask equipped with a magnetic stir bar. The mixture was purged with dry N_2 for ∼20 min prior to being immersed in a preheated oil bath at 70 °C. The copolymerization was allowed to proceed for ∼1 h prior to being terminated by exposure to air and quenching in liquid nitrogen.

Analysis Tools. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker 300 53 mm spectrometer in either deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (d_6-DMSO). CHOS elemental microanalyses were performed by Quantitative Technologies Inc. Polymer molecular weights, molecular weight distributions, and polydispersity indices were determined by SEC in *N,N*-dimethylformamide (DMF)/NEt_3 at a flow rate of 1.0 mL min^{-1} and 40 °C. The SEC system was comprised of a Waters 515 HPLC pump, a Waters 2410 RI detector, a column oven, and a PolymerLabs PLgel 5 μm MIXED-C 300 × 7.5 mm column (linear molecular weight range: 200−2 000 000 g/mol). The column was calibrated with a series of narrow molecular weight distribution poly(methyl methacrylate) standards (PolymerLabs). Data were analyzed with the Waters Empower software package.

Results and Discussion

Trithiocarbonates (TTCs) are a family of compounds that are effective mediating agents for the controlled RAFT polymerization of certain monomer classes. In particular, TTCs are especially applicable to the controlled polymerization of styrenic, acrylic, and acrylamido derivatives.[25,30,33,35−37] Recently, for example, we have been examining TTCs as RAFT agents for the controlled polymerization of acrylamide,[23] *N*-isopropylacrylamide,[22] and other structurally similar monomers. As part of our continuing studies, we decided to extend our monomer pool and examine the RAFT polymerization of commercially important functional acrylic species. Several efficient TTCs, such as **TTC1**−**TTC3** (Figure 1), have been reported in the literature.[33,36] However, to date there are no reports of the systematic evaluation of TTCs in which the nature of the substit-

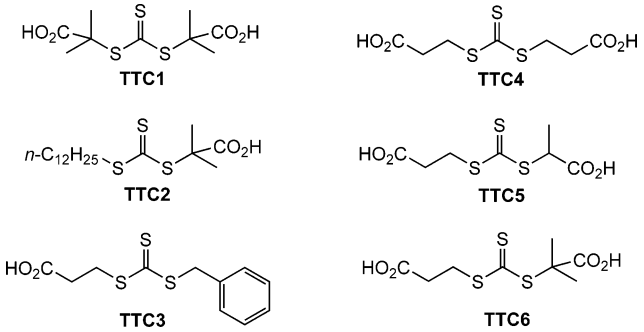
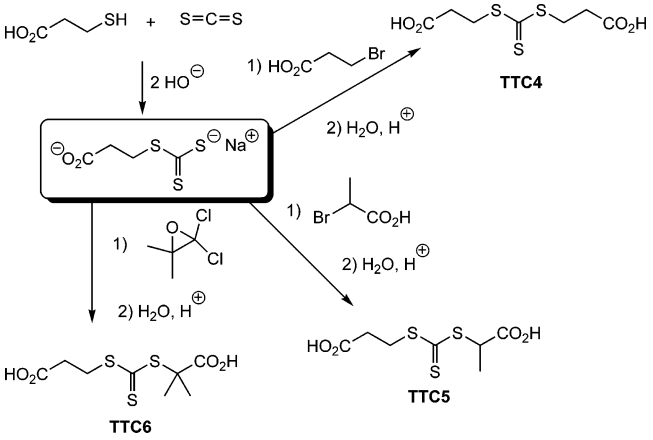


Figure 1. Chemical structures of the trithiocarbonates evaluated for the RAFT polymerization of *n*-butyl acrylate.

uents (Z and R groups) is varied. In these preliminary studies we designed and synthesized three new TTCs, namely **TTC4**, **TTC5**, and **TTC6** (Figure 1), and compared them to the previously reported species **TTC1** and **TTC3**. This was motivated by the desire to (i) conduct a fundamental study examining the systematic change in trithiocarbonate R-group structure, i.e., primary vs secondary vs tertiary alkyl species, (ii) to prepare novel dicarboxylic acid functional TTCs capable of yielding α,ω-functional polymers, and (iii) to prepare novel water-soluble RAFT agents (although this initial screening describes their effectiveness in polymerizations of a model hydrophobic acrylic monomer under bulk conditions).

Design Rationale. While **TTC1** and **TCC3** have proven to be effective RAFT agents, there are some drawbacks to each of these species, at least with respect to the research aims as outlined above. **TTC1**, while readily water-soluble, is symmetrically substituted about the TTC core (i.e., the Z and R groups are identical) and therefore acts as a difunctional RAFT agent with chain propagation occurring in both directions from the central TTC functional group. As such, it offers a very convenient route to ABA triblock copolymers but is of limited use for the preparation of AB diblock copolymers unless one cleaves the trithiocarbonate functionality postpolymerization, i.e., includes an additional synthetic step. **TTC3** was designed to facilitate chain growth in only one direction. This is by virtue of the unsymmetrical nature of the substitution about the TTC core. In this instance we can consider the $CO_2HCH_2CH_2S-$ species as the Z group and the benzylic functionality as the R group. Fragmentation of **TTC3** is clearly favored in the direction that yields the more stable benzylic radical. While **TTC3** is an effective RAFT agent[34,36] and is further highlighted here (vide infra), it does suffer from reduced aqueous solubility by virtue of the hydrophobic benzylic fragment. Additionally, it does not yield α,ω-dicarboxylic acid functional materials. These apparent "drawbacks" for **TTC1** and **TTC3** do not make these ineffective RAFT agents; on the contrary, they merely do not meet the design criteria of being highly water-soluble and capable of yielding dicarboxylic acid telechelic AB diblock copolymers directly. **TTC4**−**TTC6** were designed specifically to address the issue of preparing such telechelic materials while simultaneously evaluating the effect of the nature of the "R" group. In all instances the Z group can be considered to be the $CO_2HCH_2CH_2-S-$ species, while the R group is varied from a primary (**TTC4**) to a secondary (**TTC5**) to a tertiary (**TTC6**) functional group. Since one important factor determining the overall effectiveness of RAFT agents is the ease of fragmentation of the R group, we anticipate that, all other things being equal, the effectiveness of **TTC4**−**TTC6** should increase in the order **TTC4** < **TTC5** < **TTC6**.

Scheme 1. Synthetic Outline for the Preparation of TTC4, TTC5, and TTC6



Trithiocarbonate Synthesis. **TTC1** and **TTC3** were prepared according to literature procedures.[33,34] **TTC4**, **TTC5**, and **TTC6** were synthesized according to Scheme 1. Initially, the disodium salt of 3-dithiocarboxysulfanylpropionic acid was prepared from the reaction of the disodium salt of 3-mercaptopropionic acid with carbon disulfide. **TTC4**, **TTC5**, and **TTC6** were then obtained from the reaction of the disodium salt of 3-dithiocarboxysulfanylpropionic acid with 3-bromopropionic acid, 2-bromopropionic acid, and 2,2-dichloro-3,3-dimethyloxirane, respectively. The use of the disodium salt of 3-dithiocarboxysulfanylpropionic acid as a nucleophilic reagent is particularly advantageous since it can be prepared on a large scale and is readily isolated and stored for extended periods. The structures of these novel TTCs were confirmed by a combination of NMR spectroscopy and elemental microanalysis.

Evaluation of Trithiocarbonates in the Polymerization of *n*-Butyl Acrylate. Having prepared **TTC1**, **TTC3**, and **TTC4**−**TTC6** their effectiveness as RAFT agents was compared using the model acrylic monomer *n*-butyl acrylate (nBA). In particular, we were concerned with the effect of TTC structure and the ratio of the initial TTC concentration to the initiator concentration ($[TTC]_0$:$[AIBN]_0$), on both the kinetic and number-average molecular weight (M_n) profiles. Table 1 summarizes the experimental variables in this series of experiments.

In the initial series of experiments, the five TTCs were evaluated at 70 °C and a $[TTC]_0$:$[AIBN]_0$ of 20:1. In all instances the target molecular weight at quantitative conversion was 30 000 g/mol ([nBA]:[TTC] = 234). Polymerizations were conducted under bulk conditions, although in the case of **TTC1** and **TTC6** a small amount (∼5 vol %) of DMF was required to aid in the dissolution of the TTC. Figure 2 shows the pseudo-first-order kinetic plots for the nBA homopolymerizations employing **TTC1** and **TTC3** (A) and **TTC4**-**TTC6** (B) as well as the corresponding M_n and M_w/M_n vs conversion plots (C and D).

For **TTC1** and **TTC3** the kinetic profiles are very similar with the slopes (i.e., the apparent rate constant, K_{app}) being essentially identical. For **TTC3** the linear fit passes through the origin whereas there appears to be a small induction period of ca. 5 min in the case of **TTC1**. Such induction periods are not uncommon in dithioester-mediated RAFT systems.[17,18,21,38−40] In contrast, such induction periods are not typical of TTC-

Table 1. Summary of $[TTC]_0:[I]_0$, Experimental Molecular Weights, Polydispersity Indices, and Conversions for the Trithiocarbonate-Mediated Homopolymerizations of *n*-Butyl Acrylate at 70 °C under Bulk Conditions

	$[CTA]^a:[I]^b = 5:1$			$[CTA]^a:[I]^b = 10:1$			$[CTA]^a:[I]^b = 20:1$		
TTC	% conv[c]	M_n (g/mol)[d]	M_w/M_n[d]	% conv[c]	M_n (g/mol)[d]	M_w/M_n[d]	% conv[c]	M_n (g/mol)[d]	M_w/M_n[d]
TTC1[e]	21	5800	1.20	15	3600	1.19	10	2700	1.18
	46	8700	1.15	43	9200	1.13	33	9200	1.12
	67	11400	1.14	60	11400	1.13	62	12300	1.12
	83	13200	1.15	75	12500	1.15	92	15300	1.15
TTC3	18	6200	1.17	13	4200	1.18	16	4200	1.14
	39	10700	1.16	33	9900	1.15	27	8000	1.12
	53	14700	1.14	50	14100	1.14	65	18200	1.10
	65	17400	1.17	75	20700	1.15	71	19300	1.15
TTC4	$M_n = 200\,000-300\,000$ g/mol and $M_w/M_n = 1.90-2.10$								
TTC5	20	7200	1.15	27	8600	1.13	9	3000	1.14
	36	12900	1.14	47	13200	1.17	33	9600	1.12
	65	18800	1.14	60	16900	1.16	69	17900	1.09
	76	19800	1.15	78	19500	1.15	75	20100	1.13
TTC6[e]	18	6700	1.16	24	7200	1.15	14	3700	1.16
	50	14200	1.15	46	14000	1.14	24	8700	1.12
	68	16300	1.16	58	16700	1.14	43	12500	1.13
	86	19700	1.19	73	19700	1.15	67	18300	1.15

[a] [CTA] = concentration of RAFT chain transfer agent. [b] [I] = concentration of initiator. [c] As determined by ^{1}H NMR spectroscopy. [d] As determined by size exclusion chromatography in *N*,*N*-dimethylformamide at 40 °C. The system was calibrated with narrow molecular weight distribution poly(methyl methacrylate) standards. [e] 5 vol % *N*,*N*-dimethylformamide was added to aid in the dissolution of the TTC.

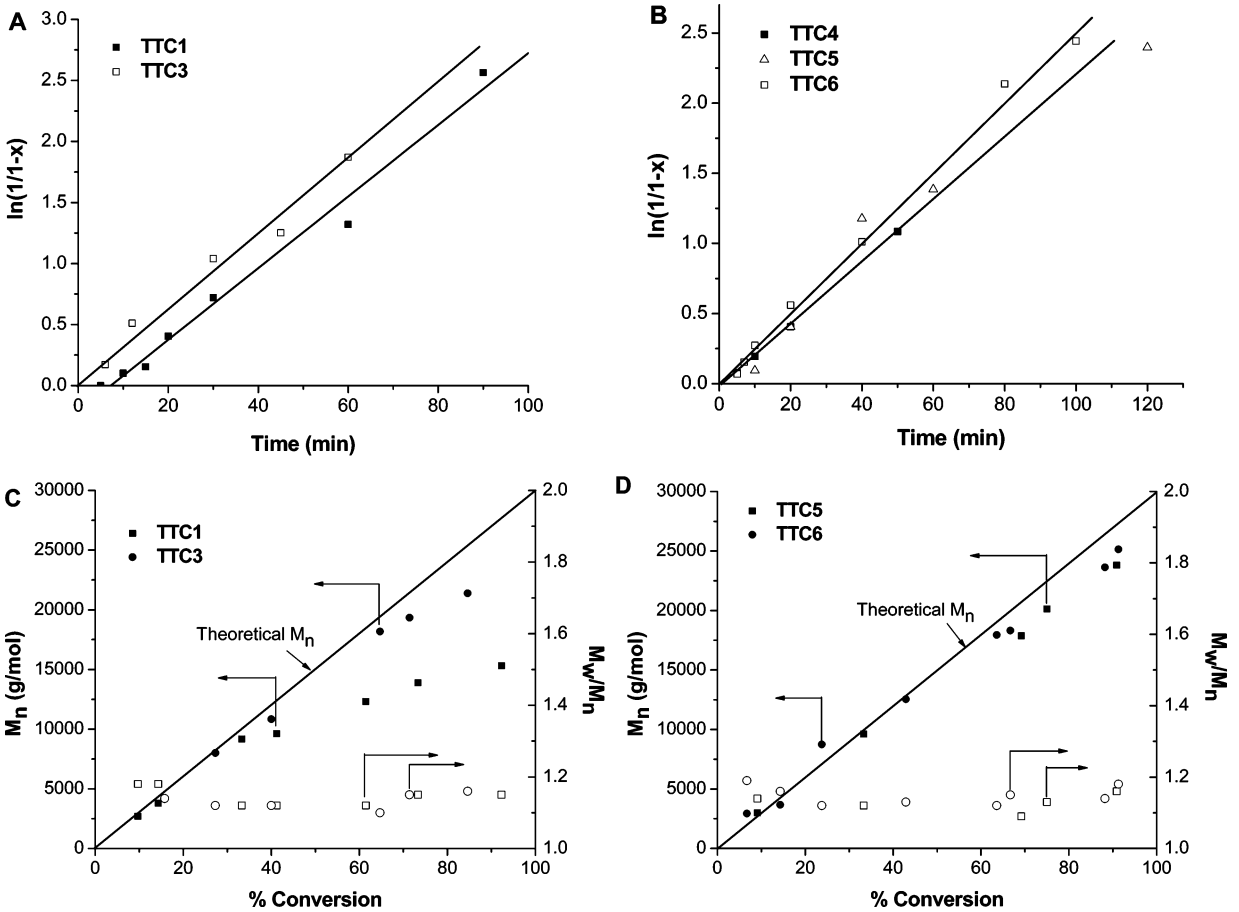


Figure 2. Pseudo-first-order kinetics plots for **TTC1**, **TTC3** (A) and **TTC4**-**TTC6** (B) for *n*-butyl acrylate at 70 °C under bulk conditions with $[TTC]_0:[AIBN]_0 = 20:1$ and the corresponding M_n and M_w/M_n vs conversion plots (C and D).

mediated systems, and we ascribe the observed small induction period here to a small amount of residual oxygen. Regardless of the cause, given the close similarity of the kinetic profiles, it is apparent that the main RAFT equilibrium is rapidly established. In the case of **TTC4**−**TTC6**, the kinetic profiles are also near-identical with all fits passing through the origin. Indeed, the kinetic profiles of the new TTCs as well as **TTC1** and **TTC3** are all similar, indicating that from a purely kinetic standpoint all the RAFT agents perform equally well, at least under the initially screened conditions. The experimentally determined apparent first-order dependence on monomer concentration is interesting since alkyl acrylates, under normal stationary free radical polymerization conditions, are well-known to deviate from this first-order dependence with [M] exponents in

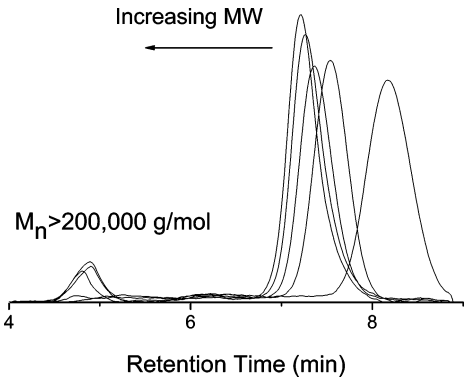


Figure 3. SEC traces (RI signal) for the bulk homopolymerization of nBA at 70 °C with **TTC1** with $[\mathbf{TTC1}]_0$:$[AIBN]_0$ = 20.

the range 1.4−1.8. Such deviations have been rationalized in terms of intramolecular chain transfer to polymer as recently discussed by Nikitin and Hutchinson.[41] However, the kinetic plot is not expected to be sensitive to the occurrence of such chain-transfer reactions.

This near-uniformity in the kinetic profiles is not, however, equally manifest with respect to the molecular weight control in these polymerizations. In the case of **TTC1** excellent agreement is observed between the theoretical and observed M_n up to ca. 30% conversion, after which a significant deviation to lower M_n values is observed. This negative deviation occurs simultaneously with the appearance of a much higher molecular weight species which is clearly visualized in the SEC traces (see Figure 3); this higher molecular weight species has a poly(methyl methacrylate) equivalent M_n of >200 000 g/mol.

Most previous studies involving the use of **TTC1** in acrylate polymerizations have typically targeted very low molecular weights. For example, in their report of the use of **TTC1** and **TTC2** as mediators in acrylic polymerizations, Lai and co-workers reported experimentally determined molecular weights in the range of ∼1100−6800 g/mol for monomers such as ethyl and butyl acrylates.[33] In the single example where a higher molecular weight ethyl acrylate homopolymer was targeted, molecular weight control was lost, and the resulting polydispersity index was 1.43. The lower than predicted molecular weights observed here for the main population of propagating chains can clearly be attributed to the presence of the higher molecular weight species. One possible explanation is that, upon reaching a critical degree of polymerization, the central trithiocarbonate core becomes so sterically hindered that the addition of a polymeric propagating chain across the C=S bond becomes difficult. Figure 4 shows a schematic representation as well as a space-filling model of a polynBA 22-mer (M_n ∼ 2800 g/mol). The accessibility to the S atom of the central C=S bond apparently becomes somewhat reduced as the DP_n increases. However, the actual degree of hindrance is anticipated to be a function of adopted chain conformation which in turn is expected to be a function of monomer structure and polymerization conditions, i.e., bulk vs solution. As such, the critical chain length at which addition to the C=S bond by a polymeric macroradical starts to become difficult may well be highly system dependent. However, further studies in which a closer examination of the effect of targeted DP_n and the resulting overall control of molecular weight will be necessary to confirm this hypothesis.

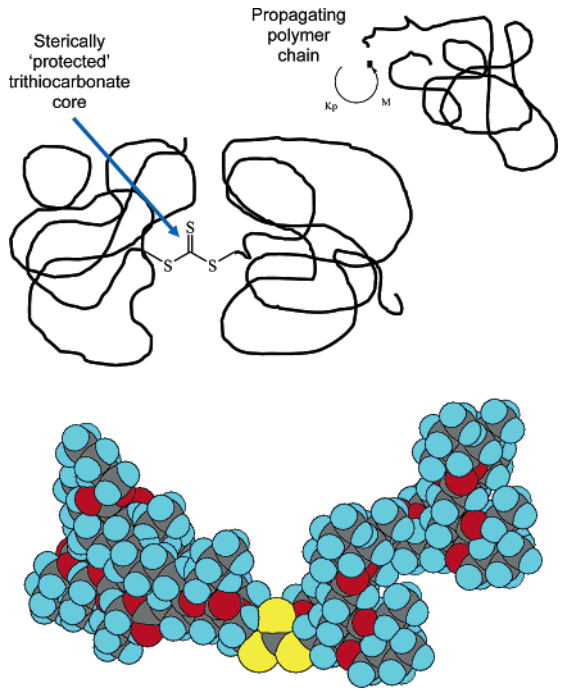


Figure 4. Schematic representation and space-filling model demonstrating the proposed steric shielding of the TTC core in **TTC1**-mediated polymerizations

However, as the accessibility to the TTC core drops, especially for higher molecular weight polymer chains, the free propagating chains have the ability to grow in an uncontrolled fashion to much higher-than-predicted molecular weights. Since the radical concentration (propagating chains in this case) is dictated by [AIBN] and since $[\mathbf{TTC1}]_0$:$[AIBN]_0$ = 20, only a very small number of these high molecular weight species are present. Even so, only a few chains need propagate to high molecular weight to effect the observed molecular weight deviation for the main population of lower molecular weight chains. The **TTC3**-mediated polymerization did proceed with good control over the molecular weight with the experimentally determined values being close to the theoretically expected values based on the fractional conversion. The evolution of M_n with conversion was linear with little/no deviation from the expected M_n values until higher conversions were attained. The minor deviations at theses higher conversions may be due to the fact that the experimentally determined molecular weights are not absolute but are relative to poly(methyl methacrylate) standards. However, we cannot dismiss the possible occurrence of undesirable chain transfer reactions (either to monomer or polymer) as a possible cause for the observed deviation.[42−44] Indeed, it is now well established that alkyl acrylates readily undergo both inter- and intramolecular chain transfer to polymer even at subambient temperatures. The occurrence of such side reactions is expected to manifest itself in the M_n vs conversion plot as a negative deviation (lower apparent molecular weight).[43] However, the generally good kinetic and molecular weight profiles observed for **TTC3** are consistent with previous reports detailing the use of this TTC in RAFT polymerizations. For both **TTC1** and **TTC3**, the polydispersities decrease with increasing conversion to final values in the range of ∼1.10−1.20, well below the theoretical lower limit of 1.50 for a normal free radical polymerization and in the range typical for RAFT-prepared (co)polymers.

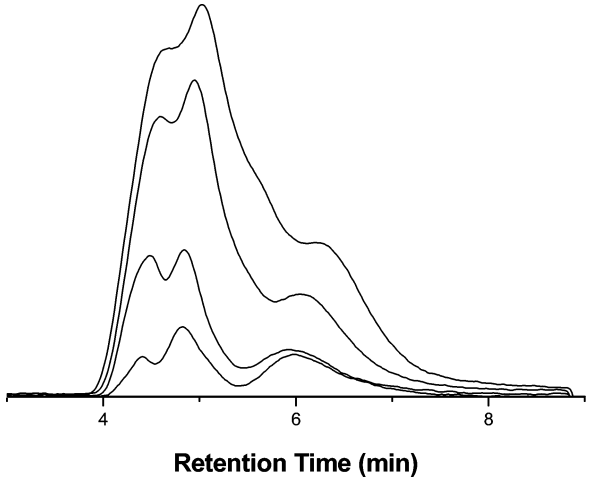


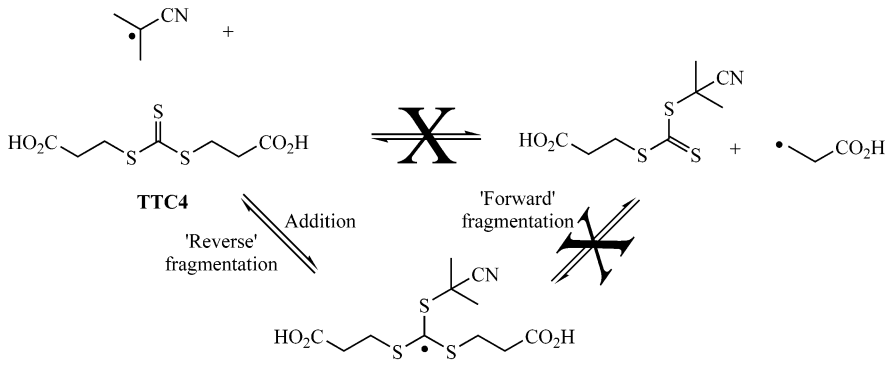
Figure 5. SEC traces (RI signals) for the bulk homopolymerization of nBA at 70 °C with **TTC4** with [**TTC4**]$_0$:[AIBN]$_0$ = 20.

Figure 2D shows the M_n and M_w/M_n vs conversion profiles for **TTC5** and **TTC6**. The molecular weight data for **TTC4** are not included since no control was observed. Figure 5 shows the SEC traces (RI signal) for the **TTC4**-mediated polymerization of nBA. The behavior of the nBA polymerization in the presence of **TTC4** is clearly much more complicated than in the case of the other TTCs. The resulting molecular weight distribution (Figure 5) is complex with, at the very least, a trimodal distribution being observed. Additionally, we note that the retention times for all the species in the molecular weight distribution remain essentially constant with their concentration simply increasing with increasing conversion. This is a feature more closely associated with conventional free radical polymerization behavior.

The inability of **TTC4** to effectively mediate the polymerization of nBA is not surprising when one considers the nature of the intermediate radical formed from the addition of either a primary (AIBN-derived) radical or oligomeric nBA radical to the C=S (see Scheme 2).

The addition of a cyanoisopropyl (CIP) radical to **TTC4** will yield the intermediate radical labeled **CIP**−**TTC4** (Scheme 2). As with any RAFT agent these addition steps are reversible. However, to function as effective mediating agents, fragmentation of the **CIP**−**TTC4** intermediate radical must be favored in the direction of the R group—indeed, this is obviously a prerequisite for effective molecular weight control; i.e., there must be a fine balance between the forward and reverse rates of addition and fragmentation and the rates of reinitiation and propagation for effective control. However, in the case of **TTC4**, the desired "forward" fragmentation will yield a primary alkyl radical, i.e., the $CO_2HCH_2CH_2^{\bullet}$ radical species. A much lower energy fragmentation pathway exists, namely the "reverse" fragmentation of **CIP**−**TTC4** to regenerate the tertiary CIP radical and **TTC4**. Clearly, of these two possible fragmentation pathways, the undesirable "reverse" fragmentation will be favored. As such, the cyanoisopropyl radical is most likely the species primarily responsible for chain initiation. While Scheme 2 depicts an extreme case in which there is no forward fragmentation, given the complex resulting molecular weight distribution observed in Figure 5, it seems likely that some chains are initiated as a result of the fragmentation in the preferred forward direction. A recent ab initio study by Coote and Radom[45] describing the effect of alkyl substituents (Z′ in $CH_3SC^{\bullet}(OZ')S-CH_2OCOCH_3$) in the xanthate-mediated polymerization of vinyl acetate clearly demonstrated that fragmentation of intermediate radicals (at least for the series of xanthates evaluated) is not only a function of resulting radical stability but also of reactant/product stabilities and can, in certain instances, lead to an unexpected fragmentation pathway as a result of this balance. However, in this study it seems likely that the majority of chains are initiated by AIBN-derived primary radicals. Since the [AIBN] is much lower than the [**TTC4**], molecular weight control is also lost (Table 1). This nonideal RAFT behavior may be compounded by the fact that even after formation of nBA oligomers, addition of these radical species to **TTC4** yields a radical intermediate with ×2 primary R groups and a secondary oligomeric nBA species, thus still favoring "reverse" fragmentation, although not, most likely, to the same extent as in the case of an AIBN-derived primary radical. Indeed, the degree of R group fragmentation might be expected to increase as more primary radicals are converted to nBA oligomeric species. While the kinetic plot (Figure 2B) for the **TTC4**-mediated homopolymerizations indicated pseudo-first-order kinetics (a feature often cited as being indicative of a controlled/living polymerization[46]), this alone clearly does not confirm controlled polymerization, as is evident in the molecular weight vs conversion profile above, but merely indicates a constant number of active species. Indeed, such pseudo-first-order kinetic behavior is also expected in a conventional free radical polymerization under steady-state conditions.[47] All things considered, therefore, we would advise against the use

Scheme 2. Possible Addition−Fragmentation Pathways for the TTC4-Mediated Polymerization of NBA Using AIBN as the Source of Primary Radicals



of **TTC4** in conjunction with AIBN as an effective CTA/initiator combination for the polymerization of nBA.

In contrast to **TTC4**, both **TTC5** and **TTC6** are very effective mediating agents (Figure 2D), yielding homopolymers with both good molecular weight control and low polydispersities. Indeed, the ability of these two new TTCs to control the molecular weight is comparable, if not superior, to that of **TTC3**. As with **TTC3**, the M_n vs conversion plots are linear and show only small deviations from the theoretical M_n at ≥90% conversion. Again, these small deviations could be due to the occurrence of undesirable inter- or intramolecular chain transfer reactions to polymer as discussed above. The enhanced control observed in the case of **TTC5** and **TTC6** vs **TTC4** is clearly related to the now favored "forward" fragmentation of intermediate radicals, i.e., TTC activation, which is a direct result of the secondary and tertiary nature, and (meth)acrylate-like structure, of the R groups in **TTC5** and **TTC6**, respectively.

Effect of $[TTC]_0$:$[AIBN]_0$. Having demonstrated that both **TTC5** and **TTC6** have the ability to mediate nBA homopolymerizations at least as effectively as other previously reported TTCs, we decided to examine the effect of $[TTC]_0$:$[AIBN]_0$ on the polymerization kinetics for these two species (see Table 1). This ratio can often be a critical factor in determining the overall success of a RAFT polymerization at least with respect to control over the molecular weight and molecular weight distribution. In the case of dithioesters a typical $[CTA]_0$:$[I]_0$ ratio is 5:1. Lower ratios, while often resulting in faster polymerizations may be less controlled, whereas higher ratios may afford better overall control but often at the expense of polymerization time.[21]Figure 6 shows the pseudo-first-order kinetic plots for the homopolymerization of nBA at 70 °C and ratios of 10:1 and 5:1 for both **TTC5** (A) and **TTC6** (B). The plots in all instances are essentially linear with the best fits passing through the origin. As expected, in both instances the polymerizations proceed more quickly at lower $[TTC]_0$:$[AIBN]_0$ ratios. This is consistent with previous reports on the effect of $[TTC]_0$:$[I]_0$ for TTC-mediated polymerizations. For example, Convertine et al.[22] recently described the room temperature polymerization of *N*-isopropylacrylamide employing **TTC2** in DMF and clearly demonstrated the kinetic effect of changing the ratio of **TTC2** to the azo initiator with lower ratios, resulting in faster polymerizations.

Perhaps the most telling indicator of a controlled/"living" polymerization is the ability to prepare block copolymers by sequential monomer addition or by isolating the first block, purifying it, and then employing it as a macroinitiating species (or macro-RAFT agent in this case) for the subsequent block copolymerization. As such, and to demonstrate the full utility of these new TTCs, we have conducted a self-blocking experiment, i.e., polymerized nBA from a polynBA homopolymer, employing a homopolymer derived from **TTC5** as the macro-RAFT agent. Figure 7 shows the SEC traces (RI signal) for the macro-RAFT agent as well as the resulting "block" copolymer. The macro-RAFT agent has an M_n of ~26 000 g/mol and polydispersity index of 1.09 with the resulting block copolymer having an experimentally determined M_n of ~150 000 g/mol and polydispersity index of 1.11. The SEC traces indicate high reinitiation efficiency with the resulting block copolymer possessing an essentially symmetrical unimodal molecular weight distribution. There is some detectable presence of lower molecular weight species (small hump on the right of the main block copolymer peak) which we ascribe to macro-RAFT agent impurity, and there is likewise a small higher molecular weight impurity which is most likely a result of undesirable termination reactions. However, both are present in small quantities relative to the main block copolymer species, and thus we conclude that the overall blocking efficiency is high.

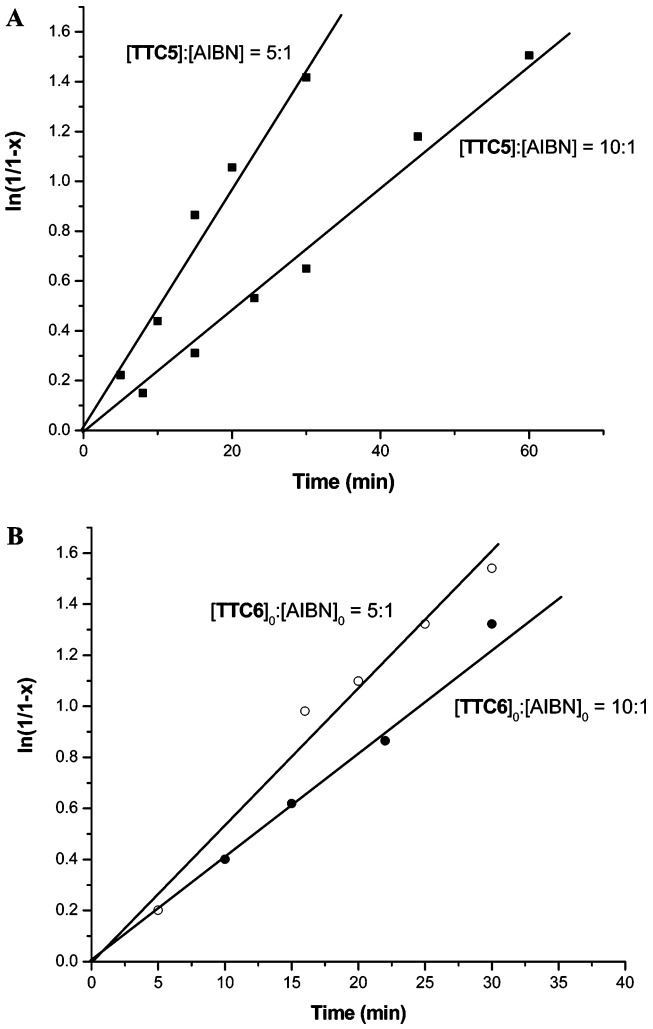


Figure 6. Pseudo first-order kinetic plots for the bulk homopolymerization of nBA at 70 °C employing **TTC5** and **TTC6** at $[TTC]_0$:$[AIBN]_0$ = 5 and 10.

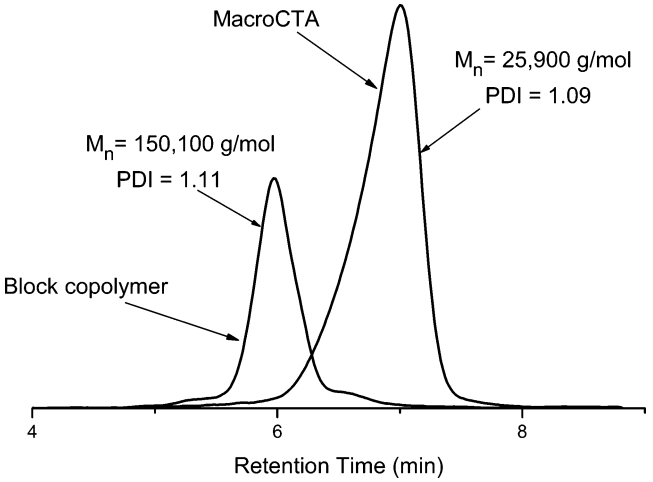


Figure 7. SEC traces (RI signals) for a poly(*n*-butyl acrylate) homopolymer (M_n = 25 900 g/mol, M_w/M_n = 1.09) prepared with **TTC5** and the resulting nBA−nBA "block" copolymer (M_n = 150 100 g/mol, M_w/M_n = 1.11).

Summary/Conclusions

Here we have reported the synthesis of three new trithiocarbonates (**TTC4**−**TTC6**) in which the nature of the substitution about the TTC functional group has been varied. We have subsequently evaluated their effectiveness as mediating agents in the RAFT homo- and block polymerization of *n*-butyl acrylate. Both **TTC5** and **TTC6**, TTCs with potential secondary and tertiary alkyl leaving (R) groups, perform as well as previously reported TTCs and yield poly(*n*-butyl acrylate) homopolymers with good molecular weight control and low polydispersities. **TTC4** was shown to be ineffective by virtue of the proposed favored "reverse" fragmentation pathway as opposed to the desired "forward" pathway required for effective molecular weight control. The use of **TTC1** as a mediating agent for the homopolymerization led to bimodal molecular weight distributions with a significantly high molecular weight impurity. We speculate that this arises due to a steric crowding effect of the central C═S bond making the addition reaction difficult and resulting in some degree of uncontrolled polymerization. However, further experiments are required to prove/disprove this. The effect of $[TTC]_0$:$[AIBN]_0$ was determined for **TTC5** and **TTC6**, and it was shown that the polymerizations were faster at the lower $[TTC]_0$:$[AIBN]_0$ ratios. Finally, we demonstrated the ability to form AB "diblock" copolymers with nBA with high reinitiation efficiency employing a poly(*n*-butyl acrylate) macro-RAFT agent. The synthesis of these new trithiocarbonates now allows the facile preparation of dicarboxylic acid telechelic poly(alkyl acrylate)s under straightforward conditions. We are currently extending our studies to the preparation of more highly functional materials.

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