Synthesis of Block and Graft Copolymers of Styrene by RAFT Polymerization, Using Dodecyl-Based Trithiocarbonates as Initiators and Chain Transfer Agents

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ABSTRACT: A series of dodecyl-based monofunctional trithiocarbonate chain transfer agents (CTAs) were successfully synthesized, toward the reversible addition-fragmentations chain transfer (RAFT) polymerization of styrene. The CTAs were used as initiators for RAFT polymerization, in the absence of the conventional free radical initiator, at higher temperature. Polystyrene (PS) of narrow polydispersity index (PDI) is synthesized. Subsequently, poly(styrene-*b*-benzyl methacrylate) diblock and poly(styrene-*b*-benzyl methacrylate-*b*-2-vinyl pyridine) triblock copolymers were synthesized from the PS macro-RAFT agent by simply heating with the second and third monomer, respectively. These experiments suggest that it should be possible to control the RAFT polymerization initiated by a CTA through the adjustment of the temperature of polymerization in such manner that initiation is tailored to proceed at faster rate (at higher tem-

INTRODUCTION Controlled/"living" radical polymerization techniques is a versatile tools for the synthesis of a verity of polymers with controlled molecular weight, molecular weight distribution (MWD), and well-defined macromolecular architectures.^{1–5} Some of the efficient methods used nowadays frequently are nitroxide-mediated polymerization⁶ (NMP), atom transfer radical polymerization^{2,7} (ATRP), reversible addition-fragmentations chain transfer^{5,8} (RAFT), single electron transfer⁹ (SET), and single electron transferreversible addition-fragmentation chain transfer (SET-RAFT).¹⁰⁻¹² Among these methods, ATRP and RAFT have emerged as the most successful techniques due to their applicability to a wide range of monomers and mild reactions conditions.^{2,13} Recently, RAFT polymerization has gained importance over the other methods mainly because of its compatibility with a wide range of functional groups such as acid, amide, amine, and epoxy containing monomers.^{14–18} Various RAFT agents (dithioesters,^{5,19} dithiocarbamates,^{20,21} trithiocarbonates,^{22–27} and xanthats^{28,29}) have been effectively used as transfer agents to controlled molecular weights, MWD, and molecular architecture of polymeric perature) in comparison to propagation (lower temperature). For the specific CTAs studied in this work, the polymerization rate of styrene was high in the case of the reinitiating cyano (CN)-substituted group (R group) compared to the other groups studied. The results further show that 4-cyano pentanoic acid group is superior to the other R groups used for the RAFT polymerization of styrene, especially based on the polydispersity at a given conversion as well as the variation in the expected and experimental number-average-molecular weights. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1066–1078

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material prepared from a wide range of monomers. Trithiocarbonate²²⁻²⁷-based chain transfer agents (CTAs) have been found to be effective for most of the RAFT polymerization of the vinyl monomers. The RAFT polymerization of styrene, ethyl acrylate, 2-hydroxyethyl acrylate, and acrylic acid were carried out successfully using S-1-dodecyl-S'- $(\alpha, \alpha'$ -dimethyl- α'' -acetic acid)-trithiocarbonate (DDMAT) as a CTA and polymers with narrow disparity (PDI \leq 1.16) were obtained.³⁰ The ambient-temperature RAFT polymerization of styrene and its functional derivatives, for example, 4-vinylbenzyl chloride, *N*,*N*-diethyl vinylbenzylamine, and 4-vinylbenzyl alcohol were carried out using (2,4,6-trimethylbenzoyl) diphenylphosphine oxide as the photoinitiator along with DDMAT under mild long wave UV-visible radiation or radiation of longer wavelength.³¹ The temperature-responsive biotinylated polymers poly(N-isopropylacrylamide) and watersoluble poly[N-(2-hydroxypropyl)methacrylamide] have been prepared in one step via RAFT polymerization using biotinylated trithiocarbonate as the RAFT agent.³² The temperature responsive poly(DMA-b-NIPAAm) was successfully prepared, in a controlled manner, at room temperature, by RAFT

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polymerization using 4,4'-azobis[2-(imidazolin-2-yl)propane] dihydrochloride (VA-044) as the initiator and S-ethyl-S'-(α, α' dimethyl- α'' -acetic acid)-trithiocarbonate as the CTA, and the polymers obtained were reported to be narrow dispersed.33 The RAFT polymerization of 4-vinylbenzaldehyde was carried out, at 70 °C, using AIBN as the initiator and a trithiocarbonate CTA (DDMAT). The resulting polymers were shown to exhibit well-defined molecular weight and narrow polydispersity index (PDI < 1.2).³⁴ The polystyrene (PS) and poly(acrylic acid) were synthesized, in a controlled manner, using DDMAT as the CTA, resulting in a trithiocarbonate end group on each of these polymers. The RAFT-generated polymers were immobilized onto the surface of the gold nanorods with or without the use of reducing agents.³⁵ The first and somewhat sketchy report on the RAFT polymerization of styrene at 110 °C, in bulk, using 2-phenylpropan-2-yl benzodithioate CTA, without the conventional free radical initiator, was reported by Chiefari et al.5 The RAFT polymerization methods is quite different from photoiniferter and thermal iniferter methods.³⁶ In thermal iniferter or photoiniferter polymerization, the results obtained suggested that these polymerization proceed via living radical polymerization mechanism. Mayo et al. have already reported that in the polymerization of styrene at higher temperature (in the range 156-190 °C), styrene acts as a self-initiator.³⁷ The RAFT polymerization of styrene at 140 °C in bulk as well as in *t*-butanol (solution) using α, α' -dimethylacetic acid trithiocarbonate CTA was reported by Lai et al.³⁰ They reported the synthesis of oligomeric PS with a number average molecular weight (M_n) of 6709 and a PDI of 1.16. Subsequently, Postma et al.³⁸ reported the thermal RAFT polymerization of styrene using *n*-butyl-based trithiocarbonates with the R group "phthalimidomethyl," in the absence of the conventional free radical initiator. They observed that the molecular weights of the polymers obtained were close to the expected values, and the PDI values were low (PDI < 1.2), at higher monomer conversion.^{38,39} The synthesis of copolymers of styrene and L-proline-functionalized styrene, in bulk, by thermal RAFT polymerization at 110 °C was carried out *S*-1-dodecyl-*S*'-(1-phenyl ethyl) trithiocarbonate using (DPET) as the CTA, without the use of the conventional free radical initiator.⁴⁰ The polymerizations were observed to proceed in a controlled manner as the PDI values of the polymers were less than 1.15. These are the only reports available in the literature on thermal RAFT polymerization carried out in the absence of the conventional free radical initiator at higher temperature. The block copolymer poly (methyl acrylate-b-isobutyl vinyl ether) was synthesized using S-1-isobutoxyethyl-S'-ethyl trithiocarbonate as the CTA in a controlled manner by RAFT polymerization.41 The block copolymer of poly(styrene-b-2-vinyl pyridine) and poly (styrene-b-4-vinyl pyridine) was synthesized using benzyl dithiobenzoate as CTA at 110 °C with AIBN as initiator.42 Poly(ethylene glycol)-b-poly(styreneboroxole) sugar responsive block copolymers, for insulin delivery applications, were also successfully synthesized by RAFT polymerization (using AIBN as the initiator, in THF, at 75 $^\circ$ C) using a trithiocarbonate-based CTA (PEG-attached DDMAT).43 It may be men-

tioned here that the addition of AIBN or any conventional free radical initiator in RAFT polymerization is a more practical approach to reduce the temperature of polymerization because it enables the generation of relatively larger concentration of the chain initiators. However, this in principle can result in homopolymers and block copolymers with the initiator fragment (in the case of AIBN, it is isobutyronitrile end group whose concentration could be slightly less than twice the concentration of the initiator taking into consideration the initiator efficiency factor). In thermal RAFT polymerizations, where the CTA functions as both the initiator and the CTA, pure homo and block copolymers can be obtained as the polymerization would involve only the insertion between the R-S bonds in the CTA. Trithiocarbonate-based CTAs are easy to synthesize compared to dithiobenzoates, and the yields obtained are very high. As the dodecyl-based trithiocarbonates showed less unfavorable odor compared to that of dithiobenzoates, they have gained more importance these days, as CTAs in RAFT polymerization.^{24,32,44,45} The crystalline nature of the dodecyl-based CTAs provide an additional advantage for its easier handling in RAFT polymerization. Recently, it was found that the water-soluble polymers synthesized using trithiocarbonate-based CTA exhibited less cytotoxicity than those based on dithiobenzoate.46

It is reported that the R group of a RAFT agent plays an important role in styrene RAFT polymerization kinetics38 whereas, in our hands, the effect of R group (from a pyrazole-based dithiocarbamate CTA) on the RAFT polymerization kinetics of styrene is negligible.⁴⁷ To the best of our knowledge, there is no report available on the kinetics of RAFT polymerization of styrene using dodecyl-based trithiocarbonates at higher temperature. The aforementioned factors prompted us to study the effect of various R groups, in dodecyl-based trithiocarbonates, on RAFT polymerization of styrene at higher temperature. We demonstrate the synthesis by RAFT polymerization of styrene and block copolymer of P(S-b-BnMA), P(S-b-2-VP) as well as graft copolymers via RAFT polymerization in an "R group" approach. It may be noted that in the literature, PS comb polymers were prepared by using dithiobenzoateattached P(S-co-p-CMS), and the resultant polymers showed multimodal GPC peaks.⁴⁸ In this new methodology, we have 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl attached pentanoic acid (CDSTSP) as pendant groups to P(S-co-p-CMS) and synthesize the graft copolymer P(S-co-p-CMS)-g-PS by the thermal RAFT polymerization method.

EXPERIMENTAL

Materials

Styrene (Aldrich, 99.9%) and benzyl methacrylate (Aldrich, 96%) were purified by passing through a column packed with activated basic alumina, which removes the inhibitor and any other acidic impurities. 2,2'-Azobis (isobutyronitrile) (AIBN, 98%) and 4, 4'-azobis (4-cyanopentanoic acid) (75%) purchased from Aldrich was recrystallized from methanol and was placed in the refrigerator (\sim 4 °C). All the other chemicals used in this study were purchased from Aldrich, 95%)





SCHEME 1 Synthesis of monofunctional dodecyl-based trithiocarbonate CTAs.

were vacuum distilled before use, and all other chemicals were used without further purification. All the solvents used in this study were purified using standard laboratory procedures.

Synthesis of Dodecyl-Based Trithiocarbonate Chain Transfer Agents

The general procedure used in the synthesis of the CTAs as shown in the Scheme 1(a,b). The detailed synthetic procedure associated with the synthesis of the docecyl-based trithiocarbonate CTAs and the summary of the results from the structural characterization studies are given below (¹H NMR and ¹³C NMR spectra are given in the Supporting Information Figs. S1–S5).

S-1-Dodecyl-S'-(1-phenyl ethyl) Trithiocarbonate

A 250-mL, three-neck, round-bottom (RB) flask (fitted with septum and reflux condenser with N₂ bubbler) was charged with 60 mL of heptane and a solution of potassium t-butoxide (1.644 g, 14.7 mmol) in 15 mL of THF. The temperature of the reaction mixture was maintained between 5 and 15 °C. n-Dodecylthiol (3.5 mL, 14.7 mmol) was added over 10 min to the RB flask, and the mixture was stirred for 45 min. To this white slurry, carbon disulfide (CS₂) (0.88 mL, 14.7 mmol) was added over 15 min, and it was stirred for a further period of 1 h. After allowing the mixture to warm to 20 °C, it was stirred for an additional period of 4.5 h. Then, 1phenyl ethylbromide (2 mL, 14.7 mmol) was slowly added, and the mixture was stirred for 24 h. It was then poured into water and extracted with ethyl acetate. The combined extracts were dried with anhydrous magnesium sulfate and filtered, and the solvent was removed by using a rotary evaporator. The crude product was separated using chromatography on silica with *n*-hexane as the eluent to provide DPET as a dark yellow color liquid and bis(dodecyl) trithiocarbonate (BDT) as a yellow color solid.

Yield of DPET = 53%. DPET-¹H NMR (CDCl₃, δ ppm, 400 MHz): δ = 7.3-7.5 (m, 5H, Ar-H), 5.4 (q, 1H, -SCH-), 3.4 (t, 2H, -SCH₂-), 1.85 (d, 3H, -SCH(CH₃)), 1.7 (quintet, 2H, -SCH₂-CH₂-), 1.3-1.5 (remaining CH₂ signals), 0.96 (t, 3H, -CH₂CH₃). ¹³C NMR (CDCl₃, δ ppm, 100 MHz): δ = 224 (C=S), 140, 128.6, 127.7, 127.6, 50, 36.7, 32, 29 (overlapping signals), 28, 23, 21, 14. Yield of BDT = 28%. BDT-¹H NMR (CDCl₃, δ ppm, 400 MHz): δ = 3.4 (t, 2H, -SCH₂-), 1.7 (quintet, 2H, -SCH₂-CH₂-), 1.2-1.47 (remaining CH₂ signals), 0.90 (t, 3H, -CH₂CH₃). ¹³C NMR (CDCl₃, δ ppm, 100 MHz): δ = 225 (C=S), 37, 32, 29 (overlapping signals), 28, 22.6, 13.5.

S-1-Dodecyl-S'-((2-ethoxycarbonyl)-ethyl) Trithiocarbonate

The synthesis of S-1-dodecyl-S'-((2-ethoxycarbonyl)-ethyl) trithiocarbonate (DECET) was performed as described in the synthesis of DPET except that ethyl α -bromopropionate (1.9 mL, 14.7 mmol) was used in the place of 1-phenylethyl bromide. The crude product was separated using chromatography on silica with 1–2% ethyl acetate in hexane as the eluent to provide DECET as a dark yellow color solid and BDT as a yellow color solid.

Yield of DECET = 56%. DECET, ¹H NMR (CDCl₃, δ ppm, 400 MHz): δ = 4.8 (q, 1H, -SCH-), 4.2 (q, 2H, -OCH₂--), 3.38 (t, 2H, -SCH₂--), 1.7 (quintet, 2H, -SCH₂--CH₂--), 1.6 (d, 3H, -SCH(CH₃)), 1.2-1.48 (remaining CH₂ signals), 0.90 (t, 3H, -CH₂CH₃). ¹³C NMR (CDCl₃, δ ppm, 100 MHz): δ = 222 (C=S), 170 (C=O), 62, 48, 37, 32, 29 (overlapping signals), 28, 23, 17, 14.

S-1-Dodecyl-S'-(2-cyanoethyl) Trithiocarbonate

NaOH (0.50 g, 12.5 mmol) was dissolved with stirring and gentle heating in a mixture of dodecanethiol (3.0 mL, 2.5 g, and 12.5 mmol), acetone (40 mL), water (5 mL), and tetrapropylammonium bromide (0.27 g, 0.10 mmol). The resulting solution was cooled in an ice bath and treated with carbon disulfide (0.75 mL, 0.95 g, 12.5 mmol). After 20 min, 2-bromopropanenitrile (1.0 mL, 0.167 g, 12.5 mmol) was added, and the mixture was stirred at room temperature for 12 h. The solution was evaporated to a quarter of the original volume. After cooling, the water phase was separated from the organic phase and washed with dichloromethane (DCM) (3 \times 50 mL). The combined organic phases were dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure and dried in vacuum, yielding a bright yellow liquid (50%). The compound was characterized by ¹H NMR and ¹³C NMR.

¹H NMR (CDCl₃, δ ppm, 400 MHz): δ = 4.8 (q, 1H, -SCH-); 3.3 (t, 2H, -SCH₂-); 2.8 (t, 2H, -SCH₂-CH₂-); 1.8 (d, 3H, -SCH(CH₃); 1.4 (m, 18H remaining CH₂ signals); 0.8 (t, 3H, -CH₂CH₃). ¹³C NMR (CDCl₃, δ ppm, 100 MHz): δ = 221.9 (C=S); 120.0 (CN); 47.4; 39.2; 37.4; 31.9; 30.6; 29.6; 29.4; 29.3; 29.2; 29.1; 28.9; 27.9; 22.7; 16.6; 14.1.

4-Cyano-4 -(dodecylsulfanylthiocarbonyl)sulfanyl Pentanoic Acid

The initial steps in the synthesis of CDSTSP were similar to that described in the synthesis of DPET. The preliminary product formed in this case (by the reaction of the potassium salt of *n*-dodecylthiol with carbon disulfide was an yellow slurry, which was reacted in portions with iodine (2.0 g, 7.9 mmol) over a 30-min period and stirred at room temperature for 14 h. Distilled water was added, and the separated organic phase was washed with a solution of sodium thiosulfate and brine solution. The organic layer was dried with anhydrous sodium sulfate and filtered. The solvent was evaporated to provide 3.7 g of BDSTD as a yellow color solid. BDSTD⁻¹H NMR (CDCl₃, δ ppm, 400 MHz): δ = 3.3 (t), 3.1 (minor triplet), 2.6 (minor triplet), 1.62 (quintet), 1.18–1.4 (remaining CH₂ signals), 0.80 (t).

A solution of 4,4'-azobis(4-cyanopentanoic acid) (3.10 g, 0.01108 mol) and the BDSTD (3.6335 g, 0.0066 mol) in ethyl acetate (50 mL) was heated to reflux for 22 h. After the removal of the volatiles *in vacuo*, the crude product was washed with water and was crystallized from heptane, to afford CDSTSP (4.162 g) as a pale yellow solid.

CDSTSP-¹H NMR (CDCl₃, δ ppm, 400 MHz): δ = 10.7 (broad, 1H, -COOH), 3.25 (t, 2H, -SCH₂-), 2.26-2.68 (m, 4H, -CH₂CH₂-), 1.81 (s, 3H, -CH₃), 1.6 (m, 2H, -SCH₂-CH₂-), 1.1-1.4 (remaining CH₂ signals), 0.80 (t, 3H, -CH₂CH₃). ¹³C NMR (CDCl₃, δ ppm, 100 MHz): δ = 217.6 (C=S), 177 (-COOH), 120 (-CN), 47, 38, 34, 32.1, 30 (overlapping CH₂ signals), 28, 26, 23.8, 21, 15.

2 -{[(Dodecylsulfanyl)carbonothioyl]sulfanyl}propanoic Acid

The initial part associated with the synthesis of 2-{[[(dodecyl-sulfanyl)carbonothioyl]sulfanyl}propanoic acid (DSCPA) was similar to that used for DCET. In this case, 2-bromopropanoic acid (1.13 mL, 1.91 g, 12.5 mmol) was added instead of 2-bromopropanenitrile. The product obtained (a precipitate) was filtered and recrystallized from petroleum ether to give the desired trithiocarbonate (DSCPA) as fine yellow platelets (3.33 g, 76%), Mp. 77.8–78.8 °C.

¹H NMR (CDCl₃, δ ppm, 400 MHz): δ = 4.8 (q, 1H, -SCH); 3.3 (t, 2H, -SCH₂); 2.8 (t, 2H, -SCH₂); 1.85 (d, 3H, -SCH (CH₃)); 1.65 (q, 2H, -SCH₂CH₂); 1.3 (m, 16H, remaining CH₂ signals); 0.8 (t, 3H, -CH₂CH₃). ¹³C NMR (CDCl₃, δ ppm, 100 MHz): δ = 221.9 (C=S); 177.0 (COOH); 47.4; 39.2; 37.4; 31.9; 30.6; 29.6; 29.4; 29.3; 29.2; 29.1; 28.9; 28.5; 27.9; 22.7; 16.6; 14.1.

RAFT polymerization of Styrene Using DPET as Initiator and Chain Transfer Agent

A stock solution of 2.0 mL (1.818 g, 17 mmol) of styrene and 0.0745 g (0.00435 mmol) of DPET was prepared, and aliquots of 3.0 mL were placed in polymerization ampoules. After the mixture was degassed under vacuum, pure nitrogen gas was introduced into the tube, which was subsequently immersed in an oil bath thermostated at 100 $^{\circ}$ C. Samples were withdrawn at different reaction times. At the end of the reaction, each ampoule was quenched in cold water and opened. The reaction mixture was diluted with THF and precipitated into excess of methanol. The polymer was dried at room temperature in vacuum for at least 24 h,

until a constant weight was obtained. The conversion of styrene was determined gravimetrically. The polymerization reaction was followed kinetically. The polymer molecular weight and PDI was characterized by GPC.

RAFT Polymerization of Styrene Using DCET, DSCPA, and DPET as Initiator and Chain Transfer Agent at Higher Temperature

A stock solution of 2.0 mL (1.818 g, 17 mmol) of styrene and 0.0288 g (0.087 mmol) of DCET was prepared in polymerization ampoules. After the mixture was degassed under vacuum, pure nitrogen gas was introduced into the tube, which was subsequently immersed in an oil bath thermostated at 140 °C (initiation; stirred for 30 min followed by lowering of temperature) and 90 $^\circ$ C (propagation). At the end of the reaction, each ampoule was quenched in cold water and opened. The reaction mixture was diluted with THF and precipitated into excess of methanol. At the end of the reaction, each ampoule was quenched in cold water and opened. The reaction mixture was diluted with THF and precipitated into a large amount of methanol. The polymer was dried at room temperature in vacuum for at least 24 h until a constant weight was obtained. The conversion of styrene was determined gravimetrically. The polymerization reaction was followed kinetically. Samples were withdrawn at different reaction times. The polymer molecular weight and PDI was characterized by GPC.

RAFT Polymerization of Styrene Using DCET and DPET as Initiator and Chain Transfer Agent at 150 $^\circ\mathrm{C}$

A stock solution of 2.0 mL (1.818 g, 17 mmol) of styrene and 0.0288 g (0.087 mmol) of DCET was prepared in polymerization ampoules. After the mixture was degassed by under vacuum, pure nitrogen gas was introduced into the tube, which was subsequently immersed in an oil bath thermostated at 150 °C. At the end of the reaction, each ampoule was quenched in cold water and opened. The reaction mixture was diluted with THF and precipitated into excess of methanol. The polymer was dried at room temperature in vacuum for at least 24 h, until a constant weight was obtained. The conversion of styrene was determined gravimetrically. The polymerization reaction was followed kinetically. Samples were withdrawn at different reaction times. The polymer molecular weight and PDI was characterized by GPC.

Synthesis of Linear Block Copolymers P(S-b-BnMA) Using Polystyrene Macro-RAFT Agent

A stock solution of 2.0 mL (2.08 g, 11.8 mmol) of benzyl methacrylate and 0.1774 g (0.039 mmol) of PS macro-RAFT agent was prepared in polymerization ampoules. After the mixture was degassed under vacuum, pure nitrogen gas was introduced into the tube, which was subsequently immersed in an oil bath thermostated at 110 °C. At the end of the reaction, each ampoule was quenched in cold water and opened. The reaction mixture was diluted with THF and precipitated into excess of methanol. The polymer was dried at room temperature in vacuum for at least 24 h, until a constant weight was obtained. The conversion of block copolymer P(S-b-BnMA) was determined gravimetrically. The polymer





SCHEME 2 Chemical structure of the monomers and CTAs used in the polymer synthesis.

molecular weight and MWD or PDI was determined by gel permeation chromatography (GPC).

Synthesis of Linear Block Copolymers P(S-b-2-VP) Using Polystyrene Macro-RAFT Agent

A stock solution of 1.5 mL (1.46 g, 13.9 mmol) of 2-vinyl pyridine and 0.0625 g (0.0195 mmol) of PS macro-RAFT agent was prepared in polymerization ampoules. After the mixture was degassed under vacuum, pure nitrogen gas was introduced into the tube, which was subsequently immersed in an oil bath thermostated at 120 °C. At the end of the reaction, each ampoule was quenched in cold water and opened. The reaction mixture was diluted with THF and precipitated into excess of hexane. The polymer was dried at room temperature in vacuum for at least 24 h, until a constant weight was obtained. The conversion of block copolymer P(S-b-2-VP) was determined gravimetrically. The polymer molecular weight and MWD or PDI was determined by GPC.

Synthesis of Linear Block Copolymers P(S-b-BnMA-b-2-VP) Using P(S-b-BnMA) Macro-RAFT Agent

A stock solution of 1.5 mL (1.46 g, 13.9 mmol) of 2-vinyl pyridine and 0.052 g of P(S-*b*-BnMA) macro-RAFT agent was prepared in polymerization ampoules, in DMF. After the mixture was degassed under vacuum, pure nitrogen gas was introduced into the ampoules, which was subsequently immersed in an oil bath thermostated at 120 °C. At the end of the prescribed time of reaction, each ampoule was quenched in cold water and opened. The reaction mixture was diluted with THF and precipitated into excess of hexane. The polymer was dried at room temperature in vacuum for at least 24 h, until a constant weight was obtained. The conversion of block copolymers P(S-*b*-BnMA-*b*-2-VP) was determined gravimetrically. The polymer molecular weight and MWD or PDI was determined by GPC.

Synthesis of P(S-co-p-CMS) Using NMP Method

The general procedure for the polymerization is as follows: styrene (3.7 mL, 32 mmol), *p*-chloromethyl styrene (*p*-CMS) (1.2 mL, 8.0 mmol), and TEMPO (0.0302 g, 0.10 mmol) were added to a dry glass tube. After the mixture was degassed

under vacuum, pure nitrogen gas was introduced into the tube, which was subsequently immersed in an oil bath thermostated at 120 °C. After a preset reaction time, the glass tube was immersed into cold water and opened, diluted with 10 mL of THF, and precipitated into 400 mL of methanol. The copolymer obtained by filtration was then dried under vacuum, at room temperature for 24 h. The polymer molecular weight and MWD or PDI was determined by GPC.

Synthesis of CDSTSP-Anchored P(S-co-p-CMS)

Poly(styrene-*co*-chloromethyl styrene) (0.7 g, \sim 0.87 mmol) was added to a RB flask containing 30 mL of THF and potassium carbonate (0.4501 g, 3.3 mmol), and the suspension was stirred gently for 10 min at room temperature. CDSTSP (0.656 g, 1.62 mmol) was dissolved in 20 mL of THF in a beaker and was then transferred to the RB flask. Tetra-*n*-butyl ammonium iodide (0.60 g, 1.62 mmol) was added to the RB flask, and the temperature was raised to 60 °C and maintained for 12 h. After cooling the reaction mixture, it was concentrated and then rinsed with water and acetone. The CTA-anchored polymer was redissolved in THF and precipitated in methanol. The yellow solid was dried under vacuum, at room temperature for 12 h.

Synthesis of P(S-co-p-CMS)-g-PS

Poly(styrene-*co-p*-chloromethyl styrene) macro-RAFT agent (0.02 g) and styrene (4 mL, 35 mmol) was added to a dry glass tube. After the mixture was degassed under vacuum, pure nitrogen gas was introduced into the tube, which was subsequently immersed in an oil bath thermostated at 110 °C. After 2 h, the glass tube was immersed into cold water, opened, diluted with THF, and precipitated into methanol. The graft copolymers obtained by filtration were then dried under vacuum, at room temperature for 24 h. The polymer molecular weight and MWD or PDI was determined by GPC.

Characterization

Molecular weights and MWD or the PDI of the polymers were determined by GPC measurements. GPC were performed at room temperature on a Water GPC system with Water 515 HPLC pump, three Phenomenox columns in series

TABLE 1 Data for the Polymerizations of Styrene with Dodecyl-Based Trithiocarbonate as CTAs in Bulk, at $100 \pm 2 \degree C$ ([Styrene]₀:[CTA]₀ = 400:1)

CTAs	Time (h)	% Conversion	<i>M</i> n (expected)	<i>M</i> n (GPC)	PDI
DPET	3.0	28.9	12,420	9,100	1.38
	9.0	47.3	20,100	14,900	1.42
	14.0	52.6	22,300	16,200	1.45
DCET	2.0	23.4	10,100	6,920	1.48
	4.0	30.1	13,200	10,940	1.37
	8.0	38.3	15,150	12,100	1.38
	10.0	46.6	22,560	15,550	1.39
DECET	2.0	23.1	10,000	7,830	1.38
	6.0	38.9	16,575	11,120	1.41
	12.0	49.5	21,000	18,300	1.43
CDSTSP	4.0	28.0	12,100	10,800	1.41
	8.0	36.5	15,600	14,400	1.41
	10.0	48.8	20,700	18,500	1.44

(guard column, 500, 10^3 , and 10^4 Å; 5 -µm particle size) and a "Waters" 2487 dual λ absorbance UV detector and 2414 RI detector with Empower software data analysis package supplied by Waters. THF was used as a solvent at a flow rate of 1 mL min⁻¹. Narrow molecular weight PS standards were used for calibrating the GPC. JASCO FTIR 410 (Japan) infrared spectrometer was used for recording IR spectra in the thin-film form (the polymer was cast on a CsCl disc from a dilute solution in THF). A Bruker AV 400 and 500 (400 and 500 MHz for proton) NMR spectrometer was used to record ¹H and ¹³C spectra and CDCl₃ was used as the solvent. Thermal analysis was performed using a TGA (TGA7 from Perkin Elmer, Q500 Hi-Res TGA from TA instruments), DSC (DSC7 from Perkin Elmer, Q200 MDSC from TA instruments) thermal analysis system between ambient and 800 °C, at a heating rate of 10 °C min^{-1} under flowing nitrogen atmosphere (50 mL min⁻¹).

RESULTS AND DISCUSSION

Synthesis of Monofunctional Trithiocarbonates

The dodecyl-based monofunctional trithiocarbonate CTAs were synthesized from dodecane thiol using the reported procedures as well as by following newer methods such as the use of potassium *t*-butoxide as base, in heptane-THF solvent mixture. The general synthetic procedure followed is given below in the form of Scheme 1. The list of CTAs synthesized is presented in Scheme 2. It is important to mention here that the synthesis of monofunctional dodecyl-based trithiocarbonate CTAs with different R groups (DPET, CDSTSP) have already been reported in literature^{49,50} but the synthesis of the aforementioned dodecyl-based monofunctional trithiocarbonates, BDT was formed as a byproduct. The CTA CDSTSP was synthesized by utilizing the previously reported procedure⁵¹ with slight modifications and the synthetic methodology is given in Scheme 1.

RAFT Polymerization of Styrene with Monofunctional Dodecyl-Based Trithiocarbonates

The thermal RAFT polymerization of styrene was carried out in bulk, at 100 \pm 2 °C, with dodecyl-based trithiocarbonate CTAs with various R groups and $[styrene]_0$: $[CTA]_0 = 400:1$. The ¹H NMR spectra of all the PS homopolymers showed signals at 3.25 ($-SC(S)SCH_2C_{11}H_{23}$) and 4.6-5.0 (-CH(Ph)SC(S)SC₁₂H₂₅) ppm, corresponding to the presence of active trithiocarbonate end functional groups. Further, it also demonstrated the presence of the reinitiating R group in all the cases suggesting that the initiation was by the thermal homolysis of the CTA than a Mayo type mechanism.³⁷ The ¹H NMR spectra of all the polymer samples are shown in Supporting Information Figures S6-S8. The expected molecular weight $(M_{n,ex})$ was calculated from the monomer conversion (which in turn was determined by the mass of the polymer formed), the initial ratio of the monomer to the CTA, the molecular weight of styrene $(M_{w,st})$ and the molecular weight of the CTA (M_{w.CTA}), as follows:

$$M_{\rm n,th} = [{\rm St}]_0 \times M_{\rm w,st} \times {\rm conversion}/[{\rm CTA}]_0 + M_{\rm w,CTA}$$

It is clear from the data presented in the Table 1 that the $M_{\rm n}$ (GPC) is less than $M_{\rm n}$ (expected) for all the polymerizations, and the PDI is between 1.37 and 1.48. This suggests that the polymerizations are not well controlled. It is also very clear from the Table 1 that, in CDSTSP-mediated thermal RAFT polymerization of styrene, the $M_{\rm n}$, GPC values are very close to the M_{n_i} expected values, in comparison with the other CTAs. The plots of number-average-molecular weight (M_n) versus monomer conversion are shown in Figure 1. As shown in Supporting Information S9, the M_n increases linearly with the monomer conversion. Although, before polymerization, high pure nitrogen was used to continuously purge each polymerization ampoule for at least 5-10 min and the CTA used for polymerization reaction were very pure in nature, the PDI values obtained are high. This suggests one of the following: that the initiation step is (not faster than propagation or even equal to it) slower than the propagation step or



FIGURE 1 Molecular weight versus monomer conversion for the thermal RAFT polymerization of styrene, in bulk, at 100 °C.



SCHEME 3 The mechanism of the thermal RAFT polymerization.

the initial stages of the polymerization proceed by conventional free radical polymerization and that controlled radical polymerization assumes significance after a certain degree of monomer conversion. The data for the CTAs DECT and DECET, which produce more reactive initiating radicals in comparison to DPET and CDSTSP CTAs, clearly suggest that the initial stages of monomer conversion is dominated by conventional free radical polymerization mechanism.

The $\ln([M_0]/[M_t])$ versus time of polymerization plots are shown in Supporting Information Figure S9. This suggests a first order dependence of the rate of polymerization with the concentration of the monomer, except during the initial stages of the polymerization. The curvature observed during the initial stages of the polymerization suggests that the polymerization might be taking place by the conventional free radical polymerization during the initial stages. During the initial stages of the polymerization, the monomer is present in very large excess in comparison to the CTA concentration and hence uncontrolled free radical addition might be taking place $(k_t^1 >> k_t^2 \text{ and } k_t^3)$ as shown in Scheme 3.

The apparent rate constant of propagation of styrene decreases in the following order CDSTSP ($k_{app} = 0.053 \text{ h}^{-1}$) > DCET ($k_{\rm app} = 0.042 \ {\rm h}^{-1}$) \sim DECET ($k_{\rm app} = 0.041 \ {\rm h}^{-1}$) ~DPET ($k_{app} = 0.037 \text{ h}^{-1}$). In the range of conversion studied at 100 °C, there is some induction period (during which the conventional free radical polymerization appears to be taking place) following which controlled radical polymerization assumes significance, for all the CTAs used here. Similar effect was observed in the RAFT polymerization of styrene (degree of polymerization = 50) mediated with 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid 3-azidopropyl ester as a CTA and AIBN as the initiator, in DMF at 70 °C, and the reason for the same was not addressed by the authors.⁵² The thermal RAFT polymerization of styrene, at 140 °C, mediated by DDMAT produces oligomers with low PDI value (PDI \sim 1.16) at higher conversion (\sim 75%).⁵ The analysis of the results reported here further indicates that induction period is the largest for DPET, which produces the most stable R radical, suggesting that the chain transfer constant may be the lowest in this case. Further, among the R groups (1-phenyl ethyl, 1-cyano ethyl and (2-ethoxy carbonyl) ethyl) investigated, there seems to be no specific and

significant role for them in terms of polymerization rate or control of polymerization as investigated for styrene monomer via thermal RAFT method at higher temperature. However in the case of 4-cyano pentanoic acid as the R group, the polymerization rate of styrene was higher compared to all the other R groups studied, and its homolysis appears to be best suited for the RAFT polymerization of styrene. Among the dodecyl-based CTAs, the 1-cyano ethyl (R group; DCET) gives polymers with low PDI compared to the others, whereas, in the case 4-cyano pentanoic acid R group (CDSTSP), the $M_{\rm n}$ GPC values are very close to the $M_{\rm n}$ expected values. The GPCs of the homopolymers as a function of the time of polymerization are shown in Supporting Information Figure S10. This suggests that the molecular weight increases with the time of polymerization for all the CTAs suggesting in turn the occurrence of controlled radical polymerization during the periods investigated.

It could be concluded from these studies that the thermal RAFT polymerization of styrene, initiated by the homolysis of the CTAs, did not proceed to the degree of control that was expected. This was perhaps due to the relatively slower rate of

TABLE 2 Data for the Polymerizations of Styrene with DCET and DPET as the CTAs and the Initiator, in Bulk at 150 ± 2 °C ([Styrene] 0:[CTA] 0 = 200:1)

CTAs	Time (min)	% Conversion	<i>M</i> n (expected)	<i>M</i> n (GPC)	PDI
DCET	30	32	6,300	3,600	1.20
	60	45	9,900	4,500	1.33
	90	53	11,300	5,500	1.26
	120	56	12,000	6,100	1.23
	150	64	13,600	6,900	1.29
	180	73	15,500	7,400	1.30
DPET	30	41	8,900	5,200	1.24
	60	49	10,600	5,900	1.29
	90	51	11,100	6,500	1.30
	120	58	12,500	7,100	1.31
	150	66	14,100	7,600	1.29
	180	72	15,300	8,400	1.41



FIGURE 2 Dependence of molecular weight versus monomer conversion (a), $ln([M]_0/[M]_t)$ versus time (b) for the thermal RAFT polymerization of styrene, using different CTAs in bulk at 150 °C.

initiation in comparison to the rate of propagation as well as due to competing conventional free radical monomer addition during the initial stages of the polymerization. To address this concern, the thermal properties of the CTAs were analyzed using TGA and DSC, under nitrogen atmosphere, to study the suitable temperature required to cleave the C-S bond. The TGA results are shown in Supporting Information Figure S11. This suggested that a temperature range 120–150 °C may be suitable for the initiation of the polymerization. The DSC studies did not indicate any other specific physical transitions in the CTAs, other than melting (where relevant, as shown in Supporting Information Fig. S12)

Based on the thermal RAFT polymerization results at 100 $^\circ\text{C}$ and the thermal analysis of the CTAs, which suggested that a

temperature range 120–150 °C may be appropriate for the homolysis of the CTAs, the thermal RAFT polymerization of styrene was performed at 150 °C, in the bulk, with DCET and DPET as the CTA for a [styrene] ₀: [CTA] ₀ ratio of 200:1. The monomer conversion and the polymer molecular weight and MWD were determined for various periods. The conversion data, molecular weight, and PDI are listed in Table 2.

It is very clear from the experimental data in Table 2 that the M_n (GPC) is less than M_n (expected) for the two CTAs (DCET and DPET) suggesting that the mechanism of thermal polymerization may not be very different from what was observed at 100 °C, that is, the occurrence of conventional free radical polymerization during the initial stages of the polymerization followed by the controlled radical



FIGURE 3 GPC traces of polystyrene obtained with increase in time of polymerization using CTAs DCET (a) and DPET (b) in bulk, at 150 °C.

TABLE 3 Data for the Polymerizations of Styrene with DSCPA, DCET, and DPET as CTAs and the initiator, in Bulk, at 140 °C (30-min Time Period) and at 90 \pm 2 °C ([Styrene]₀:[CTA]₀ = 200:1)

CTAs	Time (h) at 90 °C	% Conversion	<i>M</i> n (expected)	<i>M</i> n (GPC)	PDI
DCET	2.0	25	4,900	3,600	1.20
	3.0	29	6,400	4,700	1.27
	4.0	38	8,200	5,900	1.26
	5.0	45	9,700	7,100	1.28
	6.0	50	10,800	8,300	1.29
	7.0	58	12,400	10,100	1.35
DPET	2.0	37	8,100	6,000	1.32
	3.0	41	8,900	7,800	1.33
	4.0	48	10,400	9,900	1.21
	5.0	54	11,600	11,300	1.24
	6.0	60	12,900	12,300	1.28
	7.0	65	13,900	14,100	1.27
DSCPA	2.0	27	6,000	7,300	1.20
	3.0	34	7,400	9,500	1.18
	4.0	37	8,100	11,100	1.19
	5.0	40	8,700	12,900	1.24
	6.0	43	9,300	13,600	1.49
	7.0	48	10,400	15,100	1.61

polymerization. However, the PDI values are relatively less in comparison suggesting that higher temperature favors the chain initiation kinetics better than the chain propagation during the initial stages of the polymerization. The M_n (GPC) versus monomer conversion and the $ln([M]_0/[M]_t)$ versus time curves for these cases are shown in Figure 2(a,b). The linearity of the M_n GPC versus monomer conversion and the

 $\ln([M]_0/[M]_t)$ versus time, are both good indications of the controlled nature of the polymerization. The monomer conversion with time [Fig. 2(b)] suggests that the conventional free radical polymerization kinetics might be dominating the first 1 h of the polymerization while controlled polymerization kinetics starts beyond 1 h. The GPC traces of the polymers obtained as a function of time of polymerization are shown in Figure 3. The shifting of the peak maximum with time again suggests that the chain ends are active and that the polymerizations are controlled.

Based on the results of the thermal RAFT polymerization carried out at 100 and 150 °C and with the view to have greater control over the thermal RAFT polymerization of styrene, the initial part of the polymerization was carried out at higher temperature (140 °C) for shorter period while the later part of the polymerization was carried out at lower temperature (90 °C) for a relatively larger duration. Thus, the thermal RAFT polymerization of styrene was performed (for shorter duration at 140 °C and longer duration at 90 °C), as described earlier, in the bulk, with a [styrene]₀:[CTA]₀ of 200:1. The monomer conversion and the polymer molecular weight and MWD after various periods were determined and the same are listed in Table 3.

It can be seen from these data that the M_n (GPC) is less than M_n (expected) for the CTAs DCET and DPET although the difference appears to be very narrow in the case of DPET. The PDI remained narrow in most cases and is in the range 1.2–1.3. The plots of number-average-molecular weight (M_n) versus monomer conversion and $\ln([M]_0/[M]_t)$ versus time are shown in Figure 4(a,b). The linearity of the M_n GPC versus monomer conversion suggests that the polymerization proceeds in a controlled manner. The monomer conversion versus time plot [Fig. 4(b)] suggests that the thermal RAFT polymerization initiated by DPET proceeds without any induction time for controlled polymerization suggesting that



FIGURE 4 Dependence of molecular weight versus monomer conversion (a) $ln([M]_0/[M]_t)$ versus time (b) for the thermal RAFT polymerization of styrene, using different CTAS in bulk at 140 and 90 °C.



FIGURE 5 GPC traces of polystyrene obtained with increase in time of polymerization using CTAs (a) DSCPA (a), DCET (b), and DPET (c) bulk, at 140 and 90 °C.

the conditions identified are best suited for controlled polymerization of styrene. The GPC data for these polymerizations are shown in Figure 5. A control experiment was performed with another DSCPA as the CTA. The structure of DSCPA is similar to DCET in terms of radical stability and these results are also shown in Table 3 and Figure 5. These



SCHEME 4 Synthetic route followed for the preparation of diblock and triblock copolymers from the homopolymer of styrene via thermal RAFT polymerization at high temperature.



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Monomers	Macro-RAFT Agent	Time (h)	% Conversion	$M_{\rm n}$ (expected)	M _n (GPC)	PDI
BnMA	PS <i>M</i> _n = 4,200, PDI = 1.18	4.0	75	57,400	53,800 ^a	1.51
2-Vinyl pyridine	PS <i>M</i> _n = 4,200, PDI = 1.18	12.0	52	14,700	13,500	1.32
2-Vinyl pyridine	P(S- <i>b</i> -BnMA) <i>M</i> _n = 53,800, PDI = 1.51	11.0	43	61,200	59,900	1.58

TABLE 4 GPC Data for the Diblock and Triblock Copolymers of BnMA and 2-Vinyl Pyridine

 $^{\rm a}$ Molecular weight by MALDI-TOF = 52,800.

data (M_n (GPC) $< M_n$ (expected) and PDI increases with time) suggest that DSCPA could be a better CTA than DCET for the controlled radical polymerization of styrene.

Diblock and Triblock Copolymers

To demonstrate that the PS synthesized has active thiocarbonylthio end groups for chain extension two diblock copoly-



FIGURE 6 GPC traces of the polystyrene macro-RAFT agent and the diblock copolymers P(S-*b*-BnMA) and P(S-*b*-2-VP).

mers and one triblock copolymer were synthesized from the PS macro-RAFT agent as CTA using 2-vinyl pyridine and benzyl methacrylate monomers in bulk and in solution at 110 and 120 $^{\circ}$ C (Table 4). The thermal RAFT polymerization method used is shown in Scheme 4.

The GPC traces of the two block copolymers P(S-*b*-BnMA), P(S-*b*-2-VP), and triblock copolymer P(S-*b*-BnMA-*b*-2-VP) thus obtained are shown in Figures 6 and 7. This shows that the GPC traces of the block copolymers are shifted toward higher molecular weight while the MWDs are broad relative to the PS macro-RAFT agent. In the case of P(S-*b*-BnMA), the molecular weight is very high in comparison to P(S-*b*-2-VP), because the benzyl methacrylate monomer polymerizes faster compared to 2-vinyl pyridine, and this is also reflected by the lower PDI of the P(S-*b*-2-VP). The thermogravimetric analysis of the homopolymer and the diblock copolymer of P(S-*b*-BnMA) shows decomposition around 320 °C, corresponding to BnMA block and one from 370 to 460 °C, corresponding to the PS block (in Supporting Information Fig. S13).

Synthesis of Graft Copolymers on P(S-co-p-CMS) Side Chains via RAFT Method

The utility of the thermal RAFT polymerization toward the synthesis of graft copolymers was also explored as shown in Scheme 5. Thus, the random copolymer P(S-*co*-*p*-CMS) was obtained via NMP with the $M_{n,GPC}$ value of 17,800 and the PDI value of 1.44. The ¹H NMR spectrum of this polymer confirms its structure (data shown in Supporting Information



FIGURE 7 GPC traces of the polystyrene, P(S-*b*-BnMA) macro-RAFT agent, and the triblock copolymer P(S-*b*-BnMA-*b*-2-VP).



SCHEME 5 Synthesis of graft copolymers via RAFT polymerization from P(S-co-p-CMS).

Fig. S14; the chemical shift at 4.5 ppm is characteristic of chloromethyl protons (CH₂Cl) in *p*-CMS unit. The molar ratio (F) of S to p-CMS in P(S-co-(p-CMS)) was calculated from the results of ¹H NMR, and the F value was found to be 6.3:1. In addition to that, it was found that \sim 22 *p*-CMS units are present in a single random copolymer chain). The CTA CDSTSP was anchored onto P(S-co-(p-CMS)), and the structure of the same was confirmed by ¹H NMR spectrum (data shown in the Supporting Information Figure S15; The peak seen at 5.0 ppm is characteristic of -(CO)OCH₂Ph protons in P(S-co-p-CMS). From the ¹H NMR, it was concluded that \sim 4.6 RAFT agents were anchored on a single P(S-co-p-CMS). The thermal RAFT polymerization of styrene, in bulk, was performed with the help of the CTA-anchored P(S-co-p-CMS). The resulting P(S-co-p-CMS)-g-PS shows bimodal distribution in the GPC analysis with the $M_{n,GPC}$ value of 1,13,000 and the PDI value of 1.26. The bimodal nature of the graft copolymer obtained may be, because of the chloromethyl group's chain transfer effect. However, for styrene graft copolymer synthesis, performing RAFT polymerization in solvent medium or using azo initiator for the initiation process can lower the PDI value. As the chain transfer constant value for the R group, 4-cyano pentanoic acid is high for all types of monomers, this methodology can be utilized for anchoring functional group containing acrylic or methacrylic monomers directly on styrenic surface under suitable reaction conditions. The GPC traces of P(S-co-p-CMS) and P(S-co-p-CMS)-g-PS are given in Supporting Information Figure S16.

CONCLUSIONS

The thermal RAFT polymerization of styrene was investigated using a series of dodecyl-based monofunctional trithiocarbonate CTAs, which act both as the initiator (by thermal homolysis) and the CTA. These data suggest that it should be possible to control the RAFT polymerization initiated by the CTA by adjusting the temperature of polymerization in such manner that initiation is tailored to proceed at faster rate (at higher temperature) in comparison to propagation (lower temperature). This opens up the automation route for the RAFT polymerization of a monomer by a CTA, provided a suitable temperature for initiation and duration of initiation is identified. Thus, suitable initiation followed by lowering

the temperature for propagation and extending the duration of propagation should in principle result in the synthesis of polymers in a controlled manner. This in principle should also enable the scaled up synthesis of block copolymers of complex architecture through suitable programming of the polymerization temperature, duration, and automatic injection of monomers at the set intervals. For the specific CTAs studied in this work, the polymerization rate of styrene was high in the case of the reinitiating group 4-cyano pentanoic acid (R group) compared to the other groups studied. The results further show that 4-cyano pentanoic acid group is superior to the other R groups used for the RAFT polymerization of styrene, especially based on the polydispersity at a given conversion as well as the variation in the expected and experimental number-averagemolecular weights. The suitability of the method is demonstrated through the synthesis of diblock, triblock, and graft copolymers by the thermal RAFT polymerization method.

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