Substituent Effects on Trithiocarbonates-Mediated Polymerization of Styrene

Rong Ran, Zhi Chen, Xiao Long Wang

College of Polymer Science and Engineering, State Key Lab for Polymer Materials Engineering, Sichuan University, Chengdu 610065, People's Republic of China

ABSTRACT: In the present work, the effectiveness of five trithiocarbonates (TTCs) as mediating agents in the reversible addition fragmentation chain transfer (RAFT) polymerization and photopolymerization of styrene (St) were investigated. The five TTCs including S,S'-bis(α, α'-dimethyl-α''-acetic acid) trithiocarbonate (TTC1), bis(2-oxo-2-phenyl-ethyl) trithiocarbonate (TTC2), 3-(2-carboxyethylsulfanylthiocarbonylsulfanyl)-propionic acid (TTC3), 2-(2-carboxyethylsulfanylthiocarbonylsulfanyl)propionic acid (TTC4), and 2-(2-carboxyethylsulfanylthiocarbonylsulfanyl)-2-methylpropionic acid (TTC5) were synthesized, in which the substitution patterns (groups Z and R) of the TTCs were varied. The dynamic behavior of TTC1, TTC2, TTC4, and TTC5-mediated polymerization of St was well described by pseudo first-order kinetics. In the presence of TTC1, TTC2, TTC4, and TTC5, the polydispersity indices changed with increasing conversion in the range of 1.10–1.25 typical for RAFT-prepared (co)polymers, and were well below the theoretical lower limit of 1.50 for a normal free radical polymerization. Transfer coefficients of TTCs in St polymerization at 70°C were estimated by using the Mayo method. Density functional theory calculations successfully predicted the effect of the structure of TTCs on the activity of RAFT agents in a qualitative manner. The calculated results for RAFT agents agreed well with the experimental results. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2011–2017, 2009

Key words: trithiocarbonate; controlled polymerization; photopolymerization; styrene; density functional theory

INTRODUCTION

In the recent years, controlled/living free radical polymerization has become increasingly important in the field of polymer science in terms of both academic research and industrial application. Up to now, four ways to manipulate the free radical polymerization have been investigated: initiation-transfer-termination (iniferter),[1] nitroxide-mediated polymerization,[2] atom transfer radical polymerization (ATRP),[3] and reversible addition fragmentation chain transfer (RAFT) process.[4–7] Among the aforementioned approaches, RAFT technique is a well-known strategy for the controlled/living radical polymerization and has been extensively investigated because of its numerous monomers available under various conditions. RAFT process involves, as the key step, reversible addition-fragmentation chain transfer. With an appropriate choice of the RAFT agent and reaction conditions, RAFT polymerization can be successfully used to produce narrow polydispersity (co)polymers with controlled molecular weights and architectures.

In the RAFT polymerization, the commonly used thiocarbonylthio chain transfer agents (CTAs) are dithioester and trithiocarbonate (TTC).[6–9] Rizzardo and coworkers[10,11] have reported that the effectiveness of thiocarbonylthio RAFT agents strongly depends on the nature of the groups Z and R (Scheme 1), the monomer, and the polymerization conditions. The influence of the nature of the groups Z and R on the effectiveness of dithiobenzoate derivatives as RAFT agents was detailed in these references. Currently, TTC has attracted great attention because of its ease of synthesis and purification, especially useful for the controlled polymerization of styrene, acrylate, and acrylamide monomers and their derivatives under extremely facile conditions. However, the effect of the structure of TTCs such as groups Z and R on the activity of RAFT agents and general conclusions of the relative effectiveness of various TTCs RAFT agents in promoting living radical polymerization have still not been reported.

Research has been done on computational calculations to design effective RAFT agents. It was reported that computational quantum chemistry has been applied to calculate the properties of the ground states of a series of RAFT agents.[10–12] Already computational calculations have helped to provide an insight into structure–reactivity patterns
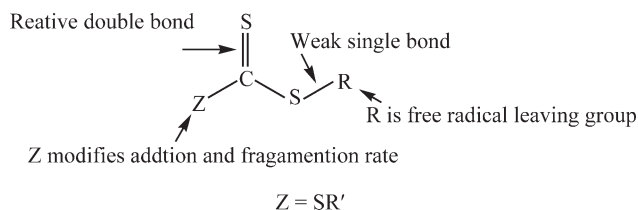
Scheme 1 Structure of RAFT agent.

in RAFT polymerization and have led to the design of a new class of RAFT agents. Moreover, computational chemistry has also made contributions to understanding of other controlled radical polymerization processes, such as ATRP,[13–15] RAFT[12,16] and iniferter.[17] Matyjaszewski and coworkers[13–15] have recently reported that the values of the absolute and relative equilibrium constants of the dissociation of alkyl (pseudo)halides (R-X) with structures relevant to dormant/propagating species in ATRP and bond dissociation energies of a variety of dithioacetates relevant to RAFT systems have been calculated using density functional theory. Ishizu et al.[17] demonstrated that density functional theory calculations provide a reliable and quantitative prediction of the trends in C—S bond dissociation energies for several model compounds such as photoinitiator.

In our previous research,[18,19] we studied the free radical polymerization of styrene and butyl acrylate in the presence of TTC and found that polymerization demonstrated controlled/living characteristics. Particularly, the controlling properties of TTC1 and TTC2 were investigated and compared using the density functional theory calculations. In the present work, we further determined the relationship between chemical structures of TTCs and their roles on controlling of polymerization. In addition, TTC

RAFT reagents were synthesized and used for the polymerization of styrene, initiated by AIBN and photoinitiation. The chain transfer constants of the TTCs were determined by the Mayo method. Density functional theory calculations are used to predict the effect of the five TTCs using five model compounds as RAFT reagents. The controlling properties of the TTCs were studied and compared with the prediction by density functional theory calculations. It was demonstrated that the results of calculations for RAFT agents precisely agreed with the experimental results. Prior to this work, there are no reports of systematic evaluation of TTCs available in which the nature of the substituents (Z and R groups) are varied by using density functional theory calculations.

EXPERIMENTAL

Materials

Styrene (St) (Shanghai Chemical Co., Shanghai, China; AR) was passed through a column of activated basic alumina (50–200 μm) to remove the inhibitor. Tetrahydrofuran (THF) and carbon disulfide were of analytical grade and used after purification. Anionic exchange resin 717 (Shanghai Resin), sodium hydroxide, chloroform, acetone (Shanghai Chemical Co.; AR), 2-bromoacetophenone, and α-hydroxy isobutyryl benzene (Darocure 1173; Acros Organics Co.) were used as received.

Synthesis of S,S′-bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (TTC1)

The structure of TTC1 is shown in Scheme 2. TTC1 was prepared according to Ref. 9. After recrystallization
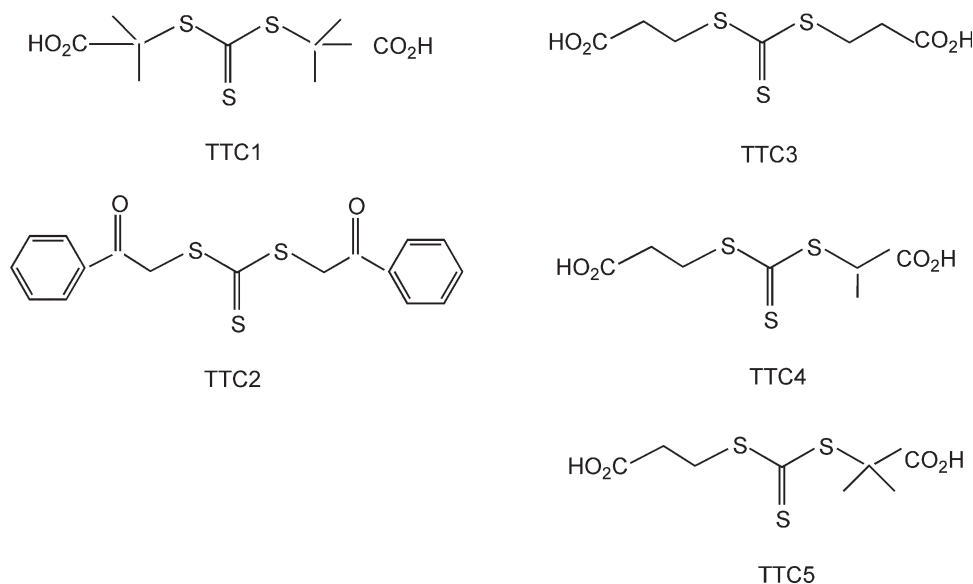
Scheme 2 Structures of trithiocarbonates.

in ethanol, the yellow product was obtained. Yield: 62.1%; mp.: 172–175°C. ^{1}H NMR (δ): 12.01 (s, ─COOH), 1.669 (s, 12H, ─CH$_3$); IR (KBr): $\nu_{(O-H)}$ 3426.66 cm^{-1}, $\nu_{(C-H)}$ 2955.71 cm^{-1}, 2918.17 cm^{-1}, 2851.09 cm^{-1}, $\nu_{(C=O)}$ 1700.59 cm^{-1}, $\delta_{(C-H)}$ 1468.83 cm^{-1}, $\nu_{(C-S-C)}$ 1286.45 cm^{-1}, $\nu_{(C=S)}$ 1063.80 cm^{-1}.

Synthesis of bis(2-oxo-2-phenyl-ethyl) trithiocarbonate (TTC2)

The structure of TTC2 is shown in Scheme 2. TTC2 was synthesized according to Ref. 19. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 4.92 (s, 4H, ─CH$_2$─), 7.4–8.0 (m, 10H, 2 aromatic H). Calcd. for C$_{17}$H$_{14}$S$_3$O$_2$: C, 58.92; H, 4.07; S, 27.77. Found: C, 59.11; H, 4.39; S, 25.97.

Synthesis of 3-(2-carboxyethylsulfanylthio-carbonylsulfanyl) propionic acid (TTC3)

The structure of TTC3 is shown in Scheme 2. TTC3 was prepared according to Ref. 20. Yield: 43.67%; mp.: 109–116°C. ^{1}H NMR (400 MHz, DMSO), (δ): 2.55, (t, 4H, ─CH$_2$─COOH), 3.50 (t, 4H, ─S─CH$_2$─), 12.5 (S, 2H, ─COOH).

Synthesis of 3-(2-carboxyethylsulfanylthio-carbonylsulfanyl) propionic acid (TTC4)

The structure of TTC4 is shown in Scheme 2. TTC4 was prepared according to Ref. 20. Yield: 41.02%; mp.: 123–126.5°C. ^{1}H NMR (400 MHz, DMSO), (δ): 1.52 (d, 3H, ─CH(CH$_3$)─COOH), 2.69 (t, 2H, HOOC─CH$_2$─), 3.55(t, 2H, ─CH$_2$─S), 4.70 (d, H, ─CH(CH$_3$)COOH), 12.7 (s, 2H, ─COOH).

Synthesis of 3-(2-carboxyethylsulfanylthio-carbonylsulfanyl) propionic acid (TTC5)

The structure of TTC5 is shown in Scheme 2. TTC5 was prepared according to Ref. 20. After recrystallization in ethanol, the yellow product was obtained. Yield: 10.04%; mp.: 178.5–182.5°C. ^{1}H NMR (400 MHz, DMSO), (δ): 1.62 (s, 6H, S─C(CH$_3$)$_2$─COOH), 2.64 (t, 2H, HOOC─CH$_2$─), 3.45 (t, 2H, HOOC─CH$_2$─CH$_2$─S─), 12.7 (s, 2H, ─COOH).

Polymerization in the presence of TTC

The polymerization was carried out in a 5-mL ampoule. The ampoule was filled with 2.0 mL monomer, TTC, and AIBN, and then flame-sealed after being bubbled with N$_2$ for 10 min to eliminate oxygen and the ampoules were immersed in a preheated oil bath at 70°C. After a predetermined time, the ampoule was opened and the reaction mixture was diluted with THF. The polymer was precipitated in a 10-fold excess of methanol (or ethanol),

recovered by filtration, and finally dried at 55°C in a vacuum until it reached a constant weight. Conversions were determined gravimetrically, and the polymerization was monitored using NMR and GPC.

Photopolymerization in the presence of TTC

The photopolymerization was also carried out in a 5-mL ampoule. The ampoule was filled with 2.0 mL monomer, TTC, and Darocure 1173, and then flame-sealed after being bubbled with N$_2$ for 10 min to eliminate oxygen, followed by UV irradiation at room temperature, with the light source of 18-W four black lamps and a distance of 4.0 cm from lamp to sample. After a predetermined time (about 15 h), the ampoule was opened and the reaction mixture was diluted with THF. A similar procedure was performed as described in the previous subsection.

Density functional theory calculations

To design the RAFT reagents, we performed density functional theory calculations (B3LYP functional using the 6-31G-(d) basis set) for the model compounds TTC1–TTC5. The C─S bond energies were calculated assuming a homolytic bond cleavage corrected with zero-point energy. Details concerning the calculations have been given elsewhere.[17]

Characterizations of polymers

The molecular weight M_n and the molecular weight distribution (MWD) were measured on a Agilent 1100 gel permeation chromatography (GPC) equipped with Pl gel column, mono-dispersed PSt as standard, and THF (1.0 mL/min) as eluent. ^{1}H NMR spectra was analyzed on a Varian Unity Inova 400 instrument with CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. Melting points of TTCs were measured on an X4 Melting Point Microscope Instrument.

RESULTS AND DISCUSSION
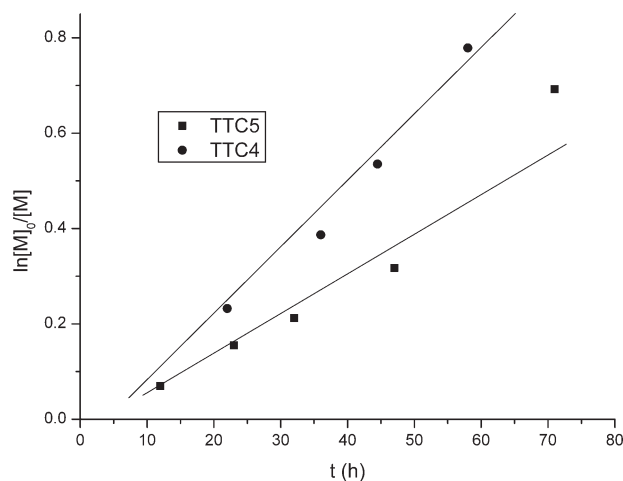
Styrene polymerization in the presence of TTCs

To examine the effect of the TTC structure on RAFT polymerization, styrene polymerizations in the presence of RAFT agents TTC1–TTC3 were carried out in bulk at 70°C with AIBN as initiator. Figure 1 shows the pseudo first-order kinetic plots which pass through the origin. Figure 2 shows the M_n and M_w/M_n versus conversion profiles for TTC1–TTC3. The molecular weight data for TTC3 is not similar to other TTCs because no control was observed. The molecular weight feature of polymerization in the presence of TTC3 is more closely associated with
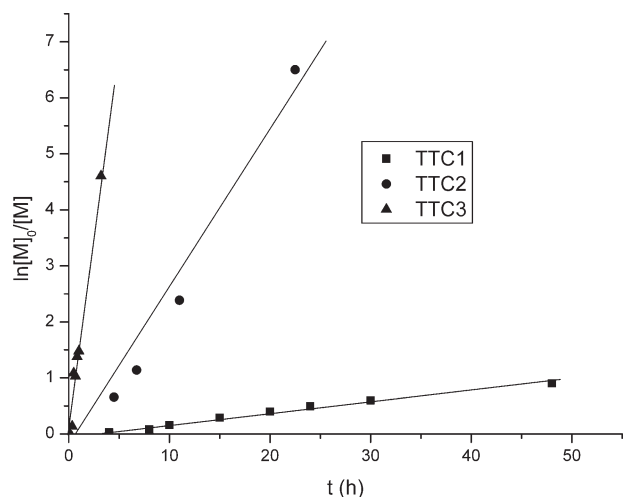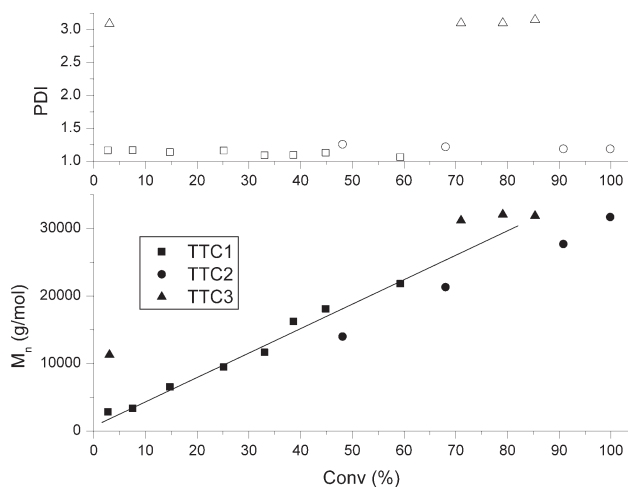
Figure 1 Plots of $\ln[M]_0/[M]$ versus time of styrene polymerization in bulk initiated with AIBN, in the presence of different trithiocarbonates at 70°C ($[St]_0 : [TTC]_0 : [AIBN]_0 = 1000 : 2 : 1$).

Figure 3 Plots of $\ln[M]_0/[M]$ versus time of styrene photopolymerization in bulk initiated with Darocure 1173, in the presence of different trithiocarbonates at room temperature ($[St]_0 : [TTC]_0 : [1173]_0 = 2000 : 10 : 1$).

conventional free radical polymerization behavior. In contrast to TTC3, TTC1 and TTC2 are effective mediating agents, yielding homopolymers with both molecular weight control and low polydispersity indices (PDIs).

Styrene photopolymerizations in the presence of RAFT agents TTC4–TTC5 were carried out in bulk and initiated by UV at room temperature using Darocure 1173 as initiator. Figure 3 shows the pseudo first-order kinetic plots for TTC4–TTC5, in which an induction period of 5 h is observed. Such induction periods are common in dithioester-mediated RAFT systems.[21–25] Indeed, the kinetic profiles of the TTCs are all similar, indicating that experimentally there is

apparent first-order dependence on monomer conversion. From a purely kinetic stand-point all the RAFT agents perform equally well, at least under the initially screened conditions. Besides, the M_n and M_w/M_n versus conversion profiles for TTC4–TTC5 were demonstrated in Figure 4. These results also demonstrated the linear evolution of the number-average molecular weight with conversion, and the PDIs changed with increasing conversion in the range of 1.10–1.25 typical for RAFT-prepared (co)polymers and were well below the theoretical lower limit of 1.50 for a normal free radical polymerization. These results were consistent with controlled/"living" polymerizations and also demonstrated that TTC4 and TTC5 were effective mediating agents.
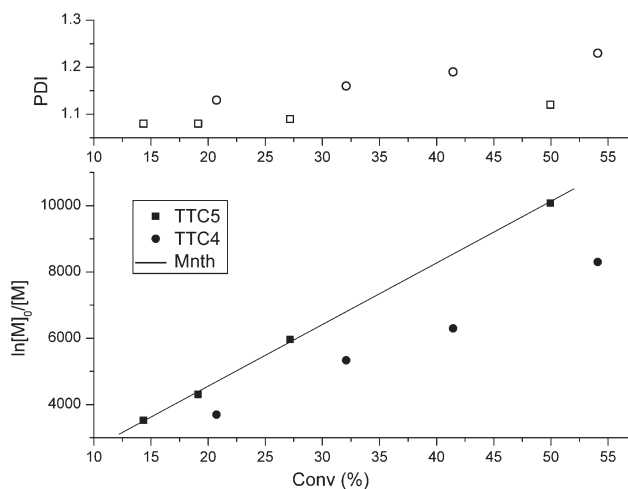

Figure 2 Relationships of M_n, PDI with conversion of styrene polymerization in bulk initiated with AIBN, using different trithiocarbonates at the same conditions given in Figure 1.

Figure 4 Relationships of M_n, PDI with conversion of styrene photopolymerization in bulk initiated with Darocure 1173, in the presence of different trithiocarbonates at room temperature. Conditions are same as Figure 3.
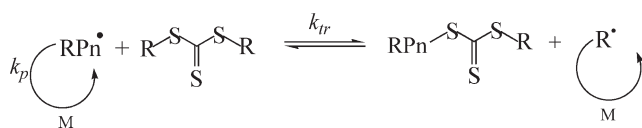
**Scheme 3** Reversible transfer in RAFT polymerization.

Transfer coefficient estimation

In RAFT reaction systems, a conventional radical initiator is needed together with the specific transfer agent known as RAFT agent. The activation process is based on a reversible chain transfer reaction between an active macromolecule and a RAFT agent, leading to the exchange of the ω-end group (Scheme 3). To achieve control, the transfer coefficient of the RAFT agent is required to be more than 1.5.[26]

The Mayo eq. (1)[27] may be used to estimate the transfer coefficients of transfer agents in circumstances where the consumption of transfer agents and monomer are negligible. For the case of TTCs, these conditions are easily met in low conversion polymerizations.

$$\frac{1}{DP} = \frac{(1+D)k_t[M^{\bullet}]}{k_p[M]} + C_M + C_s\frac{[S]}{[M]} \qquad (1)$$

Equation (1) [M], [M·], and [S] shows the concentrations of monomer, radical, and solvent. DP is the degree of polymerization, D is the coefficient of termination by disproportionation, and C_s is the transfer coefficient of the solvent. The first term on the right-hand side and the second term is the reciprocal degree of polymerization in the absence of a solvent $(\overline{X_n})_0$. Making this substitution, we arrive at the simple expression of eq. (2).
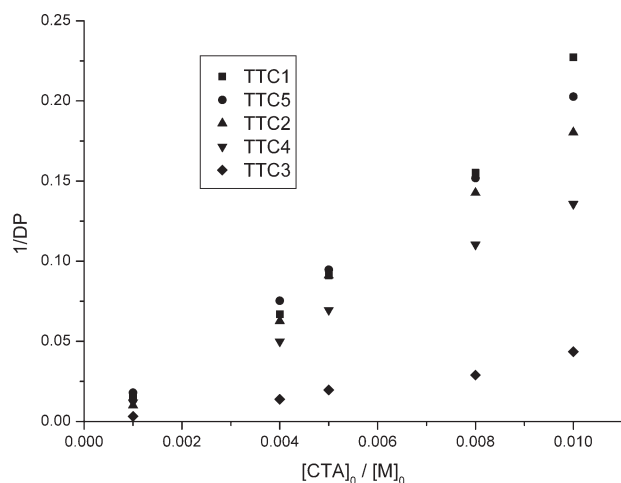
Figure 5 Mayo plots for the determination of the chain transfer constant of different trithiocarbonates in bulk styrene polymerization initiated with AIBN at 70°C.

TABLE I
Chain Transfer Constant of Trithiocarbonate for Polymerization of Styrene

Trithiocarbonate	C_{tr}
TTC1	23.2
TTC2	19
TTC3	4.32
TTC4	13.9
TTC5	20.2

$$\frac{1}{DP} = \frac{1}{(\overline{X_n})_0} + C_s\frac{[S]}{[M]} \qquad (2)$$

The transfer constant is easily evaluated; it represents the slope of the line obtained by plotting the reciprocal of the degree of polymerization (after a small extent of reaction) against the ratio of solvent (or CTA) to monomer concentrations (Fig. 5).

We have used this method to estimate transfer coefficients of TTCs in St polymerization at 70°C. The transfer coefficients of TTCs based on the Mayo equation were reported in Table I.

The chain transfer coefficients decrease in the series TTC1 > TTC5 > TTC2 > TTC4 > TTC3. TTC1, TTC5, TTC2, and TTC4 have transfer coefficients in St polymerization of more than 10. TTC3 appears relatively ineffective in St polymerization because it has much lower transfer coefficients (4.32).

## Density functional theory calculation results

We indicated that for TTC1 to TTC5, variation in the reactivity of the C=S toward free radical addition should be small and the magnitude of the transfer coefficient should be dependent primarily on the structure of TTCs. To provide a qualitative assessment of the effect of the structure on the transfer coefficient, we calculated the C—S bond dissociation energies, bond lengths of TTC1 to TTC5, and atomic spin densities for corresponding radicals produced using density functional theory calculations. These data are provided in Table II. Figure 6 shows the

TABLE II
Results of Density Functional Theory for Model Trithiocarbonates Calculated Assuming a Homolytic Bond Cleavage at 3LYP/6-31G(d) Corrected With Zero-Point Energy

Trithiocarbonates	C—S BDE (kJ/mol)	C—S bond length (Å)	Atomic spin densities for radicals
TTC1	179.23	1.865	0.8521
TTC2	216.27	1.836	0.8991
TTC3	246.86	1.833	1.1796
TTC4	201.25	1.864	0.9447
TTC5	134.22	1.899	0.8521

BDE, bond dissociation energies.
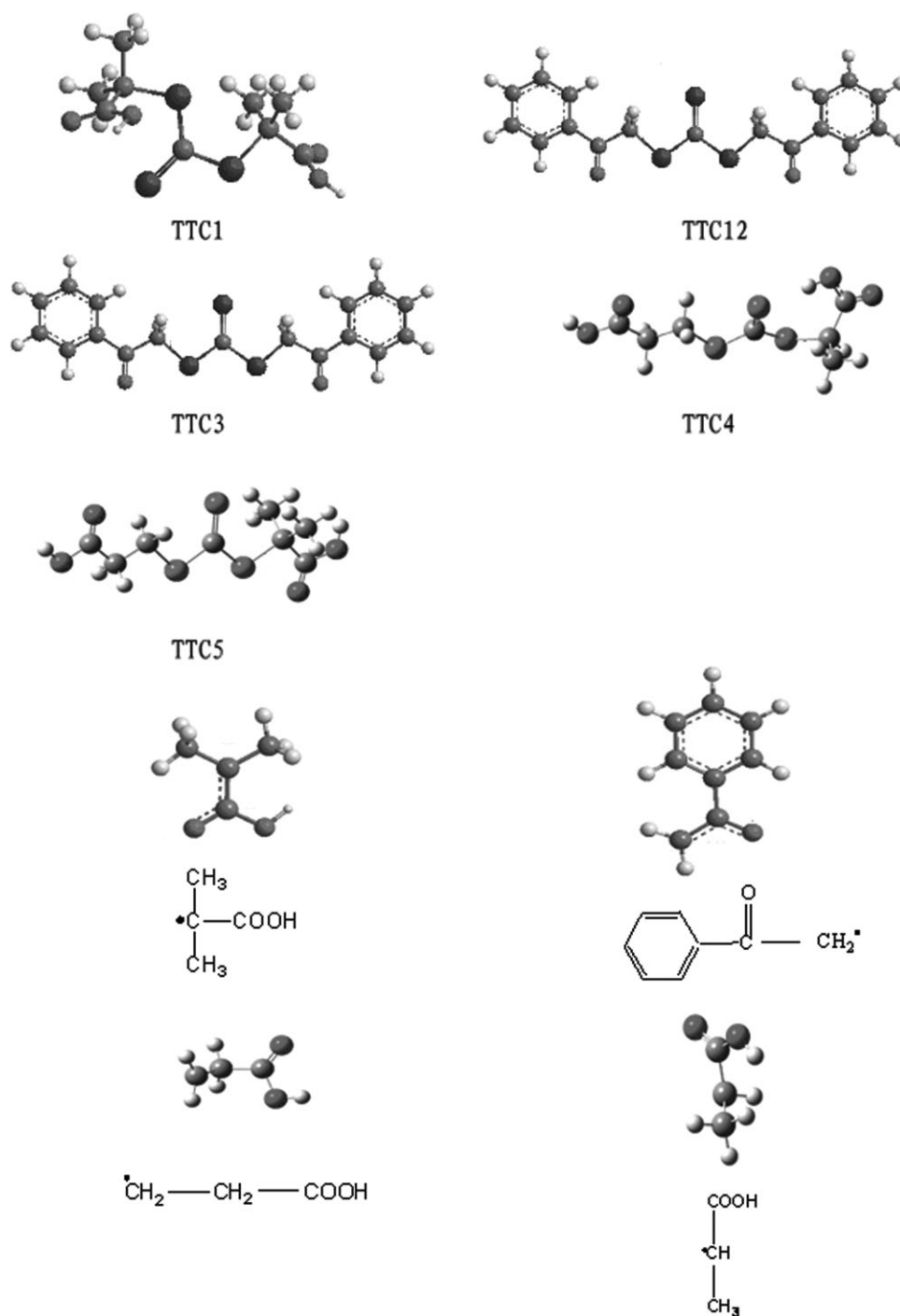
Figure 6 Views of the optimized geometries for trithiocarbonates and radical.

optimized geometries of the structure of five TTCs and radicals.

Steric factors are important in determining bond dissociation energies. It can be anticipated that this should be reflected in longer lengths for the broken C—S bond in the ground state for which steric factors are greater. It can be found that the stability of radical decrease $C(CH_3)_2COOH > \sqrt{}CH_2COC_6H_5 > \sqrt{}CH(CH_3)COOH > \sqrt{}CH_2CH_2COOH$ is due to the steric, polar, and spin delocalization factors. On the other hand, the total atomic spin density at the C1 atom (Table II) was calculated to be slightly higher CH_2CH_2COOH (1.1796) $> \sqrt{}CH(CH_3)COOH$ (0.9447) $> \sqrt{}CH_2COC_6H_5$ (0.899) $> \sqrt{}C(CH_3)_2COOH$ (0.852). Our results allow us to conclude that a radical with the larger atomic spin density of the C1 atom has shorter lifetimes and consequently larger reactivity. The effects of the five TTCs on the controlled polymerization predicted by these data increase in the following order: TTC3 < TTC4 < TTC2 < TTC1 ≈ TTC5.

In styrene polymerization, we found that the transfer coefficient decreases in the series TTC1 > TTC5 > TTC2 > TTC4 > TTC3 (see Table I) as the steric factors of R or Z groups become greater. The results validate the trends with bond dissociation energies seen with the density functional theory calculations.

CONCLUSIONS

The polymerizations and photopolymerizations of styrene with TTCs (TTC1–TTC5) as RAFT agent were investigated. In the polymerizations, the observed linear relationship in the pseudo first-order rate plot for TTC1, TTC2, TTC4, and TTC5-mediated polymerization of St, in conjunction with the linear increase of M_n versus conversion, confirms the living characteristics. For TTC1 and TTC5 the molecular weights of PSt obtained from GPC agree with the theoretical molecular weights [M_n (th.)], indicating that the molecular weights of PSt can be well controlled by the ratio of monomer consumed to TTC1 and TTC5. The measured PDIs (M_w/M_n) are very low and decrease with conversion. However, the radical system initiated by TTC2 and TTC4 showed less living polymerization characteristics consistent with the lower molecular weight than predicted. TTC3 was shown to be ineffective. In styrene polymerization at 70°C, transfer coefficients of TTCs were estimated by using Mayo method. The results showed that the transfer coefficient increases in the series TTC3 > TTC4 > TTC2 > TTC5 > TTC1 as the steric factors of R or Z groups become greater. The density functional theory calculations for RAFT agents supported such experimental data.

References

1. Otsu, T.; Matsunaga, T.; Kuriyama, A.; Yoshioka, M. Eur Polym J 1989, 25, 643.
2. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 2987.
3. Wang, J. S.; Matyjaszewski, K. Macromolecules 1995, 28, 7901.
4. Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559.
5. Chong, Y. K. B.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1999, 32, 2071.
6. Rizzardo, E.; Chiefari, J.; Mayadunne, T. A. R.; Moad, G.; Thang, S. H. Polym Prepr (Am Chem Soc Div Polym Chem) 1999, 2, 342.
7. Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, A. H. Macromolecules 2000, 33, 243.
8. Hong, J.; Wang, Q.; Lin, Y. Z.; Fan, Z. Q. Macromolecules 2005, 38, 2691.
9. Lai, J.; Filla, T. D.; Shea, R. Macromolecules 2002, 35, 6754.
10. Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. Macromolecules 2003, 36, 2256.
11. Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. Macromolecules 2003, 36, 2273.
12. Coote, M. L. Macromolecules 2004, 37, 5023.
13. Gillies, M. B.; Matyjaszewski, K.; Norrby, P. O.; Pintauer, T.; Poli, R.; Richard, P. Macromolecules 2003, 36, 8551.
14. Matyjaszewski, K.; Poli, R. Macromolecules 2005, 38, 8093.
15. Lin, C. Y.; Coote, M. L.; Petit, A.; Richard, P.; Poli, R.; Matyjaszewski, K. Macromolecules 2007, 40, 5985.
16. Coote, M. L.; Elizabeth, H. K.; Ekaterina, I. I. Macromol Rapid Commun 2006, 27, 473.
17. Ishizu, K.; Khan, R. A.; Ohta, Y.; Furo, M. J Polym Sci Part A: Polym Chem 2004, 42, 76.
18. Rong, R.; You, Y.; Tao, W. J Appl Polym Sci 2007, 105, 398.
19. Rong, R.; Tao, W.; Tao, G.; Jian, G.; Zhi, C. Polym Int 2008, 57, 28.
20. Ran, W.; McCormick, C. L.; Andrew, B. L. Macromolecules 2005, 38, 9518.
21. Donovan, M. S.; Sanford, T. A.; Lowe, A. B.; Sumerlin, B. S.; Mitsukami, Y.; McCormick, C. L. Macromolecules 2002, 35, 4570.
22. McCormick, C. L. Macromolecules 2001, 34, 6561.
23. Donovan, M. S.; Sumerlin, B. S.; Lowe, A. B.; McCormick, C. L. Macromolecules 2002, 35, 8663.
24. Quinn, J. F.; Barner, L.; Barner-Kowollik, C.; Rizzardo, E.; Davis, T. P. Macromolecules 2002, 35, 7620.
25. You, Y. Z.; Hong, C. Y.; Bai, R. K.; Pan, C. Y.; Wang, J. Macromol Chem Phys 2002, 203, 477.
26. Muller, A. H. E.; Zhuang, R.; Yan, D.; Litvenko, Cz. Macromolecules 1995, 28, 4326.
27. Mayo, F. R. J Am Chem Soc 1943, 65, 2324.