Reversible Addition–Fragmentation Chain Transfer Polymerization of Styrene Using a Novel Thiophene Dithioester as the Reversible Addition–Fragmentation Chain Transfer Agent

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ABSTRACT: Benzyl thiophene-2-carbodithioate and 2-methyl-2-(4-methylcyclohex-3-enyl)propyl thiophene-2-carbodithioate were synthesized. The reversible addition–fragmentation chain transfer polymerizations of styrene with benzyl thiophene-2-carbodithioate and 2-methyl-2-(4-methyl-cyclohex-3-enyl)propyl thiophene-2-carbodithioate as chain-transfer agents and with 2,2'-azobisisobutyronitrile as an initiator were carried out. The polymerization kinetics were investigated. An *ab initio* calculation method was used to explore the differences between benzyl thiophene-2-carbodithioate and benzyl benzodithioate. The structure of the obtained polymers was characterized with ^{1}H-NMR. Chain-extension experiments of the obtained polymer with styrene were carried out. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2357–2362, 2007

Key words: functionalization of polymers; living polymerization; polystyrene; radical polymerization

INTRODUCTION

Research in the field of controlled/living radical polymerizations (LRPs) has increased significantly over the last few decades.[1,2] LRP can give control of polymer architectures similar to that observed with more drastic systems (complex experimental procedures and limited polymerizable monomers) such as living anionic polymerization, living cationic polymerization, and coordination polymerization. To date, the major processes of LRP are nitroxide-mediated polymerization (NMP),[3] atom transfer radical polymerization (ATRP),[4] and reversible addition–fragmentation chain transfer (RAFT) polymerization.[5,6] RAFT polymerization appears to be the most versatile process in terms of the reaction conditions, the variety of monomers for which polymerizations can be controlled,[7–9] the tolerance to functionalities,[10–12] and the range of polymeric architectures that can be produced.[13–15]

The simplified RAFT process mechanism is depicted as commonly accepted in the literature[16,17] in Scheme 1. The structures of R and Z groups have a great effect on the properties of the RAFT agent. Some good research articles have shown detailed results.[18,19] Furthermore, the structures of R and Z in the RAFT agent exist in the end part of the final polymer after the polymerization. In this manner, the polymer's end group can be predesigned through the selected structures of the RAFT agent. Our group has reported the successful synthesis of 1,3-benzodioxole-, anthracene-, and pyrene-end-capped polymers via RAFT polymerization.[20–22]

Thiophene is a very useful group in the preparation of conducting polymers, such as polythiophene, which has attracted much interest because of its wide range of practical applications in several areas such as rechargeable batteries,[23,24] sensors,[25,26] light-emitting diodes,[27,28] optical displays,[29,30] and electrochromic devices.[31] However, the poor physical and mechanical properties have limited its practical applications.[32] The syntheses of conducting polymer composites and graft and block copolymers have been shown to be effective ways of compensating for certain deficiencies of conducting polymers, such as

Scheme 1 Simplified RAFT process commonly accepted in the literature.

poor mechanical and physical properties. A number of techniques for the preparation of polymers with desired end groups have been developed, such as the functional initiator approach,[33] ATRP,[34] and NMP.[35]

In this study, two novel thiophene dithioesters were synthesized and used as RAFT agents to carry out styrene RAFT polymerizations. Polymers end-labeled with thiophene were successfully prepared, and this provides a powerful tool for the synthesis of vinyl and thiophene block copolymers to improve the properties of polythiophene.

EXPERIMENTAL

Materials

All chemicals (analytical-grade) used in this study were purchased from Shanghai Chemical Reagents Co., Ltd. (Shanghai, China), and J&K–Acros (Beijing, China). Styrene was washed with an aqueous solution of sodium hydroxide (5 wt %) three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, the styrene was distilled under reduced pressure and kept in a refrigerator under 4°C. Other materials were used without further purification.

Synthesis of the RAFT agents

Benzyl thiophene-2-carbodithioate (BTCT) and 2-methyl-2-(4-methylcyclohex-3-enyl)propyl thiophene-2-carbodithioate (MCPT) were synthesized through the coupling of thiophene-2-carboxylic acid with phenyl methanol and 2-methyl-2-(4-methylcyclohex-3-enyl)propan-1-ol under P_4S_{10} according to the literature,[36–38] respectively. A typical preparation procedure for BTCT can be described as follows: Thiophene-2-carboxylic acid (1.29 g, 10 mmol), phenyl methanol (1.09 g, 10 mmol), P_4S_{10} (2.22 g, 5 mmol), and 40 mL of benzene were added to a 100-mL, three-necked round flask. The solution was stirred at room temperature and bubbled with argon for half an hour and at 82°C for about 12 h under an argon atmosphere. The reaction solution was filtered after cooling, and the filtrate was washed with deionized water until it was clear. The organic solution layer was dried with anhydrous $NaSO_4$ for 24 h. The solvent was removed by rotation evaporation. The crude product was purified twice by column

chromatography on silica oxide with mixed petroleum ether and ethyl acetate as the eluent, first with a 40 : 1 ratio and second with a 100 : 1 ratio. The final product of BTCT and MCPT was a red, crystal solid.

BTCT

^{1}H-NMR (CDCl$_3$): 4.61 (s, 2H); 6.94–7.81 (m, 8H). ANAL. Calcd: C, 57.64%; H, 4.00%. Found: C, 57.15%; H, 4.05%.

MCPT

^{1}H-NMR (CDCl$_3$): 1.02 (s, 6H); 1.88 (s, 3H); 1.51–2.08 (m, 7H); 3.75 (d, 2H); 5.47 (m, 1H); 7.01–7.86 (m, 3H. ANAL. Calcd: C, 61.04%; H, 6.44%. Found: C, 60.56%; H, 6.80%.

Polymerizations

The following procedure was typical. A master batch of 8 mL (69.5 mmol) of styrene, 139.2 mg (0.556 mmol) of BTCT, and 45.6 mg (0.278 mmol) of 2,2′-azobisisobutyronitrile (AIBN) was prepared, and aliquots of 1 mL were placed in ampules. The contents were purged with argon for approximately 10 min to eliminate the oxygen. Then, the ampules were flame sealed. The polymerization reaction was performed at the appropriate temperature. After the determined reaction time, each ampule was quenched in ice water and opened. The reaction mixture was diluted with a little tetrahydrofuran (THF; ca. 2 mL) and precipitated in a large amount of methanol (ca. 300 mL). The polymer was obtained by filtration and dried at room temperature under a vacuum to a constant weight. The conversion of styrene was determined gravimetrically.

Chain extension of polystyrene (PS)

A predetermined quantity of PS, obtained by the polymerization of styrene by a RAFT process, was dissolved in styrene. The contents were bubbled with argon for 20 min. The rest of the procedure was the same as that described previously, except that the RAFT agent was replaced by the PS synthesized previously.

Characterization

The number-average molecular weights (M_n's) and polydispersity indices (PDIs) of the polymers were determined with a Waters 1515 gel permeation chromatograph equipped with a refractive-index detector (Milford, MA) using HR 1, HR 3, and HR 4 columns with a molecular weight range of 100–500,000 calibrated with PS standard samples. THF was used as
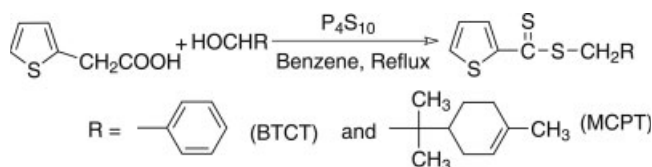
Scheme 2 Synthesis route of the RAFT agents.

the eluent at a flow rate of 1.0 mL/min at 30°C. ^{1}H-NMR spectra of the polymers were recorded on a VARIAN 400 MHz NMR instrument (Palo Alto, CA) using CDCl$_3$ as a solvent and tetramethylsilane as the internal standard. Elemental analyses of C, H, and N were measured with an EA1110 CHND-S (Carlo-Erba, Italy).

Calculations of the molecular orbitals

The calculations were carried out with the Gaussian 03 (Palo Alto, CA) (revision D 01) program package (see ref. 15) on an HP XW6200 workstation with two central processor units and 3 GB of memory. The molecular orbitals were calculated by the density function theory (DFT) with Becke's three-parameter functional with the Lee, Yang, and Parr correlation functional method (B3LYP) and the basic set 6-31G with the d function added to heavy atoms [DFT B3LYP/6-31G(d)].

RESULTS AND DISCUSSION

To synthesize the thiophene-end-labeled polymers, two dithioesters with a thiophene group as the Z group and different R groups were designed and synthesized. The structures of these two dithioesters, BTCT and MCPT, are shown in Scheme 2. The struc-
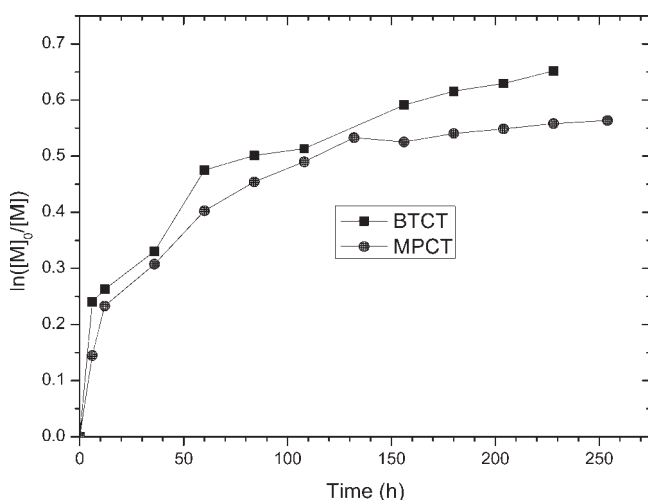

Figure 1 Kinetic plots of styrene RAFT polymerization using BTCT and MPCT as the CTAs and AIBN as the initiator with the molar ratio of [Styrene]$_0$/[CTA]$_0$/[AIBN]$_0$ = 250 : 2 : 1 at 90°C in bulk.
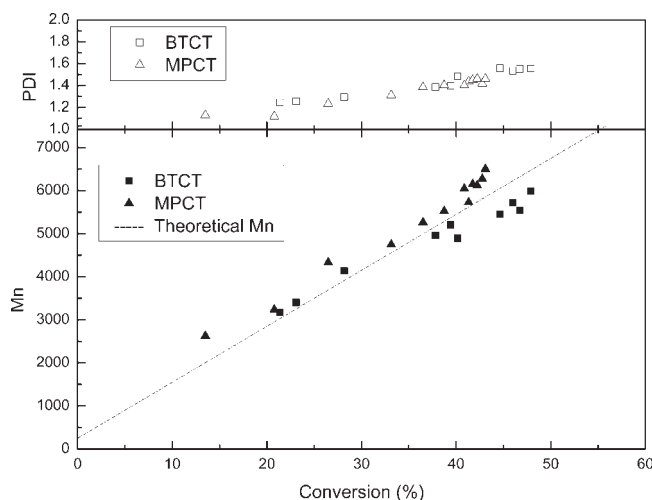

Figure 2 Dependence of M_n and PDI on the conversion for the RAFT polymerization of styrene using BTCT and MPCT as RAFT agents. See Figure 1 for the conditions.
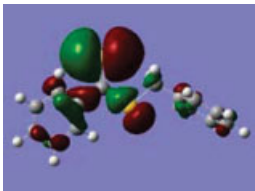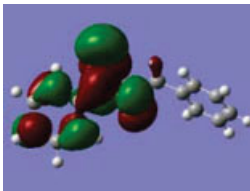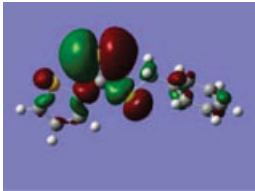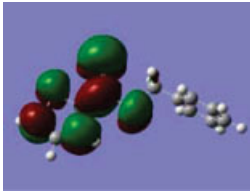
tures of these two compounds were confirmed with ^{1}H-NMR and elemental analysis. The RAFT polymerization of styrene using BTCT and MCPT as the chain-transfer agents (CTAs) and AIBN as the initiator was carried out. Figures 1 and 2 show the results for the kinetics, molecular weights, and PDIs with a molar ratio of [Styrene]$_0$/[CTA]$_0$/[AIBN]$_0$ = 250 : 2 : 1 at 90°C in bulk. The results in Figure 1 show that the two CTAs had similar kinetics in these cases. It shows a fast polymerization rate in the beginning period. The polymerization rate dropped to a relatively low level after about 10 h because of the exhaustion of AIBN. However, the overall polymerization rate of these two CTA-mediated styrene RAFT polymerizations was very low. Only about 50 and 45% polymer was obtained after 250 h of polymerization at 90°C with BTCT and MPCT, respectively. The reason for the abnormally low polymerization rate was further investigated via the *ab initio* based molecular orbital methods.

Many publications have reported that, for polymerizations with thiocarbonylthio compounds [S=C(Z)SR], the PDI and the degree of molecular weight control obtained under a particular set of reaction conditions depend on the nature of groups Z and R.[18,19] R is a homolytic leaving group, and the radical R must efficiently reinitiate polymerization to produce chain transfer. Z is a group that modifies
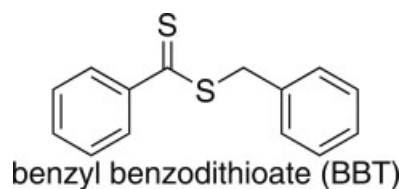
Scheme 3 Structure of BBT.

TABLE I
HOMOs and LUMOs of BTCT and BBT

	HOMO	LUMO
BBT		
BTCT		

the reactivity of the thiocarbonylthio compound and the derived adduct radical. Here we selected benzyl benzodithioate (BBT; Scheme 3) as a molecule comparable to BTCT to carry out the calculation. *Ab initio* calculations were performed with the Gaussian 03 package at the DFT B3LYP/6-31G(d). Table I shows the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of BBT and BTCT. The HOMO and LUMO energies, partial charges on sulfur, and dipole moments of BTCT and BBT are summarized in Table II. The results show that both the HOMO and LUMO energies of BTCT are lower than those of BBT, and this would result in a high transfer coefficient.[18] The AIBN-generated primary free radical would tend to react with BTCT to form the free-radical intermediate. However, the results in Table II also show that BTCT has a strong atomic charge on the thio atom of the C=S bond and a longer dipole moment than BBT, and this would result in a stable free-radical intermediate. The longer lifetime of the stable free-radical intermediate formed in the RAFT polymerization would result in the lower overall polymerization rate.

Figure 2 shows that the molecular weight increased linearly with the conversion. The M_n value obtained by gel permeation chromatography (GPC) was very close to the theoretical one. The PDI remained at a low value (1.1–1.4). These results indicated that the molecular weight of the PS could be

well controlled in BTCT- and MPCT-mediated RAFT polymerizations.

As shown in Scheme 1, the R and Z groups of the RAFT agent would remain in the polymer's end after the RAFT polymerization. The ^{1}H-NMR spectrum of the obtained polymer is shown in Figure 3. In Figure 3(A), the signals in the range of δ = 7.53–7.75 in the PS obtained via the BTCT-mediated RAFT polymerization could be attributed to the thiophene group attached to the polymer end. In Figure 3(B), the spectrum of PS prepared from the MPCT-mediated RAFT polymerization shows signals at δ = 7.53–7.75 ppm and δ = 4.82–4.96 ppm, which were the absorption of the proton at the polymer end's thiophene ring (serving as a Z group) and the double bond in cyclohexene (serving as an R group), respectively. The appearance of the thiophene ring and cyclohexene proton signals indicated that the moieties of the RAFT agent remained intact at the chain end of PS. The samples used for NMR analyses were carefully purified by successive dissolution/precipitation cycles with THF and methanol.

Furthermore, if we suppose that every polymer chain end is labeled with one thiophene ring, the molecular weight of the polymer can be calculated from the peak integral value with the following equation:

$$M_n = \left(\frac{I_{6.3-7.4}}{5} \Big/ \frac{I_{7.53-7.75}}{2} \right) \times \text{MW}_{\text{styrene}} + \text{MW}_{\text{CTA}}$$

where $I_{6.3-7.4}$ is the integral of the signals at 6.3–7.4 ppm, which concerns the benzene ring in PS, and $I_{7.53-7.75}$ is the integral of the signals at 7.6–8.2 ppm, which concerns the thiophene ring at the end of PS. $\text{MW}_{\text{styrene}}$ and MW_{CTA} are the molecular weights of the styrene and CTA, respectively. The molecular weights calculated from this method are 3295 in Figure 3(A) and 2709 in Figure 3(B) and are very close to the GPC-obtained ones (3170 and 2880, respectively). Figure 3(B) also shows the signal of the proton in cyclohexene, which serves as an R group in MPCT. Therefore, the molecular weight can be calculated through the integral value of this proton too. The value has been calculated to be 3946. It is much larger than the GPC-obtained one (2880), and this indicates that not all the polymer chains contained cyclohexene in the terminal. The RAFT polymerization in these cases was initiated by AIBN, which had

TABLE II
HOMO and LUMO Energies, Partial Charges on Sulfur, and Dipole Moments of BTCT and BBT

	Energy (eV)			Atomic charge			Dipole moment
	HOMO	LUMO	Gap	=S	—S	C=S (A)	
BBT	−5.885	−2.183	3.702	−0.155	0.225	1.58	2.3578
BTCT	−5.975	−2.427	3.548	−0.161	0.217	1.56	2.9396

a structure different from the R group of MPCT. As a result, there was a part of the polymer chain end-capped with the moiety of AIBN. Not all the polymer was end-capped with the R group.

The chain-extension behaviors of the obtained polymers were determined. Figure 4 shows the GPC traces of the original PS and the chain-extended polymers with styrene as the second monomer. The chain extension was carried out by the addition of the obtained PS (macro-RAFT agent) to a solution of fresh styrene and AIBN with the molar ratio of $[Styrene]_0/[macro\text{-}RAFT]_0/[AIBN]_0 = 250 : 2 : 1$. The polymerization was carried out at $90°C$ for 2.5 h and resulted in 54 and 48% conversions for the PS samples made with BTCT and MPCT as the RAFT agents, respectively. The GPC traces of the original macro-RAFT agent and the chain extended polymer listed in Figure 4 show that the molecular weight increased from 3500 and 2880 g/mol for the original polymer to 9120 and 6830 g/mol for the polymers after chain extension, whereas the PDI increased from 1.33 and 1.16 to 1.58 and 1.38, respectively. However, there were tails of the original polymer in the GPC curves of the chain-extended polymers, which indicated that the thiophene dithioester end-capped polymers had poor livingness even with high percentages of the end dithio groups.

CONCLUSIONS

Two novel dithiobenzoates containing thiophene structures in the Z group, BTCT and MPCT, were designed and successfully synthesized. The structures were confirmed via ^{1}H-NMR and elemental analysis. RAFT polymerizations of styrene using
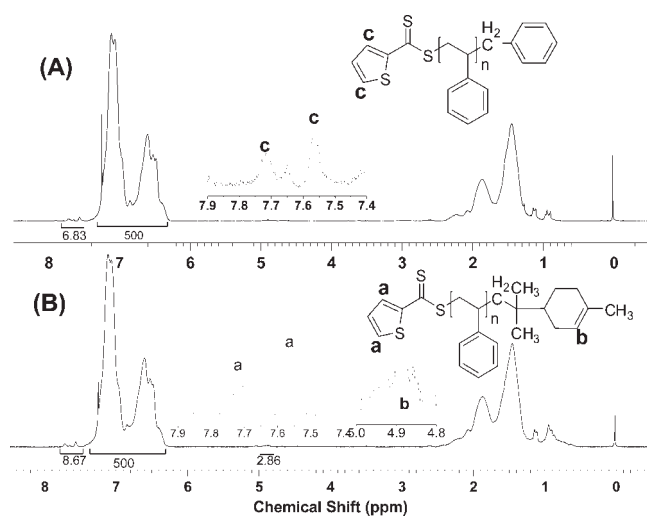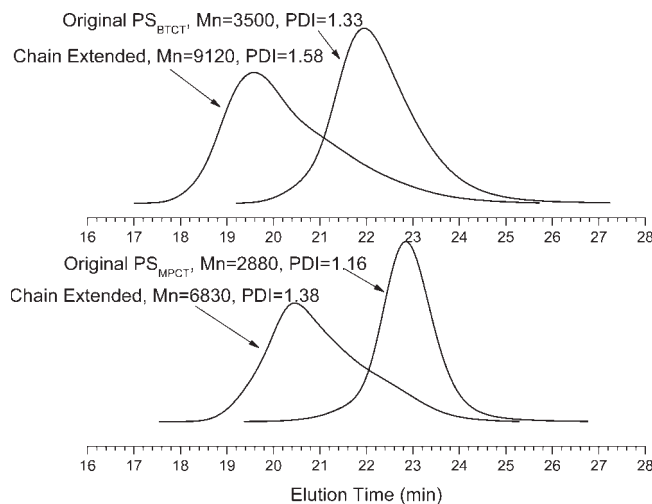
Figure 4 GPC traces of the original PS and the chain-extended polymers. PS_{BTCT} and PS_{MPCT} are the PS samples obtained with BTCT and MPCT as the RAFT agents, respectively.

BTCT and MPCT as RAFT agents and AIBN as an initiator were carried out. The obtained polymers showed controlled molecular weights. The PDIs were below 1.5. The polymerization rate was very low. *Ab initio* calculations for BTCT with the thiophene Z group showed lower LUMO energy levels, higher atomic charges on the thio atom, and longer dipole moments than those for BBT with the benzene Z group. The structure of the obtained polymer was characterized with ^{1}H-NMR spectroscopy, which demonstrated that the obtained polymers were end-capped with thiophene groups in one terminal at a high level. The chain extension of the obtained PS showed the poor livingness of the terminal dithio group. The easy and successful preparation of the thiophene-end-labeled polymer provides a useful tool for the modification of the conducting polymer polythiophene.

References

1. Matyjaszewski, K. ACS Symp Ser 1998, 685.
2. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 2987.
3. Hawker, C. J. Acc Chem Res 1997, 30, 373.
4. (a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. Macromolecules 1995, 28, 1721; (b) Wang, J S.; Matyjaszewski, K. J Am Chem Soc 1995, 117, 5614; (c) Kamigaito, M; Sawamoto, M. Chem Rev 2001, 101, 3689; (d) Matyjaszewski, K; Xia, J. Chem Rev 2001, 101, 2921.
5. Chiefari, J.; Chong, Y. K.; Ercole, F.; Kristina, 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.
6. Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Pat. Appl. WO 9801478 Al (1998).
7. Zheng, G.; Pan, C. Polymer 2005, 46, 2802.
8. Perrier, S.; Davis, T. P.; Carmichael, A. J.; Haddleton, D. M. Chem Commun 2002, 2226.

Figure 3 ^{1}H-NMR spectra of PS obtained by RAFT polymerizations with AIBN initiated at $90°C$: (A) with BTCT as the RAFT agent ($M_n = 3170$, PDI = 1.13) and (B) with MPCT as the RAFT agent ($M_n = 2880$, PDI = 1.14).

9. Zhu, J.; Zhu, X.; Cheng, Z.; Lu, J.; Liu, F. J Macromol Sci Pure Appl Chem 2003, 40, 963.
10. Mitsukami, Y.; Donovan, M. S.; Lowe, A. B.; McCormick, C. L. Macromolecules 2001, 34, 2248.
11. Taton, D.; Wilczewska, A. Z.; Destarac, M. Macromol Rapid Commun 2001, 22, 1497.
12. Convertine, A. J.; Sumerlin, B. S.; Thoma, D. B.; Lowe, A. B.; McCormick, C. L. Macromolecules 2003, 36, 4679.
13. Stenzel-Rosenbaum, M. H.; Davis, T. P.; Fane, A. G.; Chen, V. Angew Chem Int Ed 2001, 40, 3428.
14. Shinoda, H.; Matyjaszewski, K.; Okrasa, L.; Mierzwa, M.; Pakula, T. Macromolecules 2003, 36, 4772.
15. Cheng, Z.; Zhu, X.; Fu, G. D.; Kang, E. T.; Neoh, K. G. Macromolecules 2005, 38, 7187.
16. Perrier, S.; Takolpuckdee, P. J Polym Sci Part A: Polym Chem 2005, 43, 5347.
17. Moad, G.; Rizzardo, E.; Thang, S. H. Aust J Chem 2005, 58, 379.
18. 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.
19. Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. Macromolecules 2003, 36, 2256.
20. Zhou, N.; Lu, L.; Zhu, X.; Yang, X.; Wang, X.; Zhu, J.; Cheng, Z. J Appl Polym Sci 2006, 99, 3535.
21. Zhou, N.; Lu, L.; Zhu, X.; Yang, X.; Wang, X.; Zhu, J.; Zhou, D. Polym Bull 2006, 57, 491.
22. Zhou, N.; Lu, L.; Zhu, J.; Yang, X.; Wang, X.; Zhu, X.; Zhang, Z. Polymer 2007, 48, 1225.
23. Bittihm, R.; Ely, G.; Woeffier, F.; Munstedt, H.; Narmann, H.; Naegele, D. Makromol Chem Makromol Symp 1987, 8, 51.
24. Mermillod, M.; Tanguy, J.; Petiot, F. J Electrochem Soc 1986, 133, 1073.
25. Hwang, L. S.; Ko, J. M.; Rhee, H. W.; Kim, C. Y. Synth Met 1993, 55, 3671.
26. Slater, J. M.; Watt, E. J.; Freeman, J.; May, J. P.; Weirm, D. J. Analyst 1992, 117, 1265.
27. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Angew Chem Int Ed 1998, 37, 403.
28. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L; Holmes, A. B. Nature 1990, 347, 539.
29. Gustafsson, J. C.; Inganas, O.; Anderson, A. M. Synth Met 1994, 62, 17.
30. DePaoli, M. A.; Panero, S.; Passerini, S.; Scrosati, B. Adv Mater 1990, 2, 480.
31. Sotzing, G. A.; Reynolds, J. R.; Steel, P. J Chem Mater 1996, 8, 882.
32. Tarkuc, S.; Sahin, E.; Toppare, L.; Colak, D.; Cianga, I.; Yagci, Y. Polymer 2006, 47, 3001.
33. Alkan, S.; Toppare, L.; Hepuzer, Y.; Yagci, Y. Synth Met 2001, 119, 133.
34. Sahin, E.; Camurlu, P.; Toppare, L.; Mercore, V. M.; Cianga, I.; Yagci, Y. Polym Int 2005, 54, 1599.
35. Papila, O.; Toppare, L.; Hacaloglu, J. J Macromol Sci Pure Appl Chem 2006, 43, 655.
36. Dureault, A.; Gnanou, Y.; Taton, D.; Destarac, M.; Leising, F. Angew Chem Int Ed 2003, 42, 2869.
37. Dureault, A.; Taton, D.; Destarac, M.; Leising, F.; Gnanou, Y. Macromolecules 2004, 37, 5513.
38. Sudalai, A.; Kanagasabapathy, S.; Benicewicz, B. C. Org Lett 2000, 2, 3213.