Synthesis and Characterization of Dendrimer-Star Polymer Using Dithiobenzoate-Terminated Poly(propylene imine) Dendrimer via Reversible Addition-Fragmentation Transfer Polymerization

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ABSTRACT: Two new reversible addition-fragmentation transfer (RAFT) agents with 8 and 16 terminal dithiobenzoate groups on the surface of poly(propylene imine) dendrimers (generation 2.0 and 3.0, respectively) were prepared, and successively they were used in the RAFT polymerization to produce well-defined dendrimer-star polymers. The polymerization kinetics were confirmed to pseudo-first-order behavior. The polymerizations displayed excellent molecular weight control and produced polymer with low polydispersities (<1.3). The synthetic method was also suitable for the preparation of dendrimer-star block copolymers.

Introduction

Dendrimers are monodispersive molecules with a globular shape, well-defined, and perfectly branched structure, and they possess a precise number of terminal functional groups which provide high surface reactivity.[1] Dendrimer-star polymers, in which many linear homo or block copolymer chains are attached to the dendrimers, have been developed because they combine the properties of star polymers with those of dendrimers. They can be used in controlling the guest reactivity in dendrimer host in response to the change of external stimuli,[2,3] extraction applications,[4] stabilizers for colloids,[5] DNA delivery, and electrokinetic capillary chromatography.[6] Two general methods have been used to prepare dendrimer-star polymers. One is to link monofunctional linear polymers onto the dendrimer surface.[2,5−7] The other is the growth of arm polymer chains from the surface of dendrimer by "controlled/living" polymerizations. Surprisingly, only a few dendrimer-star polymer examples have been synthesized via living polymerizations, including anionic polymerization,[8] ring-opening polymerization (ROP),[9] and atom transfer radical polymerization (ATRP).[10] However, anionic and cationic polymerizations suffer from rigorous requirements, and some functional monomers cannot be used by ATRP method.

In the past five years, a significant development in controlled/living radical polymerization came about with the use of thiocarbonylthio compounds ZC(S)SR as chain-transfer agents (CTAs) in the so-called reversible addition-fragmentation transfer (RAFT) polymerization.[11] The controlled/living growth of the chains is achieved by the alternation of the activation and deactivation of the CTA between dormant and active moieties. Among the various types of RAFT agents prepared, only a few of them have been applied for star polymer synthesis.[12−15] Two types of multifunctional CTAs can be employed in RAFT process: those involving the reaction of the linear chains with the functional core (core is a part of Z-group) and those implying an outward growth of arms from the core (core is a part of R-group), following "arm-first" and "core-first" approaches, respectively. These two approaches are complementary with their respective merits and drawbacks.[12−15] For the synthesis of star polymers with dendritic or hyperbranched cores, the RAFT agent was connected to the core via Z-group.[16−18] Gnanou et al. recently described the synthesis of hybrid dendrimer-star polymers via the RAFT process by the "arm-first" approach. In this case, the core acts as the Z-group of the RAFT agent. The growth occurs at the nexus of the core and the arm. As the molecular weight of the arm builds up, a remarkable "shield effect" was found, which prevents formation of a well-defined dendrimer-star polymer.[16] Different from the "arm-first" approach reported, in this article, we present a "core-first" RAFT approach to prepare well-defined dendrimer-star polymers and block copolymers using dithiobenzoate-terminated poly(propylene imine) (PPI) dendrimer as multifunctional RAFT agent that is the attachment of the RAFT agent on the dendrimer via R groups.

Experimental Part

Materials. Polypropylenimine octaamine dendrimer (DAB-8-Am, generation 2.0) and polypropylenimine hexadecaamine dendrimer (DAB-16-Am, generation 3.0) were purchased from Aldrich. 4,4′-Azobis-(4-cyanopentanoic acid) (Fluka, > 98%), *N*-hydroxysuccinimide) (Fluka, >97%), and dicyclohexylcarbodiimide (DCC) (>98%, Shanghai First Reagent Co.) were used without further purification. Methyl acrylate (MA, >99%) and styrene (St, >99%) were purchased from the Shanghai First Reagent Co. were distilled under reduced pressure to remove the inhibitor. Azobisisobutylnitrile (AIBN, Shanghai First Reagent Co, 95%) was purified by recrystallization from ethanol. Tetrahydrofuran (THF) was refluxed for 24 h over sodium and distilled prior to use. Dichloromethane (DCM) and ethyl acetate (EA) were dried over CaH_2 and distilled prior to use. All other reagents were of analytical grade purchased from Shanghai First Reagent Co. and used as received without purification. Dithiobenzoic Acid (DTBA) was prepared according to the method described in ref 19 in 67% yield. ^{1}H NMR (300 MHz, δ, ppm, $CDCl_3$): 8.05 (d, 2H, *o*-Ar*H*), 7.60 (t, 1H, *p*-Ar*H*), 7.40 (*t*, 2H, m-Ar*H*).

Synthesis of 4-(4-Cyanopentanoic Acid) Dithiobezoate (1). The target compound was prepared according to a modi-

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Table 1. Results and Conditions of the Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization of Styrene Using Dendritic RAFT Agent 3[a]

entry	time (h)	conversion (%)	$M_{n(linearchain)}$ (GPC)[b]	$M_{n(star)}$ (GPC)[b]	PDI[c]	$M_{n(arm)}$ (NMR)[d]	$M_{n(star)}$ (NMR)[e]	$M_{n(star)}$ (th)[f]	$M_{n(arm)}$[g] hydrolysis
1	5	13.6	8 300	36 600	1.07	6 800	57 300	59 500	7 500
2	10	37.8	20 100	79 800	1.09	20 300	165 300	160 000	20 000
3	16	46.2	22 200	93 600	1.14	23 900	194 000	195 000	23 100
4	24	53.6	26 800	109 000	1.21	25 400	206 000	226 000	26 300
5	40	69.0	32 900	131 000	1.25	33 100	267 700	290 000	32 500

[a] Conditions: in tetrahydrofuran (THF), temperature = 120 °C, [St]/[RFAT agent **3**] = 4000 ([St]/[dithiobenzoate functions] = 500). [b] Calculated based on the GPC method, in which narrow PDI polystyrene standards were used in the calculation. [c] Evaluated from GPC in THF. [d] The number-average molecular weight of the arm in the dendrimer star polystyrene $M_{n(arm)}$ (NMR), calculated from ^{1}H NMR based on eq 1. [e] The number-average molecular weight of dendrimer-star polystyrenes, calculated from ^{1}H NMR based on eq 2. [f] Calculated from the following equation: $M_{n\ (star)}$ (th) = [St]/[RAFT agent] × M_{St} × conversion + $M_{RAFT\ agent}$, where [St] and [RAFT agent] are initial concentrations of St and RAFT agent and M_{St} and $M_{RAFT\ agent}$ are molecular weights of St and RAFT agent. [g] GPC measurement of the hydrolysis product.

fication method of Thang et al.[20] The DTBA (4.62 g, 30 mmol) and a catalytic amount of I_2 (50 mg) were dissolved in 15 mL of ethyl acetate in a 100-mL two-neck flask. Into this solution, a solution of dimethyl sulfonyl oxide (DMSO) (1.2 g, 15 mmol) in 5 mL of ethyl acetate was added slowly while stirring vigorously. The reaction mixture was stirred in the dark for 10 h. Without further purification, the crude disulfide was used directly in the next step. 4,4′-Azobis-(4-cyanopentanoic acid) (6.3 g, 23 mmol) and 15 mL of ethyl acetate was added into the flask. The reaction solution was heated at reflux for 18 h. The ethyl acetate was removed under reduced pressure. The crude product was isolate by silica gel column chromatograph using ethyl acetate: hexane (1:2) as eluent. Those fractions in pink red were combined. The solvent was removed in vacuo to give a red solid **1** (5.0 g, yield = 44% for two steps). ^{1}H NMR (300 MHz, δ, ppm, $CDCl_3$): 7.91 (d, 2H, *o*-Ar*H*), 7.58 (t, 1H, *p*-Ar*H*), 7.41 (*t*, 2H, m-Ar*H*), ∼2.40−2.80 (m, 4H, −CH_2CH_2-), 1.95 (s, 3H, −CH_3).

Synthesis of 4-Cyano-4-((thiobenzoyl)sulfanyl) Pentanoic Succinimide Ester (2). The compound **1** (2.04 g, 7.3 mmol) and *N*-hydroxyl succinimide (0.84 g, 7.3 mmol) were dissolved in 15 mL of anhydrous DCM. Dicyclohexylcarbodiimide (DCC) (1.51 g, 7.3 mmol) was added in one portion to the solution. The reaction mixture was stirred at room temperature in the dark for 16 h. A white byproduct was filtrated out. The filtrate was concentrated, and the concentrated liquid was purified through a silica gel column with ethyl acetate: hexane (1: 4, v/v) as eluent. A red solid **2** (2.5 g) was obtained in a yield of 91%. ^{1}H NMR (300 MHz, δ, ppm, $CDCl_3$): 7.93 (d, 2H, *o*-Ar*H*), 7.58 (t, 1H, *p*-Ar*H*), 7.41 (*t*, 2H, m-Ar*H*), 3.20 (m, 2H, −OC−CH_2−CH_2−C(CN)(CH_3)−), 2.86 (s, 4H, −OC−CH_2−CH_2−CO−), ∼2.31−2.74 (m, 2H, −CH_2−CH_2−C(CN)-(CH_3)−),1.93 (s, 3H, −CH_3).

Synthesis of Dendritic RAFT Agent 3. A solution of DAB-8-Am (0.23 g, 0.30 mmol) in 5 mL of anhydrous DCM was added slowly to the solution of 4-cyano-4-((thiobenzoyl)-sulfanyl) pentanoic succinimide ester 2 (1.02 g, 2.7 mmol) in 10 mL of DCM. The reaction mixture was stirred at room temperature in the dark for 48 h. After DCM was removed, the residue was purified by pouring the dendritic RAFT agent in DCM into hexane three times. The small molecular byproduct and the unreacted starting material were removed. After dried in a vacuum oven at 40 °C for 24 h, dendritic RAFT agent 3 (1.04 g) was obtained in 95% yield. ^{1}H NMR (300 MHz, δ, ppm, $CDCl_3$): 7.88 (d, 16H, *o*-Ar*H*), 7.55 (m, 8H, *p*-Ar*H*), 7.38 (m, 16H, m-Ar*H*), 3.28 (m, 16H, −CO−NH−CH_2−), ∼2.70−2.90 (m, 32H, −C−CH_2−CH_2−CO−NH−), ∼2.45−2.60 (m, 36H, −N−CH_2−CH$_2$−CH_2−N−), 1.92 (s, 24H, −CH_3), ∼1.76−1.88 (m, 28H, −N−CH$_2$−CH_2−CH$_2$−N−).

Synthesis of Dendritic RAFT Agent 4. The dendritic RAFT agent **4** was synthesized from DAB-16-Am in 94% yield by the same method used to prepare dendritic RAFT agent **3**. ^{1}H NMR (300 MHz, δ ppm, $CDCl_3$): 7.90 (m, 32H, *o*-Ar*H*), 7.62 (m, 16H, *p*-Ar*H*), 7.40 (m, 32H, m-Ar*H*), ∼3.15−3.35 (m, 32H, −CO−NH−CH_2−), ∼2.81−3.02 (m, 64H, −C−CH_2−CH_2−CO−NH−), ∼2.50−2.75 (m, 84H, −N−CH_2−CH$_2$−CH_2−N−), 1.93 (s, 48H, −CH_3), ∼1.70−1.88 (m, 60H, −N−CH$_2$−CH_2−CH$_2$−N−).

Table 2. RAFT Polymerization of Styrene using 3 or 4 as RAFT Agents with Different Ratios of [St]/[RAFT Agent][a]

entry	[St]/[RAFT agent]	conversion (%)	$M_{n(star)}$ (GPC)[b]	PDI[c]	$M_{n(star)}$ (th)[d]
6[e]	2 400	24.5	28 000	1.07	64 100
7[e]	800	21.3	13 600	1.18	21 200
8[e]	400	22.7	8 900	1.26	11 700
9[f]	4 800	20.4	35 300	1.17	96 300
10[f]	1 600	23.6	13 000	1.29	43 500

[a] Conditions: in tetrahydrofuran, temperature = 120 °C. [b] Calculated based on the GPC method, in which narrow PDI polystyrene standards were used in the calculation. [c] Evaluated from GPC in THF. [d] Calculated from the following equation: $M_{n\ (star)}$ (th) = [St]/[RAFT agent] × M_{St} × conversion + $M_{RAFT\ agent}$, where [St] and [RAFT agent] are initial concentrations of St and RAFT agent and M_{St} and $M_{RAFT\ agent}$ are molecular weights of St and RAFT agent. [e] Dendritic RAFT agent **3** as CTA. [f] Dendritic RAFT agent **4** as CTA.

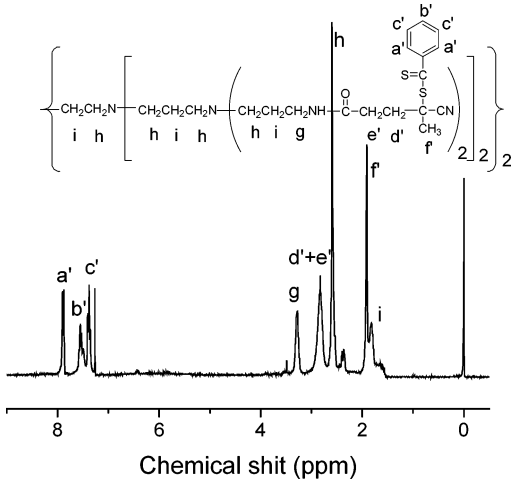
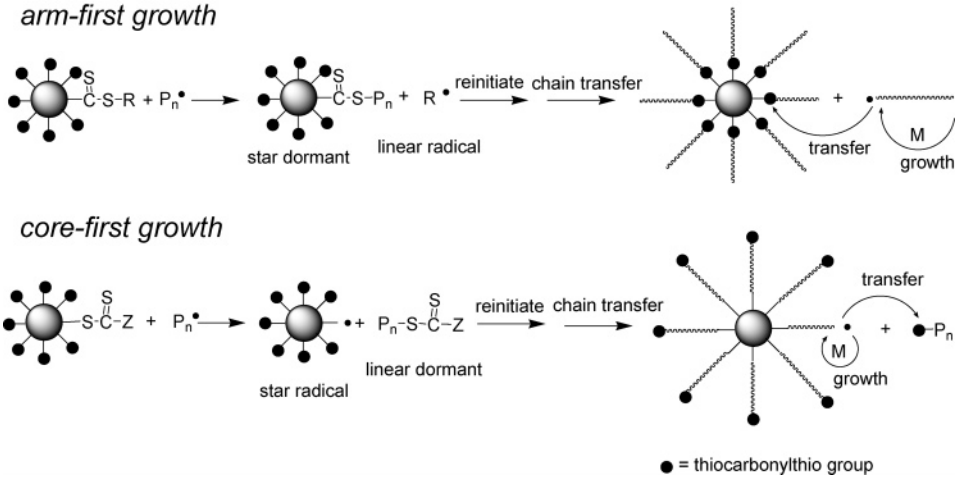


Figure 1. ^{1}H NMR spectrum of dendritic RAFT agent 3.

Polymerization. A typical polymerization procedure for synthesizing the dendrimer-star polymer is as follows. A glass tube was charged with a solution of dendritic RAFT agent 3 (12 mg, 3.8 × 10^{-6} mol) and freshly distilled St (1.6 g, 1.5 × 10^{-2} mol) in 1.5 mL of THF. After the polymerization mixture was degassed by three freeze−evacuate−thaw circles, the tube was sealed under a vacuum. The polymerization was carried out at 120 °C without AIBN for 10 h. The reaction was stopped by plunging the tube into ice water. The dendrimer-star PSt was precipitated by adding the polymer solution in THF into petroleum ether (bp ∼30−60 °C) and then collected by filtration. The polymer obtained was dried in a vacuum oven at 40 °C for 24 h in a yield of 37.8%. M_n(GPC) = 79 800; M_w/M_n = 1.09. ^{1}H NMR (300 MHz, δ ppm, $CDCl_3$): 7.9 (*o*-Ar*H*

Scheme 1. Two Types of Multifunctional RAFT Agents Used in the Synthesis of Star Polymers



of dithiobenzoate group), 7.5 (*p*-Ar*H* of dithiobenzoate group), ~6.4−7.3 (Ar*H* of St units, and *m*-Ar*H* of dithiobenzoate group), 4.9 (−CH_2−C*H*−S−), 3.1 (−CO−NH−CH_2−), 2.7 (−C−CH_2−CH_2−CO−NH−), 1.7 (−CH_2−C*H*− of St unit).

Hydrolysis of the Dendrimer-Star PSt, [Den(PSt)$_8$]. The dendrimer-star PSt, Den(PSt)$_8$, with M_n = 93 600, PDI = 1.14 (0.20 g, entry 3 in Table 1), was dissolved in anhydrous THF (10 mL), and then the solution was treated with 1 mL of sodium methoxide solution (0.46 g, 20 mmol Na reacted with 10 mL anhydrous MeOH). The mixture was heated at 65 °C for 1 day. Subsequently water (0.5 mL) was added, and the mixture was reheated at 65 °C for an additional day. Diluted HCl was added to neutralize the reaction mixture. The hydrolyzed linear polymer was then precipitated in methanol. After it was filtrated and dried in a vacuum oven for 24 h, white powder (0.16 g) was obtained with M_n = 23 100, PDI = 1.40 (GPC).

Preparation of Dendrimer-Star Diblock Copolymer, [Den(PSt-*b*-PMA)$_8$]. A typical polymerization procedure for synthesizing dendrimer-star AB diblock copolymer is as follows. A glass tube was charged with the dendritic polymer Den(PSt)$_8$ with M_n = 28 000, PDI = 1.07 (0.21 g, entry 6 in Table 2), AIBN (1.0 mg, 6.0 × 10^{-6} mol), fresh MA (1.0 g, 1.2 × 10^{-2} mol) and THF (1.0 mL), then the polymerization mixture was degassed by three freeze−evacuate−thaw cycles. The tube was sealed under a vacuum. The block polymerization was carried out at 90 °C for 5 h. The dendrimer-star diblock copolymer Den(PSt-*b*-PMA)$_8$ was precipitated by adding the mixture into petroleum ether (bp ~30−60 °C) and collected by filtration. The polymer obtained was dried in a vacuum oven at 40 °C for 24 h in yield of 36% with M_n = 15 6000, PDI = 1.35. ^{1}H NMR (300 MHz, δ ppm, $CDCl_3$): 7.9 (*o*-Ar*H* of dithiobenzoate group), ~6.4−7.3 (Ar*H* of St unit), 4.9 (−CH_2−C*H*−S−), 3.7 (−O−CH_3 of MA units), ~1.3−2.3 (−CH_2−C*H*− of PSt and PMA unit).

Characterization. ^{1}H NMR (300 MHz) spectra were recorded on a Bruker 300 nuclear magnetic resonance (NMR) instrument, using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal reference. The molecular weight, M_n (GPC) and molecular weight distribution (MWD) were determined at 30 °C on a Waters 515 gel permeation chromatography (GPC) equipped with microstyragel columns, 10^3, 10^4, and 10^5 Å. Standard narrow polydispersity polystyrenes were used in the calibration of molecular weight and molecular weight distribution and THF as eluent at a flow rate of 1.0 mL/min. Infrared spectra were recorded on a Bruker VECTOR-22 IR spectrometer.

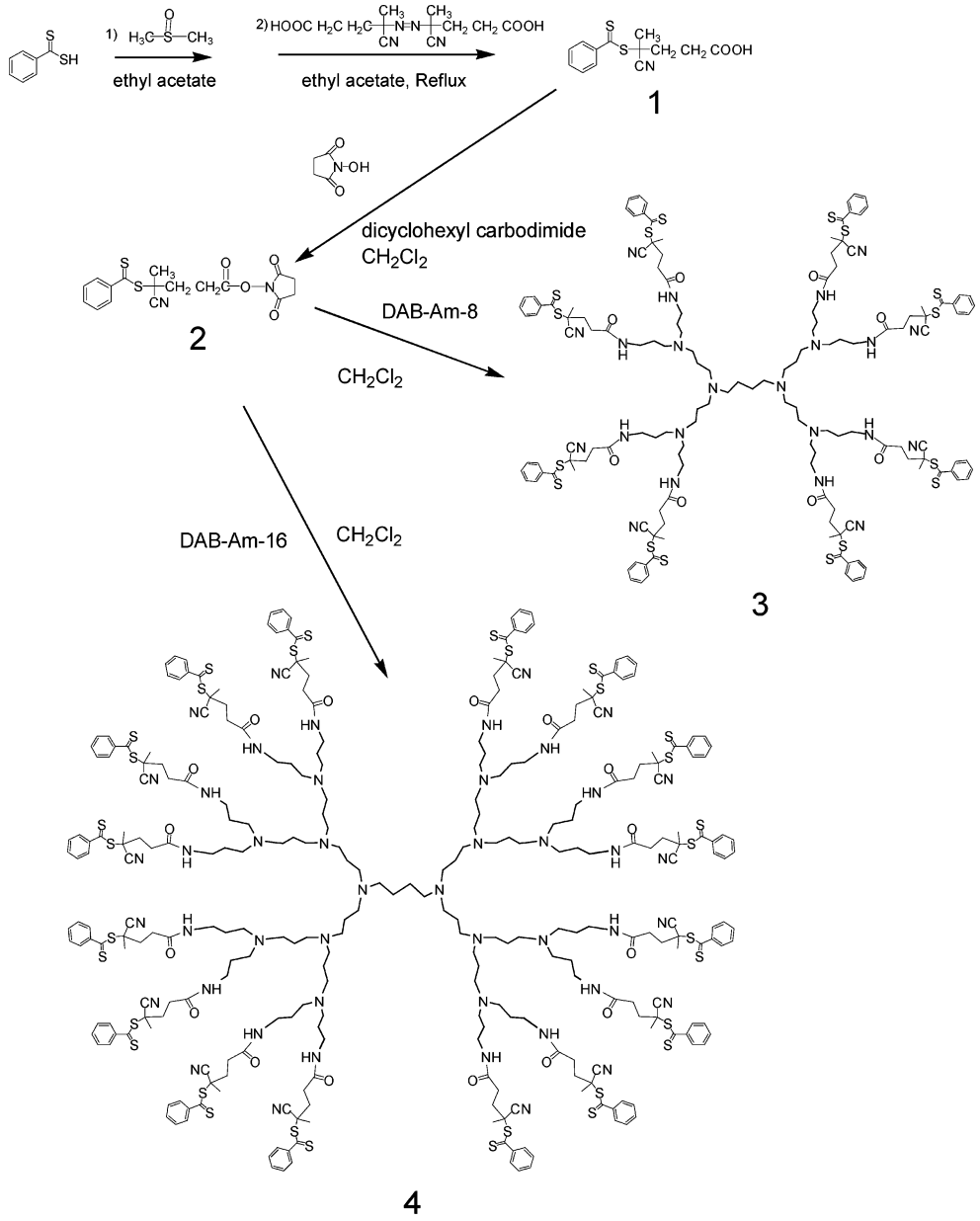
Results and Discussions

Synthesis of Dendritic RAFT Agents 3. Aforementioned in the introduction, there are two types of multifunctional RAFT agents used in the synthesis of star polymers (Scheme 1): (1) The multifunctional RAFT agents with the Z-group as a part of the core will allow the growth of arms away from the core during polymerization (*arm-first growth*). (2) For those RAFT agents with the R-group as a part of the core, chain growth must occur on the surface of core (*core-first growth*). Gnanou group used a 12-armed dendritic RAFT agent in the preparation of dendrimer-star polystyrene via arm-first growth.[16] They found that, with the progress of polymerization, the growing linear chains experienced a higher probability of irreversible terminations occurring by couplings of polystyryl radicals, forming dead linear polymers free of any thiocarbonylthio groups. Therefore we selected the dithiobenzoyl-terminated dendrimers **3** and **4** as RAFT agents, in which the R-group is a part of the core.

The dendritic RAFT agents **3** and **4** were synthesized according to Scheme 2. The PPI dendrimers with the terminal dithiobenzoate groups were prepared by coupling reaction of 4-cyano-4-((thiobenzoyl)sulfanyl) pentanoic succinimide ester **2** with amine groups on the surface of DAB-8-Am or DAB-16-Am. We selected compound **2** as a coupling reagent for two reasons: (1) compound **2** contains dihiobenzoate group which is a suitable RAFT agent for St and (2) the succinimide ester group of compound **2** is easier to react with amine group. Generally, compound **1** was prepared via a two-step procedure from DTBA.[21] We omitted the separation procedure after the oxidization reaction of DTBA, and the yield of compound **1** was not affected.

To ensure complete transformation of all eight amine groups in DAB-8-Am into dithiobenzoyl groups, an excess of the compound **2** was used. The unreacted compound **2** and byproduct *N*-hydroxyl succinimide could be removed by precipitation from hexane. Figure 1 shows the typical ^{1}H NMR spectrum of the resulting dithiobenzoate-teminated dendrimer CTA **3**. The signals at δ = 7.88 (a′), 7.58 (b′), and 7.38 (c′) ppm are assigned to the ortho, para, and meta aromatic protons relative to the dithiobenzoate group, respectively. Compared to the ^{1}H NMR spectrum of the starting PPI dendrimer DAB-8-Am, the peak (g) of the methylene protons next to carbimide on the surface of dendrimer obtained from the reaction with compound **2** moves from 2.78 to 3.28 ppm. In addition, the signals at δ = 2.50 (h) and 1.80 ppm (i) are ascribed to the methylene protons in the PPI dendrimer. The integration ratio of the peaks a′: b′: c′: d′: e′: f′: g: h: i is almost equal to 16:8:16:

Scheme 2. Synthesis of Two Dendritic RAFT Agents



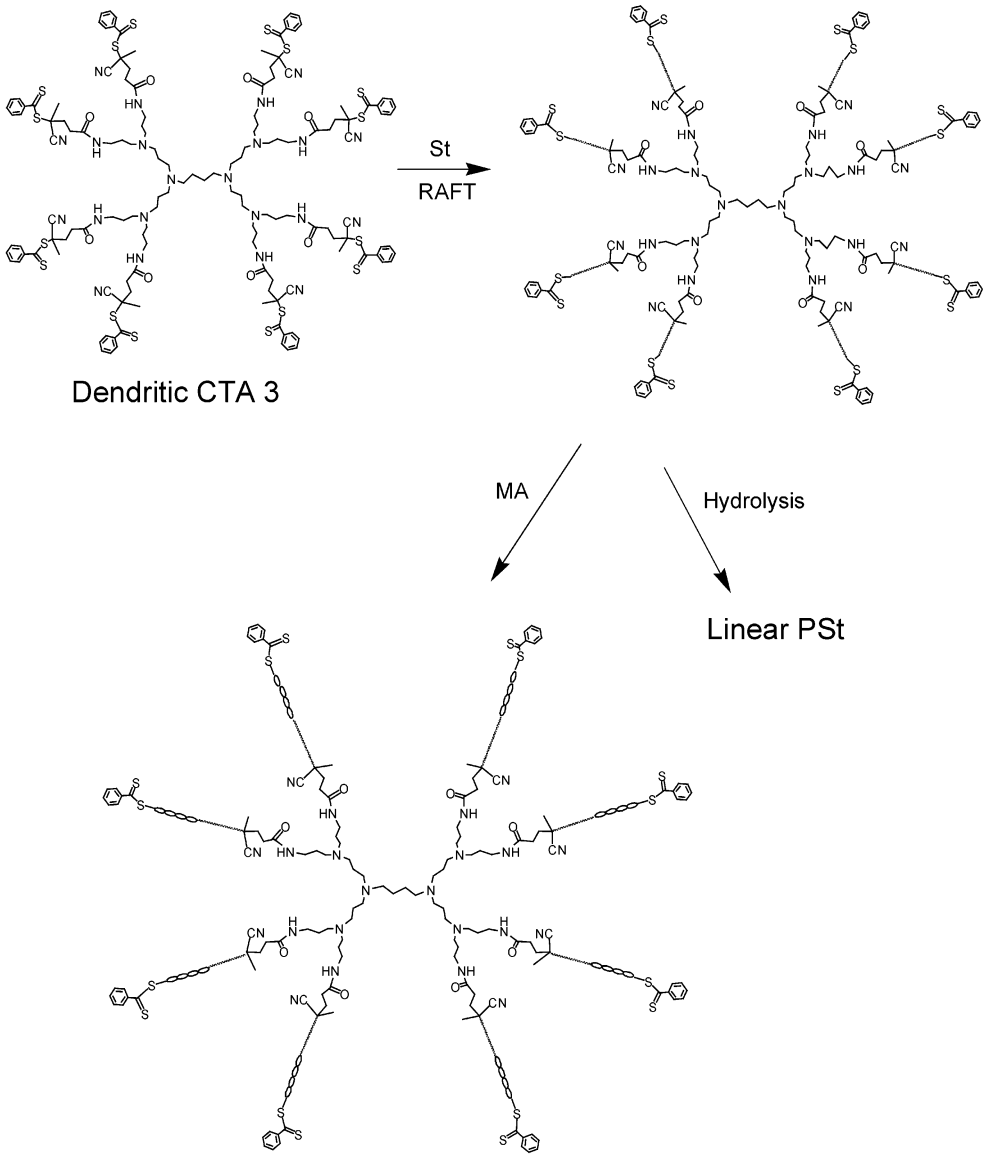
DAB-Am-8 = polypropylenimine octaamine dendrimer
DAB-Am-16= polypropyleniminehexadecaamine dendrimer

16:16:24:16:36:28. This evidence shows that all of the eight amine groups have turned to imide groups, indicating the formation of eight dithiobenzoate-terminated dendritic RAFT agent **3**. With the similar reaction condition, we synthesized the 16 dithiobenzoate-terminated dendritic RAFT agent **4** from DAB-16-Am. The FT-IR spectra of the dithiobenzoate-terminated dendritic CTA **3** and **4** are shown in Figure 2. The characteristic bands for the RAFT agents **3** and **4** are clearly observed in the IR spectra: C=S, 1048 cm^{-1}; C=O, 1649 cm^{-1}; C≡N, 2230 cm^{-1}; N−H, 3430 cm^{-1}.

RAFT Polymerization of St Using Multifunctional Dendritic RAFT Agents. The dendrimer-star $Den(PSt)_8$ was prepared by RAFT polymerization of St in the presence of dendritic RAFT agent **3** (Scheme 3). Because the dendritic RAFT agent **3** cannot dissolve in St, toluene, and anisole, all polymerizations were carried out in THF. It was reported that, at the higher temperature and without a radical initiator, the molecular weight of star is as expected.[12] We therefore selected a polymerization temperature of 120 °C, with no addition of radical initiator for better control of molecular weight of the star polymers. The results and conditions of the RAFT polymerization are listed in Table 1. The molecular weight increased with increasing conversion up to 69%, which is different from that observed by Gnanou.[16] With the core-first growth process, the RAFT agent **3** reacted rapidly with a propagating radical ($P_{n\bullet}$) to form a linear thiocarbonylthio polymer chain [S=C(Ph)S−P_m] which will leave from the core, and the fragmented star radicals (R•) on the surface of the core can initiate the polymerization of St. The star radicals will not be shielded by PSt because the radicals and RAFT sites are consistently on the surface of the dendrimer-star polymers.

The pseudo-first-order kinetic plot of the polymerization of St in the presence of dendritic RAFT agent **3** is shown in Figure 3, indicating the concentration of

Scheme 3. RAFT Polymerization and Block Copolymerization with Dendritic RAFT Agent and Hydrolysis of the Dendrimer-Star



chain radicals is constant during the polymerization. However, the straight line does not pass through zero. This inhibition of polymerization may be ascribed to slow fragmentation and/or slow reinitiation of the leaving group in the early stage of polymerization.[22−24] A well-controlled molecular weight is confirmed by linear increase of the molecular weight of the dendrimer-star PSt obtained with conversion as shown in Figure 4 , and the molecular weight distribution is narrow (PDI = 1.07−1.25).

Although this RAFT polymerization displayed living character, linear PSt always exists along with propagation of the dendrimer-star PSt. This can be observed by following the polymerization by GPC. Figure 5 shows the GPC curves of the polymers obtained at different conversions. The GPC curves of all the polymer samples in Figure 5 demonstrate two peaks: the high molecular weight peak is dendrimer-star PSt, Den$(PSt)_8$, and the lower molecular weight peak is linear PSt, which will be verified later. Both molecular weights increase with conversion, and the relative amount of linear PSt in the polymers increases as polymerization progresses. On the basis of the integral values of the two peaks, the contents of linear PSt were calculated; they are 0.8% for the polymers obtained at 13.6% conversion, 4.8% at conversion of 37.8%, and 12.4% at 69%. These phenomena should be related to the RAFT polymerization mechanism with multifunctional dendrimer RAFT agent. The livingness of RAFT polymerization is due to establishing the equilibrium between the propagating radical ($P_{n\bullet}$) and dormant chain [S=C(Z)S−P_m]. Different from ATRP, in this equilibrium reaction, split of the adduct formed by the attack of chain radical on dormant chain will release a new dormant chain and a new propagating chain.[11,20]

For the polymerization initiated by multifunctional RAFT agents, we propose a mechanism of "core-first" approach (Scheme 4) based on the mechanism with a monofunctional RAFT agent. At the initial stage, the attack of a propagating radical ($P_{n\bullet}$) on the multifunctional RAFT agent will produce a radical on star core, and it will initiate the polymerization. As the reaction proceeds, the equilibrium of the active species on the linear and dendrimer-star chains with dormant linear and dendrimer-star chains is established in Scheme 4. Thus the star polymer growth might be accompanied

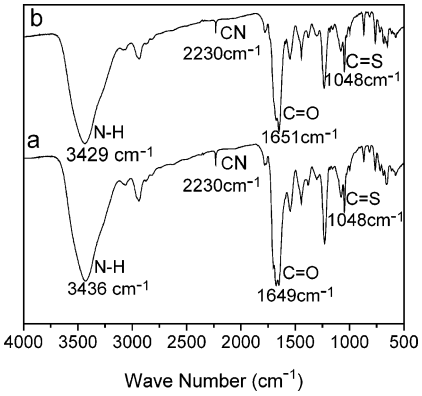


Figure 2. IR spectra of dendritic RAFT agents 3 (a) and 4 (b).

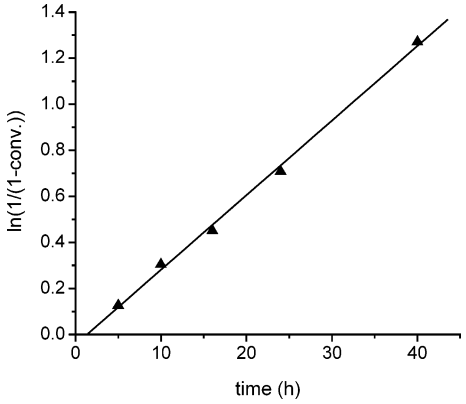


Figure 3. Pesudo-first-order kinetic plot of the preparation of dendrimer-star polystyrene at 120 °C in tetrahydrofuran in the presence of dendritic RAFT agent **3**. ([St]/[RAFT agent **3**] = 4000).

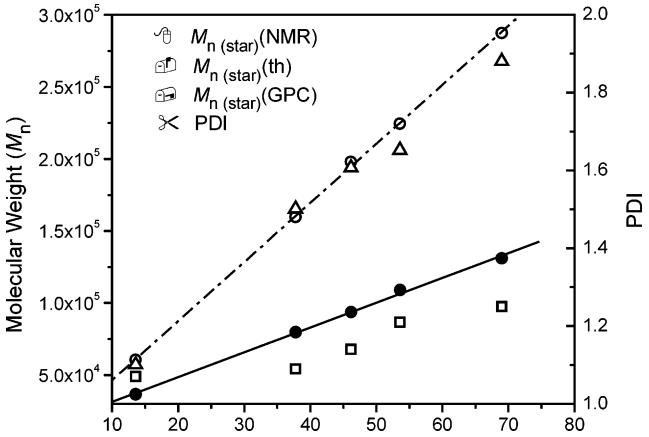


Figure 4. Evolution of the molecular weight and PDIs with conversion for the RAFT polymerization of styrene at 120 °C in tetrahydrofuran in the presence of dendritic RAFT agent **3** ([St]/[RAFT agent **3**] = 4000).

with a parallel polymerization of single chains. It is reasonable that the linear polymer should have an identical molecular weight to each of the arms attached to the dendrimer. The linear PSt propagated with the propagation of dendrimer-star PSt was shown in Figure 5.

For estimating the molecular weights of each arm and the star, the ^{1}H NMR spectra of dendrimer-star PSts, Den(PSt)$_8$ obtained after removal of the linear PSt were measured. Figure 6 is a typical ^{1}H NMR spectrum of the dendrimer-star PSt, Den(PSt)$_8$ (entry 1 in Table 1). Except for the characteristic signals of PSt, those signals

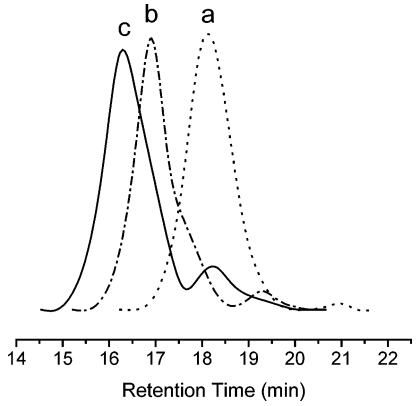
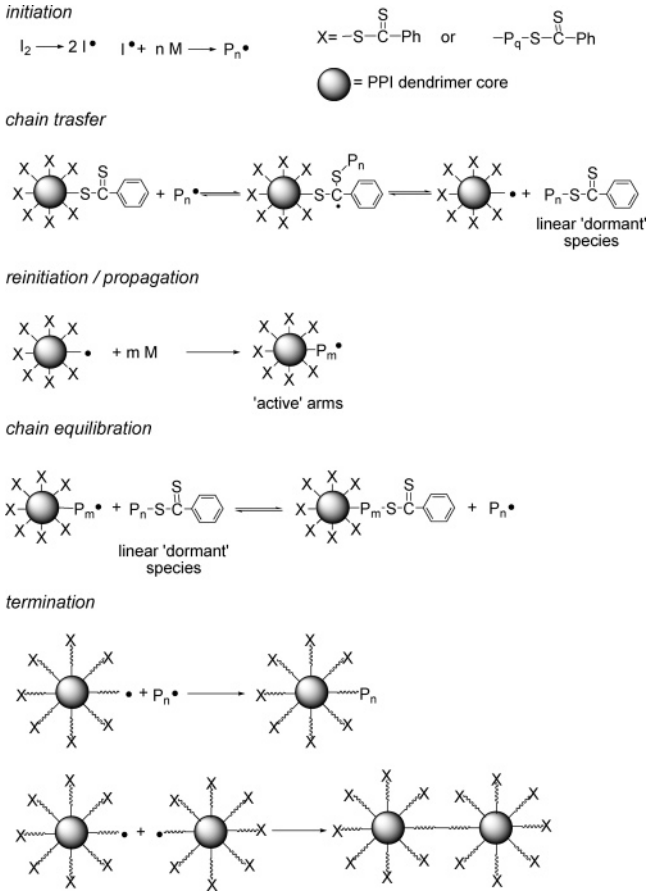


Figure 5. Evolution of GPC chromatograms for the RAFT polymerization of styrene at 120 °C in tetrahydrofuran in the presence of dendritic RAFT agent **3** ([St]/[RAFT agent **3**] = 4000): (a) entry 1 in Table 1; (b) entry 2 in Table 1; (c) entry 5 in Table 1.

Scheme 4. Mechanism of RAFT Polymerization with Dendritic RAFT Agent via "Core-First" Approach



at δ = 7.9 (a), 7.5 (b), 3.1 (d), 2.7 (e + f) ppm originated from the dendritic RAFT agent **3** appear still. The other signals from the dendrimer are overlapped with the characteristic signals of the PSt. While a new signal around δ = 4.7 ppm (c) ascribed to the methine proton of St next to dithiobenzoyl group appears in Figure 6, which might result from the cleavage of C−S bond, and the formation of a new C−S bond between St unit and dithiobenzoyl group in the RAFT process. The number-average molecular weight of each arm, $M_{n\ (arm)}$(NMR) can be calculated according to eq 1

$$M_{n(arm)}(\mathrm{NMR}) = [\,2I_{1.7}/(\,3I_{3.1})]M_{St} \qquad (1)$$

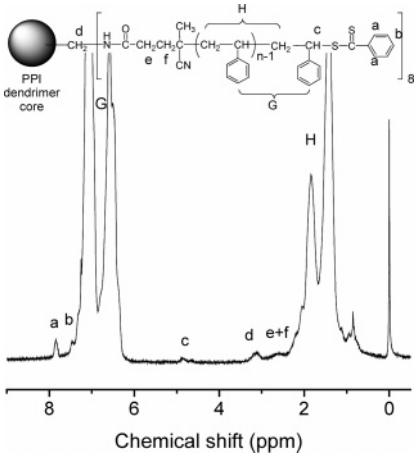


Figure 6. ^{1}H NMR spectrum of the dendrimer-star polystyrene with $M_{n\ (star)}$(GPC) = 36 600 (Table 1, entry 1) using dendritic agent 3 as the CTA.

with $I_{1.7}$ and $I_{3.1}$ relative integrations of the $-CH_2-CH-$ protons ($\delta = \sim 1.3-2.0$ ppm) of the PSt backbone and of the $-CH_2-CONH-$ protons ($\delta = 3.1$ ppm) of arm ends of PPI dendrimers. The number-average molecular weight of dendrimer-star PSts, $M_{n\ (star)}$(NMR), can be calculated based on eq 2

$$M_{n\ (star)}(\mathrm{NMR}) = M_{n\ (arm)}(\mathrm{NMR})n + M_{\mathrm{dendriticRAFTagent}} \quad (2)$$

with $M_{\mathrm{dendriticRAFTagent}}$ the molecular weight of dendritic RAFT agent and n the number of branches of the star. The calculated results are listed in Table 1 and also shown in Figure 4. The $M_{n(star)}$(GPC) of dendrimer-star PSt is less than their $M_{n\ (star)}$(th) and $M_{n\ (star)}$(NMR) values because the molecular weights are calibrated based on the linear polystyrene standards and they have different hydrodynamic characters. $M_{n(star)}$(th) values were calculated based on the feed molar ratio of St/dendritic RAFT agent and conversion of monomer. The $M_{n\ (star)}$(NMR) values of the dendrimer-star PSts agree with $M_{n(star)}$(th) at lower conversions. But at higher conversions, such as at 53.6 and 69% conversions, the $M_{n(star)}$(NMR) values are lower than the correspondent $M_{n(star)}$(th)s because of the higher percentage of linear PSt (Figure 5).

To confirm that the linear chain has an identical molecular weight to each of the arms attached to the core of the star, we hydrolyzed the dendrimer-star PSt in sodium methanol. The amide bond of the dendrimer-star PSt was cleaved to afford the linear PSt. The molecular weight of each arm can be directly obtained from its GPC curve (Figure 7). The GPC traces of the hydrolyzed product showed exactly the same molecular weight of the linear products. A shoulder on higher molecular weight was observed, and it may be due to incomplete hydrolysis or occurrence of some irreversible terminations, including coupling reactions between star and linear chain radicals, as shown in Scheme 4. The exact reason is not clear at present.

The influence of the molar ratio of RAFT agent **3** to St on RAFT polymerization was investigated. The results are summarized in Table 2. The 16-armed dendritic RAFT agent **4** was also used in the RAFT polymerization of St, and the results are also listed in Table 2. We can see that the molecular weights of the dendrimer-star PSts, Den(PSt)$_{16}$, obtained increased

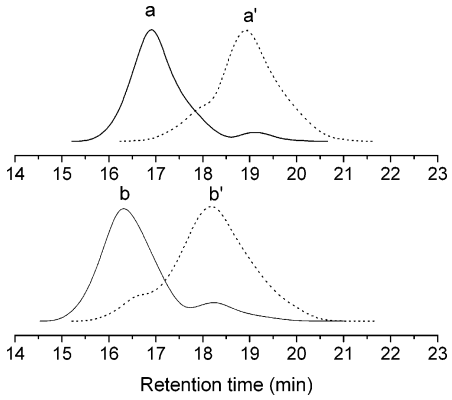


Figure 7. GPC chromatograms of polystyrene dendrimer-star (solid line) and the resulting linear polystyrene after hydrolysis (dash line): (a) $M_{n\ (star)}$(GPC) = 93 600, PDI = 1.14 (Table 1, entry 3); (a′) M_n = 23 100, PDI = 1.40; (b) $M_{n(star)}$(GPC) = 131 000, PDI = 1.25 (Table 1, entry 5); (b′) M_n = 32 500, PDI = 1.45.

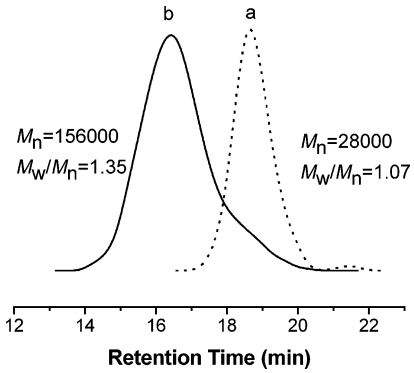


Figure 8. GPC chromatograms of dendimer-star diblock copolymer PSt-*b*-PMA (solid line) using dendrimer-star polystyrene (dash line) as macro CTA: (a) M_n(GPC) = 28 000, PDI = 1.07 (Table 2, entry 6); (b) M_n(GPC) = 156 000, PDI = 1.35.

with the molar ratio increase of St/dendritic RAFT agents in both cases.

Dendrimer-Star Block Copolymer, Den(PSt-*b*-PMA)$_8$. One key aspect of living radical polymerization is its application in the preparation block copolymers. The GPC curve of the dendrimer-star block copolymer obtained shown in Figure 8 demonstrates clearly the occurrence of the chain extension because its curve is shifted to a higher molecular weight position, and a shoulder at the low molecular weight appearing in Figure 8b may be ascribed to linear block copolymer formed during the block copolymerization based on the RAFT polymerization mechanism discussed above. In addition, a small amount of dead polymers in the macro RAFT agent may not excluded. To confirm further the formation of S(PSt-*b*-PMA)$_8$, the ^{1}H NMR spectra were measured and a typical spectrum is shown in Figure 9. In addition to the characteristic signals of PSt, the signal at $\delta = 3.7$ (D) ppm is ascribed to the ester methyl protons of MA units, confirming the formation of Den(PSt-*b*-PMA)$_8$. We can also find the signal at $\delta = 7.9$ (a) assigned to the ortho aromatic protons of dithiobenzoyl groups, which must result from RAFT block polymerization of MA.

Conclusion

Two multifunctional dithiobenzoate-terminated PPI dendrimer RAFT agents were synthesized, and they

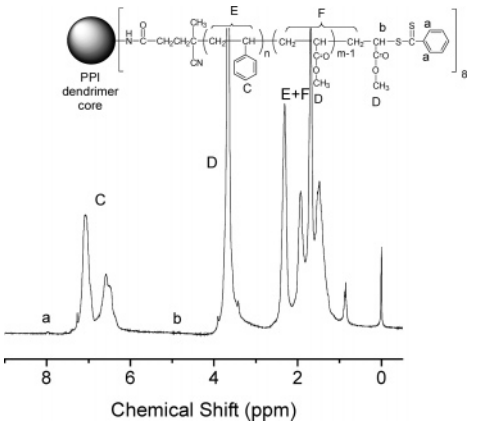


Figure 9. ^{1}H NMR of dendrimer-star block copolymer PSt-*b*-PMA (M_n(GPC) = 156 000, PDI = 1.35).

were successfully used in the preparation of well-defined dendrimer-star polymers via "core-first" RAFT approach. The polymerization displays living characters. With the propagation of the dendrimer-star polymer, the linear polymer grows in parallel, and its relative amount to dendrimer-star polymer increases also (12.4% at 69% conversion). Since each arm in dendrimer-star polymers and linear polymers both have the same possibility to propagate, they have similar molecular weights. This was confirmed by the hydrolysis of the dendrimer star polymer. No shielding effect was observed in the polymerization system because the chain radicals and RAFT sites existed consistently on the surface of dendrimer-star polymer. The dendrimer-star block copolymer, Den(PSt-*b*-PMA)$_8$, was successively prepared by the RAFT polymerization of MA using macro RAFT agent, and the linear block copolymer was observed during the block copolymerization.

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