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# Controlled Chain Branching by RAFT-Based Radical Polymerization

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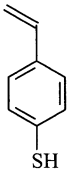
ABSTRACT: Styrene radical polymerization was carried out in the presence of a polymerizable dithioester, benzyl 4-vinyldithiobenzoate, which possesses a dithioester group and a polymerizable double bond. Branched polystyrene was formed during the polymerization, as indicated by multimodal GPC curves of the products. The branched polystyrene contains a dithiobenzoate C(=S)S moiety at each branch point and thus can be analyzed by cleavage with amine. After cleavage, the GPC profiles became narrow. The molecular weight of the cleaved product increased linearly with monomer conversion, illustrating a living fashion of the polymerization. Solution property obtained by simultaneous online measurements of viscosity and light scattering indicates that the viscosity of the branched product decreased remarkably as compared to the linear polystyrene of equivalent molecular weight. The copolymerization behavior of styrene and benzyl 4-vinyldithiobenzoate was investigated by FT-IR monitoring during the polymerization. The results show that the latter was incorporated homogeneously into polystyrene chain. Therefore, branched polystyrene was synthesized with controlled architecture in the light of the length and narrow distribution of primary chains as well as the degree and the distribution of branching along the polymer chain.

## Introduction

Synthesis of well-defined branched vinyl polymers remains a challenge in polymer chemistry. Traditionally, branched vinyl polymers have been produced in radical polymerization through chain transfer to polymer and by terminal double bond polymerization (TDBP).[1] In the latter, the terminal double bonds were formed by chain transfer to monomer and by biradical disproportion termination. However, the architectures of the resulting polymers are uncontrollable in terms of degree of branching (DB) and molecular weight of the primary chains. Multifunctional monomers, such as divinylbenzene[1] and chain transfer monomers (CTMs) **1**[2] and **2**,[3] were used as branching agent in free radical polymerization to control DB. The CTMs are advantageous over divinyl monomers in that they lead to extensive branching without gelation. It was predicted theoretically[4] that homogeneously branched polymers, in which all of the primary chains have equal branch densities and connect randomly to each other, can be produced by the CTM approach. However, the primary chain length is polydisperse due to the uncontrolled radical polymerization, with a Schulz−Flory most probable distribution even in a continuous feed reaction.[4]

Branched vinyl polymers were also prepared by copolymerization of conventional monomers with those that are able to undergo self-condensing vinyl polymerization (SCVP). SCVP was developed by Fréchet and co-workers[5] to prepare hyperbranched polymers using an *ini*tiator mono*mer*, *inimer*, which consists of a double bond and a latent initiating site for vinyl polymerization. It was then used to control the degree of branching in the synthesis of highly branched and hyperbranched polyacrylates[6−9] and polystyrene[10,11] by tuning the ratio of conventional comonomer to SCVP inimer. Hawker and co-workers[10] found that **3**, an inimer containing an initiating moiety for controlled/“living” radical polymerization, is able to control the length and length distribution of primary chains in the highly branched structure.



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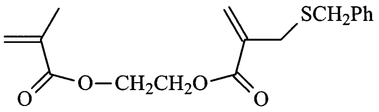

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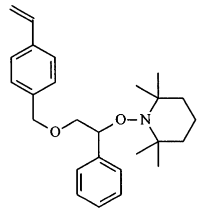

**3**

Controlled/“living” radical polymerization has progressed rapidly in the past decade. The basic mechanism is to protect highly active growing radicals through a reversible activation/deactivation process using some chemical species. In addition to the extensively investigated stable free radical mediated polymerization (SFRP)[12] and atom transfer radical polymerization (ATRP),[13] a dithioester mediated system was recently developed by Moad and co-workers in which the reversible activation/deactivation is achieved through a reversible addition−fragmentation chain transfer (RAFT) process.[14] The process involves the addition of propagating radical to dithioester, **4**, and subsequent fragmentation of the resulting intermediate **5** at either of its two arms to regenerate a propagating radical (Scheme 1). Since this chain transfer process is fast, each chain has equal probability to propagate, giving rise to a very narrow molecular weight distribution.[14]

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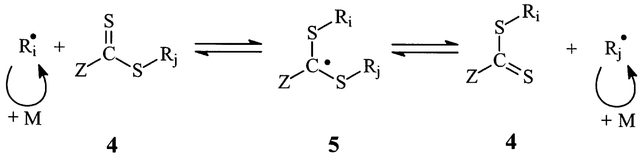
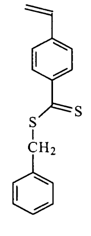
**Scheme 1. Mechanism of RAFT Process**

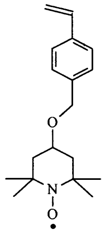


M: monomer
Z: (substituted)phenyl ring
$R_i^{\bullet}$ and $R_j^{\bullet}$: propagating radicals

In this paper, we synthesized a RAFT monomer, **6**, which consists of a dithioester moiety and a double bond, and copolymerized it with styrene to prepare highly branched polystyrene. The branched structure was controlled in terms of molecular weight and polydispersity of primary chains as well as the degree of branching (DB) and the distribution of branch points along the primary chain. The structure **6** not only is different from **1** and **2** in that it can mediate controlled/"living" radical polymerization due to the dithioester moiety but also is different from SCVP inimers since it cannot initiate polymerization. Therefore, initiation by a radical initiator or by thermal initiation of styrene is necessary. Furthermore, the location of dithioester moiety at branch point facilitates the analysis of the resulting polymers by aminolysis. Our previous work demonstrated that polymerizable nitroxyl stable radicals, such as **7**[15] and **8**,[16] act as branching agents in radical polymerization as well. However, the dithioester pendent group in the present work has wider monomer tolerance, and the synthetic principle can be extended to the synthesis of polyacrylates, etc.



**6**



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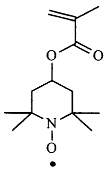


**8**

## Experimental Section

**Materials.** Styrene (Shanghai Yonghua Special Chemicals, 99%) was distilled under reduced pressure. Tetrahydrofuran (Shanghai Feida, 99.5%) was dried over $CaH_2$ and distilled from Na/benzophenone. 2,2′-Azobis(isobutyronitrile) (AIBN) (Shanghai 4th Factory of Chemicals, 99%) was recrystallized from methanol. 4-Bromostyrene (ACROS, 96%) was dried over $CaH_2$. Carbon disulfide (Shanghai 4th Factory of Chemicals, 99%) was purified by vigorously shaking with $KMnO_4$ (0.4 wt % based on $CS_2$), followed by filtration and distillation to collect a colorless fraction. Benzyl bromide (Shanghai Wulian Chemicals, 98%) was used as received. Bromobenzene (Shanghai Chemical Reagent Co. Ltd., 99.5%) was dried over $CaCl_2$ and distilled before use.

**Measurements.** The number-average molecular weight, $M_n$, and polydispersity index, PDI, of all samples were measured by gel permeation chromatography (GPC) through three Waters Styragel columns (pore size: $10^2$, $10^3$, and $10^4$ Å) in series calibrated by narrow polystyrene standard. THF was used as the eluent at a flow rate of 1 mL/min at 40 °C. The elution of the sample was detected by a Waters 410 RI detector. Additional measurements of $M_n$ and PDI were performed on a Waters 590 GPC system equipped with two AM GEL columns (5 $\mu$m, linear, molecular range 5000−$10^6$ g/mol), a Waters 410 RI detector, and a Viscotek model T60 detector that gives both viscosity data and light scattering (LS) results, using THF as the eluent at a flow rate 1 mL/min at 30 °C (LS angle, 90°; laser wavelength, 670 nm).

$^1$H NMR measurements were carried out on a Bruker (500 MHz) NMR instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the reference. UV−vis spectra were recorded on an Agilent-8453 instrument using $CCl_4$ as solvent. GC-MS was measured on a Finnigan Voyager instrument. Element analysis was carried on a Heraeus 1106 instrument.

Monomer conversions were determined by thermogravimetric analysis (TGA) of samples taken from the reaction mixture on a NETZSCH TG-209 instrument under a nitrogen atmosphere. The temperature was elevated from 25 to 510 °C at a rate of 20 K $min^{-1}$. The weight loss above 275 °C gave the polymer content.

In copolymerization study, monomer conversions of styrene and **6** were measured at different times by a Magna-550 FT-IR instrument using a KBr pellet of fixed thickness.

**Syntheses of Dithioesters.** *Benzyl 4-Vinyldithiobenzoate,* **6**. An ice-bathed Grignard solution prepared from 4-bromostyrene (9.15 g, 50 mmol) and magnesium ribbon (1.32 g, 55 mmol) in 35 mL of THF was vigorously stirred while a solution of carbon disulfide (3.80 g, 50 mmol) in 20 mL of dry THF was dropped in. The resulting dark red mixture was warmed at 50 °C for 1 h before cooled to room temperature. A solution of benzyl bromide (9.41 g, 50 mmol) in 20 mL of THF was then dropped in. The temperature was maintained at 50 °C for 4 h. The whole process was conducted under a nitrogen atmosphere.

After distillation of the solvent, the resulting thick red oil (about 10 mL) was mixed with 50 mL of 10% aqueous solution of $NH_4Cl$ and extracted with ethyl ether (3 × 30 mL). The organic layer was dried on $MgSO_4$ overnight and condensed. The resulting red oil was purified by chromatography through an $Al_2O_3$ (neutral, 60 mesh) column (eluent: cyclohexane) and recrystallization from petroleum ether. Red crystals: yield 4.7 g (35%, based on 4-bromostyrene); mp 49.3 °C. UV−vis max ($CCl_4$): 332 and 507 nm. $^1$H NMR: $\delta$ (ppm) 4.59 (s, 2H, C**H**$_2$,), 5.38 (d, 1H, C**H**$_2$=CH, $J = 10.9$ Hz), 5.86 (d, 1H, C**H**$_2$=CH, $J = 17.5$ Hz), 6.73 (q, 1H, $CH_2$=C**H**), 7.24−7.40 (m, 7H, Ar**H**), 8.00 (d, 2H, Ar**H**, $J = 6.7$ Hz). FT-IR: $\nu$ (cm$^{-1}$) = 1230 and 1053 (C=S), 3088, 916, 990 (=C−H), 1660 (C=C vinyl). GC-MS (EI): $m/e$ = 77, 91, 147, 237, 270. Calcd for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22; S, 23.71. Found: C, 71.91; H, 5.31; S, 23.95.

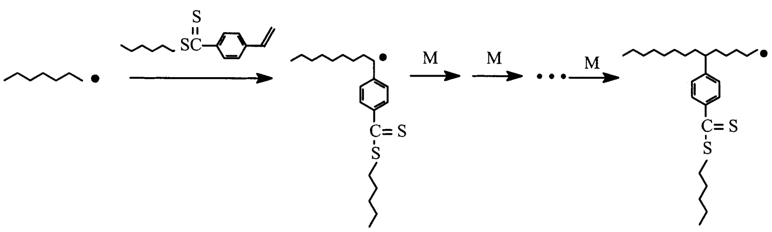
*Benzyl Dithiobenzoate,* **9**. The procedure is similar to that in the literature.[17−19] The product is red oil. Yield: 60% (based on bromobenzene). UV−vis max ($CCl_4$): 302 and 504 nm. $^1$H NMR: $\delta$ (ppm) = 4.59 (s, 2H, C**H**$_2$), 7.31−7.39 (m, 7H, Ar**H**), 7.51 (t, 1H, Ar**H**(para)), 7.98−8.00 (d, 2H, Ar**H**(ortho), $J = 8.0$ Hz). FT-IR: $\nu$ (cm$^{-1}$) = 1226 and 1044 (C=S). GC-MS (EI): $m/e$ = 77, 91, 121, 211, 244. Calcd for $C_{14}H_{12}S_2$: C, 68.81; H, 4.95; S, 26.24. Found: C, 68.59; H, 5.14; S, 24.99.

**Polymerization.** The polymerizations were carried out in bulk at various molar ratio of dithioester to monomer, 1/10, 1/50, 1/100, 1/200, and 1/300. Taking the 1/300 system as an example, a solution of **6** (0.27 g, 1.0 mmol) in styrene (31.20 g, 0.30 mol) was degassed by three freeze−pump−thaw cycles. Then the mixture was thermostated at 120 °C under a nitrogen atmosphere. The samples taken from the system at reaction times of 0.5, 1, 2, 3, 5, 7, 9, 11, 16, and 24 h were quenched into liquid nitrogen to stop the polymerization. Monomer conversion (at 24 h): 83% (by TGA). The final reaction mixture was precipitated into methanol, and a pink solid was obtained. $M_n = 21.7 \times 10^4$ (by LS) and $6.45 \times 10^4$ g/mol (by GPC); PDI = 4.6 (by LS) and 9.3 (by GPC).

The copolymerization study was carried out under the same reaction conditions. The reaction mixture at different times was injected into a KBr cell of fixed thickness for the measurement of FT-IR.

**Cleavage of the Product.** A solution of resulting branched polymer (1 g, $M_{n,GPC}$ = 84 900, PDI = 1.99) and 1 mL of ethylamine in THF (3 mL) was stirred at ambient temperature

**Scheme 2. Chain Branching during the Polymerization**



for 24 h under a nitrogen atmosphere. Then the mixture was dropped into large amount of methanol, and a white solid was precipitated. The solid was washed with water to neutral and redissolved in 3 mL of THF, followed by a period of 4 h at 40 °C with stirring in the presence of acetic acid (2 mL) and zinc powder (1 g). A white solid was obtained after precipitation from methanol, washing with water to neutral, and drying in a vacuum. White powder: yield 0.67 g; $M_{\mathrm{n,cleave}} = 29\,800$; PDI = 1.16. The results of cleavage are summarized in Figure 3.

## Results and Discussion

All polymerizations, except the homopolymerization of **6**, were initiated by thermal initiation of bulk styrene. We did not observe an induction period in any cases, indicating that the equilibrium of the reversible addition−fragmentation is fast, and the initial consumption of growing radicals in the formation of the intermediate is negligible. However, the polymerization is obviously slow when the amount of dithioester is high (entries 5−7 in Table 1). The retardation was also observed by other groups and explained according to different pathways. The CSIRO group[20] attributed the retardation to the slow fragmentation of the intermediate radical and/or the slow initiation of the expelled radical. Davis' group[21] observed, by a carefully designed radiation/waiting experiment, that the resulting radical in the radiation survived the waiting period. Therefore, they deduced that there is a storage reservoir of either radical or nonradical intermediate, which consume part of growing radicals. Monteiro[22] and Fukuda[23] proposed a cross-termination between propagating and intermediate radical, which causes a retarded polymerization. The results in the present work, i.e., the retardation without induction period, were correlated to a cross-termination process. A larger amount of dithioester leads to larger concentration of the intermediate and therefore higher termination rate between intermediate and growing radicals. However, it should be pointed out that the other two postulations are also reasonable, although not in this case, with respect to the different structure of dithioesters and the reaction conditions. The present work is focused on the synthesis of branched polymers and will not tackle this issue in detail. The final products for all systems except the homopolymer of **6** were soluble in THF without any hint of network formation.

*1. Chain Branching during the Polymerization.* As an example, Figure 1 compares the GPC profiles of the resulting polymers of the systems using benzyl dithiobenzoate (reference) and **6** as RAFT agents on a constant ratio of dithioester/monomer = 1/300. While the former shows the character of a living polymerization, the latter became multicomponent and thus very broad as the reaction proceeds. This indicates that chain branching took place during the polymerization, in which **6** plays the role of branching agent (Scheme 2). For the formation of a branch point, two steps are obviously necessary, i.e., the "growth" of a branch by propagation of a living chain end-capped by dithioester and its connection to the main chain by TDBP of the styrenic moiety. A T-shaped branch point is thus formed regardless of the sequence of the two steps. Since all living chains start to grow simultaneously, the main process of branching is the TDBP of polymeric dithioesters with increasing length. Some monomeric dithioester, **6**, may polymerize at the initial stage. The resulting pendent dithioester moiety also acts as a RAFT agent.

Because of the chain branching reaction, the molecular weight distribution of the resulting polymer is ever-broadening as the polymerization proceeds, a tendency predicated[24] and reported[25] previously. In Figure 1, the GPC profile contains a number of distinguishable shoulders instead of a broad band, indicating different branching generations. The tailing peak corresponds to primary chains, as illustrated by the cleavage results (see next section). The leading peak at the position of $M_{\mathrm{p,GPC}} \approx 5 \times 10^5$ g/mol corresponds to the component formed by connection of two highly branched clusters through TDBP or biradical coupling. It should be noted that the real $M_{\mathrm{p}}$ of this component should be much higher than the apparent GPC value since GPC is essentially based on hydrodynamic volume, which is lower for branched polymer than for linear one at the same molecular weight.

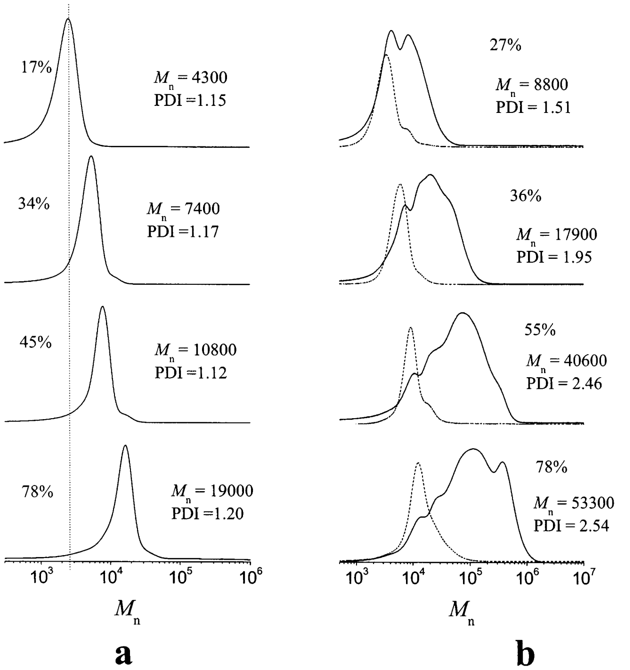
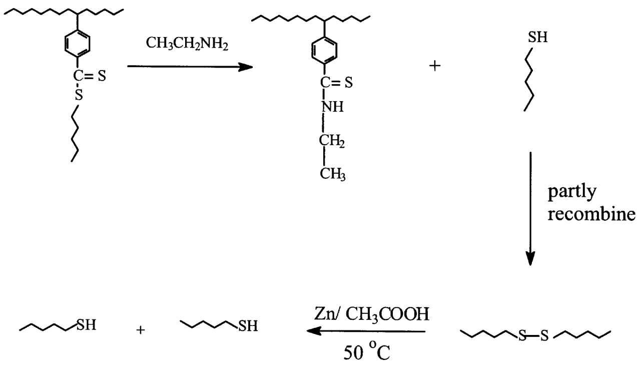


**Figure 1.** GPC traces of styrene polymerization mediated by benzyl dithiobenzoate (a) and **6** (b) at the same ratio of $[\text{dithioester}]_0/[\text{St}]_0 = 1/300$. The percentage indicates monomer conversion. The dashed lines in (b) are for cleaved product after aminolysis/reduction.

**Scheme 3. Aminolysis and Subsequent Reduction of the Branched Product**



We proved that chain branching occurs during the polymerization by cleavage of the products. As shown in Scheme 3, the branched structure can be broken by aminolyzing the dithioester moiety[26] at the branch point.

The cleavage was carried out using ethylamine as the aminolysis agent. The pink branched product became white after precipitation. However, the GPC profile of the resulting product shows a bimodal distribution, the molecular weight of one peak approximately doubling another. We suspect that two of the resulting polymers with $\omega$-mercapto groups recombine to form a persulfide bond. Therefore, we carried out a reference aminolysis experiment using linear polystyrene possessing a dithioester end group prepared by styrene polymerization mediated by benzyl dithiobenzoate, **9**. As shown in Figure 2, the fraction of the doubled molecular weight increases along with the reaction time due to the coupling between the resulting mercapto end groups. After reduction, the coupled product was cleaved again, as indicated by the dashed line in Figure 2. Thus, a reducing agent, Zn/acetic acid, was also added to the reaction mixture after the aminolysis of the branched polymers. The mixture was then warmed for 4 h, and a unimodal GPC profile was obtained.

After cleavage, the molecular weight depends linearly on monomer conversion and on the ratio of monomer to dithioester. The measured molecular weight agrees with the theoretical weight predicted from the feed ratio of styrene and **6**. In addition, the PDI of primary chains remains low, around 1.2 at high conversion. The results are shown in Figure 3. All these polymerization behaviors are consistent with those previously reported by using dithioesters without vinyl group.[14a]

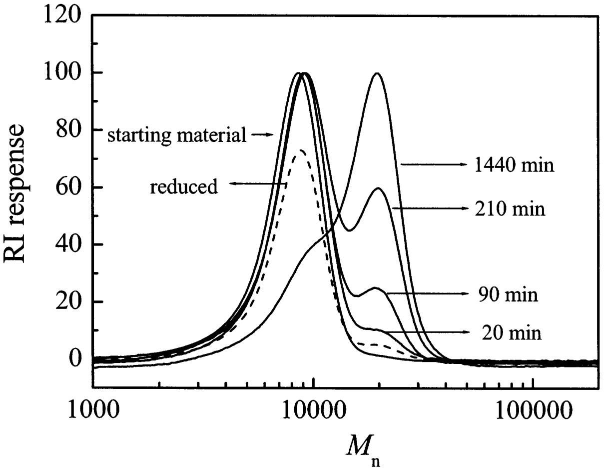


**Figure 2.** Monitoring the GPC evolution during the process of aminolysis and the subsequent reduction with Zn/$CH_3COOH$ at 50 °C for 4 h. The starting material is a linear polystyrene prepared by benzyl dithiobenzoate (1 equiv) mediated polymerization of styrene (100 equiv). The treating time with ethylamine at room temperature was indicated in the figure. The dashed line is the result after reduction.

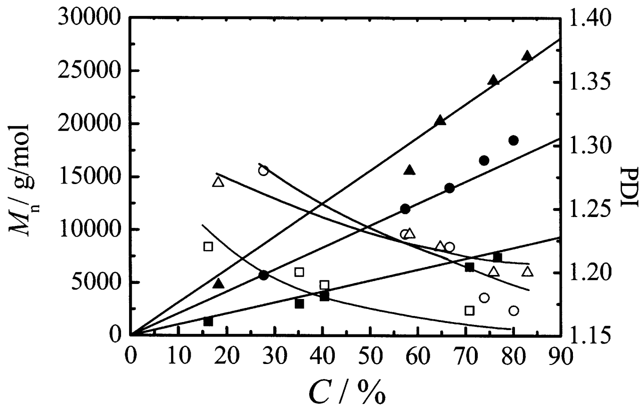


**Figure 3.** Dependence of $M_n$ and PDI of the cleaved product on total conversion, $C$, of styrene and **6**. Polymerization parameters: $[\mathbf{6}]_0/[St]_0 = 1/300$ (▲), 1/200 (●), and 1/100 (■). The lines guiding the molecular weight are theoretical values. The lines guiding the polydispersity are fitted curves. Temperature: 120 °C. Thermal initiation.

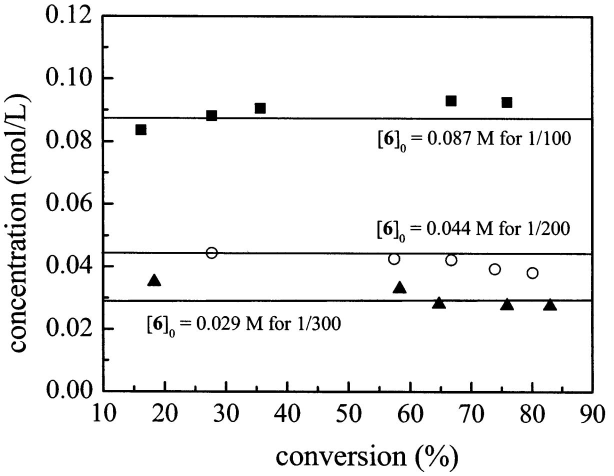


**Figure 4.** Concentration of living chains vs conversion in living radical polymerization of styrene in the presence of **6** by thermal initiation at 120 °C at the various ratios of $[\mathbf{6}]_0/[St]_0 = 1/300$ (▲), 1/200 (○), and 1/100 (■). The lines represent different values of $[\mathbf{6}]_0$.

Although the polymerization was initiated by thermal initiation, the number of living chains was kept nearly constant during the polymerization. Figure 4 shows that the calculated concentration of living chains is roughly equal to the feed amount of dithioester, indicating that the number of chains generated by the thermal initiation of styrene and the number of chains terminated biradically are negligible as compared to the number of living chains in the reaction medium.

*2. Control of Branch Length and Branch Density.* As discussed above, the branch length, or the molecular weight of primary chains, as well as the branch length distribution, can be well controlled by RAFT process. The relatively narrow distribution is a consequence of living polymerization of both attached and unattached primary chains, indicating that both the polymerized

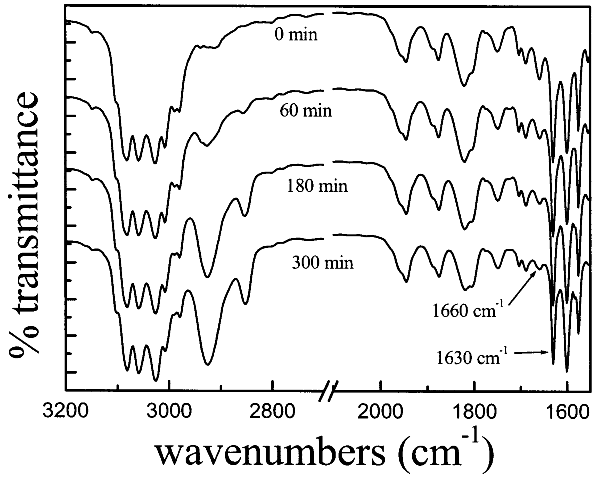


**Figure 5.** IR spectra of the reaction mixture at different times of styrene polymerization mediated by **6**, with $[\mathbf{6}]_0/[\mathrm{St}]_0 = 1/10$.

and unpolymerized dithioesters act as RAFT agent with similar reactivity.

The number of branches depends on both the feed ratio of monomer to polymerizable dithioester as well as the polymerization conversion. It is not difficult to understand this if we regard polymerizable dithioesters as $AB_2$ monomers that play the role of branching agent.[1] As the polymerization proceeds, more and more double bonds in dithioesters polymerized to form branching points, as indicated by the broadening of GPC profiles in Figure 1. Therefore, the larger amount of polymerizable dithioester used in the polymerization, and the higher the conversion, the higher the branching density in the resulting polymer.

The distribution of branch points along the main chain was obtained by copolymerization study of **6** and styrene at a relatively higher feed ratio of **6**/styrene, i.e., 1/10 and 1/50. The conversions of monomer pairs were obtained by monitoring the evolution of peak height at 1630 cm$^{-1}$ (C=C stretch in styrene) and at 1660 cm$^{-1}$ (C=C stretch in **6**). To eliminate the effect of the fluctuation of the sample thickness, the spectra were rescaled by fixing the peak height at 1600 cm$^{-1}$ of the phenyl ring, whose concentration is constant throughout the polymerization.

Figure 5 shows the IR spectra of the reaction mixture at different reaction times. Clearly, the peak height at 1630 and 1660 cm$^{-1}$ decreases relative to that of 1600 cm$^{-1}$ along with the reaction time, while new peaks at 2920 and 2850 cm$^{-1}$ assigned to main-chain C−H stretch appear and strengthen during the polymerization. Since the feed amount of **6** is much lower than that of styrene, Jaacks' equation holds in this case,[27]

$$\log \frac{[\mathrm{St}]_t}{[\mathrm{St}]_0} = r_{\mathrm{st}} \log \frac{[\mathbf{6}]_t}{[\mathbf{6}]_0} \qquad (1)$$

where $[\mathrm{St}]_t$ and $[\mathbf{6}]_t$ are the concentrations of styrene and **6** at time $t$, respectively, and $r_{\mathrm{st}}$ is the reactivity ratio of styrene. In the analysis, we replaced the concentration of styrene and **6** by the peak height at 1630 and 1660 cm$^{-1}$, respectively.

Equation 1 was plotted in Figure 6 for the measurement at different times. The data points fall on a straight line, indicating that the incorporation rate of **6** was constant and, consequently, homogeneous random branching along the main chain was formed. Since the slopes for both cases are quite close, the incorporation amount of **6**, and therefore the degree of branching, depends strongly on $[\mathbf{6}]_0$, the initial feed amount of dithioester.

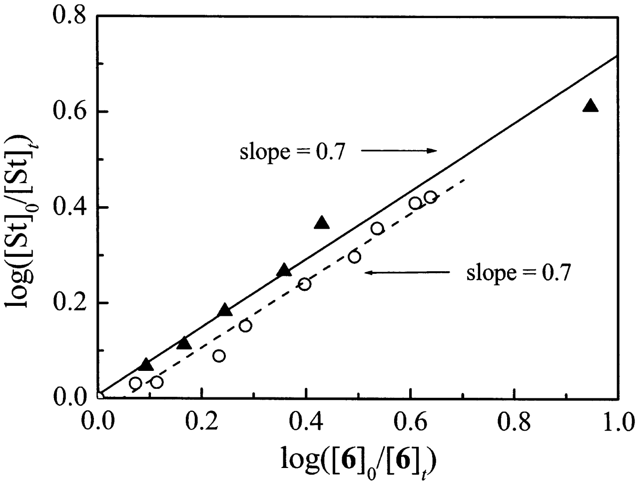


**Figure 6.** Double-logarithmic relations of $[\mathrm{St}]_0/[\mathrm{St}]_t$ against $[\mathbf{6}]_0/[\mathbf{6}]_t$ in living radical copolymerization of styrene and **6** at 120 °C. $[\mathbf{6}]_0/[\mathrm{St}]_0 = 1/10$ (▲) and 1/50 (○).

*3. Solution Properties of the Branched Polystyrene.* The solution properties of branched polymers, such as $M_n$ dependence of intrinsic viscosity and the radius of gyration, are remarkably different from their linear analogues due to the compact character of the branched structure.[28] More specifically, the value of the exponential in the Mark−Houwink relation for branched polymer is apparently smaller than that for the linear one.[29] The effect of architectural branching is also expressed by the contracting factor, $g'$,[28] which is defined as

$$g' = \frac{[\eta]_{\mathrm{b}}}{[\eta]_{\mathrm{l}}}$$

where $[\eta]_{\mathrm{b}}$ and $[\eta]_{\mathrm{l}}$ are the intrinsic viscosity of branched and linear polymers of identical molecular weight, respectively.

The dependence of intrinsic viscosity on molecular weight was determined by GPC equipped with a viscosity detector and a 90 °C light scattering detector. In the analysis, we assume that each slice of GPC profile represents a narrow disperse fractionated component with homogeneous branch density. The Mark−Houwink equation for the $i$th slice of GPC profile can be written as

$$[\eta]_i = KM_{\mathrm{w},i}^{\ \alpha_i}$$

Figure 7 shows the double-logarithm plots of $[\eta]_i$ against $M_{\mathrm{w},i}$. Obviously, the viscosity of the branched products is lower than that of the linear reference, especially at higher molecular weight. It is interesting to note that, while some plots are straight lines (run 2), some appear to have a transition point (runs 3 and 4), indicating that high molecular weight clusters with larger branch density have been formed for the system with larger feed amount of polymerizable dithioester. It is also possible that the biradicals coupling took place between branched macromolecules, and within the branched macromolecule (intramolecularly) at high monomer conversion, leading to higher branch density

**Table 1. Polymerizations and the Analytical Results of the Products**

| run | styrene/g, mmol | dithioester/g, mmol | C,[b] % (time, h) | $M_{n,LS}/10^4$ g/mol | PDI | $[\eta]_w$[c]/dL/g | α[d] | $R_{g,w}$[e]/nm | $g'$[f] |
|---|---|---|---|---|---|---|---|---|---|
| 1[a] | 5.50, 52.9 | 0.04, 0.18 | 94.0 (32) | 2.94 | 1.13 | 0.18 | 0.73 | 5.96 | / |
| 2 | 5.20, 49.9 | 0.05, 0.17 | 83.0 (24) | 21.78 | 4.60 | 0.55 | 0.45 | 23.78 | 0.18 |
| 3 | 41.60, 399 | 0.54, 2.00 | 80.1 (24) | 15.79 | 9.85 | 0.54 | 0.50 | 25.38 | 0.13 |
| 4 | 5.20, 49.9 | 0.14, 0.50 | 76.7 (24) | 11.08 | 9.07 | 0.51 | 0.48 | 22.32 | 0.17 |
| 5 | 5.20, 49.9 | 0.27, 1.00 | 79.9 (200) | 2.23 | 2.22 | 0.14 | 0.52 | 5.87 | 0.49 |
| 6 | 2.11, 20.3 | 0.55, 2.02 | 74.8 (200) | 0.42 | 2.08 | 0.04 | 0.33 | 2.15 | 0.43 |
| 7[g] | 0, 0 | 0.49, 1.82 | 57.2 (48) | 0.37 | 2.14 | 0.04 | 0.35 | 2.04 | 0.46 |

[a] Reference system using benzyl dithiobenzoate as RAFT agent. [b] Monomer conversion. [c] Weight-average intrinsic viscosity. [d] Mark–Houwink value. [e] Weight-average radius of gyration. [f] Contraction factor. [g] Homopolymerization of **6** in the presence of AIBN (0.0030 g) at 78 °C.

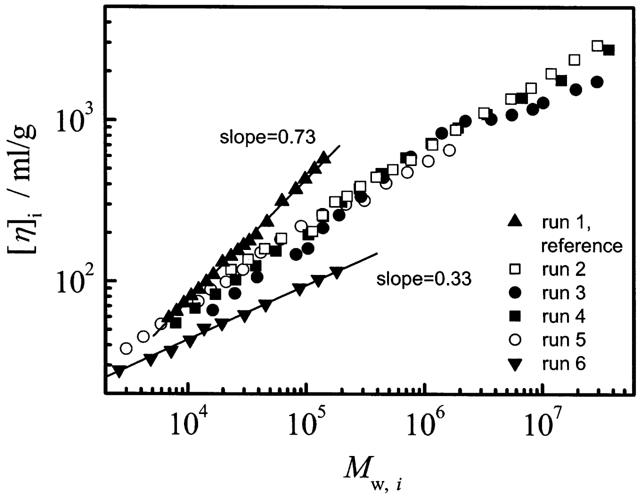


**Figure 7.** Mark–Houwink plots of branched products from styrene polymerization in the presence of **6**. $[\mathbf{6}]_0/[\mathrm{St}]_0 = 1/300$ (□), 1/200 (●), 1/100 (■), 1/50 (○), and 1/10 (▼); $[\text{benzyl dithiobenzoate}]_0/[\mathrm{St}]_0 = 1/300$ (▲) (as linear reference).

which is reflected in the Mark–Houwink relations. Table 1 gives the weight-average Mark–Houwink exponentials for the final products of various polymerization systems. Those of branched polymers are smaller, from 0.33 to 0.52, whereas that of the reference is 0.73, within the typical range for linear polymers.[1] The product of the system with $[\mathbf{6}]_0/[\mathrm{St}]_0 = 1/10$, and the homopolymer of **6** give Mark–Houwink values of 0.33 and 0.35, respectively, quite close to that of hyperbranched polystyrene,[30] 0.43.

The contraction factor, $g'$, is obtained as a dimensionless ratio of the measured intrinsic viscosity of the branched products to that of linear references calculated according to the following relations:[31]

$$[\eta]_l = 0.98 \times 10^{-4} M_w^{\,0.746} \quad \text{for } M_w = (10.0\text{–}100.0) \times 10^4 \text{ g/mol}$$

$$[\eta]_l = 1.70 \times 10^{-4} M_w^{\,0.687} \quad \text{for } M_w = (2.0\text{–}10.0) \times 10^4 \text{ g/mol}$$

$$[\eta]_l = 6.03 \times 10^{-4} M_w^{\,0.553} \quad \text{for } M_w < 2.0 \times 10^4 \text{ g/mol}$$

Table 1 shows that, although less than unity, the magnitude of $g'$ does not show a dependence on the feed ratio of dithioester to monomer. The reason can be due to the broad distribution of the products, which varies not only in molecular weights but also in branching density. It is difficult to obtain products for various systems with comparable molecular weight and molecular weight distribution. Therefore, it seems that for the broad disperse branched samples $g'$ may not give precise results related to the architecture of polymer chains.

## Conclusions

Controlled chain branching was achieved by copolymerization of styrene with a polymerizable dithioester, **6**, which plays the role of chain branching agent. Although additional initiating radical is necessary, the newly initiated chains compose a negligible fraction as compared to the total amount of living chains. The polymerization is thus well controlled by dithioester moieties of both polymerized and unpolymerized **6**. The growth of primary chains is through a living fashion; i.e., the molecular weight increases linearly with monomer conversion, and the dispersity remains low. The degree of branching depends on both the conversion and the ratio of monomer to **6**. Copolymerization study by FT-IR demonstrated that **6** polymerizes at a constant rate along with styrene, indicating a homogeneous distribution of branch units along the polymer chain. The branched product show decreased intrinsic viscosity than those of linear polystyrene.

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## References and Notes

(1) Flory, P. J. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(2) Tung, L. H.; Hu, A. T.; McKinley, S. V.; Paul, A. M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2027.
(3) Yamada, B.; Konosu, O.; Tanaka, K.; Oku, F. *Polymer* **2000**, *41*, 5625.
(4) (a) Tobita, H. *Macromolecules* **1997**, *30*, 1685. (b) Tobita, H. *Macromolecules* **1997**, *30*, 1693.
(5) Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080.
(6) Matyjaszewski, K.; Gaynor, S. G.; Kulfan, A.; Podwika, M. *Macromolecules* **1997**, *30*, 5192.
(7) Matyjaszewski, K.; Gaynor, S. G.; Müller, A. H. E. *Macromolecules* **1997**, *30*, 7034.
(8) Matyjaszewski, K.; Gaynor, S. G. *Macromolecules* **1997**, *30*, 7042.
(9) Simon, P. F. W.; Müller, A. H. E.; Pakula, T. *Macromolecules* **2001**, *34*, 1677.
(10) Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763.
(11) Gaynor, S. G.; Edelman, S. Z.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079.
(12) For example: (a) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Pat. 4,581,429, 1985. (b) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. K.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987. (c) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185.
(13) (a) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901. (b) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (c) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.

(14) (a) Chiefari, J.; Chong, Y. K.; 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. (b) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071. (c) Hawthorne, D. G.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 5457. (d) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977.

(15) Tao, Y.; He, J.; Wang, Z.; Pan, J.; Jiang, H.; Chen, S.; Yang, Y. *Macromolecules* **2001**, *34*, 4742.

(16) Li, C.; He, J.; Cao, J.; Yang, Y. *Macromolecules* **1999**, *32*, 7012.

(17) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. Patent WO 98/01478, 1998.

(18) Tabak, G.; Pham, Y. N.; Levesque, G.; Haraoubia, R. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 117.

(19) Jensen, K. A.; Pedersen, C. *Acta Chem. Scand.* **1961**, *15*, 9.

(20) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993.

(21) (a) Barner-Kowollik, C.; Quinn, J. F.; Nguyen, T. L. U.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2001**, *34*, 7849. (b) Barner-Kowollik, C.; Quinn, J. F.; Morsley, D. R.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1353. (c) Barner-Kowollik, C.; Vana, P.; Quinn, J. F.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1058.

(22) Monteiro, M. J.; Brouwer, H. *Macromolecules* **2001**, *34*, 349.

(23) Kwak, Y.; Goto, A.; Tsujii, Y.; Murata, Y.; Komatsu, K.; Fukuda, T. *Macromolecules* **2002**, *35*, 3026.

(24) Mueller, A. H. E.; Yan, D.; Wulkow, M. *Macromolecules* **1997**, *30*, 7015.

(25) Matyjaszewski, K.; Gaynor, S. G.; Mueller, A. H. E. *Macromolecules* **1997**, *30*, 7034.

(26) (a) Delere, M.; Levesque, G. *Macromolecules* **1990**, *23*, 4733. (b) Tabak, G.; Pham, T. N.; Levesque, G. *Polymer* **1998**, *39*, 5561. (c) Bonnans, P. C.; Levesque, G.; Toulin, V. *React. Funct. Polym.* **2001**, *47*, 77.

(27) Jaacks, V. *Makromol. Chem.* **1972**, *161*, 161.

(28) For a recent review: Burchard, W. *Adv. Polym. Sci.* **1998**, *143*, 113.

(29) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.

(30) (a) Ishihama, Y.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993**, *26*, 744. (b) Ishihama, Y.; Sawamoto, M.; Higashimura, T. *Polym. Bull. (Berlin)* **1990**, *23*, 361.

(31) The measurement of linear polystyrene standards in the following reference was carried out at the same condition with that in this work. Huang, Y.; Bu, L.; Zhang, D.; Hao, L.; Su, C.; Xu, Z. *J. Funct. Polym.* **2000**, *13*, 182 (in Chinese).

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