

Synthesis of Polystyrene Microgel with a Hyperbranched Polyglycerol Scaffold as Core: Effect of Shell Congestion

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Received 16 November 2006; accepted 2 April 2007

DOI 10.1002/app.26933

Published online 30 August 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two hyperbranched polyglycerols (PG) (**1a**: $M_n = 2000$, **1b**: $M_n = 8000$), both with 61% of the overall hydroxyl groups being transformed into trithiocarbonates (**2a**, **2b**, with 16 and 65 OH groups being replaced by trithiocarbonates, respectively), can be used as a reversible addition-fragmentation chain transfer (RAFT) agent. Polymerization of styrene mediated by **2a/2b** was in a living manner, resulting in star-like, amphiphilic, core-shell structured polymers with 16 arms (**3a**) and 65 arms (**3b**), respectively. It was found that for system mediated by **2b**, more serious side reaction (radical-radical coupling) occurred than that by **2a**, most probably due to their dif-

ference in shell congestion. A shell-crosslinked polymer could be prepared in the presence of divinylbenzene via a one-pot route at solid content up to 20%, but analysis proved the crosslinking was incomplete. Furthermore, the 65-arm-star polymer (**3b**) more tended to undergo macroscopic rather than intramolecular crosslinking than the 16-arm-star polymer (**3a**) did. The phenomenon might again be attributed to their difference in shell congestion. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3688–3693, 2007

Key words: microgel; star polymers; living polymerization; core-shell polymers; crosslinking

INTRODUCTION

Core-shell structured polymer^{1–4} is receiving increasing interest due to its potential in various branches of science and technology, where the core can confer topology void, H-bonding interaction, ionic interaction, hydrophobic/hydrophilic interaction, and/or coordination interaction with the guest objects, and the shell can confer protection, compartment, and solubilization. Hyperbranched polyglycerol (PG)^{5,6} is a useful scaffold for the construction of core-shell structured polymer. PG is a one-pot synthesized, cost-effective polymer, whose dense population of hydroxyl groups on the surface constitutes a platform of chemical modification, and simple modification of PG can lead to amphiphilic core-shell structured polymer with interesting property. The modified PGs have been used as nanocapsule for entrapping guest molecules⁴ and as template for synthesis of elemental/compound metal nanoparticles.^{7,8} Also, PG can be used as a scaffold to set up well-defined, onion-like polymer particle. For example, part of the hydroxyl groups of PG are transformed into trithiocarbonates, which are effective

reversible addition-fragmentation chain transfer (RAFT)⁹ agent, and the latter has been used to mediate the polymerization of a variety of monomers in a controlled/living manner, leading to core-shell structured polymer object, where the core and shell are connected by the labile trithiocarbonate.^{10–12} Crosslinking is desirable to stabilize the structure, but is generally difficult for most polymers except for those bearing crosslinkable groups. Crosslinking via polymerization of divinyl monomers is an alternative way and applicable to general polymers.

The thiocarbonylthio RAFT chain transfer agent, with a general formula of RSC(S)Z (where R is leaving group), has been widely used to synthesize polymer with well-defined structure and/or various topologies, including core-shell structured polymer. Dendrimer and hyperbranched polymer have been successfully used as a multifunctional scaffold for the preparation of multiarm core-shell structured polymer,^{10–15} where two approaches have been developed, i.e., Z-approach (the multifunctional core as part of the Z group of RSC(S)Z) and R-approach (the multifunctional core as part of the R group of RSC(S)Z). Either route has merits and drawbacks. For polymer resulted from Z-approach, the core and shell are connected by the labile thiocarbonylthio groups, thus crosslinking is generally desirable. Particularly for Z-approach, side reaction of radical-radical coupling is generally encountered. It is known that this is due to the steric hindrance of the shell,

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which prevents the active radical species from efficient recombination to the thiocarbonylthio groups, but the effect of shell congestion has not been systematically studied. On the other hand, Hawker and coworkers,¹⁶ in 2001, first reported one-pot synthesis of core-crosslinked, star-like polymer, taking advantage of nitroxide mediated living radical polymerization technique. This concept has been applied to other systems, leading to a variety of novel polymer objects, and specific for the RAFT mediated system, either shell crosslinked microgel or core-crosslinked microgel can be resulted, greatly depending on the structure of the RAFT chain transfer agent.^{17–19} Shell-crosslinked polymer appears to be more interesting and promising than its core-crosslinked counterpart.¹ Although the route proposed by Hawker and coworkers is straightforward and uniform particles can be obtained, the reaction conditions exert a subtle influence on the quality of the particles, thus parameter optimization is necessary, and is time-consuming due to the multiplicity of variables. In contrast, for the route employing scaffold, the particle number is predetermined, and the size distribution is generally narrow without parameter optimization. Here we employ a PG derivative as scaffold to synthesize star-like polystyrene via Z-approach, and consequently to synthesize shell crosslinked polymer in the presence of divinylbenzene. The influence of shell congestion on the side reaction and shell crosslinking is studied for the first time using model compounds.

EXPERIMENTAL

Materials

Styrene (99%, Sinopharm Chemical Reagent, Shanghai) and divinylbenzene (DVB) (Shanghai Shengzhong Chemical DVB: 55%, 4-vinyl-ethylbenzene: 36%, ethylbenzene: 3.26%) were purified by distillation under reduced pressure before use. Benzoylated dialysis tubing (D-7884, MWCO 1200) was obtained from Sigma.

Two PG samples, PG₂₆ and PG₁₀₆ (for nomenclature, see note*): with $M_n = 2000$ (VPO), $M_w/M_n = 1.4$ (GPC) (**1a**) and $M_n = 8000$ (VPO), $M_w/M_n = 1.42$ (GPC) (**1b**) were prepared according to literature.⁵ ¹HNMR (CD₃OD, δ /ppm): 0.79 (t, CH₃ of 1,1,1-tris(hydroxymethyl)propane, the core molecule of PG), 1.25 (q, CH₂ of 1,1,1-tris(hydroxymethyl)propane, the core molecule of PG), 3.0–4.1 (m, CH and CH₂ of monomer unit).

*Nomenclature: PG_x-(PS_y)_z, x and y represented degree of polymerization of PG and PS, respectively, z represented the number of PS arms attached on each PG scaffold.

Synthesis of trithiocarbonate functionalized PG

The synthesis of trithiocarbonate-functionalized PG (**2a**, **2b**) was carried out by (1) esterification part of the OH groups of PG with 3-mercapto-propionic acid, ¹H NMR (CDCl₃), δ /ppm: signals independent of PG, 1.63(s, SH), 2.59(t, OCOCH₂CH₂SH), 2.68(t, OCOCH₂CH₂SH). Meanwhile, the new signal at 5.15 ppm was ascribed to the CHOH of PG after OH was esterified, and the enhanced signal intensity at 4.07 ppm was ascribed to the CH₂OH of PG after the OH was esterified, (2) transformed of the residual thiol groups into trithiocarbonates, and purified by dialysis against chloroform, as described previously.¹⁰ ¹HNMR, signals independent of PG (CDCl₃) (δ /ppm): 2.75 (br, CH₂S), 3.67 (OCOCH₂CH₂S), 4.56 (s, CH₂Ph), and 7.24 (br, Ph). ¹³C NMR (CDCl₃) δ /ppm: 31.37 (CH₂S), 33.00 (CH₂C), 41.54 (CH₂Ph), 127.83, 128.72, 129.28, 134.82 (Ph), 170.74 (C=O), 218.91 (C=S), and 63.21, 64.22, 65.77, 68.56, 69.49, 70.57, 71.72, 72.92, 79.15 for PG.

Thermal polymerization of styrene mediated by **2a**, **2b**

A typical procedure was as follows: A solution of 0.5 g of **2a** and 5 mL of styrene was prepared, the mixture was charged evenly in five tubes, and each tube was degassed by bubbling with nitrogen for 15 min, sealed and reacted at 120°C for a certain time. The polymer was recovered by precipitation from methanol, purified by repeating dissolution in tetrahydrofuran and precipitation from methanol. Some samples were further purified by dialysis against chloroform for 24 h to remove the low molecular weight side products.

Shell-crosslinking of the PG-(PS)_n

Shell-crosslinking was carried out at PS/DVB/St = 1/2.4/16 (molar ratio, where DVB was the actual moles, PS was the moles of the linear arms) in DMF. Typically, 1 g polymer of PG₂₆-(PS₁₅)₁₆,* 0.28 g DVB mixture and 0.88 g of styrene was mixed with 2.8 g of DMF, the mixture was degassed and heated at 120°C for 12 h. The mixture was dissolved in chloroform, filtered and precipitated in excessive diethyl ether. The polymer was purified by repeating dissolution in chloroform and precipitation from ether, respectively.

One-pot synthesis of shell-crosslinked PG-(PS)_n

A solution of 0.2 g of **2a** in 2 mL of styrene was prepared, degassed and reacted at 120°C for 24 h, then a degassed solution of 0.2 mL of DVB in 3 mL of

DMF was injected and the reaction continued for another 12 h.

Aminolysis of the amphiphilic polymer

Typically, 2 mL of *n*-butylamine was added to a solution of 1 g of polymer in 12 mL of chloroform and the solution was stirred for 24 h at room temperature in a sealed reactor. The polymer was recovered and purified by dissolution in chloroform and precipitation from methanol, respectively.

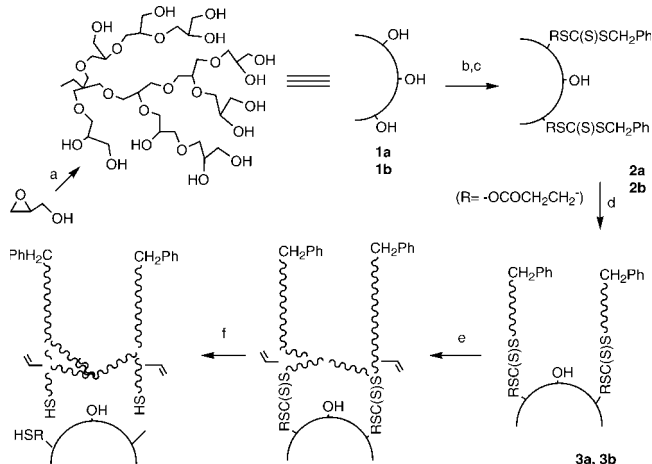
Measurement

^1H and ^{13}C NMR were recorded on DRX 500. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) were determined by Gel permeation chromatography (GPC) using Waters 150-C, calibrated with standard poly(styrene), eluent: tetrahydrofuran, flow rate: 1 mL/min, sample concentration: 10 mg/mL, injection volume 200 μL . UV-Vis spectra were recorded on Perkin-Elmer λ -2. Molecular weight of the polystyrene sample was measured using vapor pressure osmometry, experiment was carried out using a Knauer Vapor Osmometer at 35°C with chloroform in a concentration range of 5–10 mg/mL, and benzil was used for calibration.

RESULTS AND DISCUSSION

Living radical polymerization of styrene mediated with 2a, 2b

The synthesis was outlined in Scheme 1. Two PG samples were prepared with $M_n = 2000$ (**1a**, about 27



Scheme 1 Outline of the synthesis of Shell-crosslinked star-like polymer. Reaction conditions: (a) 1,1,1-Tris(hydroxymethyl)propane, KOCH_3 , 95°C; (b) 3-mercaptopropionic acid, $\text{HfCl}_4 \cdot 2\text{THF}$, 120°C; (c) triethylamine, CS_2 , benzyl bromide; (d) styrene, 120°C; (e) DMF, divinylbenzene, styrene, 120°C; (f) *n*-butylamine, chloroform.

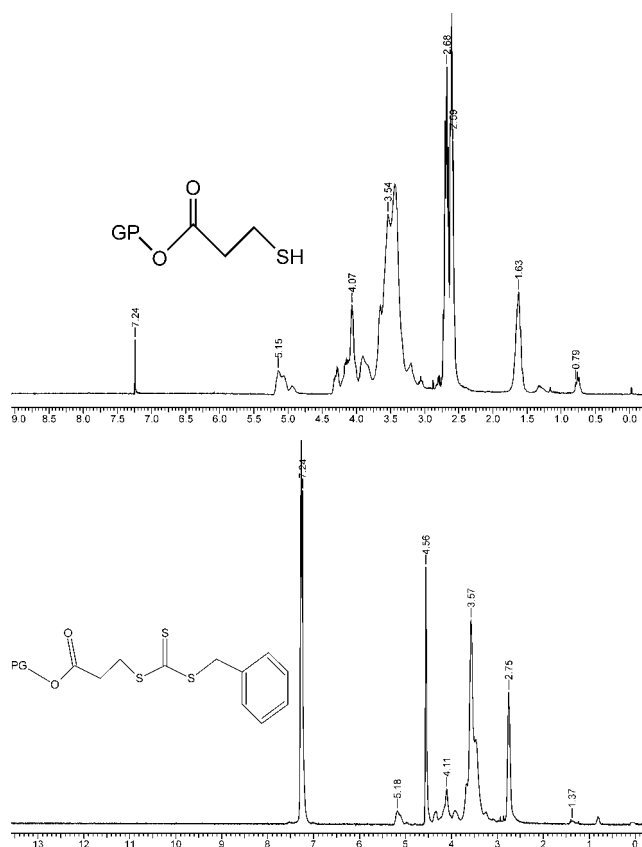


Figure 1 ^1H NMR (CDCl_3) of PG_{26} with partial hydroxyl groups being esterified with 3-mercaptopropionic acid (top) and further transformed to trithiocarbonate (bottom).

OH groups/polymer) and 8000 (**1b**, about 109 OH groups/polymer), respectively. In the derivation of the hydroxyls of PG into trithiocarbonates, two-step chemical reaction was carried out. In Step 1, the hydroxyls were esterified with 3-mercaptopropionic acid (1.06 equiv of hydroxyl of PG). The product was characterized by ^1H NMR (Fig. 1), where new signals were found at 1.63(s, SH), 2.59(t, $\text{OCOCH}_2\text{CH}_2\text{SH}$), 2.68(t, $\text{OCOCH}_2\text{CH}_2\text{SH}$). By comparing the integration area of signal at 1.63 ppm (SH) with that at 0.79 ppm, the degree of esterification could be derived, and in current experiment, it was 65%. In Step 2, the thiols were efficiently transformed into trithiocarbonate, and the polymer was purified by dialysis against chloroform. From the ^1H NMR, new signals were found at 4.56 (s, CH_2Ph), and 7.24 ppm (br, Ph), while the protons of $\text{OCOCH}_2\text{CH}_2\text{S}$ downshifted to 2.75 (br, $\text{OCOCH}_2\text{CH}_2\text{S}$) and 3.67 ppm ($\text{OCOCH}_2\text{CH}_2\text{S}$). In Figure 1, by comparing the ^1H NMR integration area of signal at 2.75 ppm with that at 4.56 ppm (s, CH_2Ph), the amount of thiol groups that were transformed into trithiocarbonate could be derived to be about 94%. Overall, 61% of the hydroxyl groups of PG were transformed into trithiocarbonates for both **1a** and

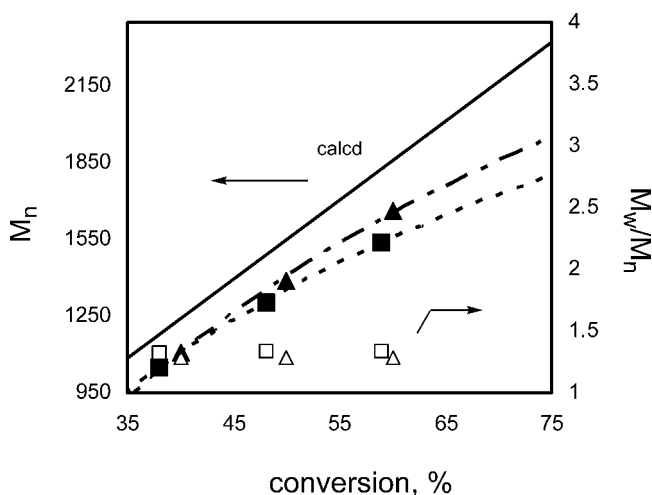


Figure 2 Dependence of M_n , M_w/M_n of the linear PS (obtained from aminolysis of the star polymer) on conversion of St mediated by **2a** (\blacktriangle , \triangle) and **2b** (\blacksquare , \square), respectively. Conditions: $[St]/[\text{trithiocarbonate}] = 30/1$ (molar ratio), bulk, 120°C . (the curves are fitted line).

1b. The modification led to PGs with 16-sites (**2a**) and 65-sites (**2b**) substituted by trithiocarbonates per molecule, respectively (Scheme 1).

2a and **2b** were used to mediate the thermal bulk polymerization of styrene at 120°C , and the resulting polymer was subjected to aminolysis before GPC measurement. It is known that GPC measurement is based on the hydrodynamic size of the polymer, thus the apparent molecular weight of a polymer can be of great difference due to their topology (such as linear and star-like polymer). To obtain a linear polymer, the star-like polymer was subjected to aminolysis, so that the arms could be cleaved from the scaffold. After aminolysis, the polymer decomposed to linear polystyrene polymers along with a hyperbranched scaffold polymer. In our experiment, the latter made up less than 10 wt % of the total mass of the star-like polymer. The resulting polymers were then analyzed by both GPC and VPO. The results were shown in Figure 2. Here the molecular weight distribution (M_w/M_n) was obtained from GPC measurement, and the number-average molecular weight (M_n) was obtained from VPO measurement. It could be found from Figure 2 that the M_n increased nearly linearly with the conversion of the monomer, and the molecular weight distribution was narrow (between 1.2 and 1.4), indicating the living character of the polymerization. On the other hand, the theoretical molecular weight of a polymer arm could be derived, assuming that one trithiocarbonate produced one polymer arm. From Figure 2, it could be found that the measured molecular weight value was slightly lower than the calculated one. To

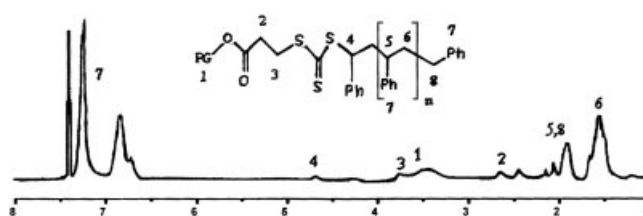
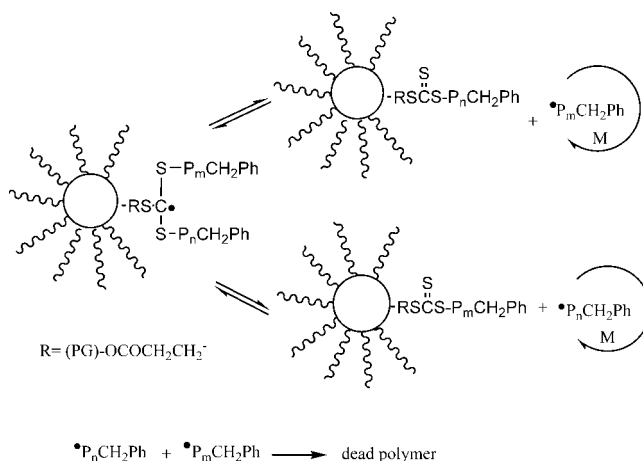


Figure 3 ^1H NMR (CDCl_3) of a **2a** mediated polymer of which the polymerization degree of each arm was about 10.

learn the reason, it is necessary to know whether all the trithiocarbonates take part in the polymerization. To do this, a polymer obtained at low conversion of styrene was obtained, purified, and subjected to ^1H NMR measurement. The monitoring was focused on the CH_2 of the $[\text{SC}(\text{S})\text{SCH}_2\text{Ph}]$ at 4.56 ppm (Fig. 1). When a styrene monomer inserted into the trithiocarbonate, the chemical structure would change to $[\text{SC}(\text{S})\text{S}(\text{CHPhCH}_2)\text{CH}_2\text{Ph}]$, new signal of CH should appear downfield. Figure 3 showed that, when the average polymerization degree of each arm was about 10, the signal at 4.56 ppm disappeared, while a new signal appeared at 4.70 ppm. It could be concluded that all the trithiocarbonate involved in the polymerization, thus **2a** would lead to a 16-arm star polymer while **2b** to a 65-arm one. Therefore, the deviation of the measured molecular weight from the calculated one was ascribed to the side reaction of radical-radical coupling, which was usually encountered in similar systems.¹⁵ The mechanism was shown in Scheme 2. Figure 4 showed a typical GPC trace of the polymer sample before dialysis, the minor peak, which corresponded to lower molecular weight polymers, was due to radical-radical coupling. The side product could be removed by dialysis, after dialysis [Fig. 4(b)], the low molecular weight polymer was removed. From the integration



Scheme 2 Synthesis of star-like polymer via Z-approach.

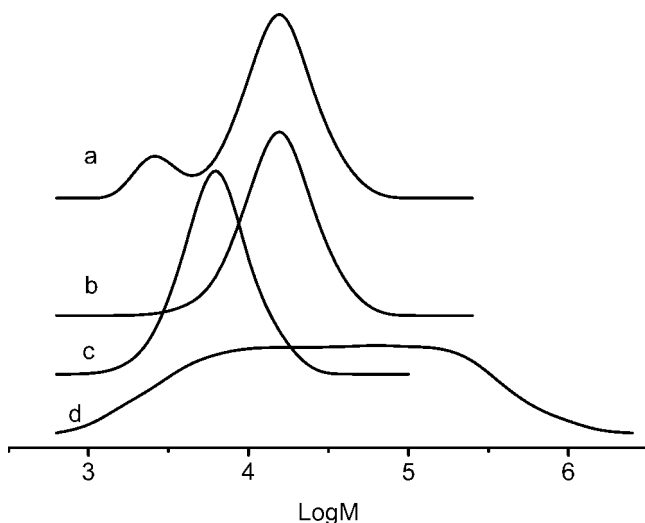


Figure 4 GPC traces of star-like polymer mediated by **2a** at 50% conversion of styrene, (a) as prepared, (b) after dialysis against chloroform, (c) after shell-crosslinked with divinylbenzene, (d) after aminolysis of the shell-crosslinked polymer.

area of GPC traces, it could be derived that the side reaction could make up 15% of the overall area.[†] Meanwhile, it was noticed that the side reaction (radical–radical coupling) was more serious for **2b** mediated system than for the **2a** mediated one. It was noticed that at almost the same conversion of styrene (59% for **2b** and 60% for **2a**), the radical–radical coupling contributed 11 wt % to the polymer mass for the **2a** mediated system, but 15% for the one mediated by **2b**. We tentatively attributed this difference to shell congestion, i.e. the PS arms on **2b** were denser than that of **2a**. It is known mathematically that for a globe, the ratio of its surface area/volume decreases with the increase of its diameter. On the other hand, it has been proved that the hyperbranched polyglycerol generally adopts a compact, globular shape.⁶ Thus for the pair of **2a/2b**, both of which 61% of the hydroxyl groups were transformed into trithiocarbonate and later into polystyrene, the density of the substitution on **2b** was higher than those on **2a**. The higher density of shell formed a steric hindrance that prevented the leaving of active radical species from efficient recombination with the chain transfer agent, i.e. trithiocarbonate groups, thus radical–radical coupling was favored (Scheme 2).

[†]Owing to the radical coupling, the GPC chromatograms generally showed bimodal traces [see Fig. 4(a)], where the minor peak corresponded to the side product due to radical coupling. The respective area of the two peaks could be obtained, employing the Gaussian peak splitting technique (software: Origin 5.0). Here in the article the area fraction contributed by the minor peak was used as a scale to evaluate the degree of side reaction.

Shell-crosslinking of the star-like polymer

Polymer **3a** and **3b** were amphiphilic core-shell structured polymers, of which the shell and core were connected by the trithiocarbonates. It is known that trithiocarbonate is susceptible to alkaline environment, and shell crosslinking can stabilize the structure, so here DVB is used as a crosslinker. In experiment, it was found that **3b** was easier to undergo macroscopic crosslinking than **3a**. To probe the mechanism, a pair of model compounds of **3a** and **3b** were prepared as $\text{PG}_{26}\text{-(PS)}_{15}\text{16}$ and $\text{PG}_{106}\text{-(PS)}_{14}\text{65}$.^{*} The polymer was first subjected to dialysis to remove the low molecular weight contaminant [Fig. 4(b)], then subjected to crosslinking under condition of PS/DVB/St = 1/2.4/16 (molar ratio, where DVB was the actual moles and PS was the moles of the linear arms) at solid content of 20% (in dimethylformamide) and at 120°C. Consequently, $\text{PG}_{106}\text{-(PS)}_{14}\text{65}$ soon led to macroscopic crosslinking, while $\text{PG}_{26}\text{-(PS)}_{15}\text{16}$ underwent intramolecular crosslinking, and the yield of polymer was 1.05-fold of the polymer before crosslinking. The above result was repeatable. As could be seen from the two model compounds, the substitution ratio of hydroxyls (0.61), the length of the PS arm (polymerization degree of 15 vs. 14) were almost the same, the only difference between them, as was pointed out previously, was the shell congestion. Based on these results, the macroscopic crosslinking was most probably due to the radical polymerization occurred outside the shell as a conventional radical process.

For $\text{PG}_{26}\text{-(PS)}_{15}\text{16}$, GPC showed that after crosslinking, $M_n = 7600$ and $M_w/M_n = 1.29$, was in sharp contrast to $M_n = 12000$ and $M_w/M_n = 1.32$ before crosslinking. As expected, the crosslinking led to a much lower apparent molecular weight of the polymer. To see the completeness of crosslinking, the shell crosslinked polymer was subjected to aminolysis, which reductively cleaved the trithiocarbonates. Experimentally, when the signal due to trithiocarbonate centering on 350 nm in UV-Vis spectra completely disappeared, it was regarded that all the trithiocarbonate groups had been reduced. The polymer was then recovered and subjected to GPC measurement. Figure 4(c) showed the results, from which it could be found that after aminolysis, the molecular weight distribution became very wide, $M_n = 14,600$ and $M_w/M_n = 9.26$. The polydispersity would remain narrow while the apparent molecular weight would become much larger were the shell sufficiently crosslinked and trithiocarbonates completely cleaved. When this did not happen, it indicated that the crosslinking was insufficient. Meanwhile, the measured molecular weight spanned from several thousand to several million (the minor fraction of polymer with very large molecular weight

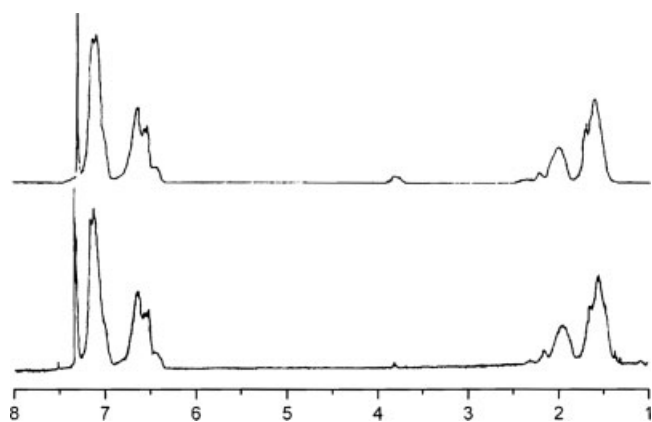


Figure 5 ^1H NMR (CDCl_3) of the one-pot synthesized $\text{PG}_{26}\text{-(PS)}_n$ before (up) and after (bottom) shell crosslinking with DVB.

might produce through partial thiol coupling between the polymers because the theoretic molecular weight of a microgel was about 10^5), indicating the crosslinking was incomplete. To get a full appreciation of this route, parameters (including the structure of the scaffold and the reaction conditions) optimization is necessary. Although this has not yet been carried out, our results at least showed that the shell congestion was an important parameter. Lower the shell congestion (substituting ratio) should be favorable for intramolecular crosslinking. Interestingly, Stenzel and coworkers¹⁸ have shown an example of successful crosslinking of similar structure but in a highly dilute solution.

A one-pot synthesis of shell-crosslinked polymer from **2a** was carried out at solid content of 20%, as described in the experimental part. 1.21 g ($\sim 51\%$) of polymer was obtained, $M_n = 6600$ and $M_w/M_n = 1.27$. Figure 5 showed the ^1H NMR spectra before and after crosslinking. Before crosslinking, the signal of PG scaffold could be observed around 3.7 ppm, while after crosslinking, the signal of PG scaffold became very weak, indicating shell-crosslinking occurred, but it could be expected that the crosslinking was also insufficient.

CONCLUSION

Trithiocarbonate functionalized hyperbranched polyglycerol can be used as a scaffold to synthesize mul-

tiarm, star-like polystyrene. The polymerization proceeds in a living manner. However, the shell congestion of the scaffold is an important factor. Higher congestion of shell is more unfavorable for the efficient recombination of the radical species with the chain transfer agent, which will lead to more serious side reaction (radical–radical coupling). Furthermore, it is found from model compounds that the star-like polymer with higher shell congestion tends to undergo macroscopic crosslinking rather than intramolecular crosslinking in the presence of divinyl monomer.

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