

Liquid-phase catalytic thermal cleavage of thiocarbonylthio end-groups for polymers synthesized by RAFT polymerization: Influences of different solvents

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ABSTRACT: Catalytic thermal cleavage of thiocarbonylthio end-groups for RAFT synthesized polymers is usually accompanied by other side reactions such as chain-scission and crosslinking. Occurrence of these side reactions depends on polymers, end-groups, and oxidation–reduction property of reaction media in a liquid phase. Herein, well-defined hydrophilic poly(4-vinylpyridine) (P4VP) and hydrophobic polystyrene (PS) are synthesized via a controlled RAFT polymerization in the presence of S-1-Dodecyl-S'-(R,R'-dimethyl-R''-acetic acid) trithiocarbonates (DDMAT). Then their thiocarbonylthio end-groups are cleaved through catalytic thermolysis in a liquid phase. Under the catalysis of Cu(0), all S-containing groups can be removed at 165 °C in 3 h. To study the effect of solvent on thermolysis and microstructure of polymer, nitrobenzene of oxidation property and diethylene glycol of reduction property are chosen as solvents. Because of oxidizing property of nitrobenzene, Z groups of RAFT agent are eliminated at the same time that thiocarbonylthio end-groups are removed. Therefore crosslinking among multipolymer chains occurs. While diethylene glycol is used as a solvent, no crosslinking occurs. Diethylene glycol is superior to nitrobenzene for synthesis of well-defined polymer without S-containing groups. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43992.

KEYWORDS: crosslinking; degradation; functionalization of polymers; structure–property relations

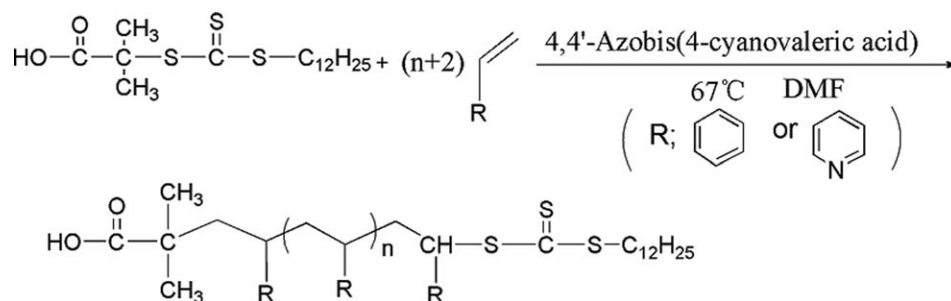
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INTRODUCTION

Since addition-fragmentation transfer agents were used to control radical polymerization in 1980's, reversible addition-fragmentation chain transfer (RAFT) polymerization served as one of the most versatile living radical polymerization methods in the presence of various addition-fragmentation transfer agents.^{1,2} A wide range of monomers including monomers with chelating capacity can be polymerized at mild operation conditions in a living manner mediated by RAFT agents and the polymerization process can be carried out in solution or heterogeneous media. In particular, thiocarbonylthio end-groups are tethered at the end of polymer chains synthesized by RAFT polymerization. These S-containing end-groups act as a functional precursor and can be further modified to produce functional polymer.³ Nonetheless, these S-containing end-groups bring negative effect to microstructure and application of well-defined polymer in most cases.^{4,5} For instance, polymer synthesized by RAFT is colorful and even sulfide and special smell is released over time or upon heating because of the decomposition of thiocarbonylthio end-groups. The application of RAFT polymers in optical-electronic field is also restricted because of

fluorescence quenching effect of thiocarbonylthio end-groups.⁶ Therefore, the effective modification and removal of S-containing end-groups is becoming more necessary. So far, various methods have been tried and reported.⁷ Thiocarbonylthio groups undergo reaction with nucleophiles and ionic reducing agents to provide thiol groups^{8,9}; thiocarbonylthio end-groups can be oxidized to thiolo-carbonate, carboxyl, or hydroxyl groups by various oxidizing agents.^{10,11} Removal of S-containing end-groups can be also accomplished by UV irradiation¹² or aminolysis reaction with the reagents of amine.^{13–15} Therein, thermolysis based on the thermal instability of thiocarbonylthio end-groups is economical and feasible because of complete thiocarbonylthio end-groups removal and without additional agents.^{16–21} However, the dominant mechanism of end-group loss depends on both the particular polymer and the type of thiocarbonylthio group. Perrier *et al.* reported the thermal stability of several RAFT agents.²² Trithiocarbonates are less stable than dithiobenzoates and both R group and Z group affect the thermal stability of RAFT agents. In the presence of metal catalysts such as Cu(0) or Fe(0), the thermal cleavage of thiocarbonylthio end-groups can be conducted at lower temperature.²³ Furthermore, in the presence of radical trapper, the



Scheme 1. RAFT polymerization of 4VP or St.

cleavage temperature can be decreased to ambient temperature.²⁴ However, solid thermolysis of polymer catalyzed by metal catalysts is difficult and slow because of mass transfer hindrance in the view of engineering. Though the introduction of radical trapper effectively decreases the thermolysis temperature, long reaction time and subsequent separation are needed. How to achieve the rapid thermolysis in liquid phase is a challenge to an engineer.

Herein, hydrophilic poly(4-vinylpyridine) (P4VP) and hydrophobic polystyrene (PS) are prepared via a RAFT polymerization. Considering the adaptability and lower thermolysis temperature, S-1-Dodecyl-S'-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (DDMAT) is chosen as RAFT agent. Nitrobenzene or diethylene glycol act as reaction media and thiocarbonylthio end-groups of P4VP and PS are cleaved in liquid phase through catalytic thermolysis. The effect of solvent on the cleavage efficiency and microstructure of the product is studied.

EXPERIMENTAL

Materials

Styrene (St, 99%) and 4-vinylpyridine (4VP, 95%) were purchased from J&K and used after reduced pressure distillation. N,N-dimethyl formamide (DMF, 99.9%), nitrobenzene (99%), diethylene glycol (99%), copper powder (Cu(0), 99.99%, 400 meshes), 4,4'-Azobis(4-cyanovaleric acid) (98%) (V501) were

purchased from J&K and used as received. S-1-Dodecyl-S'-(R,R'-dimethyl-R''-acetic acid) trithiocarbonates (DDMAT) was synthesized according to the literature.²⁵

Measurements

Molecular weight (M_n and M_p) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) against a PS standard on an Agilent 1100 series RI detector (Agilent 1100, USA). DMF was used as the eluent at a flow rate of 1 mL/min. ¹H-NMR (400 MHz) spectra were recorded on a Bruker AC 400 instrument, using deuterated chloroform ($CDCl_3$) as the solvent. Sulfur content was measured by FLASH EA 1112 element analyzer (Thermo, USA). The ultraviolet absorption of P4VP and PS solution in DMF were measured with UV-Vis spectrophotometer at 25 °C with wave length from 200 to 600 nm (2450, Shimadzu, Japan).

Synthesis of DDMAT

1-Dodecanethiol (20.2 g, 0.10 mol), acetone (58.0 g, 1.0 mol), and tricaprilylmethylammonium chloride (1.0 g, 2.5 mmol) were added into a three-necked flask at 0 °C under N_2 . Sodium hydroxide solution (50 wt %, 8.4 g, 0.105 mol) was added over 10 min. After the mixture was stirred for additional 20 min, carbon disulfide (7.6 g, 0.10 mol) in acetone (10.0 g) was added over 30 min, and the color turned red gradually. After

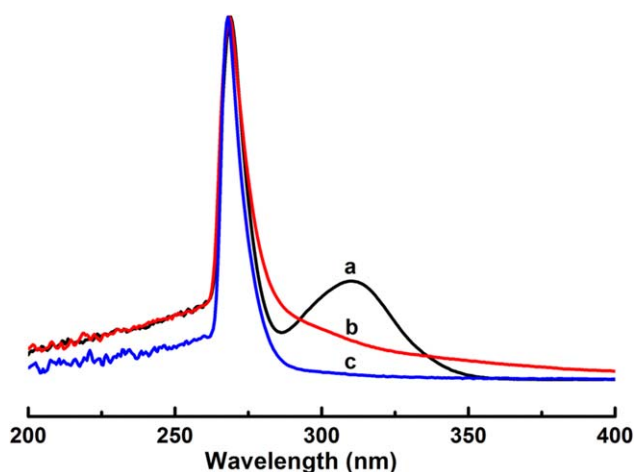


Figure 1. UV-Vis spectra of (a) P4VP capped with thiocarbonylthio group, (b) P4VP after cleavage in nitrobenzene and (c) P4VP after cleavage in diethylene glycol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

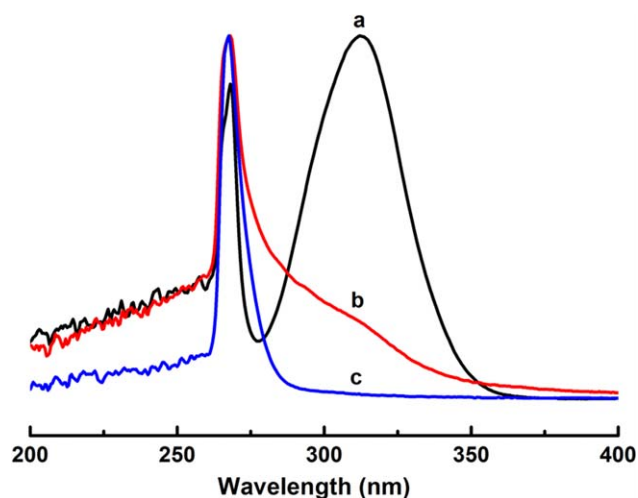


Figure 2. UV-Vis spectra of (a) PS capped with thiocarbonylthio group, (b) PS after cleavage in nitrobenzene, and (c) PS after cleavage in diethylene glycol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Results of Element Analysis

Sample	Before reaction S (W %)	In nitrobenzene S (W %)	In diethylene glycol S (W %)
P4VP	0.250%	0.027%	0.018%
PS	2.290%	0.310%	0.120%

chloroform (17.8 g, 0.15 mol) was added, sodium hydroxide solution (50 wt %, 40 g) was added drop-wise over 20 min. The mixture was stirred overnight. Deionized water (200 mL) was added, followed by 80 mL of concentrated HCl to acidify the aqueous solution. After evaporating acetone, the solid was collected and redissolved in 300 mL of 2-propanol. The solution was concentrated after filtration and the resulting solid was recrystallized from hexane to afford 12.0 g of yellow crystalline solid. Yield: 32.9%, $^1\text{H-NMR}$ (in CDCl_3): 0.89 (t, 3 H), 1.30–1.5 (m, 18H), 1.6–1.7 (m, 2H), 1.7–1.8 (s, 6H), 3.2 (t, 2H).

Polymerization

RAFT polymerization of St or 4VP was carried out according to Scheme 1. Monomer (St or 4VP) (55.0 g) and DDMAT was dissolved in DMF (150 mL). The solution was degassed via three freeze–pump–thaw cycles under N_2 at 0°C . After the temperature increased to 67°C , the initiator (V501) was added and the polymerization started. The molar ratio among monomer, RAFT agent, and initiator was set as 2000:5:1. After 6 h, the polymerization was terminated by pouring into cold methanol (ether) and the polymer was isolated by centrifugation. The product was dried at 25°C in a vacuum oven for 24 h.

Catalytic Thermal Cleavage of S-Containing End-Groups

Polymer (10.0 g) capped with thiocarbonylthio group (PS or P4VP) was dissolved in nitrobenzene or diethylene glycol

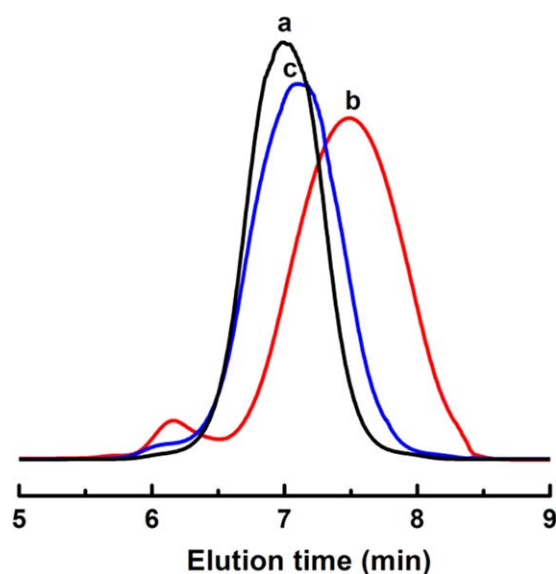


Figure 3. GPC curves of (a) P4VP capped with thiocarbonylthio group, (b) P4VP after cleavage in nitrobenzene, and (c) P4VP after cleavage in diethylene glycol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

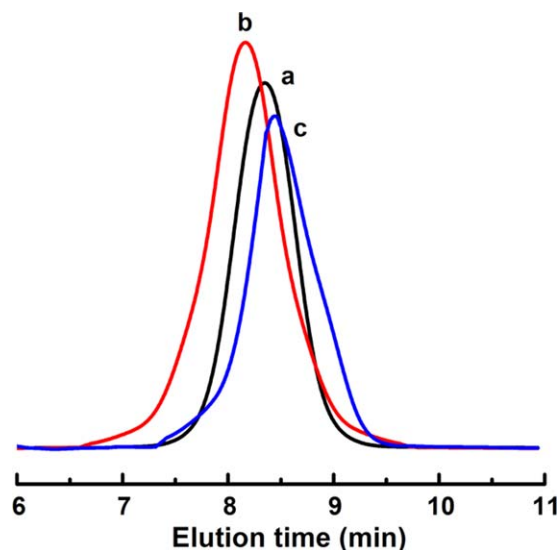


Figure 4. GPC curves of (a) PS capped with thiocarbonylthio group, (b) PS after cleavage in nitrobenzene, and (c) PS after cleavage in diethylene glycol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(50 mL). After adding $\text{Cu}(0)$ (0.5 g), the slurry was agitated at 165°C under N_2 for 3 h. $\text{Cu}(0)$ was removed by centrifugation and the polymer was precipitated in methanol or ether. After washing with methanol or ether (20 mL*3), the product was dried at 25°C in a vacuum oven for 24 h.

RESULTS AND DISCUSSION

Because of trithiocarbonates with a strong $\pi \rightarrow \pi^*$ transition around 308 nm in DMF, UV-Vis spectra is used to detect the presence of trithiocarbonate groups.²⁶ As shown in Figures 1

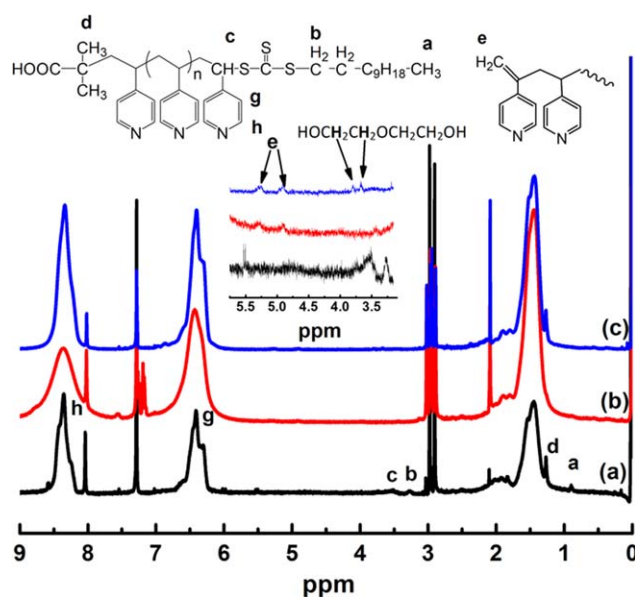


Figure 5. $^1\text{H-NMR}$ spectra of (a) P4VP capped with thiocarbonylthio group, (b) P4VP after cleavage in nitrobenzene, and (c) P4VP after cleavage in diethylene glycol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Results of GPC Characterization

Sample	M_n	M_p	PDI	Crosslinking degree
P4VP capped with thiocarbonylthio group	39,000	64,000	1.27	
P4VP in nitrobenzene	289,000	304,000	1.33	4%
P4VP in diethylene glycol	25,000	29,000	1.45	
P4VP in diethylene glycol	34,000	50,000	1.32	
PS capped with thiocarbonylthio group	4200	5100	1.18	
PS in nitrobenzene	6100	6400	1.08	87%
PS in diethylene glycol	3700	4500	1.25	

and 2, the UV signal for both P4VP and PS vanish at 308 nm after thermolysis in diethylene glycol. This indicates that trithio-carbonate groups decompose during thermolysis catalyzed by Cu(0).

To further quantize sulfur content in polymer, element analysis is used to characterize the change of sulfur content before and after the thermolysis. The results are listed in Table I. The data indicate that sulfur removal in diethylene glycol is more effective than in nitrobenzene. When the thermolysis is carried out in diethylene glycol, sulfur content of P4VP is reduced by 92.8% and that of PS were reduced by 94.8%. When the thermolysis is carried out in nitrobenzene, sulfur content of P4VP is reduced by 89.2% and that of PS were reduced by 86.5%. From the above data analysis, it can be concluded that sulfur in PS is easier to be removed than in P4VP.

To study the possible chain-scission and crosslinking during the thermolysis, GPC is used to characterize chain length changes of polymers. The GPC curves of P4VP and PS are, respectively, shown in Figures 3 and 4 and the results calculated based on PS

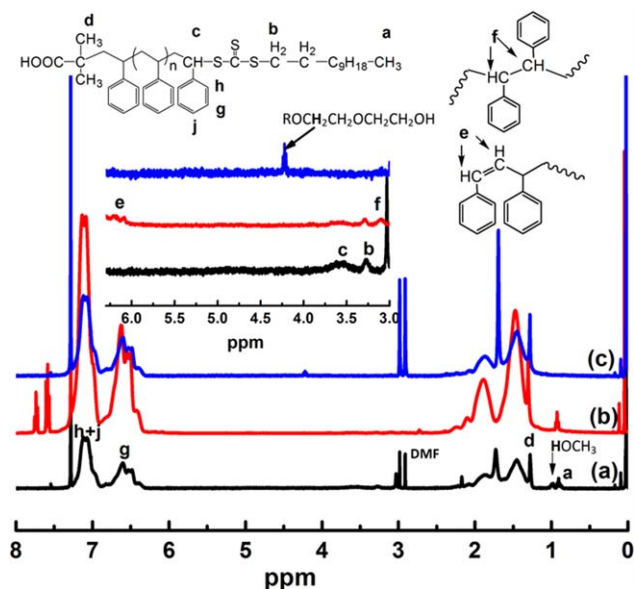


Figure 6. $^1\text{H-NMR}$ spectra of (a) PS capped with thiocarbonylthio group, (b) PS after cleavage in nitrobenzene, and (c) PS after cleavage in diethylene glycol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

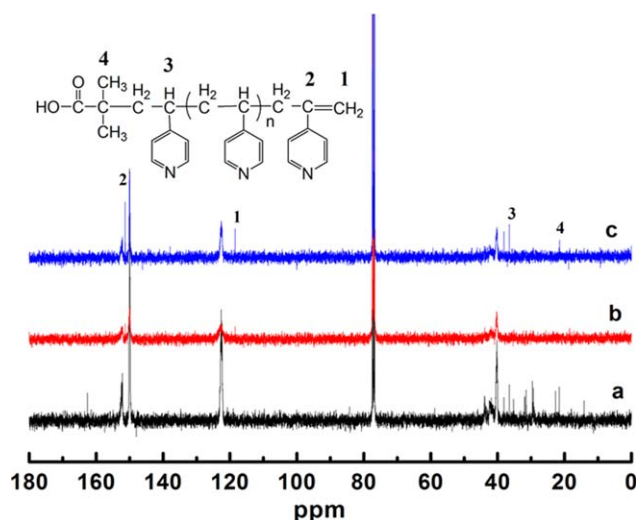


Figure 7. $^{13}\text{C-NMR}$ spectra of (a) P4VP capped with thiocarbonylthio group, (b) P4VP after cleavage in nitrobenzene, and (c) P4VP after cleavage in diethylene glycol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

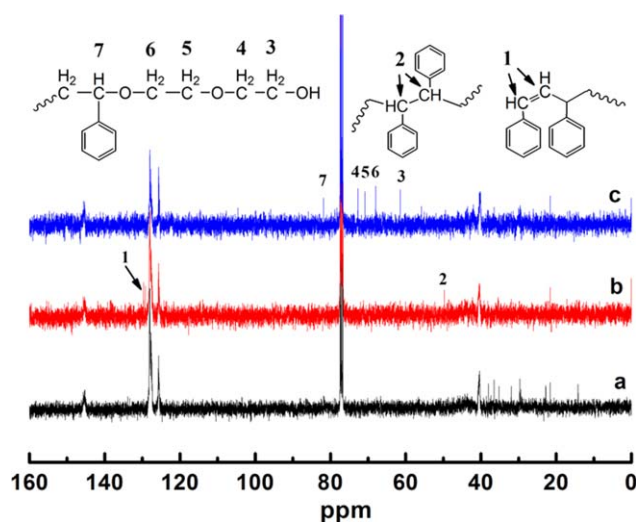
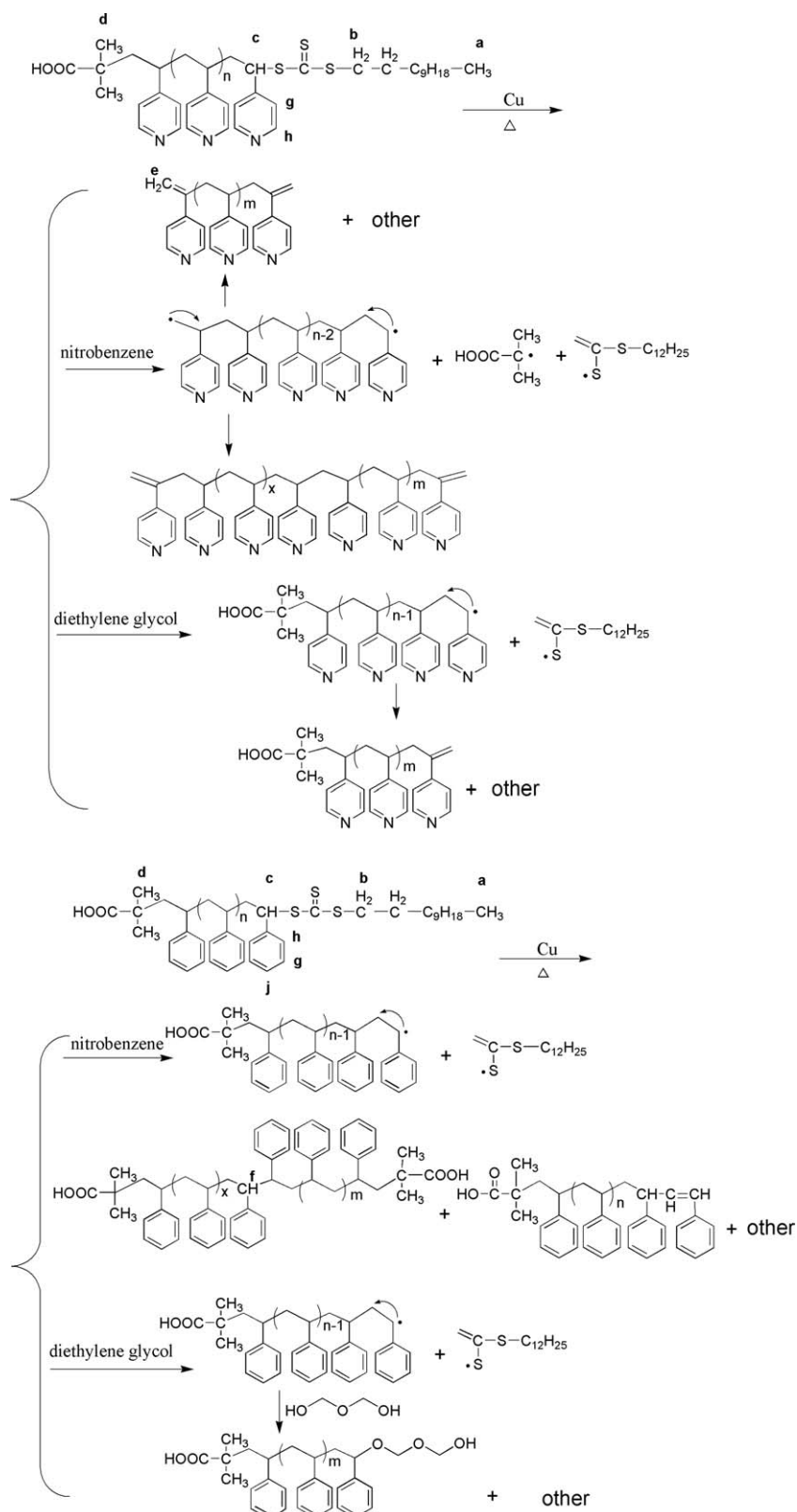


Figure 8. $^{13}\text{C-NMR}$ spectra of (a) PS capped with thiocarbonylthio group, (b) PS after cleavage in nitrobenzene, and (c) PS after cleavage in diethylene glycol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2. Catalytic thermolysis of P4VP and PS.

standard are listed in Table II. When diethylene glycol is used as the solvent, molecular weights of P4VP and PS decrease after thermal cleavage as shown in Figures 3(c) and 4(c). If only

C₁₃H₂₆S₃ groups are cleaved, the corresponding mass loss should be 0.71% for P4VP ($M_n = 39,000$ g/mol, $M_w/M_n = 1.27$). In fact, the mass loss reached to 35.9% in nitrobenzene and

12.8% in diethylene glycol. While the expected mass loss is 6.62% upon just cleavage of $C_{13}H_{26}S_3$ groups for PS ($M_n = 4200$ g/mol, $M_w/M_n = 1.18$), the actual mass loss is 11.9% in diethylene glycol. Therefore, there must be polymer degradation during the thermolysis. Usually the degradation is initiated at weak C–S link sites along polymer chains²⁷ and low PDI values imply that RAFT polymer chains degrade in the mode of end-initiated unzipping rather than in the mode of random chain scission in the presence of Cu(0). When nitrobenzene is used as the solvent, there exists shoulder peak on the curve for P4VP [Figure 3(b)] and the peak on the curve for PS wholly shifts to left [Figure 4(b)]. These polymer chains with high molecular weight can be ascribed to crosslinking among long-chain radicals during the thermolysis because radicals are generated at polymer chain ends upon cleavage of thiocarbonylthio end-groups.^{17,25} In Figure 3(b), the molecular weight of crosslinked P4VP is far more than double of P4VP. It can be ascribed to crosslinking among multi-P4VP chains because Z groups are cleaved at the same time that thiocarbonylthio groups are removed according to unstable nature of ternary carbon bond in Z group of DDMAT. The molecular weight of the P4VP in Figure 3(c) ($M_n = 34,000$ g/mol) is more than in Figure 3(b) ($M_n = 25,000$ g/mol) because P4VP chain radicals are easier terminated in diethylene glycol than in nitrobenzene, because diethylene glycol of weak reduction can quench free radicals. To explain the crosslinking difference between P4VP and PS, the radical stability theory is adopted. Because of induced withdrawing effect and conjugated effect of nitrogen atom in pyridine rings, the electron donating ability of pyridine group is weaker than benzene group in the same conditions. Therefore the radical ($-\text{CH}(\text{Ph})\text{CH}\cdot$) is more stable than the radical ($-\text{CH}(\text{Py})\text{CH}\cdot$) and PS radicals is more easily crosslinked than P4VP chain radicals. So the percentage of crosslinked PS [Figure 4(b,c)] is more than that of crosslinked P4VP [Figure 3(b,c)]. In solution, because of high activity of radicals, P4VP chain radicals lose hydrogen radicals and generate chains with unsaturated terminus that can be understood from Figure 5. Because of the steric stabilization and the radical activity, PS chain radicals are easier to react with diethyleneglycol radicals rather than polymer chain radicals itself. In nitrobenzene, PS chain radicals will crosslink in the absence of other radicals which results in the wholly shift to left of GPC curve for PS [Figure 4(b)]. Furthermore, low PDI indicates that crosslinking may proceed in a quasi-living manner.

To explore the position of bond-breaking and the microstructure change of polymer, $^1\text{H-NMR}$ is also used to characterize polymer chains before and after the thermolysis. Their spectra are shown in Figures 5 and 6. In the spectra of Figures 5(a) and 6(a), the area ratio between characteristic peak “b” ($\text{S}=\text{CSCH}_2\text{CH}_2-$) and “c” ($-\text{CHSC}=\text{S}$) is equal to 2 which implies that every P4VP or PS chain is capped with thiocarbonylthio group. In Figure 5(b,c), the vanishing of the characteristic peak “b” ($\text{S}=\text{CSCH}_2\text{CH}_2-$) of thiocarbonylthio group and emerging the characteristic peak “e” of unsaturated terminus indicate that thiocarbonylthio groups are cleaved. Moreover, the disappearance of characteristic peak “d” ($\text{HOOC}(\text{CH}_3)_2-$) in Figure 5(b) confirms that Z groups are eliminated upon ther-

molysis in nitrobenzene. In nitrobenzene, both Z groups and R groups of P4VP are ruptured in thermal decomposition. This will result that the molecular weight of the product is multiplied or the polymer chain is rapidly degraded. The position deviations of GPC peak [Figure 1(b)] are also explained. However, the characteristic peak “d” ($\text{HOOC}(\text{CH}_3)_2-$) in Figure 5(c) still exists, which indicates that partial Z groups still cap with polymer chains when the thermolysis is carried out in diethylene glycol. For PS, characteristic peaks “e” of unsaturated terminus and characteristic peaks “f” of crosslinking are also observed in Figure 6(b). The absence of characteristic peaks of double bonds in Figure 6(c) should be ascribed to termination of radicals by diethylene glycol. The others are similar to P4VP. To get more clear idea about the chain end species of P4VP and PS as well as the exact mechanism of the removal of thiocarbonylthio groups in different solvents, $^{13}\text{C-NMR}$ is used to analyze the microstructure of P4VP (Figure 7) and PS (Figure 8). The $^{13}\text{C-NMR}$ spectrum of “1” and “2” (Figure 7) shows the appearance of signals attributed to unsaturated chain ends at δ_C 118 and 152. The $^{13}\text{C-NMR}$ spectrum of PS sample b shows signals at δ_C 129 and 49 which are considered to correspond to the unsaturated chain ends and coupling (Figure 8). In addition, the styrenyl group adjacent to the diethylene glycol appears as the signals at δ_C 82 in the $^{13}\text{C-NMR}$ spectrum in Figure 8(c). Finally, the catalytic thermolysis is very complicated and the possible mechanism can be speculated as shown in Scheme 2.

CONCLUSIONS

Well-defined hydrophilic P4VP and hydrophobic PS are synthesized via a living RAFT polymerization in the presence of DDMAT. Their thiocarbonylthio end-groups can be cleaved through catalytic thermolysis in a liquid phase. Under the catalysis of Cu(0), S-containing groups can be removed at 165 °C in 3 h. When nitrobenzene is used as a solvent, crosslinking among multipolymer chains occurs because of removal of Z groups and PS chains are easier to crosslink than P4VP chains. When diethylene glycol is used as a solvent, no crosslinking occurs. In the future, the kinetic of catalytic thermolysis in a fixed bed reactor will be published.

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