



Synthesis of Narrow Polydispersity Block Copolymers of PtBA-PS by Novel RAFT Polymerization Technique

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Abstract. The synthesis of narrow disperse polystyrene (PS) and poly-*t*-butylacrylate (PtBA) was carried out by copolymerization using benzyl dithiobenzoate as the chain transfer agent (CTA). Benzyl dithiobenzoate as a reversible addition-fragmentation chain transfer (RAFT) agent has high transfer coefficient in polymerization of styrene to produce PS with higher molecular weight than that of calculated, in contrary with polymerization of *t*-butylacrylate to produce PtBA. These results were attributed to instability the benzyl dithiobenzoate as RAFT agent under the reaction conditions. PS as a macro-CTA is not active for *t*-butylacrylate polymerization due to low transfer coefficient. On the other hand PtBA as the macro-CTA is active to polymerize styrene to produce PtBA-PS block copolymer with high transfer coefficient if PtBA as macro-CTA have narrow polydispersity. The RAFT agent appears to degrade over a period of time when it is left at room temperature, which was evident from the results of PtBA

Keywords: *benzyl dithiobenzoate; copolymerization; narrow polydispersity; polystyrene; poly-*t*-butylacrylate; RAFT agent.*

1 Introduction

The preparation of polymers of predetermined molecular weight with narrow molecular weight distribution and tailored structure such as block, graft, and star copolymers has become a major aspect of polymer chemistry in recent years¹. These well-defined polymers offer a vast range of new and advanced materials for applications in biomedical material, photoelectronics, and so on.

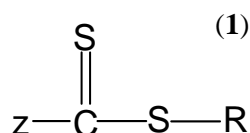
The control on macromolecule structure has been achieved by various methods, such as anionic, cationic, and controlled/living radical polymerization¹. Living radical polymerization has several advantages over other living polymerization methods, including a wide range of monomers with various functional groups, facile copolymerization, undemanding reaction condition, and feasibility in presence of water.

There are three systems that have been proved to be most efficient: nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and (RAFT). However, the ATRP and NMP free-radical polymerization

techniques have a certain disadvantages. In particular these polymerization techniques applicable to only a limited range of monomers and require reagents that are expensive and/or difficult to remove, require special polymerization condition such as high reaction temperature, and/or show sensitivity to acid or protic monomers. Also the use of these methods in the synthesis of block copolymer and other structures of complex architecture has been limited by the fact that the processes are not compatible with certain monomers and reaction conditions ^{2,3}. In particular, recent works suggests that NMP ⁴, although it can be successfully used for making block copolymers based on styrene and derivatives ^{5,6}, but it can not be applied to other systems such as the polymerization of methacrylate monomers because of fast β -H abstraction. Using ARTP, for the polymerization of acidic monomers, like methacrylic acid is limited, leads to a further difficulty in removal of the catalyst, therefore the products are often contaminated with metal ion ^{7,8}. These factors have provided the impetus of research for obtaining new and better methods.

Recently, it was reported that a RAFT “living” radical polymerization offers exceptional versatility in providing polymers with predetermined molecular weight and very narrow polydispersity. This is obtained by the polymerization in the presence of a suitable dithiocarbonyl compound (1) that acts as a highly efficient reversible addition-fragmentation chain transfer (RAFT) agent ^{2,8}. A typical raft agent contains dithiocarbonyl group attached with Z and R groups on either side. Where Z acts as an activating group that modifies the reactivity of the thiocarbonyl group toward radical addition and R acts as a good free radical leaving group. The polydispersity and the degree of molecular weight control depend on the nature of these groups Z and R. These polymerizations can be carried out in bulk, solution, emulsion, or suspension using standard reaction condition.

Dithiocarbonyl compound:

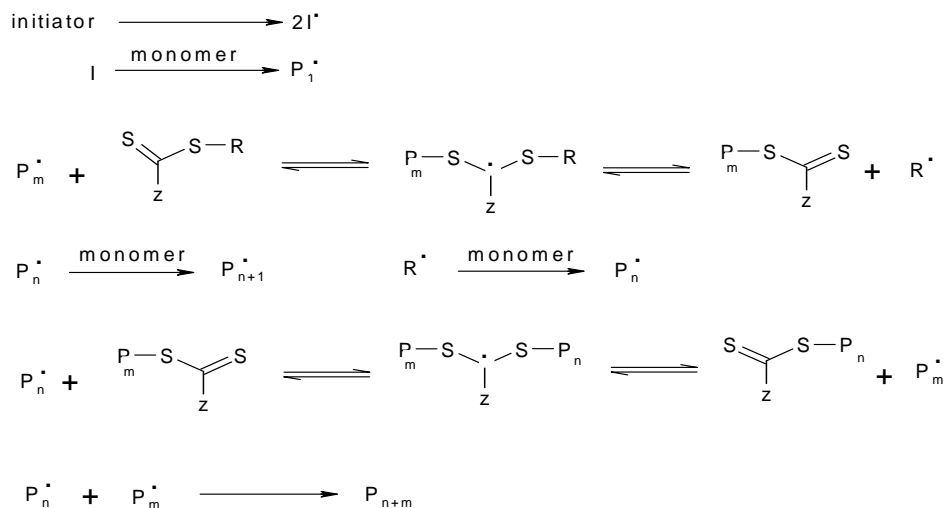


R: Free radical leaving group

Z: Activating group

To ensure a high transfer constant, Z group should make the C=S double bond active towards radical addition viz., aryl and alkyl groups. The R group should be a good free radical leaving group such as cumyl and cyanoisopropyl groups, and as an expelled radical R^\bullet should be effective in re-initiating free-radical polymerization ^{2,8}.

A simplified mechanism of RAFT polymerization developed by Rizzardo et al.⁹ is given below:



It involves a reversible chain transfer process in which a thiocarbonylthio agent is rapidly transformed into a polymeric thiocarbonylthio compound by reaction with a propagating radical (P_m^{\bullet}). The radical liberated (R^{\bullet}) reacts with a monomer to produce a new propagating radical (P_n^{\bullet}). Chain extension of polymeric thiocarbonylthio compound occurs by the same process. The thiocarbonylthio group is transferred between dormant and active chains, thus maintains the living character of the polymerization. Because the majority of chains in the product polymers have thiocarbonylthio terminal groups, polymerization can be continued in the presence of a second monomer to give a block copolymer. The living character of the RAFT process is indicated by: a). The narrow polydispersity product, (b). A linear molecular weight-conversion profile, (c). The predictability of the molecular weight from the ratio of monomer consumed to transfer agent, (d). The ability to produce blocks or higher molecular weight polymer by further monomer addition^{3,10}.

Recent work of Rizzardo et al.^{8,10} reported the effect of varying the free radical leaving group (R^{\bullet}) and the reactivity modifying group (Z) of dithiobenzoate derivatives on polymerization of several monomers: styrene, methyl methacrylate (MMA), methyl or butyl acrylate (MA or BA). The experimental results showed that The RAFT agents with electrophilic Z substituents with lone pairs directly conjugated to the $C=S$ double bond ($O-$, $N=$) have low transfer coefficients and relatively ineffective. However, electron-withdrawing groups on O or N increase the activity of RAFT agents significantly. In

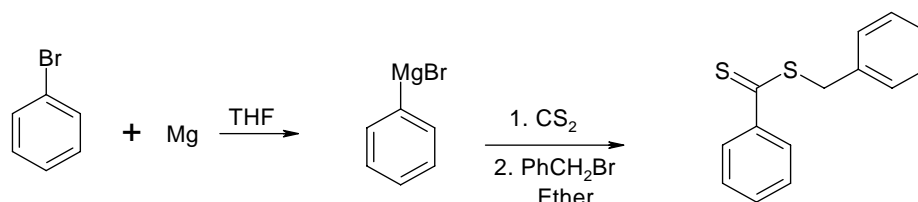
polymerizations of MMA, BA, and styrene, the ability of the RAFT agents to promote living radical polymerization depends strongly on the nature of R. A major factor determining the transfer coefficient of dithiobenzoate derivatives is the way the intermediate partitions between starting material and product which is in turn determined by the relative leaving group ability of R[•] and the propagating radical. In addition, steric factors, radical stability, and polar factors appear important in determining the leaving group ability of R[•]. They also reported that polymerization of styrene in the presence of benzyldithiobenzoate-poly(methylmethacrylate) (PMMA) as the macro-CTA was successful in giving a narrow polydispersity block copolymer P(S-co-MMA). However, block copolymer synthesis involving polymerization of MMA by using benzyldithiobenzoate-polystyrene (PS) as the macro-CTA was unsuccessful. Other research¹¹ reported that polystyrene (PS) and poly(4-vinylpyridine) (P4VP) as well as its copolymers were obtained by using dibenzyl trithiocarbonate as the chain transfer agent. The polymerization rate appeared to be lower for the polymerization of styrene using P4VP as the macro-CTA to form P4VP-PS-P4VP triblock copolymer compared with the polymerization of 4-vinylpyridine using PS as the macro-CTA to form PS-P4VP-PS triblock copolymer. This was attributed to the lower transfer coefficient of the P4VP macro-CTA to styrene compared with those of PS macro-CTA to 4-vinylpyridine.

In this paper, we report on the use of benzyldithiobenzoate as the chain transfer agent to synthesize the narrow disperse polystyrene and poly-t-butylacrylate (PtBA) in various compositions of monomer-RAFT agent, and show the living character of this chain transfer agent by copolymerization of styrene and t-butyl acrylate monomers to produce PS-PtBA diblock copolymers.

2 Experimental

Materials

Carbon disulfide (CS₂) was passed over anhydrous Na₂SO₄ and further dried by refluxing with P₂O₅, then followed by distillation. Benzyl bromide (C₅H₆CH₂Br) and Bromobenzene (C₅H₆Br) were fractional distilled under reduced pressure before using. Tetrahydrofuran (THF) was dried with sodium metal until a characteristic blue color, then distilled. Styrene and t-butylacrylate monomers were washed repeatedly with aqueous NaOH to remove inhibitors, then washed with distilled water and dried over anhydrous sodium sulfate and distilled fractionally under reduced pressure prior to use. 2,2'-azoisobutyronitrile (AIBN) was recrystallized from chloroform and methanol and stored in the dark at about -10°C until used.

Preparation of Benzyl Dithiobenzoate

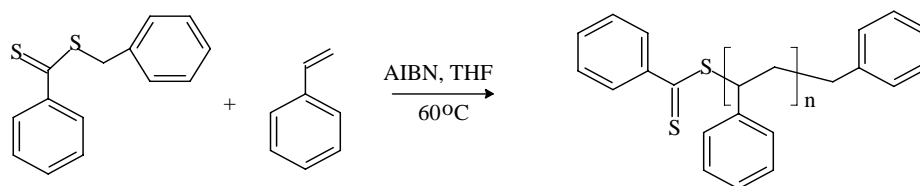
A solution of phenylmagnesium bromide made from 7.85 g of bromobenzene and 1.25 g of magnesium turning in 37.5 mL dry tetrahydrofuran (THF) was warmed to 40°C. Then 3.8 g of carbon disulfide was added over 15 minutes. 0.96 g of benzyl bromide was then added to the dark brown solution over 15 minutes after which the reaction temperature was increased to 50°C, and maintained for 45 minutes. 190 ml ice-cold water was added and the mixture was extracted with 250 mL of diethyl ether. The combined ether extracts were washed with 125 mL of distilled water and 62.5 mL of brine, and then it was dried over anhydrous sodium sulfate. After removal of solvent by vacuum distillation produced benzyl dithiobenzoate as red oil. The compound was further purified via column.

Preparation of Polymers**Synthesis of Narrow Disperse Polystyrene**

Two stock solutions A and B were prepared. Solution A contains 15 mL of styrene and 4.225 mg of 2,2'-azoisobutyronitrile (AIBN) and solution B contains 100 mg of benzyl dithiobenzoate and 4 mL of THF.

Variation of [Monomer]/[RAFT]

Aliquots from the above solutions (2.5 mL of solution A and calculated amount of solution B) were transferred to 5 ampoules. The ampoules were degassed with three freeze-pump-thaw cycles and then sealed under vacuum. The sealed ampoules were immersed in an oil bath thermostat at 60°C for a period of 24 hours time (Table 1). After the reaction time, the polymerization was stopped by cooling rapidly. The excess monomer was removed at ambient temperature under vacuum to leave a residue that was weighed to determine conversion and analyzed by GPC.



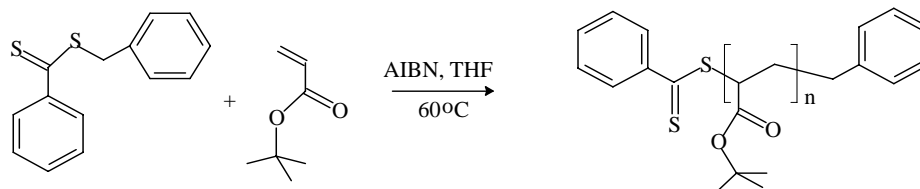
Variation of Polymerization Time

Using the best result from table I i.e., monomer/RAFT agent ratio with 1000, we varied the polymerization time and did the experiments (Table 2). Aliquots of 2.5 mL of solution A and a 0.21 mL of solution B were transferred to 4 ampoules. The ampoules were degassed with three freeze-pump-thaw cycles, and vacuum sealed. The sealed ampoules were immersed in an oil bath thermostat at 60°C for varying times. After the reaction time, the polymerization was stopped by cooling rapidly. The excess monomer was removed at ambient temperature under vacuum to leave a residue that was weighed to determine conversion and analyzed by GPC.

Synthesis of Narrow Disperse Poly-t-butylacrylate

Two stock solutions were prepared. Solution A contains 15 mL of t-butylacrylate and 1.93 mg of 2,2'-azoisobutyronitrile (AIBN) and solution B contains 100 mg of benzyl dithiobenzoate and 4 mL of THF.

Variation of [Monomer]/[RAFT]:



Aliquots of the above solutions, 2.5 mL of solution A and calculated amount of solution B were transferred to ampoules. The ampoules were degassed with three freeze-pump-thaw cycles, and vacuum sealed. The sealed ampoules were immersed in an oil bath thermostat at 60°C for a period of 5h. After the reaction time, the polymerization was stopped by cooling rapidly. The excess monomer was removed at ambient temperature under vacuum to leave a residue that was weighed to determine conversion and analyzed by GPC (Table 3).

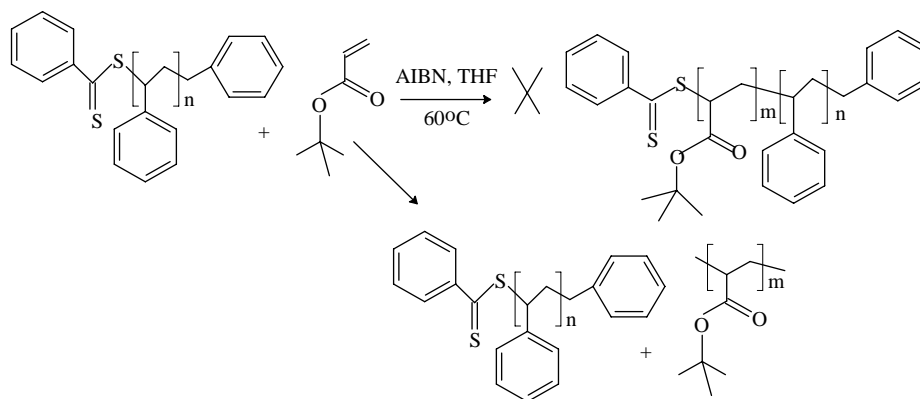
Variation of Polymerization Time

Synthesis of Poly-t-butylacrylate by varying polymerization time at a fixed [Monomer]/[RAFT] concentration of 1000 was carried out in the similar way. 2.5 mL of solution A and 0.167 mL of solution B were transferred to ampoules.

The ampoules were degassed with three freeze-pump-thaw cycles, and vacuum sealed. The sealed ampoules were immersed in an oil bath thermostat at 60°C for varying amounts of time. After the reaction time, the polymerization was stopped by cooling rapidly. The excess monomer was removed at ambient temperature under vacuum to leave a residue that was weighed to determine conversion and analyzed by GPC (Table 4 & 5).

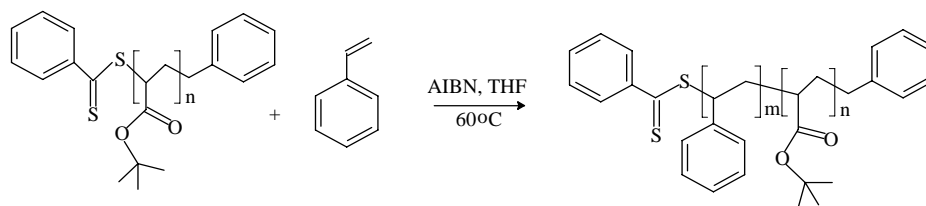
Synthesis of block copolymers

50 mg of the polystyrene-dithiobenzoate ($\overline{M}_n = 2400$) was dissolved in THF and the solution transferred to an ampoule and evaporated the THF, then 2 mL of solution B was added. The ampoule was degassed with three freeze-pump-thaw cycles, and sealed.



Then the sealed ampoule was immersed in an oil bath thermostat at 60°C for 6 hours. After the reaction time, the polymerization was stopped by cooling rapidly. The excess monomer was removed at ambient temperature under vacuum to leave a residue that was weighed to determine conversion and analyzed by GPC (Table 6).

85 mg of the poly-t-butyl acrylate-dithiobenzoate ($\overline{M}_n = 34100$) was dissolved in THF and the solution transferred to two ampoules and evaporated the THF, then 1 ml of styrene and 0.28 mg of AIBN were added. The ampoules were degassed with three freeze-pump-thaw cycles, and sealed, then heated in oil bath at 60°C for 16 and 24 hours, respectively. After the reaction time, the polymerization was stopped by cooling rapidly. The excess monomer was removed at ambient temperature under vacuum to leave a residue that was weighed to determine conversion and analyzed by GPC (Table 7).



Characterizations

GPC was carried out with a Viscotek TDA instrument in THF and CHCl_3 solvents, at 35°C , with solvent flow of $1\text{ mL}/\text{min}$. Calibration was done with polystyrene standards, and \overline{M}_n and \overline{M}_w of the homo and block polymers were accordingly calculated. The glass transition temperature (T_g) of these polymers was measured using Rheometric Scientific DSC machine. The instrument was calibrated with indium. The ^1H NMR was done on 400 MHz Bruker machine in CDCl_3 solvent.

3 Results and Discussion

Benzyl dithiobenzoate was prepared by reaction of a phenyl Grignard reagent with carbon disulfide and further treating with benzyl bromide. It was purified via distillation and column chromatography. The purity established by ^1H NMR analysis and TLC. Polymerizations were conducted at 60°C either in the bulk or in THF solution for various reaction times and composition of monomer/RAFT agent

Homopolymers (PS and PtBA)

Polymerization of styrene monomer by using benzyl dithiobenzoate as RAFT agent was found to give both narrow polydispersity and good molecular weight control (Table 1 and 2). We noted that the yields and molecular weights of polystyrene (PS) as a function of the polymerization time tend to increase, and the polydispersities becomes narrow. This shows the high transfer coefficient of RAFT agent in the polymerization. In most of the cases in the Tables 1 & 2, there is good agreement between the molecular weights determined by GPC and those calculated from conversion assuming one dithiocarbonyl group per chain. Although molecular weight is calculated based on the assumption that all chains contain one dithiocarbonyl moiety, it is important to realize that a small number of dead chains could be produced by radical-radical termination.

The correspondence between the experimentally determined and calculated molecular weight indicates complete consumption of the initial RAFT agent. The benzyl dithiobenzoate as the RAFT agent provides a narrow polydispersity product with the increasing of monomer/RAFT ratio suggesting the increasing of transfer coefficient in high monomer/RAFT ratio. However, molecular

weights are significantly higher than expected based on the ratio of monomer/RAFT agent and conversion. This may be attributed to the instability of benzyl dithiobenzoate under the reaction condition causing the concentration of the reagent to be lower than expected.

| [M]/[RAFT] | Mass (g) | Conversion (%) | \bar{M}_n (GPC) | \bar{M}_w | \bar{M}_w/\bar{M}_n | \bar{M}_n (Calc) |
|------------|----------|----------------|-------------------|-------------|-----------------------|--------------------|
| 100 | 2.90 | 12,76 | 1770 | 2400 | 1.35 | 1330 |
| 200 | - | - | 2870 | 3510 | 1.23 | - |
| 300 | 2.60 | 11,44 | 5470 | 6630 | 1.21 | 3570 |
| 700 | 3.80 | 16,72 | 15360 | 19020 | 1.24 | 12170 |
| 1000 | 4.00 | 17,60 | 21730 | 25280 | 1.16 | 18305 |

Temperature of polymerization: 60°C, Time of polymerization: 24 hours, Volume of styrene used: 2.5 mL

(2.2725 g), Mass of AIBN: 0.704 mg, \bar{M}_n (calc): $[M]/[RAFT] \times \text{Conversion} (\%) \times \bar{M}_n$ (monomer)

Table 1 Molecular weights and polydispersity index of polystyrene synthesized via RAFT polymerization by varying ratio of monomer/RAFT.

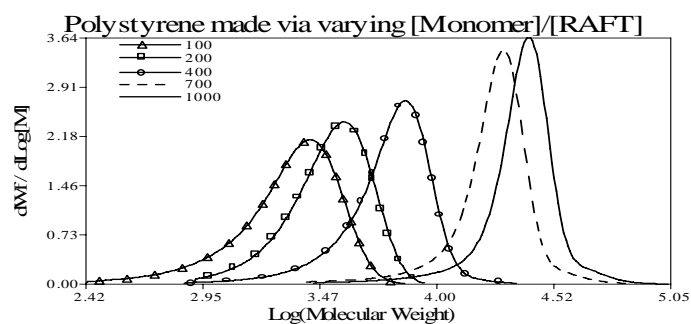


Figure 1 Evolution of GPC chromatograms of polystyrene by varying monomer/raft ratio from 100-1000.

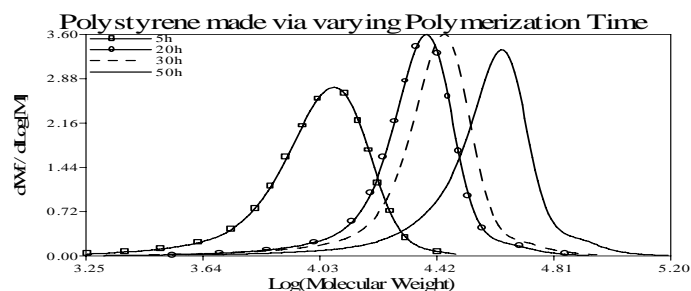


Figure 2 Evolution of GPC chromatograms of PS by varying polymerization time from 5 to 50 hours.

| Time (hours) | Mass (g) | Conversion (%) | \overline{M}_n (GPC) | \overline{M}_w | $\overline{M}_w / \overline{M}_n$ | \overline{M}_n (Calc) |
|--------------|----------|----------------|------------------------|------------------|-----------------------------------|-------------------------|
| 5 | 1.50 | 6.6 | 9530 | 11210 | 1.18 | 6865 |
| 20 | 3.80 | 16.72 | 20590 | 23500 | 1.14 | 17390 |
| 30 | 4.10 | 18.04 | 22860 | 27010 | 1.18 | 18760 |
| 50 | 5.20 | 22.88 | 34010 | 41080 | 1.21 | 23795 |

Temperature of polymerization : 60°C, [M]/[RAFT] : 1000, Volume of styrene used : 2.5 mL (2.2725 g),

Mass of AIBN : 0.704 mg, \overline{M}_n (calc) : [M]/[RAFT] x Conversion (%) x \overline{M}_n (monomer)

Table 2 Molecular weights and polydispersity index of polystyrene synthesized via RAFT polymerization by varying polymerization time.

| [M]/[RAFT] | Mass (g) | Conversion (%) | \overline{M}_n (GPC) | \overline{M}_w | $\overline{M}_w / \overline{M}_n$ | \overline{M}_n (Calc) |
|------------|----------|----------------|------------------------|------------------|-----------------------------------|-------------------------|
| 100 | 0.049 | 2.24 (oil) | - | - | - | 290 |
| 500 | 0.450 | 20.57 | 17400 | 20830 | 1.20 | 13180 |
| 1000 | 0.859 | 39.27 | 39390 | 50700 | 1.49 | 50330 |
| 1500 | 1.008 | 46.06 | 49390 | 78360 | 1.59 | 88590 |

Temperature of polymerization : 60°C, Time of polymerization : 5 hours, Volume of t-butylacrylate used :

2.5 mL (2.1875 g), Mass of AIBN : 0.321 mg, \overline{M}_n (calc) : [M]/[RAFT] x Conversion (%) x \overline{M}_n (monomer).

Table 3 Molecular weights and polydispersity index of poly-t-butylacrylate synthesized via RAFT polymerization by varying ratio of monomer/RAFT.

| Time (hours) | Mass (g) | Conversion (%) | \overline{M}_n (GPC) | \overline{M}_w | $\overline{M}_w / \overline{M}_n$ | \overline{M}_n (Calc) |
|--------------|----------|----------------|------------------------|------------------|-----------------------------------|-------------------------|
| 6 | 0.635 | 29.03 | 34080 | 45060 | 1.32 | 37210 |
| 16 | 1.119 | 51.15 | 47880 | 66000 | 1.38 | 65560 |
| 20 | 1.213 | 55.45 | 44390 | 66410 | 1.50 | 71070 |
| 24 | 1.289 | 58.93 | 43330 | 70860 | 1.64 | 75530 |

Temperature of polymerization: 60°C, [M]/[RAFT]: 1000, Volume of t-butylacrylate used: 2.5 mL (2.1875 g),

Mass of AIBN: 0.55 mg, \overline{M}_n (calc) : [M]/[RAFT] x Conversion (%) x \overline{M}_n (monomer),

Table 4 Molecular weights and polydispersity index of poly-t-butyl-acrylate synthesized via RAFT polymerization by varying polymerization time.

In polymerization of t-butylacrylate monomer we observed that, when the ratio of monomer/RAFT is 100, the product polymer is an oil formed in very low yields and is of low molecular weight. However, if the ratio of monomer/RAFT increase, the molecular weights and yields of Poly-t-butylacrylate (PTBA) obtained increase regularly, but the polydispersity tends to become broad (Table 3). In addition, upon increasing the polymerization time the molecular weights and yields of the polymers increase, while the polydispersity tends to become

broad (Table 4). These results indicate a lower transfer coefficient of benzyl dithiobenzoate as a RAFT agent in polymerization of t-butylacrylate. We also noted that molecular weights are significantly lower than expected based on the ratio of monomer/RAFT agent and conversion. This may be attributed to the instability of benzyl dithiobenzoate under the reaction condition due to the concentration of the reagent to be higher than expected.

We also tried to polymerize t-butylacrylate monomer under different condition to obtain PtBA with lower molecular weight and narrow polydispersity (Table 5). In fact, the rate of polymerization is slower than that obtained in previous polymerization, and the polymer products have lower molecular weights and yields, and relatively narrow polydispersities. These results indicated that the reactivity of RAFT agent has decreased. This may be due to inadvertent degradation of the RAFT agent with time, leading to the formation of products that appear to retard the polymerization.

| Time (hours) | Mass (g) | Conversion (%) | \overline{M}_n (GPC) | \overline{M}_w | $\overline{M}_w / \overline{M}_n$ | \overline{M}_n (Calc) |
|--------------|----------|----------------|------------------------|------------------|-----------------------------------|-------------------------|
| 4 | 0.054 | 2.47 | 1762 | 2257 | 1.28 | 1583 |
| 6 | 0.116 | 5.31 | 2750 | 3484 | 1.27 | 3403 |
| 12 | 0.308 | 14.10 | 11120 | 12270 | 1.10 | 9036 |
| Control | - | - | 43770 | 79650 | 1.82 | - |

Temperature of polymerization: 60°C, [M]/[RAFT] : 500, Volume of t-butylacrylate used : 2.5 mL (2.1875 g), Mass of RAFT : 8.33 mg, Mass of AIBN : 0.321 mg, \overline{M}_n (calc) : [M]/[RAFT] x Conversion (%) x \overline{M}_n (monomer), Control: No RAFT agent was used

Table 5 Molecular weights and polydispersity index of poly-t-butylacrylate synthesized via RAFT polymerization by varying polymerization time.

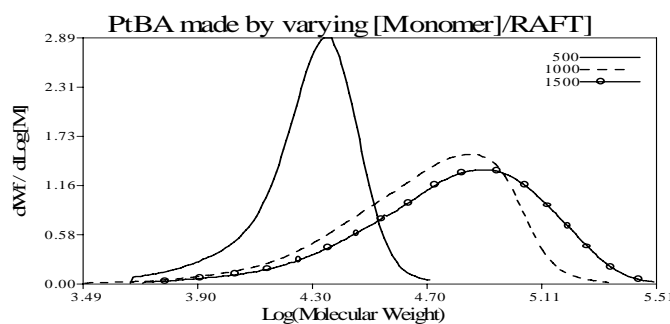


Figure 3 Evolution of PtBA mol wt by varying monomer/raft ratio between 500-1500.

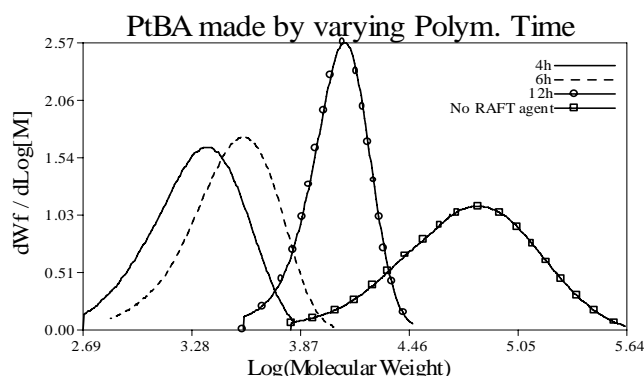


Figure 4 Evolution of mol wt of poly-t-butylacrylate by varying the polymerization time between 4 -12 h and also a control experiment without raft agent.

Block Copolymers

The experimental results revealed that the polymerization behavior for extending the polymers was different when using PS as the macro-CTA for the synthesis of PS-PTBA block copolymers than when using PtBA for the synthesis of PtBA-PS block copolymers. It was found that the conversion reached 44 % after 6 hours for making PS-PtBA block copolymer using PS as the macro-CTA, but the GPC results reveal two separate homopolymers with the molecular weights 2330 and 72860, respectively (Table 6 and Fig 5).

| Mass (g) | Conversion (%) | \overline{M}_n (GPC) | \overline{M}_w | $\overline{M}_w / \overline{M}_n$ |
|----------|----------------|------------------------|------------------|-----------------------------------|
| 0.803 | 44.45 | 2007 | 2330 | 1.16 |
| | | 54900 | 72860 | 1.33 |

PS-CTA (50 mg, \overline{M}_n : 1771, \overline{M}_w : 2391), Volume of t-butylacrylate used: 2 mL, Mass of AIBN: 0.44 mg, Temperature of polymerization: 60°C, and Polymerization time: 6 hours

Table 6 Molecular weights and polydispersity index of PS-PtBA block copolymer synthesized using PS as a macro-CTA.

This result indicates that PS, as the macro-CTA is not active for t-butylacrylate polymerization. This is because the PS-CTA is not a good homolytic leaving group in polymerization of t-butylacrylate, so that by addition of t-butylacrylate monomer in the PS-CTA, the polymerization cannot be continued to give block copolymers, and the t-butylacrylate monomer was polymerized itself to give a homopolymer PtBA.

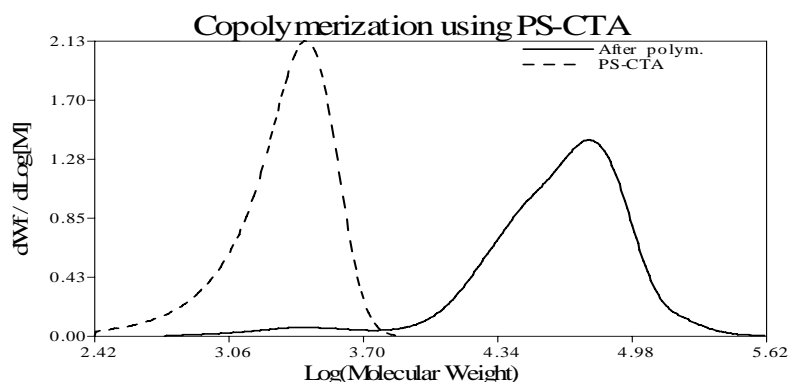


Figure 5 GPC chromatogram showing two separate homopolymers, PtBA and PS.

| Time (hours) | Mass (g) | Conversion (%) | \overline{M}_n (GPC) | \overline{M}_w | $\overline{M}_w / \overline{M}_n$ |
|--------------|----------|----------------|------------------------|------------------|-----------------------------------|
| 16 | 0.089 | 8.95 | 87630 | 132000 | 1.51 |
| 24 | 0.142 | 14.29 | 94930 | 149200 | 1.57 |

PtBA-CTA (85 mg, \overline{M}_n : 34080, \overline{M}_w : 45060), Volume of t-butylacrylate used: 1 mL, Mass of AIBN: 0.282 mg, Temperature of polymerization: 60°C

Table 7 Molecular weights and polydispersity index of PtBA-PS block copolymer synthesized using PtBA as a macro-CTA.

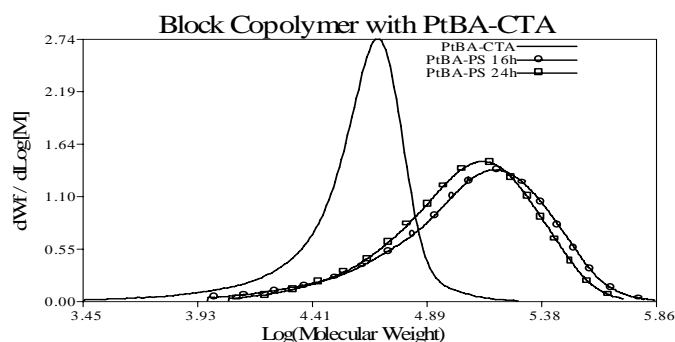


Figure 6 GPC of PtBA-PS block copolymers varying the Polym. time along with starting polymer, PtBA-CTA.

On the other hand, polymerization of styrene by using PtBA as a macro-CTA with a polydispersity index 1.32 produced block copolymers having unimodal molecular weight distribution with polydispersity index > 1.5 (Table 7 and

Figure 6 & 7). These results indicate that PtBA, as the macro-CTA is active to polymerize styrene with low transfer coefficient. The GPC results (Figure 6) show unimodal distribution. DSC data (Figure 7) also shows two separate T_g 's.

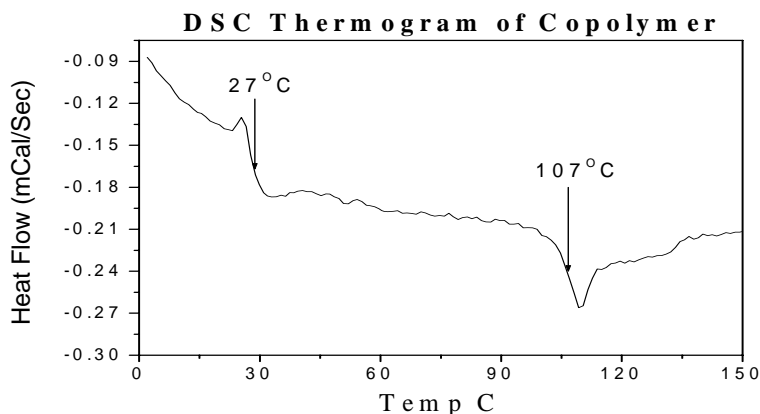


Figure 7 DSC thermogram of the copolymer PtBA-PS, showing two separate T_g 's.

We also tried one more copolymerization, where PtBA as a macro-CTA has much narrower molecular weight distribution expectedly to obtained block copolymer with narrow molecular weight distribution. The results obtained showed that polymerization of styrene by PtBA-CTA with the narrow polydispersity produced PtBA-PS block copolymer with narrower molecule weight distribution ($\overline{M}_w/\overline{M}_n < 1.2$). (Table 8 and Figure 8)

| Time (hours) | Mass (g) | Conversion (%) | \overline{M}_n (GPC) | \overline{M}_w | $\overline{M}_w/\overline{M}_n$ |
|--------------|----------|----------------|------------------------|------------------|---------------------------------|
| 6 | 0.079 | 8.69 | 25240 | 28400 | 1.13 |
| 16 | 0.355 | 37.02 | 47730 | 57000 | 1.19 |
| 24 | 0.162 | 16.89 | 43650 | 51100 | 1.17 |

PtBA-CTA (50 mg, \overline{M}_n : 11120, \overline{M}_w : 12270), Volume of t-butylacrylate used : 1 mL, Mass of AIBN: 0.282 mg, Temperature of polymerization: 60°C

Table 8 Molecular weights and polydispersity index of PtBA-PS block copolymer synthesized using PtBA as a macro-CTA.

The difference in polymerization behavior between PS-CTA and PtBA-CTA probably resulted from the difference in the transfer coefficients between PS and PTBA as macro-CTAs in polymerization of t-butylacrylate and styrene, respectively. Generally, one requirement for the formation of a narrow

polydispersity block copolymer is that the first-formed macro-CTA (A block) should have a high transfer coefficient in order to give another block (B block). This required that the homolytic leaving group ability of propagating radical A^\bullet was comparable to or greater than that of the propagating radical B^\bullet under reaction condition. In the polymerization system, when A was a PS as the macro-CTA, the transfer coefficient of Ph-C(S)S-PS in the t-butylacrylate polymerization appeared to be lower. This was attributed to the PtBA propagating radical being poor, leaving groups with a PS propagating radical and causing adduct radical PS to partition strongly in favor of starting materials. As a result, slower polymerization occurred for synthesis of PS-PtBA block copolymer from PS as the macro-CTA than for that of the PtBA-PS from PtBA as the macro-CTA. Thus, for synthesis of polystyrene-block-poly-t-butylacrylate under this polymerization conditions, it is necessary to make the PtBA block first in order to make a narrow polydispersity block copolymer.

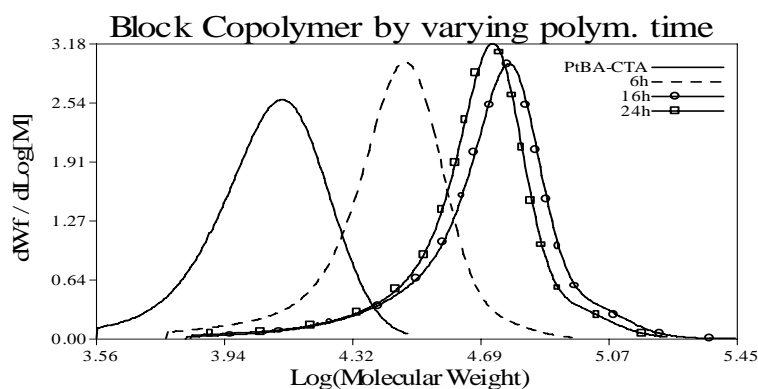


Figure 8 PtBA-PS block copolymer evolution as a function of polymerization time, along with the starting PtBA-CTA.

4 Conclusion

Benzyl dithiobenzoate as a RAFT agent has high transfer coefficient in polymerization of styrene to produce PS with higher molecular weight than that of calculated, contrary in polymerization of t-butylacrylate to produce PtBA. These results were attributed to instability the benzyl dithiobenzoate as RAFT agent under the reaction conditions. PS as a macro-CTA is not active for t-butylacrylate polymerization due to low transfer coefficient. On the other hand PtBA as the macro-CTA is active to polymerize styrene to produce PtBA-PS block copolymer with high transfer coefficient if PtBA as macro-CTA have narrow polydispersity. The RAFT agent appears to degrade over a period of

time when it is left at room temperature, which was evident from the results of PtBA.

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