Preparation of amphiphilic block copolymers by Reversible Addition Fragmentation Chain Transfer polymerization

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Abstract: Polystyrene macromolecular chain transfer agent (PS-CTA) was firstly synthesized by RAFT of styrene (St) in THF using benzyl dithiobenzoate (BDT B) as chain transfer agent and azobisisobutyronitrile (AIBN) as initiator. It was found that the molar ratio of monomers to chain transfer agents and reaction time had obvious effects on the molecular weight of PS-CTA, and the distribution of molecular weight (Mw/Mn) decreases with the increase of the ratio of chain transfer agent to initiator by using gel permeation chromatography (GPC). The amphiphilic block copolymers polystyrene-b-poly(4-vinylpyridine) (PS-b-P4VP) were synthesized using PS-CTA by RAFT. The structure, glass transition temperature (Tg) and molecular weight of the diblock copolymer were characterized by nuclear magnetic resonance (1H-NMR), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). The results showed that the structure of PS-b-P4VP was the target product. The segment ratio of PS-b-P4VP could be effectively controlled by changing the polymerization conditions in a large range.

1. Instruction
Controllable/active free radical polymerization method can passivate a large number of reactive radicals to make them dormant, establish a rapid dynamic balance between a small amount of growth radicals and a large number of dormant radicals, greatly reduce the concentration of reactive radicals, and reduce the possibility of double radical termination and chain transfer. Therefore, controllable/active free radical polymerization method provides a good way to control the structure and properties of polymers[1-2]. In 1998, Rizzardo found an active radical polymerization regulated by disulfide ester to obtain polymers with narrow molecular weight distribution, they called this polymerization method reversible addition fragmentation chain transfer (RAFT) polymerization[3]. RAFT polymerization provides a more effective and cheaper way to prepare active polymers and design polymer structures[4]. In addition, there are a wide range of monomers that can carry out RAFT polymerization, including almost all monomers suitable for other active polymerization and some monomers that can't carry out active polymerization at present. Moreover, RAFT polymerization adopts by selecting chain transfer agents with different structures, it is convenient to introduce end group functional groups into polymer materials; in addition, block and gRAFT copolymerization that can't or is difficult to obtain by other synthesis technologies can be synthesized by using macromolecular chain transfer agent.
In this paper, polystyrene macromolecular chain transfer agent (PS-CTA) was firstly synthesized by RAFT using benzyl dithiobenzoate (BDTB) as chain transfer agent. PS-CTA with controllable molecular weight and the distribution of molecular weight ($M_w/M_n$) was prepared. According to the determination results of GPC, the effects of the amount of chain transfer agent and initiator, reaction time on the conversion, molecular weight and molecular weight distribution were investigated. The synthesized PS-CTA was used to regulate the monomer 4VP for solution RAFT reaction to synthesize amphiphilic block copolymers PS-\textit{b}-P4VP.

2. Experimental

2.1. Materials
4-Vinylpyridine (4VP, Acros Organics) was dried over CaH2 and distilled at 55 oC before use. Benzyl dithiobenzoate (BDTB) was synthesized and purified according to the reported methods\cite{5}. All the other solvents and materials were purchased from Shanghai Chemical Reagent Station without further purification.

2.2. Characterization methods
Nuclear magnetic resonance (1H NMR, Bruker AVANCE III, 400 MHz) spectrum was used to identify the structures of the polymers using chloroform-d (CDCl3) as solvent and tetramethylsilane (TMS) as the internal standard. The molecular weight and distribution of the polymers were determined by gel-permeation chromatography (GPC, Agilent-1100, USA) using DMF as eluent and polystyrene as standard with a flow rate of 1 mL/min at 35 oC. The thermal properties were analyzed by differential scanning calorimetry (DSC 822e, Mettler Toledo), DSC analysis was carried out by scanning the samples at a heating rate of 10oC/min from 20oC to 180oC.

2.3. Synthesis of PS-CTA
PS-CTA was synthesized by RAFT of St using BDTB as chain transfer agent and AIBN as initiator in THF. The detailed procedure was as follows: AIBN, BDTB and 4 g St (the typical feed molar ratio was $n$[St]:$n$[BDTB]:$n$[AIBN]= 50/100/150/200:2:1) were added into the reaction flask at room temperature, and then 4 mL solvent THF was added. Stirring or ultrasonic oscillation for a period of time to mix the reactants. The sample was degassed under nitrogen purge with stirring for 30min. Then the polymerization was performed at 70 oC for scheduled time, precipitated from methanol and then filtered under vacuum. Such process was repeated twice, and the obtained powder dried in a vacuum oven overnight at 30 oC.

2.4. Preparation of amphiphilic block copolymers PS-\textit{b}-P4VP
Amphiphilic block copolymers PS-\textit{b}-P4VP was synthesized by RAFT of 4VP using PS-CTA and AIBN as initiator. The detailed procedure was as follows: PS-CTA, AIBN and 4 g 4VP (the typical feed molar ratio was $n$[4VP]:$n$[PS-CTA]: $n$[AIBN] = 1500:10:1) were added into the reaction flask, and then 4 mL solvent dimethylformamide (DMF) was added. The sample was degassed under nitrogen purge with stirring for 30min. Then the polymerization was performed at 70oC for scheduled time, the amphiphilic block copolymer was obtained after precipitated from ether, and filtered under vacuum. Such process was repeated twice, and the obtained powder dried in a vacuum oven overnight at 30oC.
3. Results and discussion

3.1. Effect of molar ratio of monomer and chain transfer agent on PS-CTA

| Tab.1 The effect of different PS-CTA ratio on the $M_n$ and PDI |
|------------------|---------------|-----------------|-----------------|------------------|
| n[St]:n[BDTB]: n[AIBN] (mol/mol) | Conversion % | $M_n(th)$ $\times 10^{-3}$ | $M_n(GPC)$ $\times 10^{-3}$ | $M_w/M_n$ |
| 50:2:1 | 23.1 | 1.98 | 6.87 | 1.08 |
| 100:2:1 | 30.1 | 3.91 | 10.1 | 1.23 |
| 150:2:1 | 20.0 | 3.90 | 10.8 | 1.23 |
| 200:2:1 | 25.5 | 6.47 | 13.9 | 1.31 |

Polymerization Conditions: 70°C, reaction time 5 h

The lower conversion of St at 5 h might be due to the slow polymerization and induction effect of chain transfer agent, the RAFT polymerization rate of St was lower than that of conventional free radical polymerization. The retarding effect might due to the fact that most of the growth radicals formed after the initiation reaction of the RAFT process were transformed into intermediate radicals, which accumulated until the addition cleavage equilibrium was established without directly initiating the growth, resulting in the retarding phenomenon. It depended on the concentration of the initial RAFT reagent, and the polymerization rate of the system decreased with the increase of RAFT reagent. The induction period also prolonged with the increase of chain transfer agent concentration, which might due to the slow reinitialization rate of leaving groups in the early stage of polymerization. It could be seen from Tab.1 the molecular weight of PS-CTA could be controlled by adjusting the ratio of initiator to monomer. Thus, it was easier to control the segment ratio of block copolymer. At the same time, it was found that the Mw/Mn with the increase of the feed ratio of monomer to chain transfer agent, so it was necessary to control the appropriate feed ratio to maintain narrow molecular weight distribution.

3.2. Effect of reaction time on PS-CTA

![Fig.1 Dependence of $M_n$ on Reaction time (Conditions: 70 °C, n[St]:n[BDTB]: n[AIBN]=200:2:1)](image)

The $M_n$ and $M_w/M_n$ of the synthesized PS-CTA were determined by GPC. The results showed that $M_n$ increased steadily with the increase of reaction time, as shown in Fig.1. It shows that the $M_w/M_n$ of the PS-CTA obtained was relatively stable under different polymerization reaction times, which accorded with the characteristics of active polymerization.
3.3. $^1$H-NMR spectrum of PS-CTA and PS-b-P4VP

![Fig.2 1H-NMR spectrum of PS-CTA(a) and PS-b-P4VP(b)](image)

Fig.2 (a) showed $^1$H-NMR spectrum of PS-CTA, it showed that the chemical shift δ4.7 and δ7.9 correspond to the methylene adjacent to sulfur on the end group and two H on the benzene ring adjacent to sulfur, which indicated that the chain transfer agent had been connected to the macromolecule. The peaks c, d and e represent the peaks of polystyrene, which proved that PS-CTA with clear structure.

Fig.2 (b) showed $^1$H-NMR spectrum of PS-b-P4VP, the two absorption peaks at δ6.4 and δ8.3 belonged to the absorption peaks of n-ortho and h-meso on the pyridine ring of P4VP chain segment, there were protons on methyl and methylene at peaks e and f. a and b were methylene adjacent to sulfur on the end group and two H on the benzene ring adjacent to sulfur respectively. The above analysis showed that the amphiphilic block copolymer PS-b-P4VP was successfully synthesized by RAFT.

3.4. DSC analysis of PS-CTA and PS-b-P4VP

The DCS curves of PS-CTA and PS-b-P4VP were shown in Fig.3. Two glass transition temperatures (T_g) appeared on the DCS curves of PS-b-P4VP in Fig.3, which belong to the T_g of PS segment and P4VP segment of PS-b-P4VP respectively. It could be preliminarily judged from the DSC curves that PS-b-P4VP was synthesized successfully.

![Fig.3 The DSC curves of PS-CTA and PS-b-P4VP](image)

4. Conclusions

PS-CTA was prepared via RAFT. With the increase of the molar ratio of monomer, chain transfer agent and initiator in the reaction system, or reaction time, Mn of PS-CTA gradually increased. The MW/Mn of the PS-CTA obtained was relatively stable under different polymerization reaction times, which
accorded with the characteristics of active polymerization. The polymerization rate in the initial reaction stage was very slow, which was significantly lower than that in the conventional free radical polymerization. The amphiphilic block copolymers PS-b-P4VP were successfully synthesized using PS-CTA by RAFT. It was expected to be used in the fields of catalysis, heavy metal loading, medical treatment and so on.

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