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RESEARCH ARTICLE

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Synthesis of 4-arm methyl methacrylate star polymer by atom transfer radical polymerization

Abstract The synthesis of 4-arm methyl methacrylate star polymer had been achieved successfully by atom transfer radical polymerization using CuCl as catalyst, 2, 2′- bipyridyl as ligand and pentaerythritol tetrakis (2-bromoisobutyrate) as the initiator. The star polymer was characterized by ^{1}H-NMR and GPC, by which the precise 4-arm structure of the PMMA was confirmed.

Keywords living radical polymerization, atom transfer radical polymerization, star polymer, methyl methacrylate

1 Introduction

Atom transfer radical polymerization (ATRP) as one of the controlled polymerization plays an important role in polymer synthesis [1–5]. Currently, star polymers have attracted considerable attention because of their unique structure and properties [6,7]. Design and synthesis of star polymers and the study on their structure-property relationship have become the forefront in macromolecular science [8–11]. Methods toward making star polymers fall into two routes, the core-first method [12,13] and the so-called arm-first method [14]. In our work, we prepared the 4-arm methyl methacrylate star polymer (4-armstar PMMA) using the initiator pentaerythritol tetrakis (2-bromoisobutyrate) as the core by the core-first method and atom transfer radical polymerization (ATRP) technique. The molecular weight and the structure of the above-mentioned polymers were characterized with ^{1}H-NMR and gel permeation chromatography (GPC).

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2 Experiments

2.1 Materials and measurements

CuCl (CP) were purified by stirring overnight in glacial acetic acid, and washing with absolute ethanol and diethyl ether, and then dried under vacuum. 2, 2′-bipyridyl (bpy, AR) and 2-bromoisobutyryl bromide (AR) were used directly without further purification. The pentaerythritol tetrakis (2-bromoisobutyrate) (AR) was dried under vacuum for 24 h at 40°C. Methyl methacrylate (MMA, AR) was distilled from calcium hydride and stored in a freezer under nitrogen before use. Acetone was dried with a molecular sieve, distilled and purged with nitrogen for 30 min before use. THF (AR) was distilled with Na before use. Triethylamine was dried with CaH_2 for 24 h and distilled before use.

The ^{1}H-NMR spectra were recorded on an AVANCF 300 Hz NMR spectrometer with $CDCl_3$ as a solvent and with tetramethylsilane (TMS) as an internal standard. GPC measurements were carried out with a Waters 2410 instrument. HPLC grade THF mixed with triethylamine (2 vol%) was used as the eluent at a flow rate of 1 mL/min. Calibration was made with polystyrene standards.

2.2 Synthesis of tetrafunctional initiator pentaerythritol tetrakis (2-bromoisobutyrate) (PT-Br)

A 100 L round-bottom flask with a magnetic stirring bar was charged with 2 g pentaerythritol and kept under nitrogen before the addition of 48 mL of THF and 9 mL of triethylamine *via* syringe transfer. After the complete dissolution of pentaerythritol, the reaction medium was cooled to 0°C under stirring. A solution of 9 mL of 2-bromoisobutyryl bromide in 12 mL of THF was slowly added. The flask was kept at room temperature for 2 days under stirring. The filtrate was diluted with 50 mL dichloromethane, and then washed sequentially with a 10% HCl aqueous solution (50 mL), a saturated $NaHCO_3$ aqueous solution (50 mL) and water (100 mL) three times. The organic layers were then dried over anhydrous

magnesium sulfate, filtered, concentrated in a vacuum oven and then crystallized in methanol two times to produce 4.5 g white crystals. Yield: 40%. Mp: 134°C–135°C. ^{1}H-NMR ($CDCl_3$, 300 MHz)δ: 1.94 (s, 24H, C(Br)–CH_3), 4.33 (s, 8H, C–CH_2–O).

2.3 Synthesis and hydrolysis of 4-arm star PMMA

CuCl (0.40 mmol), bpy (0.8 mmol), PT-Br (0.1 mmol), acetone (10 mL), water (1 mL) and MMA (40 mmol) were added into a nitrogen purged dry glass tube (25 mL) with a magnetic stirrer. The tube was then sealed with a rubber septum, cooled, evacuated and back-filled with ultra-high pure nitrogen three times. The tube was then immersed into a water bath at 35°C for 8 h. After that, the mixture was then diluted with 20 mL CH_2Cl_2, purified by passing through an alumina column two or three times, concentrated and then precipitated in methanol. The solution was then filtered, washed with methanol and dried in vacuum oven for 24 h at 50°C to obtain white 4-arm star PMMA powder.

1.0 g sample of 4-arm star PMMA was dissolved in a mixture of methanol (50 mL) and KOH solution (5%, 5 mL). The mixture was refluxed for 72 h at 60°C. The organic phase was dried over anhydrous magnesium sulfate after it was extracted with chloroform. Then, it was precipitated with methanol, filtered and dried in vacuum oven for 24 h at 40°C to obtain hydrolysate of 4-arm star PMMA.

3 Results and discussion

4-arm star PMMA was synthesized by ATRP using pentaerythritol tetrakis (2-bromoisobutyrate) as the initiator, CuCl as the catalyst, and bpy as the ligand at 35°C in acetone/water medium. The synthetic route of the star polymer is shown in Fig. 1.

In the synthesis process of tetrafunctional initiator PT-Br, excess 2-bromoisobutyryl bromide was added to ensure the complete esterification of pentaerythritol. Meanwhile, the reaction could be accelerated by the complexes of triethyla-mine with 2-bromoisobutyryl bromide [15]. Moreover, 2-bromoisobutyryl bromide was easily inactivated by hydrolysis. The reaction must be operated in a closed and dry nitrogen atmosphere. In the synthesis process of 4-arm star PMMA, the anaerobic state of the reaction system is particularly important to the structure of the polymer, because CuCl is very prone to be oxidized to terminate the "living"/controlled polymerization.

Figure 2 shows the GPC traces of the polymer after hydrolysis and the original PMMA star polymer. The M_n of the original 4-arm star PMMA is about four times as much as that of 4-arm star PMMA after hydrolysis. Thus the 4-arm structure of the PMMA was confirmed. As evidence for the tetrafunctional initiation by the tetrahalide, MMA polymerization had been initiated by an equimolar mixture of monohalide and tetrahalide. Indeed, the GPC curves show two elution peaks and their molecular weights at peak maxima are approximately in a 4/1 ratio (Fig. 3).

Table 1 shows the results of the polymerizations of MMA. MMA was all polymerized with good control using a PT-Br/CuCl/bpy catalyst system, giving low polydispersity polymer.

Figure 4 exhibits the dependence of the number average molecular weight (M_n) and the polydispersity index (PDI) of 4-arm star PMMA on monomer conversion. M_n increased linearly with the increase of the monomer conversion, while PDI remained relatively narrow, indicating, the "living" characteristic of the polymerization. It can be observed from Fig. 4 that the molecular weights measured by GPC ($M_{n,GPC}$) were much lower than the calculated values ($M_{n,theo}$). This is due to the well-konwn fact that star polymers have a lower hydrodynamic volume than linear polymers of the same molecular weight. Thus, calibration with linear standard polystyrene leads to an underestimation of the molecular weight of star polymers.

Figure 5 shows the GPC curves of the obtained 4-arm star PMMA and all are narrow and symmetrical. Moreover, the smaller PDI was, the narrower the GPC curves became. The bigger Mn was, the shorter the elution time became. The results indicated that it was in accord with the size exclusion effect of GPC and close to that expected.

^{1}H-NMR is employed to analyze the structure of 4-arm star PMMA (Fig. 6). The signals at 0.84–1.25, 1.5–2.08, 3.60 and δ = 4.02 represented-methyl groups (peek a) methylene groups (peek b), methoxy groups (peek c) and methyl groups (peek d), respectively. Moreover, the absorptions at δ = 3.74 (peek c'), δ = 2.70 (peek b'), and δ =

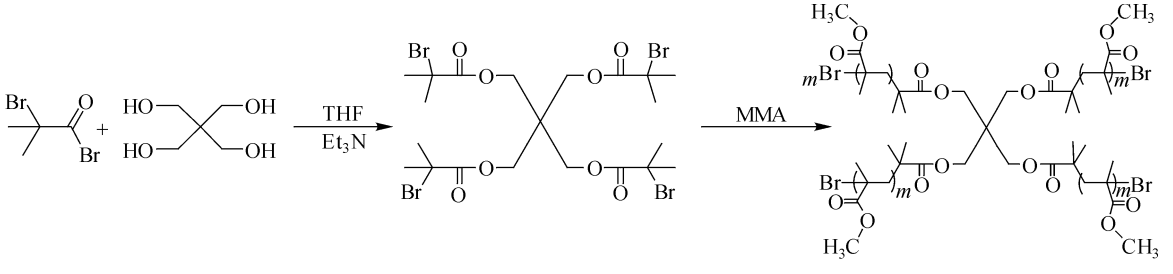

Fig. 1 Synthetic route of the star polymer

Table 1 Molecular characterization results of 4-arm star PMMA obtained by ATRP

Sample	Time/h	Conversion/%	$M_{n,\ theo}$	$M_{n,\ GPC}$	PDI
$(PMMA)_4$-1	4	45	18000	16050	1.23
$(PMMA)_4$-2	8	70	28000	25000	1.25
$(PMMA)_4$-3	12	90	36000	32690	1.24

Conditions: MMA (40 mmol), PT-Br (0.1 mmol), CuCl (0.4 mmol), bpy (0.8 mmol), acetone (10 mL), water (1 mL), temperature (35°C)

$M_{n,\ theo}$ = Conversion × $[c(Monomer)_0/c(PT\text{-}Br)_0]$ × $M_M + M_I$, M_M and M_I are respectively the molecular weight of Monomer and initiator.

1.25 (peek a') proved the presence of the end group, $–CH_2–CBr(CH_3)(COOCH_3)$. It is proof that the well-defined 4-arm star PMMA with terminal bromine was obtained.

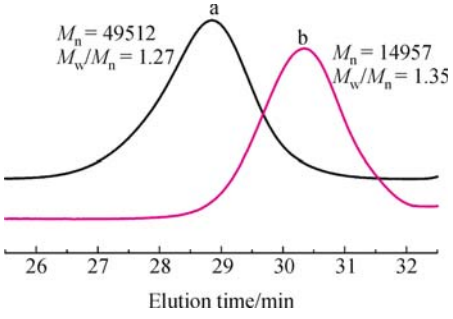

Fig. 2 GPC traces of 4-arm star PMMA **(a)** and its hydrolysate **(b)**

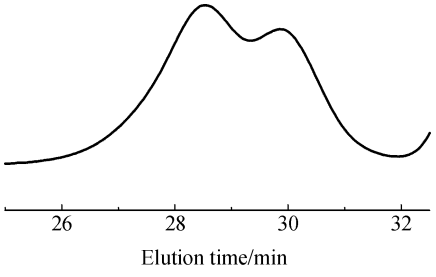

Fig. 3 GPC traces of the mixture of linear and 4-arm star PMMA, obtained by using an equimolar mixture of monohalide and tetrahalide as initiators

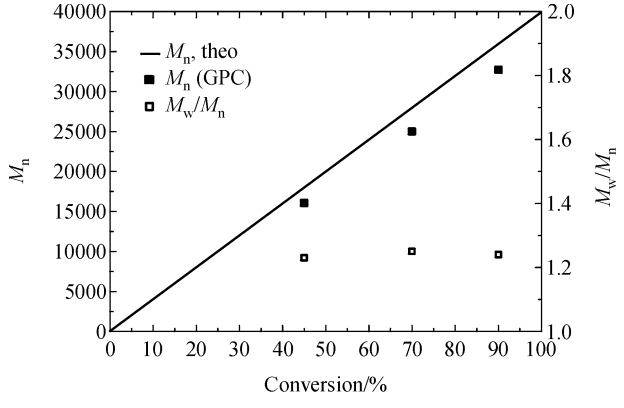

Fig. 4 M_n and M_w/M_n versus conversion for the ATRP of MMA

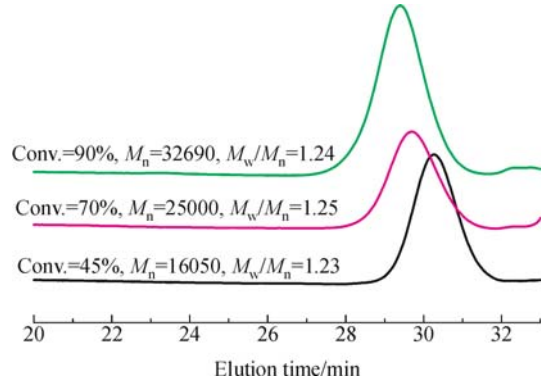

Fig. 5 Gel permeation chromatograms of a 4-arm star PMMA

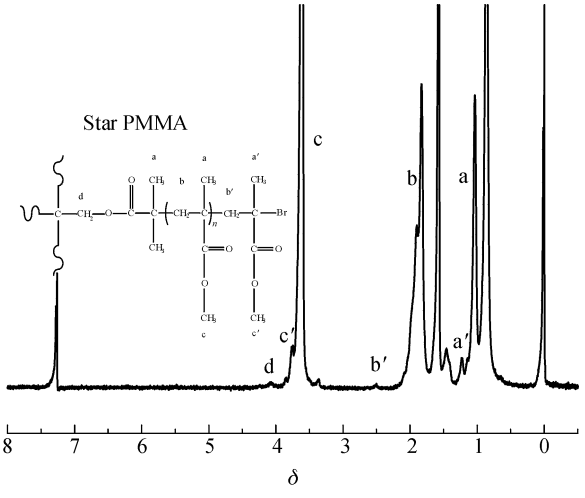

Fig. 6 ^{1}H-NMR spectra of a 4-arm star PMMA in $CDCl_3$

4 Conclusion

The synthesis of 4-arm star PMMA has been achieved successfully by the core-first method and ATRP. The results show that the polymerization with CuCl/bpy/PT-Br was closely controlled. The star polymer was characterized by ^{1}H-NMR and GPC. The results confirm that star PMMA is a 4-arm star structural polymer.

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