

SYNTHESIS OF POLY(METHYL METHACRYLATE)-*graft*-POLYSTYRENE BY
ATOM TRANSFER RADICAL POLYMERIZATION*Sheng-min Gong^a, Qun-sheng Li^b, Yan Shi^a, Zhi-feng Fu^{a**}, Shu-ke Jiao^a and Wan-tai Yang^a^a Key Laboratory for Controlled Chemical Reactions of Education Ministry, Beijing University of Chemical Technology,
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Abstract The radical copolymerization of methyl methacrylate and 2-hydroxyethyl methacrylate was carried out via atom transfer radical polymerization (ATRP) initiated by ethyl 2-bromoisobutyrate and catalyzed by CuBr/2,2'-bipyridine complex. This polymerization proceeds in a living fashion with controlled molecular weight and low polydispersity. The obtained copolymer was esterified with 2-bromoisobutyl bromide yielding a macroinitiator, poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate-*co*-2-(2-bromoisobutyryloxy)ethyl methacrylate), and its structure was characterized by ¹H-NMR. This macroinitiator was used for ATRP of styrene to synthesize poly(methyl methacrylate)-*graft*-polystyrene. The molecular weight of graft copolymer increased with the monomer conversion, and the polydispersity remained relatively low. The individual grafted polystyrene chains were cleaved from the macroinitiator backbone by hydrolysis and the hydrolyzed product was characterized by ¹H-NMR and GPC.

Key words Atom transfer radical polymerization, Graft copolymer, Styrene, Methyl methacrylate

INTRODUCTION

Graft copolymers exhibit interesting solution, mechanical, and morphological properties due to their biphasic nature and architecture. They can be used as thermoplastic elastomers and compatibilizers of polymer blends. Atom transfer radical polymerization (ATRP) has been used to prepare many graft copolymers using the macroinitiator technique. The macroinitiator could be prepared in different ways. The first method is the copolymerization of backbone monomer with a functional monomer. For example, Hawker *et al.*^[1] prepared a macroinitiator for ATRP by nitroxide-mediated free radical copolymerization of styrene with chloromethylstyrene, and Matyjaszewski *et al.*^[2] prepared a macroinitiator by conventional free radical copolymerization of vinyl chloride with vinyl chloroacetate. The second method is the chemical modification of backbone polymer. For example, Sen *et al.*^[3, 4] prepared macroinitiators by partial bromination of syndiotactic polystyrene or poly(ethylene-*co*-styrene) at benzylic positions using *N*-bromosuccinimide, Jiang *et al.*^[5] reported the preparation of macroinitiator from a commercial diblock product of poly(styrene-*b*-ethylene-*co*-propylene) by chloromethylation of polystyrene block, and Ying *et al.*^[6] reported the preparation of macroinitiator chloromethylated phenoxy poly(propylene glycol) by ring-opening polymerization of propylene oxide and glycidyl phenyl ether followed by chloromethylation.

Recently, Matyjaszewski *et al.*^[7] prepared trimethylsilyl-protected 2-hydroxyethyl methacrylate (TMS-HEMA) via ATRP and subsequently esterified the obtained polymer with 2-bromoisobutyl bromide in the presence of a catalytic amount of tetrabutylammonium fluoride, resulting in a new macroinitiator, poly(2-(2-bromoisobutyryloxy)ethyl methacrylate), with controlled molecular weight and low polydispersity. This

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macroinitiator was used for ATRP of styrene or butyl acrylate, yielding densely grafted copolymers. Brittain *et al.*^[8] also prepared graft copolymers using the same procedure but the homopolymerization of TMS-HEMA was replaced by copolymerization of TMS-HEMA with methyl methacrylate (MMA). In this paper, a more common monomer, 2-hydroxyethyl methacrylate (HEMA), which was not protected, was directly copolymerized with MMA via ATRP. Thus obtained copolymer was then esterified with 2-bromoisobutyryl bromide, yielding a macroinitiator. This macroinitiator was used for ATRP of styrene to synthesize poly(methyl methacrylate)-*graft*-polystyrene.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA) was purified according to a published procedure^[9]. Its solution in water (20% by volume) was first extracted with hexane for 5 times to remove dimethacrylate. The aqueous solution was then salted (250 g/L NaCl) and the monomer was separated from the aqueous phase by extraction with ether 4 times to remove methacrylic acid. Hydroquinone and anhydrous MgSO_4 were added to the ether solution. After the ether was removed under reduced pressure using a rotary evaporator, the monomer was stored at -15°C in a freezer. It was distilled under reduced pressure immediately prior to use. Styrene and methyl methacrylate were dried over anhydrous MgSO_4 , then distilled under reduced pressure and stored at -15°C . All solvents were dried over anhydrous MgSO_4 . CuBr (Shanghai No. 1 Chemical Regent Factory), CuBr_2 (Beijing Chemical Factory), 2,2'-bipyridine (bipy) (Beijing Shiyang Chemical Factory), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) (Aldrich), ethyl 2-bromoisobutyrate (Aldrich), and 2-bromoisobutyryl bromide (Aldrich) were used without any further purification.

Copolymerization

The ATRP copolymerization of MMA and HEMA was carried out in solution. In a typical example, 0.79 g (5.5 mmol) of CuBr and 1.72 g (11.0 mmol) of bipy were added to a 250 mL dry round-bottomed flask equipped with a magnetic stirrer. After the flask was sealed with a rubber septum, it was degassed and purged with argon three times and then kept under argon. A mixture of 2.15 g (11.0 mmol) ethyl 2-bromoisobutyrate, 70.6 g (705 mmol) deoxygenated MMA, 39.4 g (302 mmol) HEMA and 80 mL toluene were added via a syringe that had been purged with argon. After the mixture had been stirred at ambient temperature for 5 min, the flask was placed in an oil bath kept at 90°C . After 6 h, the mixture was diluted with THF, and the solution was filtered through a column of alumina to remove the catalyst. The copolymer was precipitated into a large amount of cold dimethyl ether and dried under vacuum.

Preparation of Macroinitiator

In a 500 mL round-bottomed flask filled with dry argon, 36.0 g (156.5 mmol) 2-bromoisobutyryl bromide diluted with 50 mL CH_2Cl_2 was added dropwise to a solution containing 42.3 g of the above copolymer and 15 g (187.0 mmol) pyridine and 200 mL CH_2Cl_2 at $0-10^\circ\text{C}$. After the reaction mixture was stirred overnight at room temperature, the macroinitiator was precipitated from a large amount of cold methanol and dried under vacuum.

Grafting Polymerization

The typical procedure was as follows: 4.3 g macroinitiator, 0.533 g (3.7 mmol) CuBr and 0.91 g (5.25 mmol) PMDETA were added to a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer. After the flask was sealed with a rubber septum, it was degassed and purged with argon three times and then left under argon. 70 g Deoxygenated styrene was added to dissolve the macroinitiator. After the macroinitiator had dissolved, the flask was immersed in an oil bath thermostated at 110°C . At definite time intervals, portions of the sample were withdrawn from the flask using degassed syringes to determine monomer conversion and molecular weight.

Hydrolysis of Graft Copolymer

The graft copolymer was dissolved in THF in a flask. Then, a small amount of KOH (ethanol solution) was

added. The solution was refluxed 3 days. The solution was concentrated by rotating evaporation of THF. Then, the polymer was precipitated from pure methanol and dried under vacuum.

Characterization

Monomer conversion was obtained gravimetrically. Apparent molecular weights and molecular weight distributions of macroinitiator and graft copolymers were measured by gel permeation chromatography (GPC) using a Waters 515 pump, three columns (Styragel HR1, Styragel HR3 and Styragel HT4) and a 410 differential refractometer detector. The eluent was THF and the flow rate was 1 mL/min. Narrow MW polystyrene standards were used to generate the calibration curve. $^1\text{H-NMR}$ spectra were obtained using a Bruker AC400 NMR spectrometer. CDCl_3 was used as a solvent.

RESULTS AND DISCUSSION

Copolymerization of MMA and HEMA by ATRP

The results of solution copolymerization of MMA and HEMA by ATRP are shown in Fig. 1. The number average molecular weight (M_n) of the copolymers increased linearly with conversion and their polydispersity was relatively low throughout the polymerization process. However, a discrepancy between the values of $M_{n, \text{th}}$ and $M_{n, \text{gpc}}$ is observed. This may be attributed to the analysis of GPC data using calibrations made with polystyrene standards.

The copolymer composition was analyzed with $^1\text{H-NMR}$. Figure 2 shows a typical $^1\text{H-NMR}$ spectrum of the copolymer. The signal at $\delta = 3.6$ corresponds to the methyl ester protons of MMA, and the peaks at $\delta = 3.8$ and 4.1 are assigned to methylene protons of the hydroxyethyl group of HEMA. By using the area ratio of the peaks $((b + c)/4 : a/3)$, the copolymer's composition can be calculated. For a copolymer with $M_n = 6680$, the ratio of MMA to HEMA was 10:6. This copolymer was used for the preparation of macroinitiator.

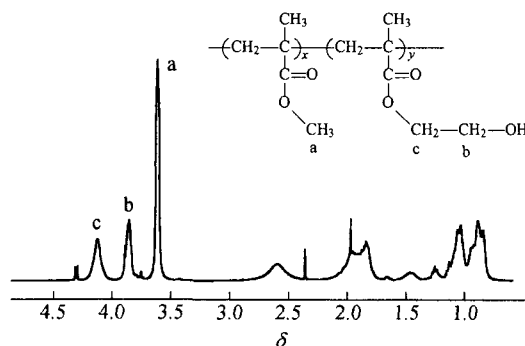
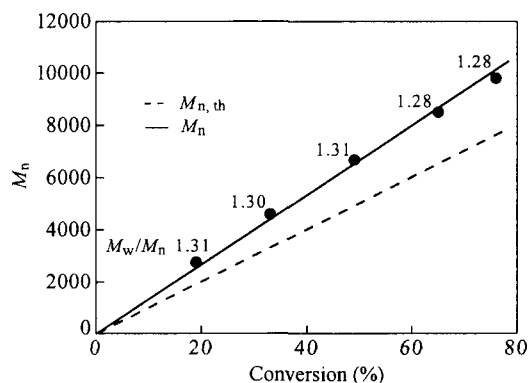


Fig. 1 A plot of molecular weight versus conversion for ATRP solution copolymerization of MMA and HEMA in toluene initiated with ethyl 2-bromoisobutyrate and catalyzed with CuBr/bipy

$[\text{I}]_0 : [\text{CuBr}]_0 : [\text{bipy}]_0 : [\text{M}]_0 = 1 : 1 : 2 : 100$ at 90°C ;
 $[\text{MMA}]_0 : [\text{HEMA}]_0 = 7 : 3$ and volume ratio of monomer to solvent = 1/0.75;

Fig. 2 $^1\text{H-NMR}$ spectrum of a random copolymer of MMA and HEMA

M_n of this copolymer determined by GPC was 6680

Preparation of Macroinitiator

The macroinitiator was synthesized by reacting 2-bromoisobutyryl bromide with the above copolymer in the presence of pyridine. After "bromination", the M_n of the macroinitiator increased from 6680 to 8570, while the polydispersity remained constant. Bromine content in the macroinitiator determined by combustion method was 12.64%. This result indicates that there are about 13.7 initiating sites along the macroinitiator chain. The number of initiating site was also calculated from $^1\text{H-NMR}$ spectrum of the macroinitiator. The signals at $\delta = 3.8$ and 4.1

corresponding to methylene protons of $-\text{CH}_2\text{CH}_2\text{OH}$ in HEMA become weaker and two new peaks at $\delta = 4.2$ and 4.4 appear, which are assigned to two different kinds of methylene protons of $-\text{COOCH}_2\text{CH}_2-\text{OOC}(\text{CH}_3)_2\text{Br}$ (Fig. 3). A similar result was obtained to that determined by the combustion method.

Graft Copolymerization

The grafting polymerization of styrene by ATRP was first carried out at 110°C in bulk using CuBr/PMDTA complex as a catalyst. The dependence of MW and polydispersity on comonomer conversion is illustrated in Fig. 4. It is obvious that the apparent M_n of graft copolymer determined by GPC increased linearly with comonomer conversion at lower comonomer conversion. However, as comonomer conversion increases, the MWs deviate from the line. A closer look at the entire MWD development throughout the grafting polymerization reveals that higher molecular weight species are formed continuously during the reaction (Fig. 5). This shows that bimolecular coupling termination between two graft copolymers occurs to a nonnegligible extent. Although bimolecular coupling termination between two growing living chains also exists in ATRP initiated by a monofunctional initiator, the MWD is unimodal throughout the reaction. But in this experiment, an intermolecular coupling between two graft copolymers will give a polymer with about 26 grafts resulting in a shoulder peak on the higher side of the GPC trace. In work on the synthesis of densely grafted copolymers and star-shaped polystyrene with eight arms by ATRP, the same phenomena were also observed^[10]. As is well known, the apparent MWs of comb-graft and star-shaped polymers measured by GPC should be lower than their real MWs due to their smaller hydrodynamic volumes. However, in this experiment, the apparent MWs at higher monomer conversions were larger than their theoretical values. This further verifies that bimolecular coupling termination between two graft copolymers indeed occurred.

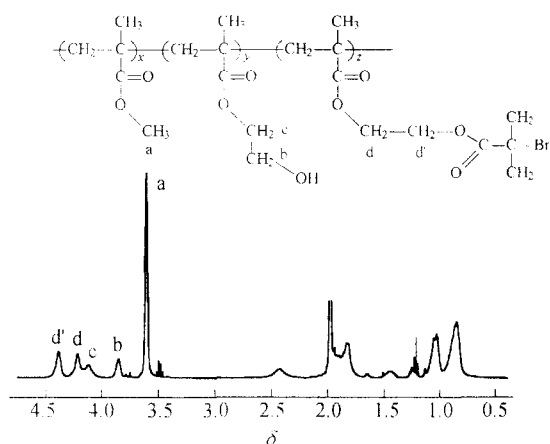


Fig. 3 ^1H -NMR spectrum of the macroinitiator M_n of this copolymer determined by GPC was 8570

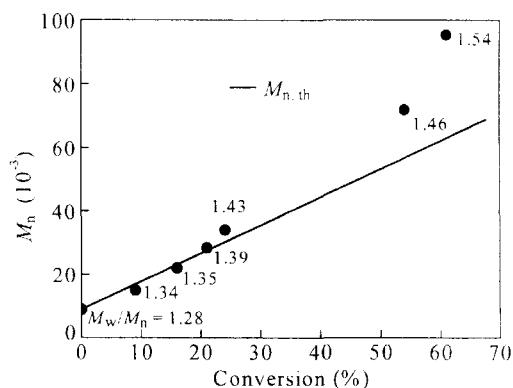


Fig. 4 Conversion dependence of apparent molecular weights for grafting polymerization
Conditions: Macroinitiator = 4.3 g (M_n of the macroinitiator was 8570 and there were 13.7 initiating sites per macroinitiator), CuBr = 3.7 mmol, PMDTA = 5.25 mmol, styrene = 70 g, and reaction temperature was 110°C

Characterization of Graft Copolymer

To determine the degree of control of the free radical grafting process by ATRP, the individual grafted polystyrene chains were cleaved from the poly(methyl methacrylate) backbones by hydrolysis. For example, a graft copolymer obtained above (the monomer conversion was 61%) was hydrolyzed using KOH in a mixture of THF and ethanol. The polystyrene graft chain was recovered by precipitation in a large excess of methanol. ^1H -NMR analysis of the isolated polymers showed the disappearance of the resonances due to the backbone, and there were only the peaks due to hydrolyzed polystyrene graft (Fig. 6).

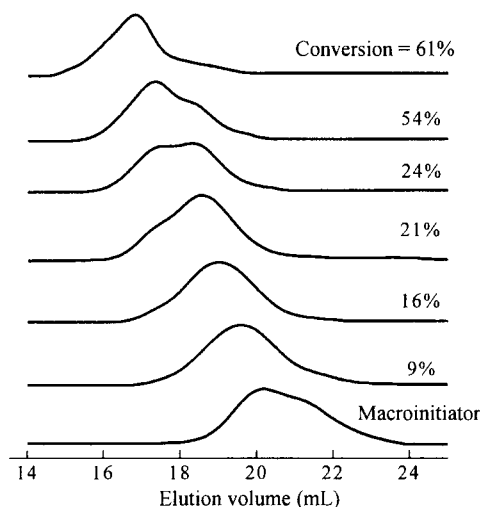


Fig. 5 GPC traces of the graft copolymers obtained at different monomer conversions
See Fig. 1 for conditions

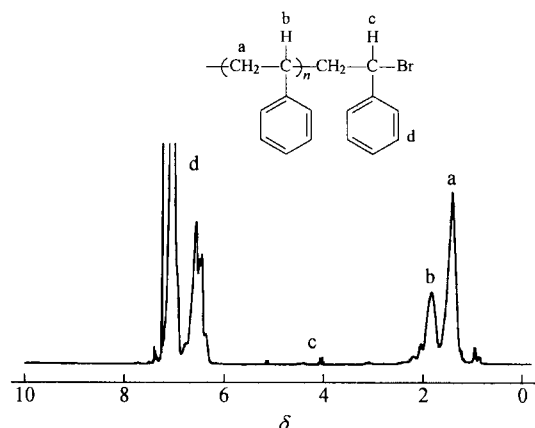


Fig. 6 ^1H -NMR spectrum of hydrolyzed polystyrene graft

The MW of polystyrene graft was determined by ^1H -NMR ($M_n = 8070$) and compared with that determined by GPC ($M_n = 6870$; polydispersity index = 1.11). These two values are rather close to the theoretical value of 6200 based on the assumption that one initiating site along the backbone generates one polymer graft chain. This demonstrates that the synthesized graft copolymer exhibits the expected structure.

CONCLUSIONS

Preparation of poly(methyl methacrylate)-*graft*-polystyrene by ATRP has been demonstrated by using the macroinitiator method. The macroinitiator was synthesized by esterifying poly(MMA-*co*-HEMA) with 2-bromoisobutyryl bromide, which was obtained by ATRP copolymerization of MMA and HEMA in a living fashion. Well-defined graft copolymer could be synthesized by maintaining a lower monomer conversion in the grafting reaction. GPC traces of the graft copolymers exhibit a bimodal distribution, indicating the occurrence of intermolecular coupling termination to a nonnegligible extent at higher monomer conversion.

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