Chinese Chemical Letters Vol. 14, No. 12, pp 1289 – 1292, 2003
http://www.imm.ac.cn/journal/ccl.html

Synthesis of Comblike Poly(methyl methacrylate) by Atom Transfer Radical Polymerization with Poly(ethyl 2-bromoacrylate) as Macroinitiator

Yan SHI[1], Zhi Feng FU[1,*], Yu Dong ZHANG[2], Shu Ke JIAO[1]

[1]Key Laboratory of Controlled Chemical Reactions, and Department of Polymer Engineering,
Beijing University of Chemical Technology, Beijing 100029
[2]Polyolefin National Engineering Research Center, Beijing Research Institute of Chemical Industry,
Beijing 100013

Abstract: Comblike poly(methyl methacrylate) was synthesized by atom transfer radical polymerization of methyl methacrylate with poly(ethyl 2-bromoacrylate) as a macroinitiator, which was prepared by conventional free radical polymerization of ethyl 2-bromoacrylate. The obtained comblike polymers were characterized by GPC and ^{1}H NMR.

Keywords: Comblike polymer, atom transfer radical polymerization (ATRP), macroinitiator, poly(methyl methacrylate), ethyl 2-bromoacrylate.

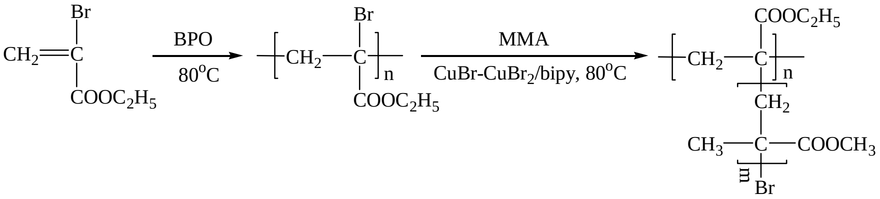
The synthesis of comblike or densely grafted macromolecules has been an area of intensive research over the past decade. Three synthetic routes to comblike macromolecules have been described in the literature: (1) “grafting onto” (attachment of living polymer chains onto reactive polymer backbones)[1-3], (2) “grafting through” (homopolymerization of macromonomers)[4,5], and (3) “grafting from” (polymerization of side chain monomers from the initiating sites on the backbones)[6]. However, all these methods involve ionic polymerization which need rigorous reaction conditions. Atom transfer radical polymerization (ATRP) developed by Wang and Matyjaszewski[7] has many advantages over ionic polymerization, such as suitable for a large variety of monomers and less stringent reaction conditions. This living free radical polymerization method has been used to make well-defined comblike polymers using “grafting from” macroinitiators[8-10]. The macroinitiators bearing ATRP initiating groups as side groups in each repeating unit could be obtained by conventional free radical homopolymerization of 2-(2-bromopropionyloxy)ethyl acrylate using azobisisobutyronitrile (AIBN) as an initiator, or by ATRP of trimethylsilyl-protected 2-hydroxyethyl methacrylate, followed by esterification with 2-bromoisobutyryl bromide to yield poly(2-(2-bromoisobutyryloxy)ethyl methacrylate).

In this work, we used a much more easily obtained monomer, ethyl 2-bromoacrylate (EBA), to prepare the ATRP macroinitiator for comblike polymer

---

[*] E-mail: fuzf@mail.buct.edu.cn

Scheme 1 Synthesis of the macroinitiator and comblike PMMA



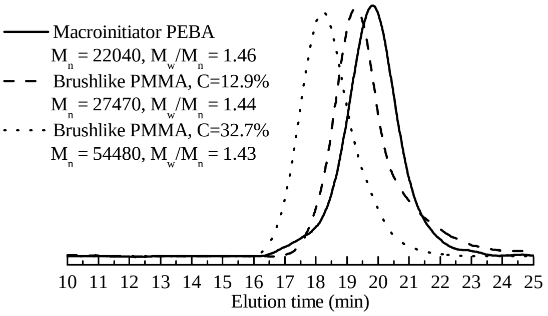
synthesis without any transformation process (**Scheme 1**).

EBA was prepared according to the literatural method[11]. Its polymerization was carried out through conventional free radical polymerization using benzoyl peroxide (BPO) as the initiator at 80°C in dioxane (EBA, 6.50 g; BPO, 0.14 g; dioxane, 8.0 mL.). After polymerization for 1 hr, the reaction mixture was poured into a large excess of cold methanol, and 4.5 g of white powdered poly(ethyl 2-bromoacrylate) (PEBA) was obtained. The average molecular weight (M_n) and polydispersity index determined by GPC calibrated with narrow distributed linear polystyrene standards were 22040 and 1.46, respectively.

The chemical environment of the bromide atoms on PEBA chain is the same as that in alkyl 2-bromoisobutyrate, which is a well-known effective initiator for ATRP of methyl methacrylate (MMA)[12]. Therefore, ATRP of MMA with PEBA as the macroinitiator is expected to generate comblike polymer. The ATRP of MMA was carried out in toluene (volume ratio of MMA to toluene was 1:1) at 80 °C with CuBr/ 2,2-bipyridine (bipy) as the catalyst, and a small amount of $CuBr_2$ was added in order to prevent the coupling reactions between different macromolecules. **Figure 1** shows the resulting GPC traces of comblike polymers obtained at different monomer conversions. It can be seen that as monomer increased, the molecular weight distributions of the obtained polymers were unimodal and shifted to higher molecular weights without contamination of the unreacted macroinitiator.

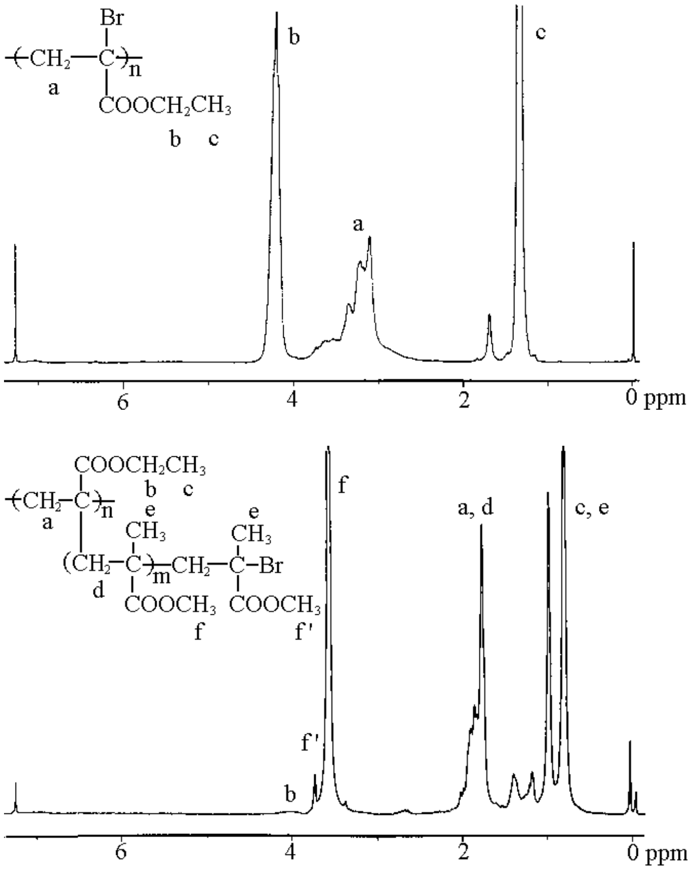
Unfortunately, no poly(methyl methacrylate) (PMMA) graft could be isolated from the PEBA backbone for characterization and determination of the functionality of the final polymer brush. ^{1}H NMR spectrum of comblike PMMA is shown in **Figure 2**. For comparison, the ^{1}H NMR spectrum of the macroinitiator PEBA is also shown. It can be found that in the ^{1}H NMR spectrum of comblike PMMA the proton at 3.1-3.5 ppm (H_a) of PEBA had completely disappeared and shifted to higher fields (1.8-2.0 ppm), whereas correspondingly, new signal at 3.7 ppm for methyl ester proton of MMA (H_f) was observed. Furthermore, the small signal (f') on the shoulder of the methyl ester proton (f) was due to the terminal methyl ester proton adjacent to the bromide atom at ω-end. The M_n of every PMMA graft chain obtained from the peak intensity ratio f/f' was 3200, which was in close agreement with the M_n (2980) calculated from the monomer over bromide atom molar ratio and monomer conversion. This shows that nearly all initiating sites along the PEBA backbone initiated ATRP of MMA and that well-defined comblike PMMA was generated.

Figure 1 GPC traces of the macroinitiator and comblike polymers obtained at different monomer conversions[a] (Molecular weights were calibrated *vs* linear polystyrene standards)



[a] Reaction conditions: [M]:[I]:[CuBr]:[$CuBr_2$]:[bipy] = 600:1:1:0.1:2.2. [I] was defined as the molar amount of bromide atom in the macroinitiator (mass of macroinitiator/molecular weight of EBA).

Figure 2 ^{1}H NMR spectra of macroinitiator PEBA (upper) and comblike PMMA (bottom)



Acknowledgments

Y. Shi thanks Beijing University of Chemical Technology for partial financial support to this work.

References

1. S. W. Ryu, A. Hirao, *Macromolecules*, **2000**, *33* (13), 4765.
2. S. W. Ryu, H. Asada, A. Hirao, *Macromolecules*, **2002**, *35* (19), 7191.
3. T. Tsoukatos, S. Pispas, N. Hadjichristidis, *Macromolecules*, **2000**, *33* (26), 9504.
4. Y. Tsukahara, S. Namba, J. Iwasa, *et al.*, *Macromolecules*, **2001**, *34* (8), 2624.
5. Y. Tsukahara, K. Tsutsumi, Y. Yamashita, S. Shimada, *Macromolecules*, **1990**, *23* (25), 5201.
6. P. Jannasch, *Macromolecules*, **2000**, *33* (23), 8604.
7. J. S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.*, **1995**, *117* (20), 5614.
8. K. L. Beers, S. G. Gaynor, K. Matyjaszewski, *Macromolecules*, **1998**, *31* (26), 9413.
9. H. G. Borner, K. L. Beers, K. Matyjaszewski, *Macromolecules*, **2001**, *34* (13), 4375.
10. G. Cheng, A. Boker, M. Zhang, G. Krausch, A. Müller, *Macromolecules*, **2001**, *34* (20), 6883.
11. C. E. Barnes, N. J. Belvidere, USP 2476528, **1949**.
12. K. Matyjaszewski, J. Xia, *Chem. Rev.*, **2001**, *101* (9), 2921.

Received 3 December, 2002