Preparation of a Copolymer of Methyl Methacrylate with a New Monomer, 2,2,6,6-Tetramethyl-4-benzyloxyl-piperidinyl Methacrylate, and Its Initiation of the Graft Copolymerization of Styrene with a Controlled Radical Mechanism

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ABSTRACT: A copolymer [P(MMA-co-TBPM)] was prepared by the radical polymerization of methyl methacrylate (MMA) and 2,2,6,6-tetramethyl-4-benzyloxyl-piperidinyl methacrylate (TBPM) with azobisisobutyronitrile as an initiator. TBPM was a new monomer containing an activated ester. Both the copolymer and TBPM were characterized with NMR, IR, and gel permeation chromatography in detail. It was confirmed that P(MMA-co-TBPM) could initiate the graft polymerization of styrene by the cleavage of the activated ester of the TBPM segment. This process was controllable, and the molecular weight of the graft chain of polystyrene increased with the increment of conversion. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 4398–4403, 2002

Keywords: copolymerization; graft copolymers; nitrooxide free radical; radical polymerization; controllability

INTRODUCTION

Recent progress in the field of grafted (or brush) copolymers has led to a need to develop efficient methods for synthesizing a wider variety of materials with the same basic architectural design. In the past few years, a variety of brushlike macromolecules have been prepared with the macromonomer method.1–6

Georges et al.7 first reported the controlled radical polymerization of styrene (St) by stable free-radical polymerization. The mechanism involves the reversible capping of the growing chain by a counter stable free radical such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Recently, various methods have been used to introduce TEMPO onto the chains of (co)polymers, and TEMPO adducts have been widely used to promote the controlled radical graft polymerization of St.8–10 According to the traditional method, the polymer or copolymer is first prepared, and then TEMPO is introduced to it.11 With this method, it is obvious that the amount and site of the activated species are very difficult to control.

The approach described here involves grafting from a copolymer synthesized by the copolymerization of methyl methacrylate (MMA) with a newly developed activated ester monomer, 2,2,6,6-tetramethyl-4-benzyloxyl-piperidinyl methacrylate (TBPM), with the copolymer used as a macronitiator. In comparison with traditional methods, the amount of TEMPO introduced into the backbone of the macronitiator was...
easier to control, and the polymerization was more efficient.

**EXPERIMENTAL**

**Materials**

4-Hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTEMPO) was prepared by the oxidation of 4-hydroxy-2,2,6,6-tetramethylpiperidine (Beijing Chaoyang Huashan Auxiliary Factory) with hydrogen peroxide, with sodium tungstate as a catalyst (mp = 71–72 °C). Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. All other reagents were purified by standard methods.

**Preparation of 4-Benzylxoxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (BTEMPO)**

The synthesis of BTEMPO is outlined in Scheme 1. HTEMPO (19.5 g, 0.113 mol), 25.4 g (0.149 mol) of benzyl bromide, 16.7 g (0.298 mol) of powdered KOH, and 5.5 g of poly(ethylene glycol) (molecular weight = 600) was added to 70 mL of benzene. The mixture was stirred violently for 5 h at 40 °C, and then the mineral was filtered. The oil layer was washed with water several times until the water was colorless, then it was dried with CaCl₂ overnight. Rude BTEMPO was obtained after benzene and excess benzyl bromide were distilled under reduced pressure. It was purified by recrystallization in hexane for a yield of 74.8%.

IR (cm⁻¹): 1597, 1497, 1463, 746, 696 (benzene ring). UV (nm): 230 (benzene ring), 450 (NO₂). mp: 63–64 °C.

**Preparation of TBPM**

BTEMPO (5.0 g, 0.02 mol) and 2.0 g of ascorbic acid were added to 40 mL of distilled water. The mixture was stirred for 8 h until the orange-red color vanished at 25 °C. Ether was used to extract the solution three times; it was combined with the organic layers, dried with MgSO₄, and filtered for the removal of the solid. Methacryloyl chloride (2.5 mL, 0.025 mol) was added dropwise to the ether solution mixed with 2.4 mL (0.02 mol) of triethylamine in an ice bath. The mixture was stirred for 4 h, washed with distilled water, and dried with CaCl₂. The solid was filtered, and the solvent was removed by distillation in vacuo. The residue crystallized from methanol to yield 3.7 g (55% yield).

NMR (δ): 7.22 (m, 5H, phenyl), 6.05 (s, 1H, CH₃=C), 5.50 (s, 1H, CH₂=C), 4.47 (s, 2H, =CH₂—O—), 3.67 (m, 1H, piperidinyl), 1.92 (s, 3H, CH₃—C=C), 1.88 (d, 2H, piperidinyl), 1.69 (t, 2H, piperidinyl), 1.18 (s, 3H, piperidinyl), 1.03 (s, 3H, piperidinyl). IR (cm⁻¹): 1746 (C=O), 1637 (C=C), 1603, 1503, 740, 698 (benzene ring). mp: 73–75 °C.

**Preparation of the Macroinitiator [P(MMA-co-TBPM)]**

To a 100-mL ampule, accurately weighed MMA, TBPM, and AIBN in a definite molar ratio were charged; the ampule was degassed by three freeze–pump–thaw cycles at 77 K and then sealed under very pure N₂ (99.99%). The ampule was placed in an oil bath at 60 ± 0.1 °C for a period of time. The copolymerized product was diluted with CHCl₃, precipitated with petroleum ether (bp = 30–60 °C), purified twice by the procedures of dissolution and precipitation with CHCl₃/petroleum ether, and then dried to a constant weight at 60 °C.

**Graft Copolymerization of St by the Initiation of P(MMA-co-TBPM)**

The preparation of the grafter copolymer can be described as follows. A charged molar ratio of St and P(MMA-co-TBPM) was placed in an ampule. The ampule was degassed by three freeze–pump–thaw cycles at 77 K and then sealed under very pure N₂ (99.99%). The ampule was placed in an oil bath at 125 ± 0.1 °C for a period of time. The graft copolymers were diluted with CHCl₃, precipitated with petroleum ether (bp = 30–60 °C). The copolymer was purified twice by the procedures of dissolution and precipitation with CHCl₃/petroleum ether, extracted with ethanol (95%) for 48 h for the removal of the small molecules, and then dried to a constant weight at 60 °C.

**Cleavage of the Grafted Polystyrene (PS) Chain**

In a 10-mL flask, LiAlH₄ (0.38 g, 10.0 mmol) in 2.4 mL of tetrahydrofuran (THF) and the graft copolymer (100 mg) in 3.6 mL of THF were introduced and then refluxed for 3 h with stirring. To the solution, 2.0 mL of ethyl acetate and distilled
water were slowly added, respectively. The broken PS chain was extracted by cyclohexane several times (10 mL × 6), and the combined extracted solutions were concentrated to about 1/3 of the original volume and then precipitated with petroleum ether (30–60 °C). The precipitant was purified by dissociation and precipitation with chloroform/petroleum ether.

**RESULTS AND DISCUSSION**

**Copolymerization of MMA with TBPM and Characterization of the Macroinitiator P(MMA-co-TBPM)**

The copolymerization of MMA and TBPM was performed with a common radical mechanism. In NMR spectra (Fig. 1) of the monomer (TBPM) and copolymer, the double bonds of TBPM at 6.05 and 5.50 ppm disappeared, and that at 4.5 ppm for protons of methylene of the benzyloxy group remained. Furthermore, protons for —COOCH₃ of MMA at 3.6 ppm were observed. In IR spectra of the copolymer, we also found that the absorption of the double bonds around 1637 cm⁻¹ for TBPM and around 1640 cm⁻¹ for MMA disappeared. All
this information confirmed that the copolymerization was conducted successfully.

The composition ratio of MMA and TBPM in the copolymer was calculated with following equation by means of NMR:

\[ r = \frac{[\text{TBPM}]}{[\text{MMA}] + [\text{TBPM}]} = \frac{A/2}{B/3 + A/2} \]

where \( r \) is the fraction of TBPM units in the copolymer, \( A \) is the peak area of the protons of methylene of the benzyloxy group at 4.5 ppm, and \( B \) is the peak area of methyl protons (-COOCH₃) of the MMA segment at 3.6 ppm. The contents of TBPM in the macroinitiator P(MMA-co-TBPM), shown in Table 1, increased with the increment of TBPM in the feed ratio of the monomers.

**Graft Copolymerization of St by the Initiation of P(MMA-co-TBPM)**

Tables 2 and 3 show the data for the graft copolymerization initiated by P(MMA-co-TBPM). The molecular weight of P(MMA-co-TBPM)-g-PS increased with the polymerization time and with the conversion of St.

The purified graft copolymers were characterized in detail with GPC and \(^1\)H NMR. In the GPC diagram, only a peak attributed to the graft copolymer was observed, and no trace of the macroinitiator P(MMA-co-TBPM) was left. In \(^1\)H NMR, the protons of the benzene ring at 6.5–7.3 ppm, attributed to the PS graft chain, appeared next to the chemical shifts of protons of P(MMA-co-TBPM), as illustrated in Figure 1.

So that the controllability of the graft copolymerization initiated by TBPM segments in P(MMA-co-TBPM) could be investigated, PS graft chains were broken from the grafter copolymer with LiAlH₄ as a reductant. It was confirmed by GPC that the molecular weight of the PS graft chain was proportional to the conversion and that the molecular weight distribution was rather narrower; in all cases, its values were within 1.21–1.5, even for a molecular weight as high as 230,000. Therefore, it can surely be said that the graft copolymerization of St initiated by P(MMA-co-TBPM) was controllable.
Effect of the Concentration of the P(MMA-co-TBPM) and TBPM Contents in P(MMA-co-TBPM) on the Graft Copolymerization of St

The concentration of the P(MMA-co-TBPM) and TBPM contents in P(MMA-co-TBPM) exerted a great influence on the graft copolymerization of St, as shown in Tables 2 and 3. For example, when the concentration of P(MMA-co-TBPM) increased from 7.5 \times 10^{-4} to 15 \times 10^{-4} mol/L, after 5 h, the molecular weight of the PS grafted chain and the monomer conversion dropped from 15.7 \times 10^4 and 18.7\% to 7.5 \times 10^4 and 14.8\%, respectively (Table 2). We also found that under similar polymerization conditions and conversions, the molecular weight of the graft copolymer and PS grafted chain decreased with the increment of TBPM in P(MMA-co-TBPM) (Table 3). In general, in common radical polymerizations, when the reaction conditions (e.g., the monomer concentration and polymerization temperature) are constant, the conversion of the monomer decreases with the decreasing initiator concentration, whereas the molecular weight of the polymer increases. However, in our system, the conversion of St and the molecular weight of the grafter and PS grafted chain increased simultaneously with the decreases in the concentration of P(MMA-co-TBPM) and in the content of TBPM in P(MMA-co-TBPM). For a low P(MMA-co-TBPM) concentration and low TBPM contents, the dormant amount from coupling of the propagating PS species with BTEMPO \cdot formed by decomposition of the TBPM segment in the copolymer was very low, so the concentration of propagating radical species was high, and the polymerization rate, molecular weight, and conversion were also higher, but the molecular weight distribution was broader. When a high P(MMA-co-TBPM) concentration and high contents of TBPM in P(MMA-co-TBPM) were used, the concentration of BTEMPO \cdot radicals was also higher, and the dormant amount from coupling of propagating PS species with BTEMPO \cdot was increased; the polymerization of St was strictly controlled because of the low concentration of propagating radicals, which led to the decrease in the molecular weight and conversion of St.

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REFERENCES AND NOTES