# Block Copolymerization of Methyl Methacrylate from Fluorine-contained Polyimide Macroinitiator by Atom-transfer Radical Polymerization

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The linear fluorine-contained polyimide macroinitiator capped with the chloromethylphenyl group at both polymer ends was synthesized and reacted with methyl methacrylate (MMA) to form an ABA-type triblock copolymer (MMA-*b*-PI-*b*-MMA) by atom-transfer radical polymerization (ATRP). The poly(methyl methacrylate) (PMMA) homopolymer was decomposed completely at ca. 400 °C, whereas the polyimide macroinitiator was thermally stable up to ca. 500 °C The MMA component in MMA-*b*-PI-*b*-MMA was selectively decomposed up to ca. 400 °C, while the polyimide component remained.

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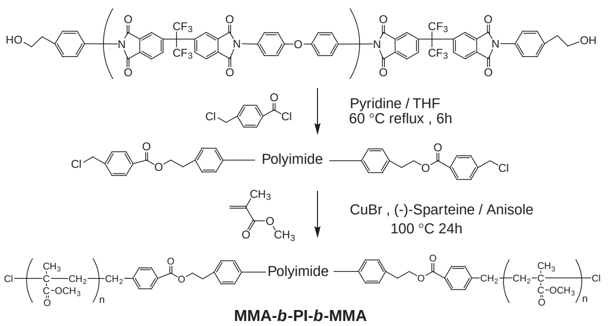
The polyimide has higher thermal and chemical resistance properties as compared to other polymers. Because polyimides synthesized from 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) show higher solubility and processibility, they are widely applied in the electronics, optics, and aerospace industries.[1] Block or graft copolymerization of polymers is one of the important methods for modifying or improving polymer properties. For example, polyimide/nylon 6-block and graft copolymers display a higher tensile strength than pure nylon 6.[2] Moreover, the micro-phase-separated block copolymers composed of a thermally stable polyimide and a thermally labile polymer are used to produce porous polyimides through the decomposition of the latter polymer. The introduction of pores into polyimides is an effective way of lowering their dielectric constant. Therefore, these porous polyimides are expected to be applied as interlayer insulation membranes of large scale integration (LSI).[3] In this article, we synthesized the linear fluorine-contained polyimide having chloromethylphenyl groups as a macroinitiator for atom-transfer radical polymerization (ATRP), and attempted to react it with MMA (i.e., thermally labile polymer unit for thermal decomposition) as a new approach to forming a triblock polyimide.

As described in Scheme 1, the linear polyimide macro-initiator having chloromethyl groups was prepared from fluorine-contained polyimide with two terminal OH groups (PI–OH).[4] The PI–OH and pyridine were dissolved in tetrahydrofuran (THF). An excess amount of 4-chloromethylbenzoyl chloride was added into the solution and was refluxed at 60 °C for 6 h. After filtration, the reaction mixture was poured into a large amount of methanol and was dried under a vacuum at 80 °C overnight. It produced a yellow-white solid of the polyimide macroinitiator (91% yield based on the weight). This macroinitiator was soluble in THF, *N*,*N*-dimethylformamide, methyl ethyl ketone, and acetone, but it exhibited poor solubility in toluene, ethyl acetate, hexane, and methanol. The number-average molecular weight ($M_n$) and the polydispersity ($M_w/M_n$) of the macroinitiator estimated by gel-permeation chromatography (GPC) analysis (polystyrene standards) were 6400 g/mol and 1.49, respectively. The $M_n$ of the macroinitiator was also determined from the number of the polymer end groups by $^{1}$H NMR (DMSO, 500 MHz). Based on the signals at $\delta$ 4.53 (–CH$_2$–O– of polymer ends), 7.24 (aromatic protons of diamine repeating unit) and 7.76 (aromatic protons of 6FDA repeating unit), the $M_n$ of the macroinitiator determined was 5500 g/mol.



**Scheme 1.**

The block copolymerization of MMA created from the polyimide macroinitiator via ATRP was conducted by using CuBr and (−)-sparteine as a ligand[5] in an anisole solution at 100 °C for 24 h.[6] The triblock copolymer (MMA-*b*-PI-*b*-MMA) exhibited good solubility even in the poor solvents for the macroinitiator, such as toluene and ethyl acetate. Figure 1 shows the GPC chromatograms of the polyimide macroinitiator and MMA-*b*-PI-*b*-MMA. The GPC trace of MMA-*b*-PI-*b*-MMA appeared at an earlier time. In addition, its trace was narrow, indicating that no side reactions occurred. The $M_n$ and $M_w/M_n$ of MMA-*b*-PI-*b*-MMA were 16000 g/mol and 1.71, respectively. The $M_n$ of MMA-*b*-PI-*b*-MMA was also determined by $^{1}$H NMR. The degree of polymerization of the MMA block was about 38 ($M_n = 3800$), and the $M_n$ of MMA-*b*-PI-*b*-MMA determined using $^{1}$H NMR was 13000 g/mol.[7] Therefore, the weight ratio of the MMA block and polyimide block in MMA-*b*-PI-*b*-MMA determined using $^{1}$H NMR was 58:42. These

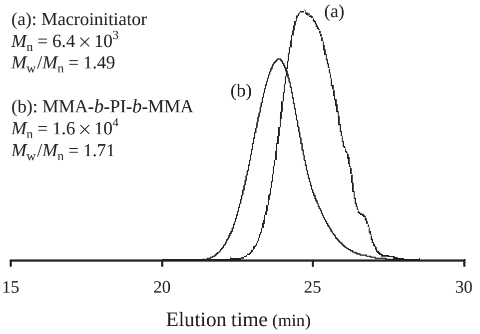


**Figure 1.** GPC curves of (a) the polyimide macroinitiator and (b) MMA-*b*-PI-*b*-MMA.

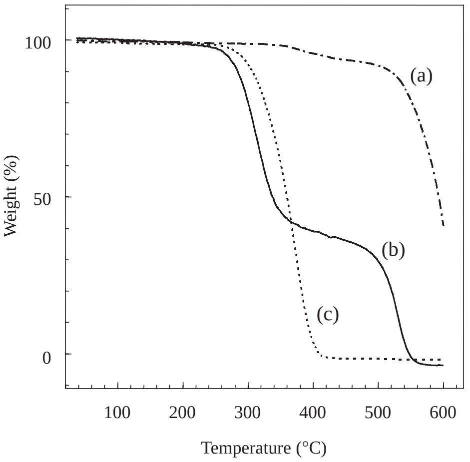


**Figure 2.** TGA curves of (a) the polyimide macroinitiator, (b) MMA-*b*-PI-*b*-MMA, and (c) PMMA homopolymer in air.

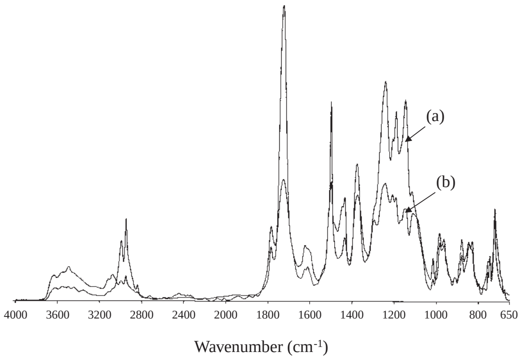


**Figure 3.** IR spectra of MMA-*b*-PI-*b*-MMA (a) before and (b) after thermal treatment at 280 °C for 1 h in air.

molecular weights from GPC and $^1$H NMR measurements were similar to those predicted by the feed molar ratio of MMA monomer to the macroinitiator ($M_n = 17200$ g/mol). This result suggests that the block copolymerization proceeded quantitatively.

The thermal behavior of MMA-*b*-PI-*b*-MMA was examined in air with thermo gravimetric analysis (TGA)[8] and was compared with that of the polyimide macroinitiator and PMMA homopolymer.[9] As presented in Figure 2, the PMMA homopolymer began to decompose at ca. 300 °C and decomposed completely at ca. 400 °C. This decomposition behavior was the same as the literature.[10] On the other hand, the polyimide macroinitiator was thermally stable until ca. 500 °C. As a result, the MMA-*b*-PI-*b*-MMA showed a two-step decomposition. The first step, beginning at ca. 280 °C, and the second step, beginning at ca. 500 °C, were due to the MMA and polyimide blocks, respectively. The weight loss was ca. 60% at 400 °C, decomposition temperature of the PMMA homopolymer. This weight ratio was consistent with that determined using $^1$H NMR.

Figure 3 shows the infrared (IR) spectra of MMA-*b*-PI-*b*-MMA before and after heat treatment at 280 °C for 1 h in air. After heat treatment, the peaks at 2800–3000 cm$^{-1}$, which are characteristic of the $CH_2$ group, disappeared in the spectrum, indicating that the MMA block decomposed.

In conclusion, the use of the fluorine-contained polyimide with chloromethylphenyl groups as the macroinitiator for ATRP was a successful route toward producing the ABA-type triblock polyimide. The thermal decomposition selectively proceeded for the thermally labile MMA block in MMA-*b*-PI-*b*-MMA. Such a block copolymer would be useful in the preparation of porous polyimides which are applied for electric materials.[3]

## References and Notes

1 a) A. K. St. Clair, T. L. St. Clair, *ACS Polym. Mater. Sci. Eng.* **1984**, *51*, 62. b) T. Matsuura, S. Ando, S. Matsui, S. Sasaki, F. Yamamoto, *Electron. Lett.* **1993**, *29*, 2107. c) T. Sawada, S. Ando, S. Sasaki, *Appl. Phys. Lett.* **1999**, *74*, 938. d) S. Matsuda, S. Ando, T. Sawada, *Electron. Lett.* **2001**, *37*, 706.

2 a) H. Ding, F. W. Harris, *Pure Appl. Chem.* **1995**, *87*, 1997. b) Y. Pae, *J. Appl. Polym. Sci.* **2006**, *99*, 300. c) Y. Pae, *J. Appl. Polym. Sci.* **2006**, *99*, 309.

3 a) J. L. Hedrick, T. P. Russell, M. Sanchez, R. Dipietro, S. Swanson, *Macromolecules* **1996**, *29*, 3642. b) J. L. Hedrick, Y. Charlier, R. Dipietro, S. Jayaraman, J. E. Mcgrath, *J. Polym. Sci., Part A* **1996**, *34*, 2867. c) D. W. Kim, S. S. Hwang, S. M. Hong, H. O. Yoo, S. P. Hong, *Polymer* **2001**, *42*, 83.

4 4,4′-Diaminodiphenyl ether (1.13 g, 5.63 mmol) and 4-aminophenethyl alcohol (0.31 g, 2.25 mmol) were dissolved in 15 mL of *N*-methyl-2-pyrrolidinone (NMP), and then 6FDA (3.00 g, 6.75 mmol) was added into the solution. After the reaction mixture was stirred under a nitrogen atmosphere at room temperature for 12 h, 3 mL of *p*-xylene was added into the yellow viscous polyamic acid solution, and it was refluxed for thermal imidization at 180 °C for 6 h. The resulting product was poured slowly into a large amount of methanol to precipitate the polyimide solid. It was then purified by repeating reprecipitation using NMP and methanol, and then was dried overnight at 80 °C in a vacuum oven to obtain the linear fluorine-contained polyimide with two terminal OH groups (PI–OH) (3.48 g, 83% yield based on the weight). The $M_n$ and $M_w/M_n$ of the polyimide were 6000 g/mol and 1.60, respectively.

5 T. Sugizaki, M. Kashio, A. Kimura, S. Yamamoto, O. Moriya, *J. Polym. Sci., Part A* **2004**, *42*, 4212.

6 Distilled MMA (1.07 g, 10.7 mmol) and (−)-sparteine (0.10 g, 0.43 mmol) in anisole (10 mL) were added to a dry 100-mL flask with a magnetic stirrer. After being degassed by three freeze–pump–thaw cycles, the polyimide macroinitiator (0.64 g, 0.10 mmol) and CuBr (0.03 g, 0.21 mmol) were charged. The reaction mixture was stirred under a nitrogen atmosphere at 100 °C for 24 h. The polymerization was terminated by the addition of THF. After which, the resulting solution was poured slowly into a large amount of methanol to precipitate the polymer solid. It was purified by repeating reprecipitation using THF and methanol, and was made to dry overnight at 80 °C in a vacuum oven to obtain MMA-*b*-PI-*b*-MMA (1.34 g, 79% yield based on the weight).

7 In the estimation of contents of the MMA units by $^1$H NMR ($CDCl_3$, 500 MHz), the signals at $\delta$ 3.60 (–O–$CH_3$ of MMA block) and 4.55 (–$CH_2$–O– of polyimide macroinitiator) were used.

8 The TGA of the powder samples (ca. 2 mg) was measured from 40 to 600 °C at a heating range of 10 °C/min in air (100 mL/min).

9 The PMMA homopolymer of standard grade ($M_n$: 11000 g/mol, $M_w/M_n$: 1.04) was purchased from Polymer Laboratories Co., Ltd.

10 T. Kashiwagi, A. Inaba, J. E. Brown, K. Hatada, T. Kitayama, E. Masuda, *Macromolecules* **1986**, *19*, 2160.

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