

# Synthesis and Thermal Properties of Poly(methyl methacrylate)-Poly(L-lactic acid)-Poly(methyl methacrylate) Tri-Block Copolymer

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**ABSTRACT:** Poly(methyl methacrylate)-poly(L-lactic acid)-poly(methyl methacrylate) tri-block copolymer was prepared using atom transfer radical polymerization (ATRP). The structure and properties of the copolymer were analyzed using infrared spectroscopy, gel permeation chromatography, nuclear magnetic resonance (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR), thermogravimetry, and differential scanning calorimetry. The kinetic plot for the ATRP of methyl methacrylate using poly(L-lactic acid) (PLLA) as the initiator shows that the reaction time increases linearly with  $\ln[M]_0/[M]$ . The results indicate that it is possible to

achieve grafted chains with well-defined molecular weights, and block copolymers with narrowed molecular weight distributions. The thermal stability of PLLA is improved by copolymerization. A new wash-extraction method for removing copper from the ATRP has also exhibits satisfactory results. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3905–3911, 2012

**Key words:** poly(methyl methacrylate)-poly(L-lactic acid)-poly(methyl methacrylate); atom transfer radical polymerization; thermal properties; wash-extraction method

## INTRODUCTION

Poly(lactic acid) (PLA) is a kind of aliphatic polyester that is polymerized by lactic acid. PLA is biodegradable, chemically inert, and biocompatible.<sup>1–4</sup> It can be obtained from sustainable biological resources and is innocuous.<sup>5</sup> The performance of PLA can be modulated by copolymerization with other monomers, making it an important biodegradable universal polymer material. PLA can be used as wrapper, fiber, and biomedical materials. However, the low glass transition temperature ( $T_g$ ) of PLA (60°C) limits its applications.<sup>6</sup> Studies<sup>7,8</sup> regarding PLA modifications for specific uses, which attempt at overcoming the drawback of thermal instability have intensified in recent years. Copolymerization is one of the principal methods.

Poly(methyl methacrylate) (PMMA) is an important polymer material because of its chemical stability, mechanical performance, as well as relatively

high thermal decomposition and glass transition temperatures. The processability, weatherability, and electrical insulating properties of PMMA are also remarkable.<sup>9</sup> Some studies have focused on addressing the limitations of PLA by preparing a PLA-PMMA copolymer. Rohman et al.<sup>10</sup> reported a method for preparing PMMA-PLA hydrolysis oligoesters by interpenetrating polymer networks. Johnson et al.<sup>11</sup> reported using the atom transfer radical polymerization (ATRP) method and a bipyridyl ( $\text{CH}_2\text{O-PLA-OC(O)C(CH}_3)_2\text{Br}$ )<sub>2</sub> initiator to prepare a bipyridyl(PLA-PMMA)<sub>2</sub> copolymer.

ATRP has its roots in organic chemistry's atom transfer radical addition.<sup>12</sup> The ATRP method has been proven effective for a wide range of monomers (styrenes, (meth)acrylates, acrylonitrile, etc.) either in bulk or in a variety of solvents (benzene, water, etc.).<sup>13</sup> The ATRP process is a transition-metal-mediated living radical polymerization of vinyl monomers. Compared with other polymerization methods, ATRP can decrease the molecular weight distribution (MWD) of a copolymer and improve the controllability of a reaction.<sup>14,15</sup> Consequently, ATRP has become an important method of polymer structure design. Compared with living ionic polymerization, ATRP has better controllability and can be applied to most monomers under mild reaction

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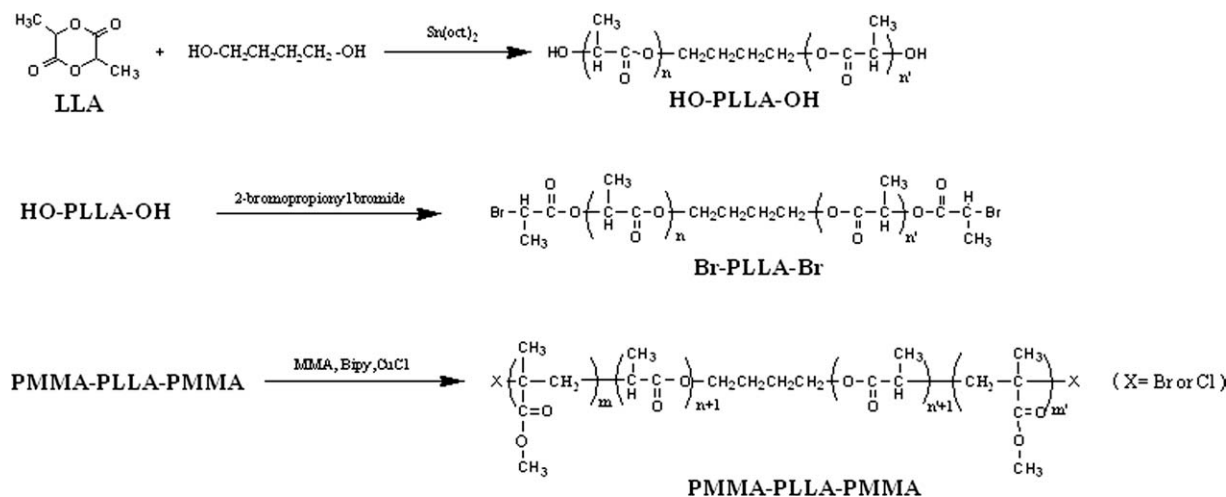


Figure 1 Synthetic route of PMMA-PLLA-PMMA.

conditions.<sup>16,17</sup> Thus, ATRP has a considerable potential use in various industries. In particular, ATRP has been successfully employed in the synthesis of a large range of previously unknown well-defined block copolymers.

In this study, L-lactide (LLA, Fig. 1) was used as the raw material, 1,4-Butylene glycol was added to obtain HO-PLLA-OH via ring opening polymerization. The initiator Br-PLLA-Br was prepared from HO-PLLA-OH with two hydroxide radicals. A PMMA-PLLA-PMMA copolymer with a controllable molecular weight was then obtained via an ATRP reaction with Br-PLLA-Br and methyl methacrylate (MMA). The purpose of this study is to improve the thermal stability of PLA by copolymerizing PMMA with dihydroxyl-terminated PLA (HO-PLLA-OH).

## EXPERIMENTAL

### Materials

Lactide acid (Anhui Fengyuan Company, China) was purified by recrystallization before use. MMA (Sinopharm Chemical Reagent, China) was vacuum-distilled from CaH<sub>2</sub> and stored under a nitrogen atmosphere at 4°C. Stannous octoate(Sn(Oct)<sub>2</sub>; Sigma, USA) and all other reagents(Tianjin Fuchen chemical reagent company) were reagent grade and used without further purification.

### Characterization

The Fourier-transform infrared (FTIR) transmission spectra of the samples were recorded from KBr-pellets (1 wt % of polymer) using a Thermo Nicolet 380 FTIR spectrometer in the domain range of 4000 to 650 cm<sup>-1</sup> at 4 cm<sup>-1</sup> resolution (1738 data points).

Nuclear magnetic resonance was taken with a Bruker AVANCE spectrometer at 400.13 MHz

<sup>1</sup>H-NMR and 75.48 MHz <sup>13</sup>C-NMR. The chemical shifts in CDCl<sub>3</sub> were reported downfield from 0.00 ppm using tetramethylsilane as an internal reference.

Gel permeation chromatography (GPC) was conducted using a Dionex P680 equipped with PLgel (Polymer Laboratories, 5μm, 300 × 7.5) and a differential refractometer (Shodex RI 101). The mobile phase was tetrahydrofuran and the flow rate was 1 mL/min at 35°C. The polymer concentration was 1 mg/mL with a 100 μL injection volume. A series of narrow MWD polystyrene standards (PSS) were used to generate a calibration curve. Average molecular masses were reported as polystyrene equivalents.

Elemental analysis was determined with a Vario MICRO Elemental Analyzer (Elementar) (using 2 mg of the sample) to elucidate the amount of C and H in the polymer. Samples of the polymers were dried in vacuum before determination.

Differential scanning calorimetry (DSC) was carried out in a Perkin Elmer Pyris I DSC. The samples were heated under a flow of nitrogen gas at 20°C/min from 0 to 250°C, quickly cooled from 250 to 0°C, and scanned at a heating rate 20°C/min from 0 to 250°C.

Thermogravimetric analysis (TGA) measurements were conducted using a Perkin-Elmer Pyris I TGA. All samples were heated under a flow of nitrogen gas from 25 to 550°C at a heating rate of 20°C/min.

### Preparation of the polylactide

LLA was synthesized using the methods of Kulkarni et al.<sup>18</sup> About 1.0 g of purified LLA, 1,4-butanediol(0.025 mol %), Sn(Oct)<sub>2</sub>(0.1 mol %) were added into a 10 mL ampule, Vacuuming and backfilling with nitrogen (five cycles) were applied to remove oxygen and the ampule was sealed under vacuum. The mixture was placed in a 130°C oven for 2 h, and the ampule was scraped after the reaction. All the

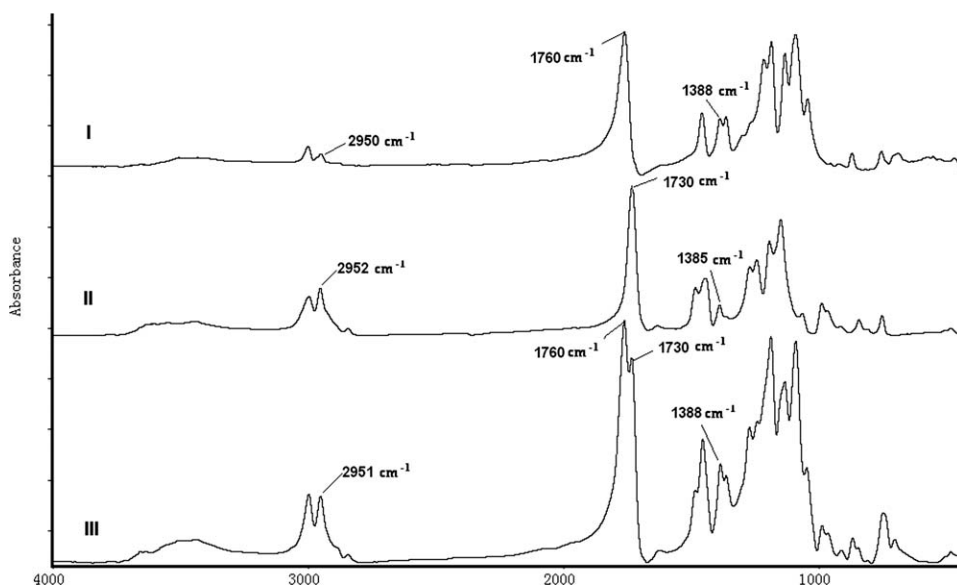


Figure 2 FTIR spectrogram of PMMA (I), PLLA (II), and PMMA-PLLA-PMMA (III).

products including glass fragment were placed in a clean conical beaker and dissolved in chloroform. The glass fragments were subsequently filtered out. The product HO-PLLA-OH was then precipitated in methanol, filtered out, and dried under vacuum until constant weight.

#### Preparation of the Br-PLLA-Br initiator

About 10 g of HO-PLLA-OH was dissolved in a reaction bulb with 40 mL of methylene dichloride (DCM). The bulb was then placed in an ice bath, added pyridine and  $\alpha$ -bromopropionyl bromide (HO-PLLA-OH : pyridine :  $\alpha$ -bromo-propionyl bromide = 1 : 5 : 10, mol) dropwise, stirred for 2 h at 0°C and 48 h at room temperature. After pyridinium was filtered out, the filtrate was collected and precipitated with methanol to obtain Br-PLLA-Br. Drying under vacuum until constant weight was reached.

#### Preparation of the PMMA-PLLA-PMMA copolymer

Br-PLLA-Br, cuprous chloride (CuCl), 2,2-bipyridyl and MMA (1 : 4 : 8.5 : 2,000 mol) were added in a 10-mL ampule. Applying vacuum and backfilling with nitrogen (five cycles) were performed to remove oxygen. The ampule was then sealed under vacuum. Polymerization was carried out at 80°C in an oven and the ampule was scraped after the reaction. All the products including glass fragments were placed in a clean conical beaker, and dissolved in DCM. The glass fragments were filtered out and the filtrate was washed with distilled water five times until the wash solution became colorless. Then the product PMMA-PLLA-PMMA was precipitated

in ethanol and dried under vacuum until constant weight.

## RESULTS AND DISCUSSION

### Characterization of PMMA-PLLA-PMMA

Figure 2 shows the FTIR spectrogram of PLLA (I), PMMA (II), and PMMA-PLLA-PMMA (III). After

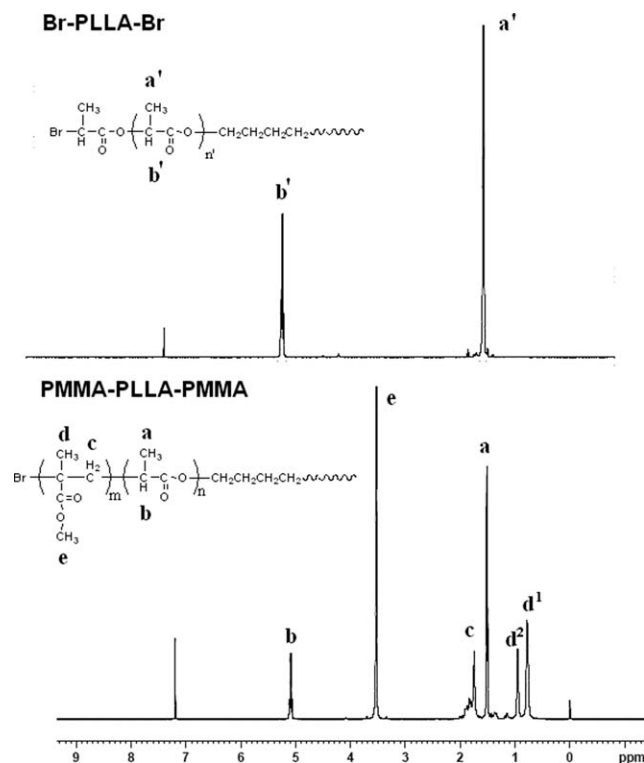


Figure 3  $^1\text{H-NMR}$  spectrogram of PLLA and PMMA-PLLA-PMMA.

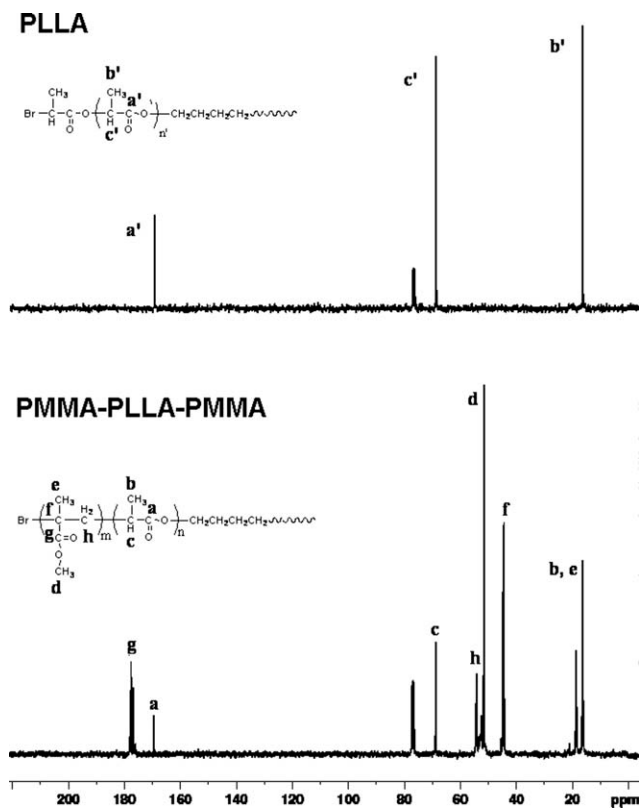


Figure 4  $^{13}\text{C}$ -NMR spectrogram of PLLA and PMMA-PLLA-PMMA.

copolymerization, the typical PMMA- $\alpha$ -methyl characteristic peak at  $1388\text{ cm}^{-1}$  and the C-H asymmetric stretching of PMMA at  $2950\text{ cm}^{-1}$  were strengthened.<sup>19,20</sup> These results suggest that the PMMA was grafted to the Br-PLLA-Br initiator. The peak at  $1760\text{ cm}^{-1}$  corresponds to the  $\text{C}=\text{O}$  stretching vibration band of PLLA, and the peak at  $1732\text{ cm}^{-1}$  corresponds to that of PMMA.<sup>21,22</sup> In the FTIR spectrogram of (III),

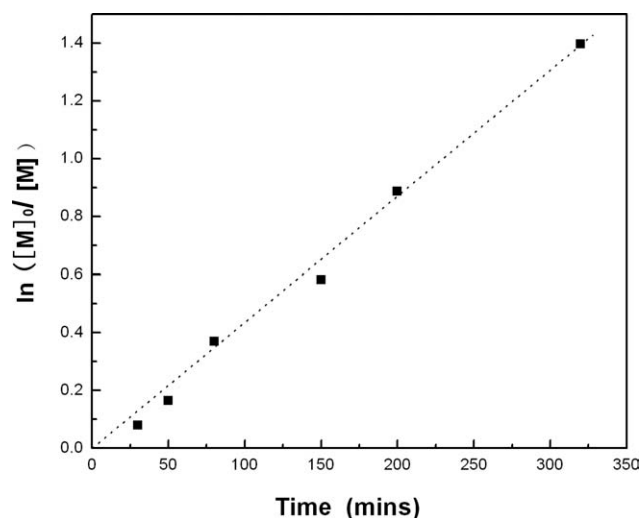


Figure 5 Kinetic plot for the ATRP of MMA with PLLA initiation.

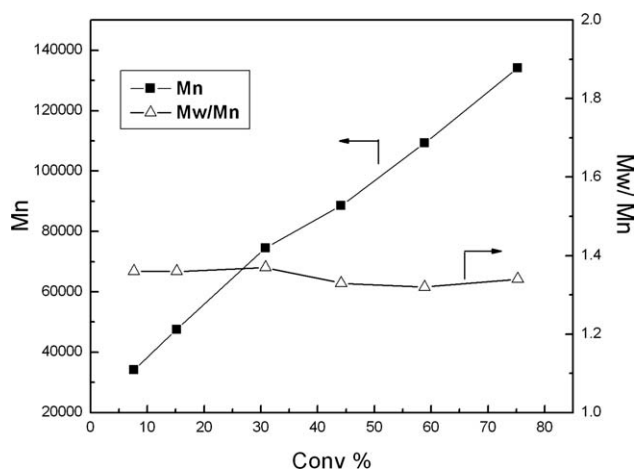


Figure 6 Dependence on conversion of the molecular weight and  $M_w/M_n$ .

the peaks at  $1760$  and  $1732\text{ cm}^{-1}$  indicated the presence of a copolymer consisting of PLLA and PMMA.

The  $^1\text{H}$ -NMR spectrogram of PLLA and the PMMA-PLLA-PMMA copolymer is shown in Figure 3. Peaks at  $\delta 1.58$  and  $5.18$  correspond to  $\text{—CH}_3$  (a) and  $\text{—CH—}$  (b) hydrogen peaks on the PLLA block,<sup>23</sup> respectively.  $\alpha$ -Methyls with different configurations have different chemical shifts in PMMA, syndiotactic methyl ( $\delta 0.78$  [d1]), and isotactic methyl ( $\delta 0.95$  [d2]). In addition, the  $\delta 1.74$  (c) and  $\delta 3.53$  (e) hydrogen peaks belong to the  $\text{—CH}_2\text{—}$  and carbomethoxy of the PMMA block, respectively.<sup>24</sup> The  $^{13}\text{C}$ -NMR spectrogram is shown in Figure 4, peaks between  $\delta 18\text{—}20$  correspond to the  $\text{—CH}_3$  (b) and  $\text{—CH}_3$  (e) of the PLLA and PMMA block. Peaks around  $\delta 170$  (a) and  $\delta 178$  (g) belong to the  $\text{—CO—}$  of the PLA and PMMA block respectively.<sup>10,25</sup> Peaks at  $\delta 44$  (f),  $\delta 52$  (d) and  $\delta 54$  (h) peaks belong to the tertiary carbon, the  $\text{—O—CH}_3$  and the  $\text{—CH}_2\text{—}$  of the PMMA block.<sup>26</sup> The GPC profiles demonstrate a single polymer peak, suggesting that a triblock copolymer was successfully synthesized without the presence of homopolymers of PLLA and PMMA. A comparison of the PLA's  $\text{—CH}_3$  peak (a) with the PMMA' carbomethoxy peak (e) in  $^1\text{H}$ -NMR shows that there are  $\sim 349$  units of MMA on each side of the PLA center block. Therefore, the NMR-calculated number average molecular weight ( $M_n$ ) of the PMMA portion is  $69\,800\text{ g/mol}$ , and the total  $M_n$  of copolymer is  $80,800\text{ g/mol}$ , which agrees well with the GPC value of  $81,900\text{ g/mol}$ .

### Synthesis of PMMA-PLLA-PMMA

In order to obtain a HO-PLLA-OH chain with appropriate molecular weight, PLLA was polymerized via the ring-opening polymerization of lactide using 1,4-butylene glycol. The dried product of HO-PLLA-OH ( $M_n = 22,200$ , MWD = 1.31, GPC) is a



TABLE I  
DSC Data for PLLA, PMMA, and PMMA-PLLA-PMMA

No.	Sample		Glass transition temperature		Cold crystallization temperature		Melting temperature	
	$M_{n\text{PLLA}}^a$ (g/mol)	$M_{n\text{PMMA}}^b$ (g/mol)	$T_g$ (°C)	$\Delta C_p$ (J g <sup>-1</sup> °C <sup>-1</sup> )	$T_{cc}$ (°C)	$\Delta H_{cc}$ (J g <sup>-1</sup> )	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )
1-1	22,220	0	58.3	0.658	117.9	34.7	165.6	51.42
1-2	22,220	790	57.5	0.540	125.3	54.8	165.2	45.6
1-3	22,220	5,325	59.5	0.379	/	/	/	/
1-4	22,220	18,510	83.1	0.316	/	/	/	/
1-5	22,220	34,050	104.3	0.262	/	/	/	/
1-6	22,220	44,340	107.4	0.288	/	/	/	/
1-7	0	20,080	124.0	0.240	/	/	/	/

<sup>a</sup>  $M_{n\text{PLLA}}$  was measured directly by GPC.

<sup>b</sup>  $M_{n\text{PMMA}}$  was calculated according to the formula:  $M_{n\text{-PMMA}} = (M_{n\text{copolymer}} - M_{n\text{PLLA}})/2$ ;  $M_{n\text{copolymer}}$  was measured directly by GPC.

white powder. The experimental mass fraction of the HO-PLLA-OH obtained by elemental analysis is as follows: C, 48.92%; H, 5.44%. The C/H mass ratio of the HO-PLLA-OH by elemental analysis is 8.99, which is consistent with the theory value of neat PLLA. Br-PLLA-Br ( $M_n = 22,200$ , MWD = 1.27, GPC) is a light yellow powder after bromination. The Br analysis obtain by halogen-free is 1.33%, the yield of bromination is nearly 100%.

As described in the Experimental section, the copolymerization of Br-PLLA-Br and MMA was carried out via ATRP. In this case, Br-PLLA-Br was used as the initiator, the reactant MMA was liquid, and no other solvent was added. The experimental mass fraction of the PMMA-PLLA-PMMA obtained by elemental analysis is as follows: C, 57.78%; H, 7.47%, which agrees well with the <sup>1</sup>H-NMR result.

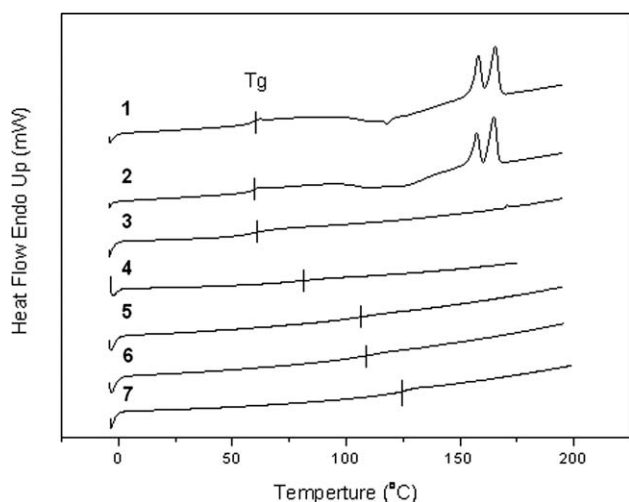


Figure 7 DSC Thermograms of PLLA, PMMA-PLLA-PMMA, and PMMA. 1. HO-PLLA-OH,  $M_n = 22,220$ ; 2. Copolymer,  $M_n = 23,800$ ; 3. Copolymer,  $M_n = 32,870$ ; 4. Copolymer,  $M_n = 59,240$ ; 5. Copolymer,  $M_n = 90,320$ ; 6. Copolymer,  $M_n = 110,890$ ; 7. PMMA,  $M_n = 200,80$ .

The kinetics plot of the ATRP reaction is shown in Figure 5. There is a linear relationship between  $\ln([M]_0/[M])$  and time. Thus, the reaction rate and monomer concentration satisfied the requirements of first order kinetics. Molecular weight increases with the conversion rate, whereas the  $M_w/M_n$  remains constant, and narrowly distributed (Fig. 6). Overall, the polymer system followed the characteristics of the ATRP, indicating that is a living polymerization.

#### Removal of Cu from crude PMMA-PLLA-PMMA

The common methods for Cu catalyst removal from ATRP products include Al<sub>2</sub>O<sub>3</sub> column chromatography, precipitation and dissolution. Although the Al<sub>2</sub>O<sub>3</sub> column is effective in removing Cu (low residue of 5.55 mg/kg), Al<sub>2</sub>O<sub>3</sub> has a strong adsorption effect on PLLA and its copolymer. Hence, the

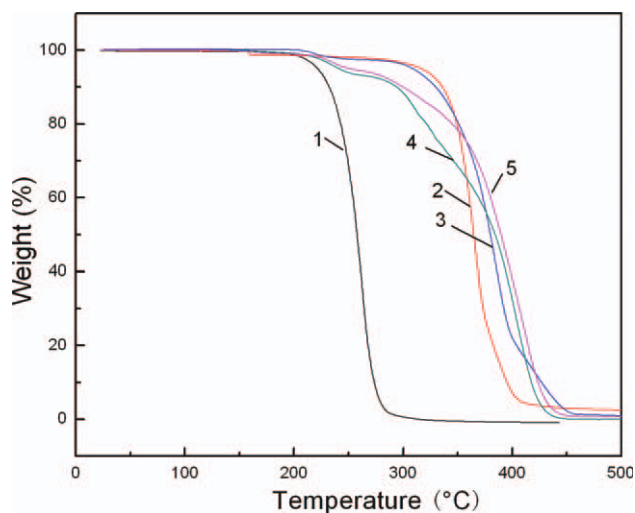


Figure 8 TGA curve of PMMA-PLLA-PMMA. 1. HO-PLLA-OH; 2. Copolymer,  $M_n = 23,800$ ; 3. Copolymer,  $M_n = 32,870$ ; 4. Copolymer,  $M_n = 81,910$ ; 5. Copolymer,  $M_n = 90,320$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE II  
Parameters of the TGA Curve for PLLA and PMMA-PLLA-PMMA

No.	Polymer	Sample		$T_i$ (°C)	$T_{1/2}$ (°C)	$T_{10\%}$ (°C)
		$M_{ncopolymer}^b$ (g/mol)	$M_{nPMMA}^c$ (g/mol)			
1	HO-PLLA-OH <sup>a</sup>	/	/	243.8	257.9	273.3
2	PMMA-PLLA-PMMA	23800	790	345.4	364.8	395.2
3		32870	5325	349	379.8	426.8
4		81910	29845	349.1	384.2	417.6
5		90320	34050	355.3	389.5	423.8

<sup>a</sup> HO-PLLA-OH,  $M_n = 22,220$  g/mol (GPC).

<sup>b</sup>  $M_{ncopolymer}$  was measured directly by GPC.

<sup>c</sup>  $M_{nPMMA}$  was calculated according to the formula:  $M_{n-PMMA} = (M_{ncopolymer} - M_{nPLLA})/2$ .

productive rate of PMMA-PLLA-PMMA is very low (52.14 %). In this paper, the filter washing-extraction method was used to remove copper ions from the products. After five times washing-extraction, the products contained virtually no Cu (residual quality = 0 mg/kg), and the productive was >85%.

### Thermal properties of the copolymer

The DSC results of the copolymers with different PMMA chain lengths are shown in Table I and Figure 7.  $T_g$  data indicate an increasing stiffness of the copolymer chain with the PMMA block content.  $T_g$  of the copolymer increased from about 55 to 107°C with increased PMMA block.<sup>27,28</sup> Although the chain length of each PMMA block in the copolymer is twice the chain length of the PMMA homopolymer, the  $T_g$  of the copolymer never reaches the  $T_g$  of the homopolymer ( $T_g = 124$ °C) because of the effect of the PLLA chain. In addition, the PLLA and PMMA blocks are highly compatible, and no phase disengagement is observed with the PMMA block ranging from 0 to 34,000. The crystal and melting peaks of the copolymer both disappear with increased PMMA block. Therefore, the copolymer transitioned from partial crystallization to an amorphous state. Increasing the copolymer chain causes the chain to intertwine. On the other hand, randomizing the PMMA block damaged the typical arrangement of the PLLA. Consequently, the degree of its crystallinity decreases.

To study the thermal stability of PLMA-PLLA-PMMA, copolymers with different molecular weights were examined by TGA. At 250°C, the pyrolysis of PLLA (Curve 1) caused it to undergo a continuous heat weight loss (Fig. 8). When the initial decomposition temperature and weight loss rate decrease from 50 to 10%, the thermal property of the copolymer is better than that of HO-PLLA-OH. Following copolymerization, the initial decomposition temperature increases from 243 to 355°C. Notably, even a short PMMA block ( $M_n = 790$  g/mol) causes

an increased initial decomposition temperature of 100°C (Table II). Intramolecular transesterification is generally accepted as the dominant thermal degradation pathway for PLA,<sup>29</sup> if hydroxyl chain end of PLA is capped, then the intramolecular transesterification will be inaccessible and PLA remain intact until the onset of alternate degradation pathways at much higher temperatures.<sup>27</sup> Therefore, changing the PMMA block length has no significant influence on the initial decomposition temperature and weight retention rate.

### CONCLUSIONS

A PMMA-PLLA-PMMA block copolymer was synthesized by a Br-PLLA-Br initiator with MMA via ATRP. The copolymerization was a first order kinetics process, indicating that the reaction had controllability and low MWD. This feature is typical of a radical polymerization via ATRP. The thermal property of the copolymer was investigated by DSC and TGA. The results indicated that compared with PLLA, the thermal properties of the copolymer significantly improved. The initial decomposition temperature increased from 244 to 350°C, and  $T_g$  increased from 58 to 107°C. In addition, using a washing-extraction method to remove Cu from the ATRP had also achieved satisfactory results.

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