

## NOTE

# Ring-opening polymerization of $\epsilon$ -caprolactone and L-lactide initiated by a hydroxy-terminated aromatic polyimide

Hisatoyo Morinaga<sup>1,2</sup>, Fumiya Tsuneishi<sup>3</sup> and Shinya Inada<sup>1</sup>*Polymer Journal* (2016) 48, 311–315; doi:10.1038/pj.2015.107; published online 11 November 2015

## INTRODUCTION

Aliphatic polyesters prepared by ring-opening polymerization of  $\epsilon$ -caprolactone (CL) and L-lactide (LA) have attracted considerable interest because they are biodegradable and biocompatible. However, it is difficult to produce aliphatic homopolyesters that fulfil practical requirements given the inherently poor properties of these polymers, such as low mechanical strength and poor heat resistance. To overcome these drawbacks, improvements have been made by preparing nanocomposites with organoclay.<sup>1–4</sup>

Aromatic polyimides (PIs) are well known as plastics used in super-engineering applications because of their high mechanical strength and thermal resistance, as well as their good biocompatibility.<sup>5</sup> We believe that an incorporation of aromatic PIs into the aliphatic polyesters could help improve the properties of aliphatic polyesters for use as biomaterials. Ding and Harris<sup>6</sup> have demonstrated that the mechanical properties of nylon 6-*block*-PI-*block*-nylon 6 copolymers are superior to those of commercial nylon 6. Takeichi and coworkers have reported that the initial decomposition temperature of poly(urethane-imide) is higher than that of polyurethane.<sup>7</sup> These reports prompted us to explore a method to prepare copolymers composed of aliphatic polyesters and aromatic PIs. The corresponding method is required to more readily introduce the PI segment into the target polyester backbone. In this note, we describe a facile synthesis of ABA-type triblock copolymers consisting of aliphatic polyesters and aromatic PIs by ring-opening polymerization of CL and LA initiated with hydroxy-terminated PI. It has been reported that PIs with hydroxy-terminated groups can be easily synthesized by reacting dianhydride, diamine and aminoalcohol.<sup>8–11</sup>

## EXPERIMENTAL PROCEDURE

### Materials

4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (99%, 6FDA, Sigma Chemical Company, St Louis, MO, USA), 4,4'-diaminodiphenyl ether

(99%, ODA, Wako Pure Chemical Industries, Osaka, Japan), *p*-aminophenethyl alcohol (85%, Wako Pure Chemical Industries) and CL (Wako Pure Chemical Industries) were used as received. LA was provided by Kyushu Institute of Technology. Dried *N*-methyl-2-pyrrolidone (NMP) was obtained from Wako Pure Chemical Industries. Other solvents were obtained from Wako Pure Chemical Industries and were used without further purification.

### Measurements

The <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H-NMR; 400 MHz) spectra were recorded on a JEOL ECX-400II spectrometer (JEOL Resonance, Tokyo, Japan) in dimethyl sulfoxide (DMSO)-*d*<sub>6</sub> using tetramethylsilane as an internal standard. Fourier transform infrared spectra of the polymers were recorded on a JASCO FT/IR-4100 spectrometer (JASCO, Tokyo, Japan). Thermal decomposition was investigated by thermogravimetry-differential thermal analysis (Thermo plus EVO2 TG8120, Rigaku, Japan) at a heating rate of 10 °C min<sup>-1</sup> in air. Glass transition temperatures were determined by differential scanning calorimetry (DSC) using a Thermo plus EVO2 DSC8230 (Rigaku, Tokyo, Japan) for poly(LA)-*b*-PI-*b*-poly(LA) and a X-DSC 7000 (Hitachi, Tokyo, Japan) for poly(CL)-*b*-PI-*b*-poly(CL) at a heating rate of 10 °C min<sup>-1</sup>, under N<sub>2</sub> gas. The number-average (*M*<sub>n</sub>) and weight-average (*M*<sub>w</sub>) molecular weights were estimated by size exclusion chromatography (SEC), which consisted of a Waters Alliance e2695 GPC system equipped with a 2414 refractive index detector (Waters, Milford, MA, USA) and poly(vinyl alcohol) gel columns (shodex Asahipak GF-310 HQ+GF-7M HQ with size exclusion limitations of 4 × 10<sup>4</sup> and 1 × 10<sup>7</sup> g mol<sup>-1</sup>, respectively) eluted with tetrahydrofuran (THF) at a flow rate of 0.6 ml min<sup>-1</sup> at 35 °C using a calibration curve based on polystyrene standards.

### Synthesis of hydroxy-terminated PI

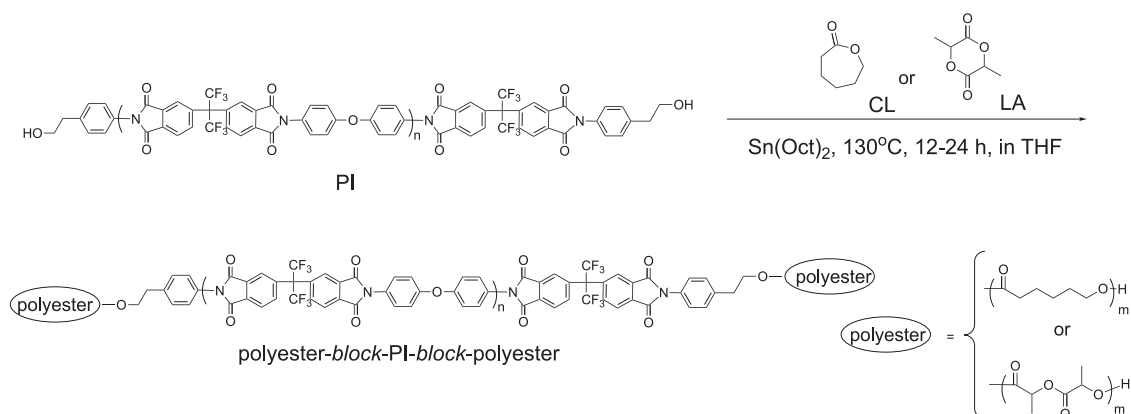
Hydroxy-terminated PI was synthesized according to previous papers.<sup>9–11</sup> 6FDA (1.50 g, 3.38 mmol) in 7.0 ml of NMP was added to 9.5 ml of NMP containing ODA (0.565 g, 2.82 mmol) and *p*-aminophenethyl alcohol (0.155 g, 1.13 mmol). The reaction mixture was stirred under argon gas at room temperature for 24 h, followed by refluxing with the addition of *m*-xylene (3 ml) at 180 °C for 6 h. Then the solution was poured into excess ethanol to

<sup>1</sup>Department of Materials Science and Engineering, National Institute of Technology, Kochi College, Kochi, Japan; <sup>2</sup>Faculty of Education and Human Sciences, Graduate Faculty of Interdisciplinary Research, University of Yamanashi, Yamanashi, Japan and <sup>3</sup>Advanced Course of Material Engineering, National Institute of Technology, Kochi College, Kochi, Japan

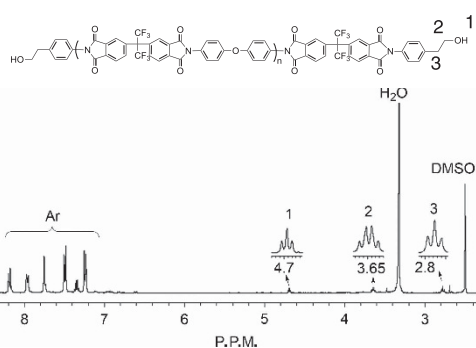
Correspondence: Dr H Morinaga, Faculty of Education and Human Sciences, Graduate Faculty of Interdisciplinary Research, University of Yamanashi, Kofu, Yamanashi 400-8510, Japan.

E-mail: hmorinaga@yamanashi.ac.jp

Received 28 July 2015; revised 18 September 2015; accepted 18 September 2015; published online 11 November 2015



**Scheme 1** Ring-opening polymerization of CL and LA initiated by PI.



**Figure 1**  $^1\text{H}$  NMR spectrum of PI measured in DMSO- $d_6$ .

precipitate the PI with hydroxy groups at both chain ends (Yield = 71% (1.57 g),  $M_n(\text{NMR}) = 5700$ ,  $M_n(\text{SEC}) = 3200$ ).

$^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz,  $\delta$ , p.p.m.): 2.78 ( $\text{HOCH}_2\text{CH}_2-$ ); 3.65 ( $\text{HOCH}_2\text{CH}_2-$ ); 4.7 ( $\text{HOCH}_2\text{CH}_2-$ ); 6.51–8.34 (aromatic ring).

### Ring-opening polymerization of CL initiated by PI

The typical procedure for the ring-opening polymerization of CL initiated by the reactive PI, shown in Scheme 1, is described as follows. Tin(II) 2-ethylhexanoate ( $\text{Sn}(\text{Oct})_2$ , 6 mg, 14.8  $\mu\text{mol}$ ) was added to a test tube containing CL (0.699 g, 6.12 mmol) and PI (0.352 g, 0.0617 mmol) in THF (1.0 ml). The reaction mixture was heated at 130  $^\circ\text{C}$  and stirred for 24 h under an argon atmosphere. The resultant polymer was purified by reprecipitation with an excess of methanol (0.64 g, Yield = 61%).

$^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz,  $\delta$ , p.p.m.): 1.00–1.71 ( $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ); 2.08–2.35 ( $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ); 2.89–2.97 ( $-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}-$ ); 3.82–4.05 ( $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ); 4.22–4.29 ( $-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}-$ ); 6.98–8.33 (aromatic ring).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz,  $\delta$ , p.p.m.): 24.5 ( $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ); 25.3 and 28.2 ( $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ); 32.6 ( $-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}-$ ); 33.8 ( $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ); 61.0 ( $-\text{C}(\text{CF}_3)_6-$ ); 63.9 ( $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ) and ( $-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}-$ ); 99.9 ( $-\text{C}(\text{CF}_3)_6-$ ); 119.5, 127.6, 129.8, 133.1, 137.7, and 156.5 (aromatic ring); 166.5 (carbonyl group of imide ring); 173.2 ( $-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ ).

### Ring-opening polymerization of LA initiated by PI

The typical procedure for the ring-opening polymerization of LA initiated by PI, as shown in Scheme 1, is described as follows.  $\text{Sn}(\text{Oct})_2$  (6 mg, 14.8  $\mu\text{mol}$ ) was added to a test tube containing LA (0.882 g, 6.12 mmol) and PI (0.352 g, 0.0617 mmol) in THF (1.0 ml). The reaction mixture was heated at 130  $^\circ\text{C}$  and stirred for 12 h under an argon atmosphere. The resultant polymer was purified by reprecipitation with excess methanol (0.63 g, Yield = 51%).

$^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz,  $\delta$ , p.p.m.): 1.17–1.54 ( $-\text{C}(=\text{O})\text{CH}(\text{CH}_3)\text{OC}(=\text{O})\text{CH}(\text{CH}_3)\text{O}-$ ); 2.91–3.01 ( $-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}-$ ); 4.13–4.23 ( $-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}-$ ); 4.29–4.40 and 5.02–5.27 ( $-\text{C}(=\text{O})\text{CH}(\text{CH}_3)\text{OC}(=\text{O})\text{CH}(\text{CH}_3)\text{O}-$ ); 6.72–8.33 (aromatic ring).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz,  $\delta$ , p.p.m.): 17.0 ( $-\text{C}(=\text{O})\text{CH}(\text{CH}_3)\text{OC}(=\text{O})\text{CH}(\text{CH}_3)\text{O}-$ ); 35.2 ( $-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}-$ ); 66.0 ( $-\text{C}(\text{CF}_3)_6-$ ); 69.2 ( $-\text{C}(=\text{O})\text{CH}(\text{CH}_3)\text{OC}(=\text{O})\text{CH}(\text{CH}_3)\text{O}-$ ) and ( $-\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}-$ ); 119.6, 124.9, 127.7, 129.9, 133.2, 133.6, 137.8, and 156.6 (aromatic ring); 166.6 (carbonyl group of imide ring); 169.7 ( $-\text{C}(=\text{O})\text{CH}(\text{CH}_3)\text{OC}(=\text{O})\text{CH}(\text{CH}_3)\text{O}-$ ).

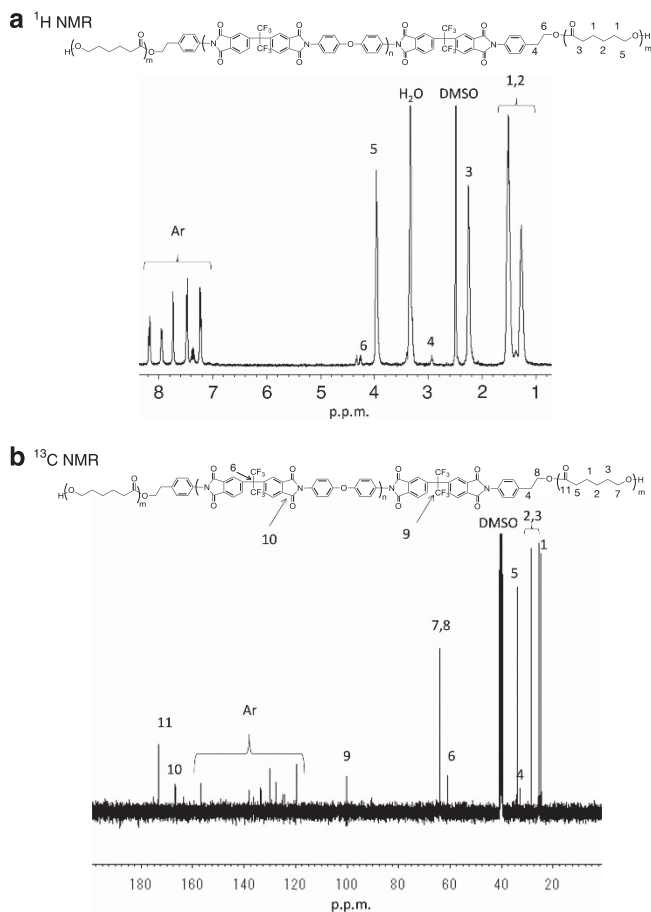
## RESULTS AND DISCUSSION

### Synthesis of hydroxy-terminated PI

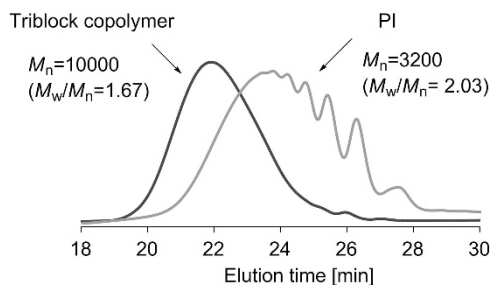
Prior to the synthesis of ABA triblock copolymers, hydroxy-terminated PI was synthesized by a polyaddition reaction. The  $^1\text{H}$  NMR spectrum of PI is shown in Figure 1. The peaks at 2.78 and 4.7 p.p.m. assignable to the protons of the  $-\text{CH}_2\text{CH}_2\text{OH}$  groups of PI are clearly observed. These results are consistent with those of previous studies.<sup>9–11</sup> The  $^1\text{H}$  NMR spectroscopic analysis reveals that the  $M_n$  (NMR) value is 5700. The  $M_n$  and  $M_w/M_n$  values estimated by SEC analysis were 3200 and 2.03, respectively.

### Ring-opening polymerization of CL initiated by PI

The ring-opening polymerization of CL was performed with PI in the presence of  $\text{Sn}(\text{Oct})_2$  at 130  $^\circ\text{C}$  for 24 h in a feed molar ratio of  $[-\text{OH in PI}]_0:[\text{CL}]_0$  of 2:100 to afford the corresponding polymer in 61% yield. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the resultant polymer are shown in Figure 2. The peaks at 1.00–1.71, 2.08–2.35 and 3.82–4.05 p.p.m. assignable to the methylene protons of poly(CL), as well as the aromatic protons of PI, were clearly observed in the  $^1\text{H}$  NMR spectrum of the resultant polymer. In addition, there was no peak at 4.7 p.p.m. attributed to the terminal hydroxy groups of PI, which implies that the ring-opening polymerization proceeded from both ends of PI. The  $^{13}\text{C}$  NMR spectrum of the resultant polymer shows peaks assignable to the methylene carbons and ester carbonyl carbons of poly(CL), as well as to the aromatic carbons of PI. These results indicate that the ring-opening polymerization of CL successfully proceeded, affording the corresponding poly(CL). This NMR spectroscopic analysis allowed us to determine the composition ratio of the resultant polymer, PI:poly(CL) = 48:52 (wt:wt), by comparing the molecular weights between the PI segment ( $M_n(\text{NMR}) = 5700$ ) and the poly(CL) segment ( $M_n(\text{NMR}) = 6300$ ). The molecular weight of the poly(CL) segment was determined by comparing the integral ratio of the peaks attributed to the methylene protons in the PI segment and the poly(CL) protons in the  $^1\text{H}$  NMR spectrum. The polymerization degree of CL at one hydroxy group of PI was 27.6.



**Figure 2** (a) <sup>1</sup>H and (b) <sup>13</sup>C NMR spectra of poly(CL)-*b*-PI-*b*-poly(CL) measured in DMSO-*d*<sub>6</sub>. Comp. (PI:poly(CL))=48:52 (wt:wt) determined by <sup>1</sup>H NMR spectroscopy.



**Figure 3** SEC profile of poly(CL)-*b*-PI-*b*-poly(CL). Comp. (PI:poly(CL))=48:52 (wt:wt) determined by <sup>1</sup>H NMR spectroscopy. A full color version of this figure is available at the *Polymer Journal* online.

The SEC profiles of the resultant polymer show a unimodal elution peak that shifted to a higher molecular weight region from that of PI (Figure 3). The SEC and NMR results reveal that the ring-opening polymerization of CL was successfully initiated from both of the hydroxy-terminated groups of PI to give the corresponding ABA triblock copolymer. The corresponding  $M_n$  and  $M_w/M_n$  values were estimated to be 10 000 and 1.67, respectively.

When the ring-opening polymerization of CL initiated by PI in a feed molar ratio of  $[-\text{OH in PI}]_0:[\text{CL}]_0 = 2:200$  was performed in a similar manner, the corresponding ABA triblock copolymer with a

**Table 1** Results of block copolymerization of CL and LA<sup>a</sup>

No.	<i>M</i>	[−OH in PI] <sub>0</sub> :[M] <sub>0</sub>		Comp. <sup>b</sup> (PI:poly( <i>M</i> ))	
		(mol:mol)	Yield (%)	(wt:wt)	<i>M<sub>n</sub></i> ( <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> ) <sup>c</sup>
1	CL	2:100	61 <sup>d</sup>	48:52	10 000 (1.67)
2	CL	2:200	69 <sup>d</sup>	30:70	12 000 (1.74)
3	LA	2:100	51 <sup>d</sup>	48:52	7700 (1.56)
4	LA	2:200	43 <sup>d</sup>	32:68	10 100 (1.42)
c.f. <sup>e</sup>	—	—	71 <sup>f</sup>	100:0	3200 (2.03)

Abbreviations: CL, ε-caprolactone; LA, L-lactide;  $M_n$ , number-average molecular weights;

$M_w$ , weight-average molecular weights; PI, polyimide.

<sup>a</sup>Polymerization time: 24 h (for CL) and 12 h (for LA).

<sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy.

<sup>c</sup>Estimated by SEC.

<sup>d</sup>Methanol-insoluble part.

<sup>e</sup>PI (macroinitiator).

<sup>f</sup>Ethanol-insoluble part.

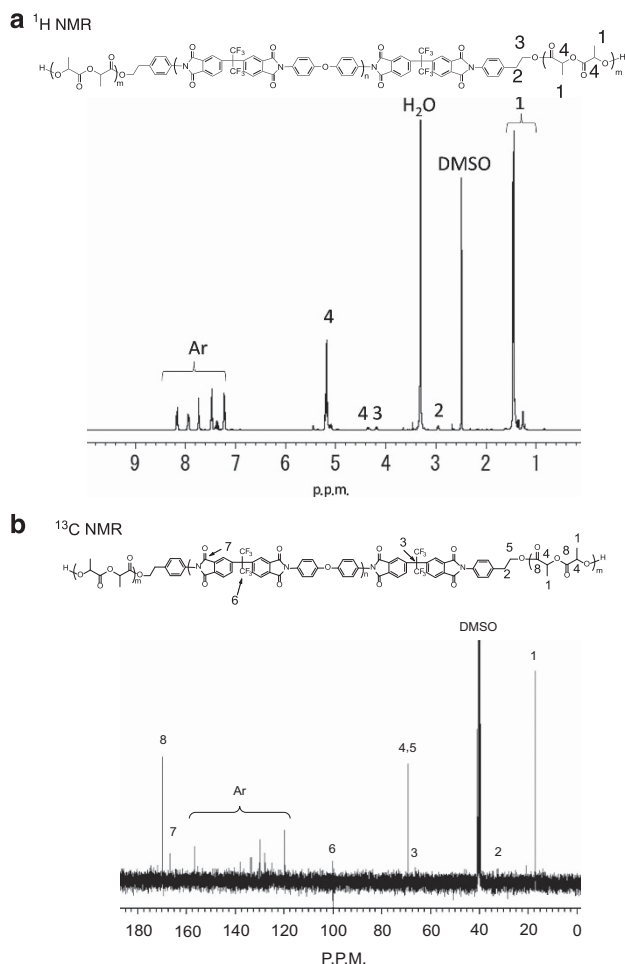
composition of PI:poly(CL) = 30:70 (wt:wt), as determined by <sup>1</sup>H NMR spectroscopy, was obtained in 69% yield. The polymerization degree of CL at one hydroxy group of PI was 58.0. The SEC result showed a unimodal peak with  $M_n = 12 000$  ( $M_w/M_n = 1.74$ ).

We attempted to prepare films of poly(CL)-*block*-PI-*block*-poly(CL) by using the solvent casting method; however, the films were too brittle to investigate their mechanical properties, likely because of the low molecular weight of the PI segment. Synthesis of triblock copolymers derived from PI with higher molecular weights is required to investigate the mechanical properties compared with pure poly(CL). We expect introducing the PI segment into poly(CL) may enhance its elastic modulus, and detailed results of these investigations will be reported elsewhere.

### Ring-opening polymerization of LA initiated by PI

In a similar procedure to that used with CL, the ring-opening polymerization of LA by PI was performed in a feed molar ratio of  $[-\text{OH in PI}]_0:[\text{LA}]_0 = 2:100$  to synthesize poly(LA)-*block*-PI-*block*-poly(LA). The resultant polymer was obtained in 51% yield (Table 1). Figure 4 shows the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the resultant polymer. In addition to the peaks ascribed to the aromatic protons of PI, peaks assignable to the methyl and methine protons of poly(LA) were clearly observed at 1.17–1.54 and 5.02–5.27 p.p.m., respectively, in the <sup>1</sup>H NMR spectrum. There was no peak at 4.7 p.p.m. attributed to the hydroxy groups of PI, which suggests that the ring-opening polymerization proceeded from both hydroxy groups. The <sup>13</sup>C NMR spectrum shows peaks at 17, 69.2 and 169.7 p.p.m. ascribed to the methyl, methine and ester carbonyl carbons of poly(LA), respectively. The composition of the polymer (PI:poly(LA)) was calculated to be 48:52 (wt:wt) based on the molecular weights of the PI segment ( $M_{n(\text{NMR})} = 5700$ ) and the poly(LA) segment ( $M_{n(\text{NMR})} = 6300$ ). The polymerization degree of LA at one hydroxy group of PI was 21.7. The SEC profile, shown in Figure 5, shows a unimodal peak of the resultant polymer. The corresponding  $M_n$  and  $M_w/M_n$  values were 7700 and 1.56, respectively. These results indicate that poly(LA)-*block*-PI-*block*-poly(LA) was successfully synthesized by the ring-opening polymerization of LA from both of the hydroxy-terminal groups of PI.

When the ring-opening polymerization of LA was performed at a feed molar ratio of  $[-\text{OH in PI}]_0:[\text{LA}]_0 = 2:200$ , the corresponding ABA triblock copolymer with a composition ratio of PI:poly(LA) = 32:68 (wt:wt) was obtained in 43% yield (Table 1). The polymerization degree of LA at one hydroxy group of PI was 41.2.



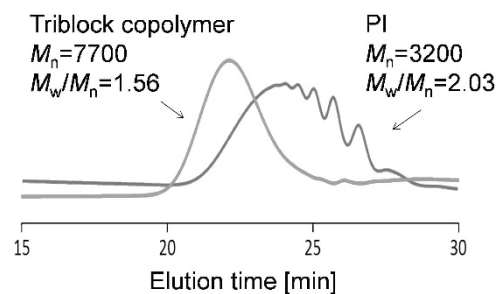
**Figure 4** (a) <sup>1</sup>H and (b) <sup>13</sup>C NMR spectra of poly(LA)-*b*-PI-*b*-poly(LA) measured in DMSO-*d*<sub>6</sub>. Comp. (PI:poly(LA))=48:52 (wt:wt) determined by <sup>1</sup>H NMR spectroscopy.

The  $M_n$  and  $M_w/M_n$  values estimated by SEC analysis were 10 100 and 1.42, respectively.

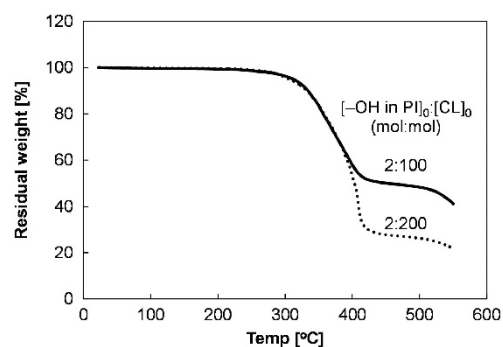
The films prepared from poly(LA)-*block*-PI-*block*-poly(LA) by the solvent casting method were also too brittle to allow investigation of their mechanical properties.

### Thermal properties

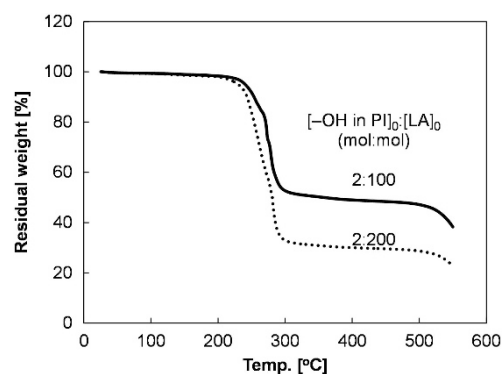
Thermogravimetric analysis was performed to investigate the thermal degradation behavior of ABA triblock copolymers composed of aromatic PIs and aliphatic polyesters. No significant difference in the onset degradation temperature was observed between the two poly(CL)-*block*-PI-*block*-poly(CL) copolymers (Figure 6). Thermogravimetric analysis curve showed a two-step degradation. In the low temperature region, below approximately 300 °C, weight loss of a few percentage points (<5%) was observed for poly(CL)-*block*-PI-*block*-poly(CL). The weight decreased abruptly upon heating at >300 °C because of thermal decomposition of the poly(CL) segment. Then a plateau was reached between approximately 420 °C and 500 °C. Weight loss was observed again at approximately 510 °C, and this was attributed to the decomposition of the PI segment. On the basis of these results, the compositions were calculated to be PI:poly(CL)=48:52 and 27:73 (wt:wt) for feed molar ratios of  $[-\text{OH in PI}]_0$ : $[\text{CL}]_0=2:100$  and 2:200, respectively. These values were close to the



**Figure 5** SEC profile of poly(LA)-*b*-PI-*b*-poly(LA). Comp. (PI:poly(LA))=48:52 (wt:wt) determined by <sup>1</sup>H NMR spectroscopy. A full color version of this figure is available at the *Polymer Journal* online.



**Figure 6** Thermal degradation of poly(CL)-*b*-PI-*b*-poly(CL).



**Figure 7** Thermal degradation of poly(LA)-*b*-PI-*b*-poly(LA).

compositions determined by <sup>1</sup>H NMR spectroscopy. In the case of poly(LA)-*block*-PI-*block*-poly(LA), as shown in Figure 7, the onset degradation temperature of the copolymer prepared at  $[-\text{OH in PI}]_0$ : $[\text{LA}]_0=2:100$  was approximately 6 °C higher than that prepared at  $[-\text{OH in PI}]_0$ : $[\text{LA}]_0=2:200$ , indicating that the ratio of the PI segment to the poly(LA) segment affected the thermal resistance. The results of thermogravimetric analysis also showed a two-step decomposition behavior (that is, the weight losses at approximately 220–310 °C and >510 °C were assigned to the thermal decomposition of poly(LA) and PI, respectively). The corresponding compositions based on the thermal decomposition behavior were calculated to be PI:poly(LA)=49:51 and 30:70 (wt:wt) for  $[-\text{OH in PI}]_0$ : $[\text{LA}]_0=2:100$  and 2:200, respectively. These values were close to the compositions determined by <sup>1</sup>H NMR spectroscopy.

DSC measurement of poly(CL)-*block*-PI-*block*-poly(CL) was performed at –100 °C to 100 °C. Glass transition temperatures ( $T_g$ ) were detected at –63.9 and –64.4 for the triblock copolymers prepared

with  $[-\text{OH in PI}]_0:[\text{CL}]_0=2:100$  and  $2:200$ , respectively. These  $T_g$  values were attributable to the poly(CL) segment.<sup>12</sup> Similarly, DSC measurement of poly(LA)-*block*-PI-*block*-poly(LA) was performed at 0–200 °C.  $T_g$  values of 41.7 °C and 39.7 °C were determined for the copolymers prepared with  $[-\text{OH in PI}]_0:[\text{LA}]_0=2:100$  and  $2:200$ , respectively, and these values were attributable to the poly(LA) segment.<sup>13</sup> These results indicate that a small improvement in heat resistance is achieved by incorporating a PI segment into an aliphatic polyester segment.

## CONCLUSIONS

ABA-type triblock copolymers composed of aliphatic polyesters and aromatic PIs were synthesized in a facile manner by the ring-opening polymerization of CL and LA initiated by hydroxy-terminated aromatic PI. The aliphatic polyester segments of the resultant copolymers showed a small improvement in thermal stability as a result of the introduced aromatic PI.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

## ACKNOWLEDGEMENTS

This research was supported by a Joint Project of Toyohashi University of Technology and Kosen for Education and Research. We thank Professor Dr Tsutomu Takeichi (Toyohashi University of Technology) for helpful discussions. We also thank Professor Dr Haruo Nishida (Kyushu Institute of Technology) for providing L-lactide.

- 1 Lee, S.-R., Park, H.-M., Lim, H., Kang, T., Li, X., Cho, W.-J. & Ha, C.-S. Microstructure, tensile properties, and biodegradability of aliphatic polyester/clay nanocomposites. *Polymer* **43**, 2495–2500 (2002).
- 2 Bordes, P., Pollet, E. & Avérous, L. Nano-biocomposites: biodegradable polyester/nanoclay systems. *Progr. Polym. Sci.* **34**, 125–155 (2009).
- 3 Jimenez, G., Ogata, N., Kawai, H. & Ogihara, T. Structure and thermal/mechanical properties of poly( $\epsilon$ -caprolactone)-clay blend. *J. Appl. Polym. Sci.* **64**, 2211–2220 (1997).
- 4 Messersmith, P. B. & Giannelis, E. P. Synthesis and barrier properties of poly( $\epsilon$ -caprolactone)-layered silicate nanocomposites. *J. Polym. Sci. A Polym. Chem.* **33**, 1047–1057 (1995).
- 5 Kanno, M., Kawakami, H., Nagaoka, S. & Kubota, S. Biocompatibility of fluorinated polyimide. *J. Biomed. Mater. Res.* **60**, 53–60 (2002).
- 6 Ding, H. & Harris, F. W. Synthesis and characterization of novel nylon 6-b-polyimide-b-nylon 6 copolymers. *Pure Appl. Chem.* **67**, 1997–2004 (1995).
- 7 Zuo, M., Xiang, Q. & Takeichi, T. Preparation and properties of novel poly(urethane-imide)s. *Polymer* **39**, 6883–6889 (1998).
- 8 Peters, E. N. Hydroxy terminated polyetherimide oligomers. U.S. Patent No. 4,611,048 (1986).
- 9 Miyata, S. & Nagai, K. Block copolymerization of methyl methacrylate from fluorine-containing polyimide macroinitiator by atom-transfer radical polymerization. *Chem. Lett.* **36**, 1114–1115 (2007).
- 10 Miyata, S., Yoshida, K., Shirokura, H., Kashio, M. & Nagai, K. Solid and thermal properties of ABA-type triblock copolymers designed using difunctional fluorine-containing polyimide macroinitiators with methyl methacrylate. *Polym. Int.* **58**, 1148–1159 (2009).
- 11 Morinaga, H., Imahashi, M. & Takeichi, T. Synthesis of aromatic polyimide bearing long alkyl chains through click reaction. *e-Polymers* **12**, 1016–1022 (2012).
- 12 De Juana, R. & Cortazar, M. Study of the melting and crystallization behavior of binary poly( $\epsilon$ -caprolactone)/poly(hydroxy ether of bisphenol A) blends. *Macromolecules* **26**, 1170–1176 (1993).
- 13 Helminen, A., Korhonen, H. & Seppälä, J. V. Biodegradable crosslinked polymers based on triethoxysilane terminated polylactide oligomers. *Polymer* **42**, 3345–3353 (2001).