Preparation of Chain-Extended Poly(hexamethylene/pentamethylene carbonate)s and Their Block Copolymerization with Poly-L-lactide into Partly Biobased Thermoplastic Elastomers

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Abstract: A commercially available carbonate oligomer, poly(hexamethylene/ pentamethylene carbonate) (PHPC), was found to involve various minor units that had been formed during the ester-exchanging polycondensation of ethylene carbonate and a mixture of 1,6-hexanediol and 1,5-pentanediol. This PHPC oligomer was chain-extended by using diphenyl carbonate as chain extender and then subjected to tin-catalyzed ring-opening polymerization of L-lactide to prepare ABA tri-block copolymers consisting of poly-L-lactide (PLLA) and PHPC as the hard A and soft B blocks, respectively. With the chain-extended PHPC as the macro-initiators, the molecular weights of the resultant copolymers became significantly higher even at increased contents of PHPC. The tri-block copolymers obtained were fabricated into polymer films by solution casting, and their properties were analyzed. It was revealed that the tri-block copolymers PLLA-PHPC-PLLA can be novel thermoplastic elastomers that are environmentally friendly in terms of utilization of carbon dioxide as feedstock.

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1. Introduction

Aliphatic polycarbonates (APC) are a class of biodegradable polymers that are attracting great interest of materials engineers because of their good biocompatibility and degradation to less acidic products.^[1-4] There are many types of APC consisting of different alkanediol units. Those consisting of diols of middle carbon-chain length (C5 - C8) are used as soft segments having low T_g , while those consisting of alicyclic building blocks can be applied as hard segments.^[5-10] The commercially available poly-(hexamethylene carbonate) (PHMC) diol and poly-(hexamethylene/ pentamethylene carbonate) (PHPC) diol, having low molecular weight and bis-hydroxyl terminals, are used as soft segments of polyurethane.^[11-13] Recently their environmental friendliness is highlighted because they are synthesized from ethylene carbonate (EC) manufactured by the use of carbon dioxide as feedstock.^[14-16] With this nature in mind, we have demonstrated that PHMC diol can be used as a macro-initiator of the ring-opening polymerization (ROP) of L-

lactide to prepare tri-block copolymers comprising poly-L-lactide (PLLA) and PHMC (PLLA-PHMC-PLLA) that have both biobased and CO₂-originated characters.^[17] Since PHMC is crystalline at ambient temperature, the properties of the PLLA-PHMC-PLLA copolymers may be significantly influenced by the temperature change. In the present study, therefore, we use amorphous PHPC diol as the macro-initiator to obtain similar PLLA-APC block copolymers, and for which the elastomeric properties are evaluated.

Here, we first analyze the microstructure of the PHPC oligomer that is industrially produced by the reaction of an alkanediol mixture and EC. Since the synthetic procedure using EC as the starting carbonate source is different from the ordinary polycondensation of diphenyl carbonate (DPC) and diols, the resultant polycarbonate is known to involve minor units different from the diol units. The well-characterized PHPC oligomer is then chain-extended with DPC as chain extender to obtain high molecular weight polymers, and which were used as the macroinitiators of the ROP of L-lactide to prepare PLLA-PHPC-PLLA tri-block copolymers (Scheme 1). The PLLA-PHPC-PLLA block copolymers obtained are finally characterized in detail to

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Scheme 1 Chain-extension of PHPC and the following synthesis of tri-block copolymers PLLA-PHPC-PLLA and PDLA-PHPC-PDLA.

confirm their elastomeric nature that is suitable for use as environmentally friendly thermo-plastic elastomer.

2. Experimental Section

2.1 Materials

L-lactide was supplied by Musashino Chemical Research Institute, Ltd. (Tokyo, Japan) and used as received. Its optical purity was 99.8 %ee. An oligomeric sample of PHPC was purchased from Asahi Kasei Chemicals Co., Ltd. Its number-average molecular weight (M_n) was reported to be 2000 Da. Its ^1H -NMR spectroscopy revealed that the real M_n (nmr) was 2150, being only slightly different from the reported one. Its gel permeation chromatography (GPC) showed that the number- ($M_n(\text{gpc})$) and weight-average ($M_w(\text{gpc})$) molecular weights were 3000 and 4500 Da, respectively, having a dispersity of $M_w/M_n=1.5$. Diphenyl carbonate (DPC) and tin octoate ($\text{Sn}(\text{Oct})_2$) were purchased from Nakalai Tesque Co. Ltd. (Kyoto, Japan). $\text{Sn}(\text{Oct})_2$ was purified by distillation under high vacuum and dissolved in a distilled toluene in a concentration of 0.1 g/ml for use as the catalyst. The other solvents such as dichloromethane (CH_2Cl_2) and methanol were commercially supplied.

2.2 Measurements

600 MHz ^1H and 125 MHz ^{13}C NMR spectra were recorded on a Bruker UltraShield Plus spectrometer.

Deuterated chloroform containing tetramethylsilane (TMS : 0.03 vol%) as the internal reference was used as the solvent. Both $M_n(\text{gpc})$ and $M_w(\text{gpc})$ were determined by GPC using a Shimadzu GPC system consisting of an LC-20AD pump and an RID10A refractive index detector. Samples were eluted out at 40 °C with chloroform as eluent at a flow rate of 0.25 mL/min through a combination of TOSOH TSKgel Super HZM-N and Super HZ-H columns. The molecular weights were calibrated with polystyrene standards from 500 to 100,000 Da. Differential scanning calorimetry (DSC) was conducted on a Perkin Elmer Diamond DSC thermal analyzer under a nitrogen flow of 20 ml/min at a heating rate of 10 °C /min for about 5.0 mg of a sample. The sample was heated from -60 to 180 °C in the first scan, quenched to -60 °C, and heated again from -60 to 180 °C in the second scan. The melting temperature (T_m) and glass transition temperature (T_g) of the sample polymer were determined from the curve of the second scan. Tensile tests of polymer films were done on a tensile testing machine (STA-1150, ORIENTEC, Co., Ltd., Japan) at room temperature with a gauge length of 10 mm at a crosshead speed of 10 mm/min. The data obtained over four test specimens were averaged for each measurement.

2.3 Chain extension of aliphatic polycarbonates

A certain amount of the commercially available PHPC oligomer ($M_n=2150$) (300 g, 0.14 mol) was mixed

with a slightly smaller molar amount of DPC (24.3 g, 0.11 mol) in a reactor. With this feed ratio (DPC/PHPC=0.81), the theoretical M_n of the resulting PHPC ($M_{n(th)}$) ought to be about 20,000 Da under a complete polycondensation reaction. The mixture was gradually heated to 200 °C without any catalyst added, and the pressure was slowly reduced to 20 Pa in a period of 15 min with the generated phenol removed. After reaching the final pressure, the mixture was kept stirring for 1 h. The viscosity of the mixture gradually increased with progress of the polycondensation. The rubbery polymer finally obtained after cooling down the reaction temperature was taken out from the flask and directly used for the subsequent copolymerization. Another PHPC sample having an $M_{n(th)}$ of 8,300 Da was also prepared likewise by changing the DPC-to-PHPC feed ratio to 0.59. The PHPC samples thus obtained are called PHPC Xk where X denotes their M_n in kDa, for example, PHPC 2.2k, PHPC 10.3k, and PHPC 22.4k where the X value ought to be approximate one near the real value.

PHPC 2.2k : ^1H NMR (600 MHz, in CDCl_3 , Figure 1) : for the main repeat units, δ : 1.42 (C_6 , $\gamma\text{-CH}_2$ of HMG), 1.47 (C_5 , $\gamma\text{-CH}_2$ of HMG), 1.75 (B_5 and B_6 , $\beta\text{-CH}_2$ of HMG and PMG), and 4.21 (A_5 and A_6 , $\alpha\text{-CH}_2$ of HMG and PMG) ; for the sub units, δ : 3.45 ($(f_1+f_1')+g_1'$, $\text{OCH}_2\text{-}$ of DHG and DPG and PHG units), 3.65 ($(E_5^*+F_6^*)+(e_3+e_3')+d_2$, $\text{OCH}_2\text{-}$ of DEG and $\text{OCH}_2\text{CH}_2\text{-}$ of EHG and EPG), 3.72 ((e_2+e_2') , $\text{OC(O)OCH}_2\text{CH}_2\text{O-}$ of EHG and EPG), and 4.3 ($(c_5'+c_6)+d_1+(e_1+e_1')$, $\text{OC(O)OCH}_2\text{CH}_2\text{O-}$ of EG, DEG, EHG, and EPG). ^{13}C NMR (125 MHz, in CDCl_3 , Fig. 2) : for the main repeat units, δ : 22.1 (C_5 , $\gamma\text{-CH}_2$ of PMG), 25.4 (C_6 , $\gamma\text{-CH}_2$ of HMG), 28.3 (B_5 , $\beta\text{-CH}_2$ of PMG), 28.6 (B_6 , $\beta\text{-CH}_2$ of HMG), 67.6 (A_5 , $\text{OCH}_2\text{-}$ of PMG), 67.8 (A_6 , $\text{OCH}_2\text{-}$ of HMG), and 155.4 (D , OC(O)O of HMG and PMG) ; for the terminal units, δ 22.1 (C_5^* , $\text{HO-}\gamma\text{-CH}_2\text{-}$ of PMG), 25.5 (C_6^* or D_6 , $^*\text{HO-}\gamma$ (or ϵ)- $\text{CH}_2\text{-}$ of HMG), 28.5 (B_5^* , $-\text{CH}_2\text{CH}_2\text{OC(O)O}$ of PMG), 28.7 (B_6^* , $-\text{CH}_2\text{CH}_2\text{OC(O)O}$ of HMG), 32.3 (D_5^* , $\text{HO-CH}_2\text{CH}_2\text{-}$ of PMG), 32.6 (E_6^* , $\text{HO-CH}_2\text{CH}_2\text{-}$ of HMG), 62.6 (E_5^* , $\text{HOCH}_2\text{-}$ of PMG), 62.7 (F_6^* , $\text{HOCH}_2\text{-}$ of HMG), and 67.9 (A_6^* , $-\text{CH}_2\text{-OC(O)O}$ of HMG) ; for the sub units, δ : 71.1 (c_5 , $-(\text{CH}_2)_5\text{OC(O)OCH}_2\text{-}$ of EG), 71.3 (c_6 , $-(\text{CH}_2)_6\text{OC(O)OCH}_2\text{-}$ of EG), 66.7 (d_2 , $-\text{CH}_2\text{OCH}_2\text{-}$ of DEG), 69.9 (d_1 , $\text{OC(O)OCH}_2\text{-}$ of DEG), 25.7 (e_4 , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of EHG), 29.4 (e_3 , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of EHG), 66.9 (e_2 , $\text{OC(O)OCH}_2\text{-CH}_2\text{O}$ of EHG), 68.4 (e_1 , $\text{OC(O)OCH}_2\text{-}$ of EHG), 22.4 (e_3' , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of EPG), 25.2 (e_4' , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of EPG), 29.2 (e_3' , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of EPG), 67.2 (e_2' , $\text{OC(O)OCH}_2\text{CH}_2\text{O}$ of EPG), 68.5 (e_1' , $\text{OC(O)OCH}_2\text{-}$ of EPG), 25.9 (f_3 , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of DHG), 28.3 (f_3 , $\text{OCH}_2\text{-}$

$\text{CH}_2\text{CH}_2\text{-}$ of DHG), and 68.0 (f_1 , $\text{OCH}_2\text{-}$ of DHG), 26.0 (f_3' , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of DPG), and 68.0 (f_1' , $\text{OCH}_2\text{-}$ of DPG).

2.4 Synthesis of ABA triblock copolymers

A typical copolymerization procedure was as follows. At first, certain amounts of L-lactide (1.1 g, 7.4×10^{-3} mol) and PHPC 22.4 k (0.9 g, 4.0×10^{-5} mol) were placed in a glass reactor and dried in vacuum at 40 °C for 2 h and at 85 °C for 1 h. The mixture was then heated at 180 °C under stirring for 10 min, and a portion of the catalyst solution (10 μL , 2.5×10^{-6} mol of $\text{Sn}(\text{Oct})_2$) in toluene was added to it. The mixture was kept stirred at 180 °C for 40 min. Then, the product was cooled, dissolved in a dichloromethane, and reprecipitated into an excess methanol. The precipitates were isolated by filtration and dried in vacuum at 80 °C for at least 6 h to obtain PLLA-PHPC-PLLA (5.6k-22.4k-5.6k in block length as described below). Other block copolymers having different compositions were prepared by changing the L-lactide to PHPC ratio in the feed with the PHPC samples having different M_n . The block lengths and compositions of the resultant PLLA-PHPC-PLLA are shown as 8.9k-10.3k-8.9k for which the average M_n values in kDa of the blocks are connected in series.

PLLA-PHPC-PLLA 2.2k : ^1H NMR (600 MHz, in CDCl_3 , Figure 5) : for the main repeat units, δ : 1.42 (C_6 , $\gamma\text{-CH}_2$ of HMG), 1.47 (C_5 , $\gamma\text{-CH}_2$ of PMG), 1.56-1.6 (I , CH_3 of the lactate unit), 1.75 (B_5+B_6 , $\beta\text{-CH}_2$ of HMG and PMG), and 4.21 (A_5+A_6 , $\alpha\text{-CH}_2$ of PMG and HMG), 4.35 (G^* , CH-OH of the terminal lactate), and 5.16 (H , CH of the lactate unit) ; for the sub units, δ : 3.45 ($(f_1+f_1')+g_1'$, $\text{OCH}_2\text{-}$ of (DHG, DPG, PHG), 3.65 ($(e_3+e_3')+d_2$, $\text{OCH}_2\text{-}$ of DEG and $\text{OCH}_2\text{CH}_2\text{-}$ of EHG and EPG), 3.72 ((e_2+e_2') , $\text{OC(O)OCH}_2\text{CH}_2\text{O-}$ of EHG and EPG), and 4.3 ($(c_5'+c_6)+d_1+(e_1+e_1')$, $\text{OC(O)OCH}_2\text{CH}_2\text{O-}$ of EG, DEG, EHG, and EPG). ^{13}C NMR (125 MHz, in CDCl_3 , Fig. 6) : for the main repeat units, δ : 22.1 (C_5 , $\gamma\text{-CH}_2$ of PMG), 25.4 (C_6 , $\gamma\text{-CH}_2$ of HMG), 28.3 (B_5 , $\beta\text{-CH}_2$ of PMG), 28.6 (B_6 , $\beta\text{-CH}_2$ of HMG), 67.6 (A_5 , $\text{OCH}_2\text{-}$ of PMG), 67.8 (A_6 , $\text{OCH}_2\text{-}$ of HMG), 69.0 (H , CH of the lactate unit), 69.2 (G^* , CH-OH of the terminal lactate) and 155.4 (D , OC(O)O of PMG and HMG) ; for the sub units, δ : 71.1 (c_5 , $-(\text{CH}_2)_5\text{OC(O)OCH}_2\text{-}$ of EG), 71.3 (c_6 , $-(\text{CH}_2)_6\text{OC(O)OCH}_2\text{-}$ of EG), 66.7 (d_2 , $-\text{CH}_2\text{OCH}_2\text{-}$ of DEG), 69.9 (d_1 , $\text{OC(O)OCH}_2\text{-}$ of DEG), 25.7 (e_4 , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of EHG), 29.4 (e_3 , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of EHG), 65.2 (E_5' , $\text{HOCH}_2\text{-}$ of EHG), 65.3 (F_6' , $\text{HOCH}_2\text{-}$ of EHG), 66.9 (e_2 , $\text{OC(O)OCH}_2\text{-CH}_2\text{O}$ of EHG), and 68.4 (e_1 , $\text{OC(O)OCH}_2\text{-}$ of EHG), 22.4 (e_3' , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of EPG), 25.2 (e_4' , $\text{OCH}_2\text{CH}_2\text{-}$ of EPG), 29.2 (e_3' , $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-}$ of EPG), 67.2

(e₂', OC(O)OCH₂CH₂O of EPG), 68.5 (e₁', OC(O)OCH₂- of EPG), 25.9 (f₃, OCH₂CH₂CH₂- of DHG), 28.3 (f₂, OCH₂CH₂CH₂- of DHG), and 68.0 (f₁, OCH₂- of DHG), 26.0 (f₃', OCH₂CH₂CH₂- of DPG), and 68.0 (f₁', OCH₂- of DPG).

2.5 Preparation of cast films

Each of the copolymers was dissolved in dichloromethane in a concentration of 0.2 g / 3.0 mL (5.0 wt%). The resultant copolymer solution was cast into a Petri dish and solidified by evaporating the dichloromethane in a semi-airtight container in a period of 12 h. The solidified film was then peeled off and thoroughly dried in vacuum at 40 °C for 8 h.

3. Results and Discussion

3.1 Fine structure of PHPC 2.2k

The commercially available sample of PHPC 2.2k is manufactured by the ester exchange reaction of EC and an excess amount of a mixture of hexamethylene glycol (HMG) and 1,5-pentamethylene glycol (PMG), respectively (Scheme 2). Here, both bis(6-hydroxyhexyl) carbonate and bis(5-hydroxypentyl) carbonates are first produced with ethylene glycol (EG) eliminated, and then they are copoly-condensed into PHPC by eliminating the excess HMG and PMG. We have found out that the PHPC 2.2k involves several ether-diol units that are formed by the decarboxylic ether formation of the hydroxyl and carbonate groups. The involvement of these minor units is less than 2.3 % in unit molar ratio as PHMC 2.2k that is also synthesized by the same

procedure.

Figure 1 shows a typical ¹H-NMR spectrum of PHPC 2.2k. In addition to the four main-chain signals (A₆, B₆, C₆ : HMG and A₅, B₅, C₅ : PMG units), several small signals are detected around δ 3.3-3.7 ppm and 4.25 ppm. The main-chain unit ratio (x : y) of pentamethylene carbonate (PMG : x) and hexamethylene carbonate (HMG : y) is 1 : 1.25 as determined by the integral ratios of signals C₆ (two methylenes) and C₅ (one methylene) from Figure 1A.

As indicated in the expanded spectrum (Figure 1A'), PHPC 2.2k contains sub-units. Scheme 3 shows the major and minor units involved together with their signal assignments. While the largest signal (E₅*+F₆*) at δ 3.65 ppm is assigned to the terminal hydroxyl-methylene protons (HO-CH₂-), the other small signals are attributed to minor units formed by the aforementioned side reactions. The signal (c+d₁+e₁+e₁') at the lowest magnetic field (δ 4.35 ppm) is assigned to the carbonate OC(O)O-CH₂- protons of the EG units derived from the EC monomer. The upper-field signals (e₂+e₂', e₃+e₃'+d₂, f₁+f₁'+g₁') are reasonably assigned to the ether O-CH₂- protons of the ether-diol units. Namely, the units of dipentamethylene glycol (DPG), ethylenoxy-pentamethylene glycol (EPG), and pentamethylenoxy-hexamethylene glycol (PHG) ought to be involved in addition to diethylene glycol (DEG), dihexamethylene glycol (DHG), and ethylenoxy-hexamethylene glycol (EHG) units (See Experimental).

Figure 2 shows a 125 MHz ¹³C NMR spectrum of PHPC 2.2k. In addition to the signals of the main-chain

Scheme 2 Polymerization scheme of EC and a mixture of HMG and PMG to obtain PHPC 2.2k.

Fig. 1 (A) A typical 600 MHz ^1H NMR spectrum of PHPC 2.2k and (A') its expanded spectrum in the magnetic field from δ 3.2 to 4.5 ppm.

Fig. 2 (A) A typical 125 MHz ^{13}C NMR spectrum of PHPC 2.2k and its expanded spectra in the magnetic field around (A') δ 66–72 ppm and (A'') δ 21–31 ppm.

Scheme 3 Major and minor units involved in the original PHPC 2.2k with their ^1H and ^{13}C signal assignments (cf. Figures 1 and 2).

repeat units (A_6 , B_6 , C_6 , D_6 : HMG and A_5 , B_5 , C_5 , D_5 : PMG units), the signals due to the 6-hydroxyhexamethylene (A_6^* , B_6^* , E_6^* , F_6^*) and 5-hydroxyhexamethylene (B_5^* , C_5^* , D_5^* , E_5^*) carbonate

terminals are detected. The other small signals are assigned to the minor units involved at the EG units (c_5 and c_6), the DEG units (d_1 and d_2), the EHG units (e_1 , e_2 , e_3 and e_4), the EPG units (e_1' , e_2' , e_3' , e_4' and e_5'), the

DHG units (f_1 , f_2 and f_3), and the DPG units (f_1' and f_3') (See Experimental). The PHG signals duplicate with the above signals, maintaining the following relations : $g_1=f_1$, $g_2=f_2$, $g_3=f_3$, $g_1'=f_1'$, $g_2'=f_2'$, $g_3'=f_3'$. It is therefore clear that the PHPC 2.2k sample involves the carbonate units of EG and ether-diols of DEG, EHG, EPG, DPG, DHG and DPG in addition to the major HMG and PMG units. The formation of these ether units is induced during the ester-exchange reaction of the hydroxyl terminals with EC.

3.2 Preparation of chain-extended PHPC

PHPC 2.2k, well characterized as above, was chain-extended by using DPC as the chain extender at different DPC/ PHPC 2.2k ratios of 0.59 and 0.81 in the feed. The polycondensation proceeded efficiently with phenol eliminated without addition of catalyst, probably because the catalyst utilized in the synthesis of PHPC 2.2k may have remained in the oligomer. The ^1H NMR spectra of the final products showed much smaller signals due to the terminal HO-CH_2 (at δ 3.84 ppm) than those of PHPC 2.2k, while the minor signals around δ 3.3-3.7 ppm and 4.3 ppm were kept identical with the original one. Figure 3 compares the expanded ^{13}C NMR spectra of the chain-extended PHPCs. It is evident that the carbon signals of the terminal groups at δ 62.7 ($\beta\text{-HOCH}_2$, E_5^*) and 62.8 ($\alpha\text{-HOCH}_2$, F_6^*) ppm become weaker with increasing the molecular weight of PHPC with the other signals due to the minor units unchanged. It is also shown that the higher the molecular weight of PHPC, the weaker the carbon signals of the β -terminal groups at δ 32.5 (for $\text{HO-(CH}_2)_5\text{-}$, E_6^*) and δ 32.7 (for $\text{HO-(CH}_2)_6\text{-}$, D_5^*) ppm. These data support the chain-extended structure of PHPC

having telechelic hydroxyl tails.

Figure 4 shows the GPC curves of the PHPC samples obtained at different DPC / PHPC 2.2k ratios in the feed. Each curve shows a unimodal curvature, and its peak top shifts to a higher molecular weight region with increasing the DPC ratio in both cases. It is therefore confirmed that the molecular weight of the chain-extended PHPC can be well controlled by changing the DPC ratio in the feed. Table 1 summarizes the typical results of the chain extension. The $M_n(\text{nmr})$ value of each PHPC Xk is comparable to the $M_n(\text{th})$ estimated from the DPC / PHPC 2.2k ratios in the feed, supporting the efficient molecular weight control. The $M_n(\text{nmr})$ values are almost half the $M_n(\text{gpc})$ values, probably because of the different hydrodynamic volumes of PHPC samples compared to that of the reference polymer.

3.3 Synthesis of ABA tri-block copolymers

The PHPC Xk samples obtained above were used as the macro initiators in the ROP of L-lactide to prepare the tri-block copolymers of PLLA-PHPC-PLLA (Scheme 1). The polymerization proceeded very quickly in bulk state by the catalysis of $\text{Sn}(\text{Oct})_2$ to give PLLA-PHPC-PLLA in high yield. Figure 5 shows a typical ^1H NMR spectrum of a PLLA-PHPC-PLLA product prepared at PHPC 22.4k / L-lactide = 20/10 in weight ratio, i.e., targeting 5.6k-22.4 k-5.6k in an average M_n series of the constituent blocks. In addition to the signals (H and I) of the PLLA units and those of the PHPC (A_5 , B_5 , and C_5 for PMG units) and PHMC units (A_6 , B_6 , and C_6 for HMG units), a small signal (G^*) due to the hydroxyl-methine proton of the PLLA block terminals is detected at δ 4.35 ppm. The

Fig. 3 Expanded 125 MHz ^{13}C NMR spectra of PHPC having different M_n , (a) PHPC 2.2k, (b) PHPC 10.3k, and (c) PHPC 22.4k.

Fig. 4 GPC curves of (a) PHPC 2.2k (control), (b) PHPC 10.3k, and (c) PHPC 22.4k. The curves were normalized for comparison.

original signal due to the hydroxy-methylene protons of PHPC 22.4k has completely been replaced by this signal, supporting the chain elongation of PLLA from the PHPC terminals. Figure 6 compares the ^{13}C NMR spectra of a tri-block copolymer [PLLA-PHPC-PLLA (3.6k-22.4k-3.6k)] and the corresponding macro-initiator PHPC 22.4k. It is confirmed that the signals due to the terminal hydroxy-methylene of PHPC (E_5^* at δ 62.6 and F_6^* at δ 62.7 ppm) have been replaced by the ester-methylene signal at lower magnetic field (E_5' at δ 65.2 and F_6' at δ 65.3 ppm) in the copolymer, supporting that the two types of PHPC tails have been connected with PLLA chains. All of these data demonstrate that the PHPC terminals can quantitatively initiate the ROP of L-lactide to form the tri-

block copolymers in a controllable manner.

Table 2 compares the integral ratios of the representative proton signals from the ^1H NMR spectra of PHPC 2.2k (Figure 3), PHPC 22.4k (not indicated), and PLLA-PHPC-PLLA (3.6k-22.4k-3.6k) (Figure 5) after the normalization in regard to the signal at δ 3.72 (e_2+e_2'). Since the integral ratios of the signals due to the minor units ($f_1+f_1'+g_1'$, $E_5^*+F_6^*+e_3+e_3'+d_2$, e_2 , and $c_5+c_6+d_1+e_1+e_1'$) are almost similar to each other among the three samples, the minor units have been retained in the chain-extended PHPC and the block copolymers. If all the hydroxyl terminals of PHPC 22.4k are linked with PLLA chains, the signal of the terminal hydroxy-methylene protons (E_5^* and F_6^*) of PHPC 20k is to be replaced by

Table 1 Results of the chain extension of PHPC 2.2k with DPC as the chain extender^{a)}.

APC	DPC/ PHPC 2k in feed	M_n (th) ^{b)}	M_n (nmr)	M_n (gpc) ^{c)}	PDI^c (M_w/M_n)
PHPC 2.2k	(control)	-	2,150	3,000	1.5
PHPC 10.3k	0.59	8,300	10,300	19,500	2.0
PHPC 22.4k	0.81	20,500	22,400	44,800	2.1

a) The polymer recovery > 99%

b) Estimated from the DPC / diol ratio in the feed

c) Measured in CHCl_3 at 40 °C.

Fig. 5 A typical 600 MHz ^1H NMR spectrum of PLLA-PHPC-PLLA (3.6k-22.4k-3.6k) (a) with an expanded spectrum in the region of δ 3.3-4.5 ppm (b).

the hydroxy-methine signal (G^* at δ 4.35 ppm) of the PLLA block terminals of PLLA-PHPC-PLLA(3.6k-22.4k-3.6k). Therefore, the signal around δ 3.65 ppm is assigned only to $(e_3+e_3') + d_2$ in PLLA-PHPC-PLLA(3.6k-22.4k-3.6k), and the following relation is established.

$$\left[\int \text{PHPC}(\delta 3.65) - \int \text{PLLA-PHPC-PLLA}(\delta 3.65) \right] / 2 \\ \doteq \int \text{PHPC}(\delta 4.35)$$

The M_n (DP) of PHPC can also be calculated by comparison of the integral ratios $(A_5+A_6) / (E^*+F^*)$, being 2,150 (15.5) and 22,400 (161.2) for PHPC 2.2k and PHPC 22.4k, respectively. They are almost correspondent to the $M_n(\text{th})$ values described above (the average molecular weight of the two repeating units of PHPC is estimated to be 139). The relative integral ratios of the signals c and d can also be estimated as below, assuming $e_1+e_1' = e_2+e_2' = e_3+e_3'$ and $d_1 = d_2$

$$(c_5'+c_6) = \{(c_5'+c_6)+d_1+(e_1+e_1')\}_{\text{PHPC20k}} - \{(e_3+e_3')+d_2\}_{\text{copolymer}} \\ d_1 = \{(e_3+e_3')+d_2\}_{\text{copolymer}} - (e_2+e_2')$$

Accordingly, the minor unit ratios of EG, DEG, (EHG+EPG), and (DHG+DPG) are roughly determined to be as follows:

$$\text{EG : DEG : (EHG+EPG) : (DHG+DPG)} \\ = (c_5'+c_6) : d_1 : (e_1+e_1') : (f_1+f_1') = 0.4 : 1.1 : 1 : 1.8.$$

The unit molar percentages of these minor units in PHPC 2.2k are therefore 0.0022, 0.0061, 0.0055, and 0.0099 (in unit ratio) for EG, DEG, (EHG+EPG), (DHG+DPG), respectively, and the total content of the minor units is assumed to be 2.3 unit mol%.

Figure 7 shows the GPC curves of the PLLA-PHPC-PLLA prepared with PHPC 22.4k at different PHPC/PLLA ratios. Each curve shows a unimodal curvature owing to the relatively narrow molecular weight distribution, and its peak shifts to higher molecular weight region with increasing the PLLA block length, suggesting the controlled block copolymerization.

Table 3 summarizes the results of the copolymerization. When PHPC 10.3k is used as the macro-initiators, the block lengths of the resultant copolymers are almost identical to those estimated from the feed ratios and monomer conversions. Their $M_n(\text{gpc})$ values are significantly larger than $M_n(\text{nmr})$ values because of the difference in hydrodynamic volume between the copolymers and the reference polymers. However, their increasing orders with increasing the PLLA composition are correspondent to each other. It should be noted that the molecular weight distribution of

Fig. 6 Typical 125 MHz ^{13}C NMR spectra of (a) PHPC 22.4k and (b) PLLA-PHPC-PLLA (3.6k-22.4k-3.6k).

Table 2 ^1H NMR signals attributed to the minor units of PHPC 2.2k, PHPC 22.4k and PLLA-PHPC-PLLA (3.6k-22.4k-3.6k)^a.

PHPC 2.2k			PHPC 22.4k			PLLA-PHPC-PLLA (3.6k-22.4k-3.6k)		
Signal	ppm	Integral ratio	Signal	ppm	Integral ratio	Signal	ppm	Integral ratio
(A ₅ +A ₆)	4.12	150.5	(A ₅ +A ₆)	4.12	177.3	(A ₅ +A ₆)	4.12	216.6
(f ₁ +f _{1'})+g _{1'}	3.45	1.5	(f ₁ +f _{1'})+g _{1'}	3.45	1.8	(f ₁ +f _{1'})+g _{1'}	3.45	2.0
(E ₅ *+F ₆ *)+(e ₃ +e _{3'})+d ₂	3.65	11.9	(E ₅ *+F ₆ *)+(e ₃ +e _{3'})+d ₂	3.65	3.2	(e ₃ +e _{3'})+d ₂	3.65	2.1
(e ₂ +e _{2'})	3.72	1.0	(e ₂ +e _{2'})	3.72	1.0	(e ₂ +e _{2'})	3.72	1.0
(c _{5'} +c ₆)+d ₁ +(e ₁ +e _{1'})	4.3	1.9	(c _{5'} +c ₆)+d ₁ +(e ₁ +e _{1'})	4.3	2.5	(c _{5'} +c ₆)+d ₁ +(e ₁ +e _{1'})	4.3	2.9
						G*	4.35	0.6
						H	5.16	30.4
DP=(A ₅ +A ₆)/(E ₅ *+F ₆ *)								
(PHPC)			15.5			161.2		
DP=H / G*								
(PLLA)						50.7		

a) The integral ratios were normalized in regard to the signal at δ 3.72 (e₂+e_{2'}).

Table 3 Results of the synthesis of tri-block copolymers PDLA-PHPC-PDLA.

PHPC	Feed ratio	Yield	Conversion	M _n ^a	M _n ^b	Composition	PHMC content	M _n ^c	PDI
(Mn)	PLLA-PHPC-PLLA	(%)	(%)	(th)	(nmr)	PLLA-PHPC-PLLA	(wt%)	(gpc)	(gpc)
10.3k	2.5k-10.3k-2.5k	81	83	15300	14300	2.0k-10.3k-2.0k	72	24500	1.6
	5.3k-10.3k-5.3k	89	91	20900	19700	4.7k-10.3k-4.7k	52	25200	1.7
	8.9k-10.3k-8.9k	90	93	28100	26300	8.0k-10.3k-8.0k	39	32100	1.6
22.4k	5.6k-22.4k-5.6k	87	74	33600	30700	3.6k-22.4k-3.6k	76	48000	1.8
	9.8k-22.4k-9.8k	85	86	42000	39300	7.9k-22.4k-7.9k	59	68200	1.7
	20.3k-22.4k-20.3k	82	88	63000	48100	12.3k-22.4k-12.3k	48	71900	1.8

a) Estimated from the monomer/ macro-initiator ratio in feed

b) Determined by ¹H-NMRc) Determined by GPC (in CHCl₃) **Fig. 7** Normalized GPC curves of PLLA-PHPC-PLLA : (d) 3.6k-22.4k-3.6k, (e) 7.9k-22.4k-7.9k, and (f) 12.3k-22.4k-12.3k.

the copolymers is rather narrower than that of macro-initiators, because of the homogeneous chain-extension from the terminals of the latters to make the M_n larger. On the other hand, the copolymers prepared from PHPC 22.4k consist of PLLA blocks having slightly shorter chain lengths than the theoretical ones estimated from the feed ratio, because of the relatively low monomer conversion remaining around 80 % in the copolymerization. In this series, again, the increasing tendencies of the M_n (nmr) and M_n (gpc) are correspondent to each other. All of these data suggest that the block lengths of the tri-block copolymers can be controlled by changing the molecular

weight of the macro-initiator (center block) and the monomer/ macro-initiator ratio in the feed.

3.4 Thermal properties of the copolymers

Table 4 summarizes the thermal properties of the PLLA-PHPC-PLLA samples analyzed by DSC. In the PLLA-PHPC-PLLA triblock copolymers having PHPC (10.3 kDa), the T_m and ΔH_m due to the crystal fusion of PLLA become higher with increasing the PLLA composition. In contrast, in the PLLA-PHPC-PLLA triblock copolymers having PHPC (22.4 kDa), the ΔH_m value becomes higher with increasing the PLLA composition, while the change in T_m is small. The T_m and

Table 4 Thermal properties of the PLLA-PHPC-PLLA tri-block copolymers (2nd heating).

Sample	PHPC contents	T _g	T _c	ΔH _c	T _m	ΔH _m	Crystallinity ^a
PLLA-PHPC-PLLA	(%)	(°C)	(°C)	(J g ⁻¹)	(°C)	(J g ⁻¹)	(%)
2.0k-10.3k-2.0k	72	-24.7	68.2	3.4	134.1	3.4	3.7
4.7k-10.3k-4.7k	52	-35.9 / 40.3	65.7	10.6	146.6	16.8	18.1
8.0k-10.3k-8.0k	39	-44.8 / 50.6	79.1	12.2	153.4	19.6	21.1
3.6k-22.4k-3.6k	76	-38.0 / 45.5	-	-	156.6	8.2	8.8
7.9k-22.4k-7.9k	59	-45.1 / 54.5	-	-	159.4	11.9	12.8
12.3k-22.4k-12.3k	48	-46.1 / 57.8	-	-	158.1	17.4	18.7

a) Determined from ΔH_m in reference to the specific ΔH_m of hc crystals (93 J g⁻¹).

ΔH_m values are higher in the copolymers of PHPC-22.4k than the copolymers of PHPC-10.3k at similar PHPC/PLLA ratios (4.7k-10.3k-4.7k and 12.3k-22.4k-12.3k), because the block length of PLLA becomes longer in the former. Since PHPC is amorphous, it can aid the PLLA blocks to crystallize by working as plasticizer, increasing the crystallinity even at lower PLLA contents (2.0k-10.3k-2.0k and 3.6k-22.4k-3.6k). The copolymers of PHPC (22.4k), having a higher molecular weight and better plasticizing effect, exhibit no crystallization exotherm even in the second scan, because of the spontaneous crystallization after the quenching of the 1st-scanned samples. These results indicate that the short PLLA and PHPC block chains (having lower M_n) are compatible while the longer PHPC and PLLA blocks (having higher M_n) are more likely phase-separated.

The PLLA-PHPC-PLLA copolymers consisting of PHPC (22.4k) as well as PLLA-PHPC-PLLA (4.7k-10.3

k-4.7k) and PLLA-PHPC-PLLA (8.0k-10.3k-8.0k) exhibit two T_g values attributable to the PLLA and PHPC blocks, whereas the PLLA-PHPC-PLLA (2.0k-10.3k-2.0k) shows only one T_g. The appearance of the two T_g is compatible with the aforementioned phase separation of the two blocks. It is therefore confirmed that the longer the PLLA blocks, the poorer the compatibility of PLLA and PHPC.

3.5 Mechanical properties of the copolymer films

The PLLA-PHPC-PLLA copolymers comprising both PHPC 10.3k and 22.4k were fabricated into polymer films by solution casting. The tensile data of the resultant PLLA-PHPC-PLLA films are summarized in Table 5. The copolymer films having PHPC compositions higher than 50 wt% exhibit elastomeric behavior, whereas the other copolymer films comprising the higher PLLA compositions showed a clear yield point. Evidently, the tensile modulus of the copolymer films increased with

Fig. 8 Temperature dependences of storage modulus and tan δ of PLLA-PHPC-PLLA films: square: 12.3k-22.4k-12.3k, triangle: 7.9k-22.4k-7.9k.

Table 5 Tensile properties of the PLLA-PHPC-PLLA films.

Sample	PLLA-PHPC-PLLA	PHPC / PLLA	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at break (%)
a'	2.0k-10.3k-2.0k	72 / 28	5 ± 1	18 ± 1	408 ± 37
b'	4.7k-10.3k-4.7k	52 / 48	17 ± 1	71 ± 2	565 ± 102
c'	8.0k-10.3k-8.0k	39 / 61	16 ± 1	288 ± 16	402 ± 140
d'	3.6k-22.4k-3.6k	77 / 23	15 ± 4	11 ± 5	858 ± 37
e'	7.9k-22.4k-7.9k	60 / 40	27 ± 2	80 ± 2	687 ± 27
f'	12.3k-22.4k-12.3k	49 / 51	31 ± 2	648 ± 31	569 ± 44
g	PLLA 53k	0 / 100	70 ± 4	2094 ± 59	10 ± 2

increasing the PLLA content. The tensile strength also showed an increasing behavior with increasing the PLLA content by which the total molecular weight of the copolymers was increased. Particularly, the copolymer films comprising PHPC 22.4k (higher-molecular-weight soft block) exhibited a clear increase in strength. On the other hand, the increase in PLLA composition in the copolymer films having PHPC 10.3k (low-molecular-weight soft block) decreased the strength slightly, because of the yield behavior shown. Similarly, the tensile elongation of the copolymer film comprising PHPC 10.3k showed an irregular decrease at high PLLA compositions whereas that of the copolymer films comprising PHPC 22.4k decreased with increasing the PLLA composition. Among the copolymer films, those consisting of PHPC 22.4k can afford the highest elongation exceeding 500-800 % that is adequate for use as thermoplastic elastomer having higher toughness. These results suggested that the copolymers comprising the soft PHPC and hard PLLA blocks can be thermoplastic elastomers whose tensile modulus and strength increase with increasing the PLLA content while the tensile elongation increases with increasing the PHPC content.

Figure 8 shows the temperature dependences of

storage modulus (E') and $\tan \delta$ of the copolymer films of PLLA-PHPC-PLLA having a long center block (PHPC 23.5k). The two $\tan \delta$ peaks shown around -40 °C and 60 °C can be attributed to the α -relaxation temperatures (T_g) of PHPC and PLLA, respectively, suggesting that the copolymer films should have a micro phase separation structure of the hard and soft segments. The E' values are 10^8 - 10^9 Pa between the two T_g . With the increased PLLA content, E' becomes higher, and the relaxation peaks are weaker. It is shown that the films of tri-block copolymers can retain their mechanical properties up to 150-160 °C. Although the E' changes around T_g is sharp, the E' can be retained up to 150 °C.

As compared with the polymer films of similar copolymers (PLLA-PHMC-PLLA) consisting of PHMC, an APC composed of single unit, the present copolymer consisting of PHPC, an APC composed of two units, have attained slightly different crystallization behavior. Table 6 compares the properties of PLLA-PHMC-PLLA and PLLA-PHPC-PLLA copolymers having long center blocks (PHMC 21.2k and PHPC 22.4k). Evidently, PLLA-PHPC-PLLA shows highly crystalline nature because of the enhanced PLLA crystallinity that is driven by the excellent plasticity of the amorphous PHPC block

Table 6 Comparison of the properties of the tri-block copolymers of PLLA-PHMC-PLLA and PLLA-PHPC-PLLA consisting of long center blocks (PHMC 21.2k and PHPC 22.4k (or 23.5k)).

PLLA-APC-PLLA		APC / PLLA	T_c (°C)	ΔH_c (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	Crystallinity ^{a)} (%)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at break (%)
PHMC	6.0k-21.2k-6.0k	64 / 36	83.4	5.9	159.8	6.9	7.4	21 ± 1	160 ± 25	688 ± 71
	13.1k-21.2k-13.1k	45 / 55	100.9	18.9	161.5	20.5	22.0	32 ± 3	410 ± 38	582 ± 61
PHPC	7.9k-22.4k-7.9k	60 / 40	-	-	159.4	11.9	12.8	27 ± 2	80 ± 2	687 ± 27
	12.3k-22.4k-12.3k	49 / 51	-	-	158.1	17.4	18.7	31 ± 2	648 ± 31	569 ± 44

a) Determined from ΔH_m in reference to the specific ΔH_m of the crystals (93 J g⁻¹).

chains. On the other hand, the PLLA-PHMC-PLLA exhibits retarded PLLA crystallinity because the crystalline PHMC blocks may interfere with the crystallization of the PLLA chains. The tensile properties, however, are almost correspondent with each other between the two systems, because the highly crystalline nature of the PHPC-containing copolymer films can be compensated by the softness of the PHPC blocks.

4. Conclusion

The commercially available PHPC diol (PHPC 2k) was found to contain various minor units in small amount that had been formed during the ester exchanging polycondensation of diols and EC. It was successfully chain-extended to obtain higher-molecular-weight PHPCs. The resultant telechelic PHPCs, retaining the two hydroxyl terminals, were subjected to the ROP of L-lactide as macro-initiators to obtain ABA tri-block copolymers PLLA-PHPC-PLLA. As analyzed by DSC, the copolymers consisting of longer soft blocks (PHPC) showed higher T_m values because the chain length of the PLLA hard blocks became longer at identical hard-to-soft block ratios. It was found out that the tensile modulus of their films decreased with increasing the content of soft blocks while the strength and elongation were affected by the total molecular weight of the copolymers. In particular, the polymer films of PLLA-PHPC-PLLA consisting of a longer soft block (PHPC 22.4k) showed the highest elongation over 700 %. These data revealed that the present block copolymers can be used as novel bio-based thermoplastic elastomers. At present, these block copolymers are partly biobased (biobased contents = PLA compositions) because the PHPC prepolymers are prepared from oil-based building blocks (EC, HMG and PMG). In the near future, however, they will be able to be fully biobased by replacing these building blocks with those of biobased origin and by using CO₂ as renewable feedstock.

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