Synthesis and Characterization of Poly(L-lactic acid)-*b*-poly(ethylene terephthalate-*co*-sebacate)-*b*-poly(L-lactic acid) Copolyesters

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ABSTRACT: Random copolyester namely, poly(ethylene terephthalate-*co*-sebacate) (PETS), with relatively lower molecular weight was first synthesized, and then it was used as a macromonomer to initiate ring-opening polymerization of L-lactide. ^{1}H NMR quantified composition and structure of triblock copolyesters [poly(L-lactic acid)-*b*-poly(ethylene terephthalate-*co*-sebacate)-*b*-poly(L-lactic acid)] (PLLA-PETS-PLLA). Molecular weights of copolyesters were also estimated from NMR spectra, and confirmed by GPC. Copolyesters exhibited different solubilities according to the actual content of PLLA units in the main chain. Copolymerization effected melting behaviors significantly because of the incorporation of PETS and PLLA blocks. Crystalline morphology showed a special pattern for specimen with certain composition. It was obvious that copolyesters with more content of aromatic units of PET exhibited increased values in both of stress and modulus in tensile test. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 161–168, 2007

Key words: block copolymers; polyesters; synthesis; PLLA

INTRODUCTION

Random poly(ethylene terephthalate-*co*-sebacate) (PETS) is a typical copolyester comprising aromatic polyester poly(ethylene terephthalate) (PET) and aliphatic polyester poly(ethylene sebacate) (PES). Copolymerization endows the resulting products PETS with modified properties in both mechanical and thermal aspects, which strongly depends on average sequence length of polyester units and degree of randomness.[1] Some researches have shown that aromatic polyesters can be degraded when they are copolymerized with aliphatic polyesters.[2] Potential applications of copolyesters as biomaterials and degradable materials are expected.

Poly(L-lactic acid) (PLLA) is a aliphatic and degradable polyester. Its biodegradability and bioenvironmental compatibility have attracted much attention in medical and pharmaceutical applications.[3–5] Its properties can be significantly enhanced and broadened by modification via copolymerization, which provides a number of advantages because the architecture and composition of the biomaterials can be tailored to control the material properties.[6]

Because regulation of the crystal structure offers an additional possibility of optimizing their properties, the synthesis of block copolyesters with crystallizing segments is an effective way to obtain new polyester materials.[7] Block copolymerization of PETS with L-lactide is for modifying the physical and biological properties, which may offer various applications. In the mean while, degradability is also expected because some studies revealed that aromatic polyesters are degraded when they are copolymerized with aliphatic polyesters,[8] and potential applications of block copolyesters as biomaterials and degradable materials are expected.

Messman et al.[9] reported the synthesis and characterization of ABA triblock copolymers derived from chloro-telechelic poly(L-lactide) combining ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP). Gadzinowski and Sonowski[10] synthesized biodegradable/biocompatible ABC triblock copolymer [poly(ethylene oxide)-poly(glycidol)-poly(L-lactide) (PEO-PGly-PLLA)], bearing hydroxyl groups in the middle block. The copolymers of polylactide with different structures such as multiblock[11,12] and star-shaped block[13,14] have been studied intensively.

Chen's research, however, is one of those few addressing the combination of PLLA with copolyesters employing PET units. Their article reveals the miscibility, thermal characterization, and crystallization of poly(L-lactide) and poly(tetramethylene adipate-*co*-terephthalate) blends.[15]

In the present work, we report the synthesis of ABA triblock copolyester PLLA-PETS-PLLA consisting of a center block of aromatic–aliphatic copolyester poly(ethylene terephthalate-*co*-sebacate) (PETS) and outer blocks of PLLA, in which random

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bishydroxylate PETS with relatively low molecular weight is used as a macromonomer to initiate ring-opening polymerization of L-lactide. Triblock copolyesters with diverse solubilities can be obtained from same reaction ampoule. Structure, composition, solubility, thermal properties, crystalline morphology, and mechanical properties are characterized, which are expected useful for further applications. The research is timely and may be of both scientific and industrial interests.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT) and ethylene glycol (EG) were kindly supplied by Chemical Petrol, China. Sebacate acid (SA) is the product of Zhonghe Chemical Plant, Tianjin, China. Derivatives titanium and stannous octate are all reagent grades and used as received. L-lactide was prepared in our laboratory by known procedures,[16] and was recrystallized from anhydrous ethyl acetate twice and then dried in vacuum for at least 24 h prior to polymerization. The pure L-lactide remained as white acerous crystals with melting point of 93.2–96.7°C after three times recrystallization from ethyl acetate.

Synthesis of PETS copolyester

Transesterification of DMT with EG and esterification of SA with EG are the process to obtain bis(hydroxyethyl)terephthalate (BHET) and bis(hydroxyethyl)sebacate (BHES), respectively. BHET and BHES weighted according to the molar ratio (5.5 : 4.5) were added to a round-bottom flask equipped with magnetic stirrer and condenser. Melting polycondensation was proceeded at (230 ± 2)°C for 30 min with titanium derivative and antioxidant 1010 under nitrogen atmosphere and vacuum condition less than 133 Pa. Resultant PETS was dissolved in chloroform and then precipitated by anhydrous methanol, washed with methanol, filtered, and dried in vacuum.

Synthesis of PLLA-PETS-PLLA triblock copolyesters

PETS and L-lactide were added to an argon-purged 20 mL ampoule. Then anhydrous toluene solution of stannous octate was syringed. When toluene was evaporated, the ampoule was sealed under vacuum condition. Copolymerization was carried out under oxygen-free and anhydrous condition at 170°C, and the chemical structure of PLLA-PETS-PLLA triblock copolyester is given in Scheme 1. After 8 h, the ampoule was broken and the copolymer was dissolved in chloroform. Then the polymers were isolated by methanol, and dried *in vacuo*. When acetone was added, part of the triblock copolyesters is soluble, and the other part shows solubility in chloroform. Triblock copolyesters with different solubilities from the same ampoule are obtained respectively, by precipitating in methanol and drying again.

Characterization

The intrinsic viscosity of copolyesters were determined in a (25.0 ± 0.1)°C thermalsat with a phenol/1,1,2,2-tetrachloroethane solution by a Ubbelohde viscometer. ^{1}H NMR spectra were recorded in deuterated chloroform (CDCl$_3$) with tetramethylsilane as internal standard on a Varian Inovia 500 MHz spectrometer. GPC measurements were carried out at room temperature in THF using a Waters 410 apparatus with PS as reference. Differential scanning calorimetry (DSC) measurement was performed on a Perkin–Elmer DSC-7 apparatus under nitrogen atmosphere using samples of about 5 mg. The sample was heated up to predetermined temperature at a rate of 10°C/min, and maintained at this temperature for 5 min, and then quenched to −50°C. The second heating run was scanned again at a rate of 10°C/min to 200°C. Polarized microcopy images were recorded by Olympus BX51 on triblock copolyesters when solvent is evaporated slowly at room temperature.

Film preparation and tensile test

Chloroform solution of triblock copolyester casting films were prepared, and the thickness were adjusted at almost 50–70 μm. Solvent evaporated at room temperature, and films were dried *in vacuo*. Tensile properties were estimated on film strips (40 × 10 mm^2) using a Testometric M350-20kN tensile testing machine (15 kgf load-cell) at 25°C and a constant cross-head speed of 5 mm/min. Each recorded value is an average of at least three specimens.
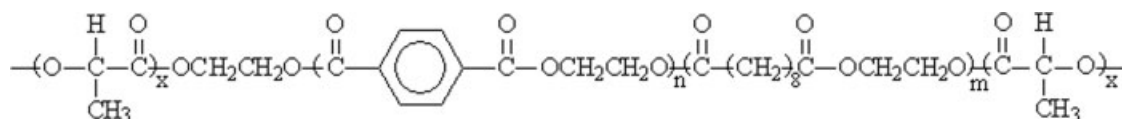
Scheme 1 Chemical structure of PLLA-PETS-PLLA.

RESULTS AND DISCUSSION

Synthesis of PETS

The intrinsic viscosity of PETS shows a lower value of 0.373 dL/g. The ^{1}H NMR spectrum is shown in Figure 1, and the assignments of proton signals are also included.

As shown in Figure 1, the strong absorbance visible at 8.109 ppm is the signal of the protons attached to benzene nucleus (T). The bands centered on 1.297 (S3), 1.596 (S2), and 2.320 (S1) ppm are characteristic to CH$_2$ protons of sebacate residue, respectively. The calculated molar ratio of PET:PES is 5.59 : 4.41, which appropriates to feed ratio 5.5 : 4.5.

Four profiles discriminated at 4.702 (X1), 4.538 (X2), 4.429 (X3), and 4.264 (X4) ppm are assigned to the protons in ethyl glycol residue, which corresponds to SES, SET or TES, and TET, respectively. The average sequence length of polyester units in PETS can be estimated using the manipulation proposed by Yamadera and Murano,[1] and the results are 3.25 and 2.73 for PET and PES units, respectively.

With transesterification mechanism, the amounts of hydroxyl end groups can be controlled by reaction time. Synthesis of PET-related copolyesters by polycondensation requires reaction time of about 150 min.[17] Thirty minutes is selected in this study for preparing PETS macromonomer with relatively lower average molecular weight to obtain relatively larger amount of hydroxyl end group. The content of the hydroxyl end groups in PETS, which were calculated by integration of the peaks at 3.990 (X5) and 3.810 (X6) ppm, respectively, were also evaluated. Protons X7 and X8 are somewhat overlapped with that of X1–X4. The average molecular weight of PETS can be obtained by

$$\overline{M}_{n,\text{PETS}} = \frac{I_T}{I_{X5} + I_{X6}} \times 192 \ + \ \frac{I_{S1}}{2(I_{X5} + I_{X6})} \times 228 + 58$$

(1)

where I refers to the integration intensity of corresponding absorbance in ^{1}H NMR spectrum, and the subscripts denote the designated protons. The constant 192 and 228 represent the molecular weight of PET and PES units, respectively. The value 58 denotes the molecular weight of end group in PETS.

The calculated value of average molecular weight for PETS is 5074.

Synthesis of PLLA-PETS-PLLA triblock copolyesters

The bishydroxylate PETS obtained above was subjected to block copolymerization with L-lactide via ring-opening polymerization. The synthesis temperature was selected at 170°C on the basis of our previ-
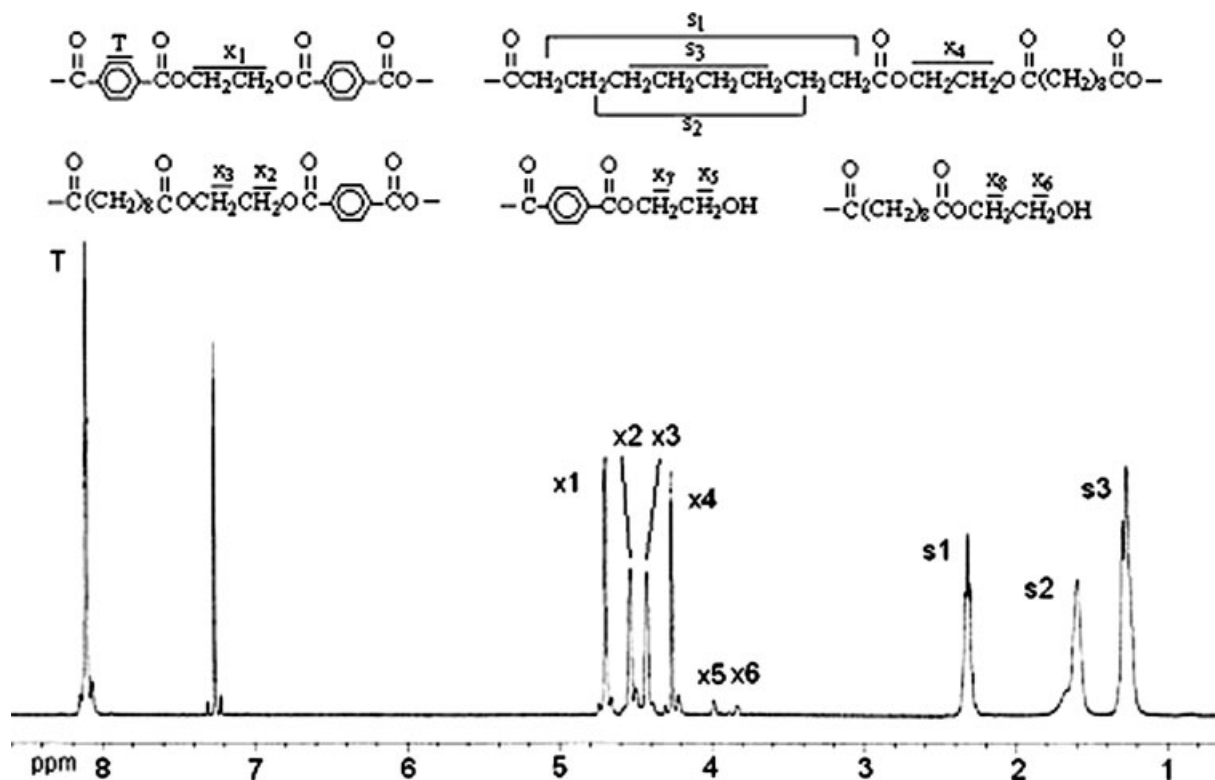

Figure 1 ^{1}H NMR spectrum of PETS.

TABLE I
Designated Samples of Copolyester

| Sample | Feed ratio (mol %) | | $[\eta]$ (dL/g) | Solubility | | Yield (%) |
	PETS	L-lactide		Acetone	Chloroform	
PETS	100	0	0.373	−[c]	+[d]	−
40PETS-C[a]	40	60	0.660	−	+	40.37
40PETS-A[b]	40	60	0.540	+	+	59.63
60PETS-C	60	40	0.566	−	+	55.92
60PETS-A	60	40	0.492	+	+	44.08

[a] Dissolved in Chloroform.
[b] Dissolved in Acetone.
[c] Insoluble.
[d] Dissoluble.

ous work on synthesis of PLLA and the melting temperature of PETS. Table I describes the block copolyesters as well as PETS. All the values of intrinsic viscosity for triblock copolyesters become larger in comparison with that of PETS, which infers the formation of block copolyesters with relative higher molecular weight. Moreover, intrinsic viscosity of triblock copolymers derived from same ratio differs from sample to sample. In detail, samples soluble in acetone show relatively higher values than those soluble in chloroform. The yields in Table I give indications that more acetone soluble block copolyesters samples are acquired when the contents of PLLA is higher in the copolyesters. In detail, 40PETS-A, which possesses relatively higher contents of PLLA, shows a yield of 59.63% for acetone soluble samples, while 60PETS-A exhibits a yield of only 44.08%.

Figure 2 shows GPC traces, and the values of molecular weight are summarized in Table III. The GPC of the block copolyesters exhibit unimodal distribution and do not show the presence of any possible homopolymerized PETS. The results derived from GPC are slightly larger than the calculated value derived from feed ratio and that obtained from NMR. The index $\overline{M}_w/\overline{M}_n$ (ranging from 1.518 to 1.799) in Table III shows that the relatively narrow dispersity of molecular weight may induce the potential applications.

^{1}H NMR analysis of PLLA-PETS-PLLA triblock copolyesters

All the ^{1}H NMR spectra for the triblock copolyesters exhibit almost the same resonances for signal of the protons, but show diverse relative intensities according to compositions and solubilities. Figure 3 depicts a typical ^{1}H NMR spectrum of triblock copolyesters for 40PET-C. Besides the proton signals in PETS, a newly appeared band presents at 5.100 ppm (L1), and the intensity in 1.596 ppm is remarkably increased, which is also due to the introducing of PLLA units (protons L2). Moreover, the signals at 3.990 and 3.810 ppm almost disappear, which confirms that most of the hydroxyl end groups in PETS have participated in the reactions with L-lactide.
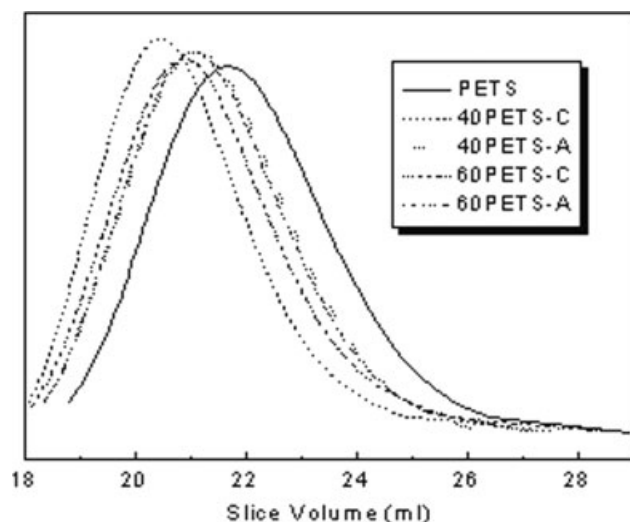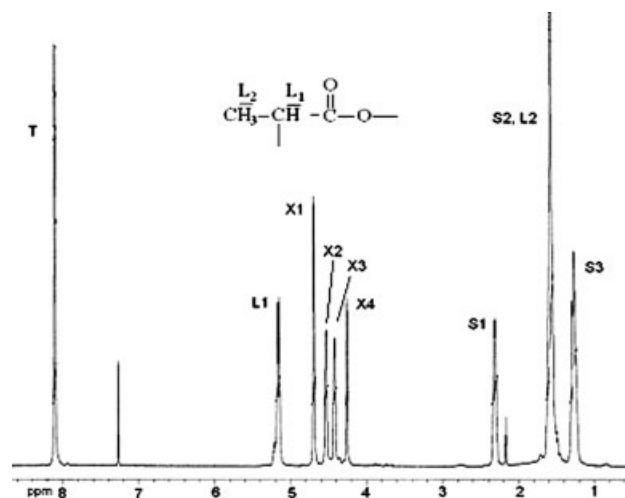

Figure 2 GPC traces of copolyesters.

Figure 3 ^{1}H NMR spectrum of 40PETS-C.

TABLE II
Degree of Randomness of PETS and Compositions for Triblock Copolyester

Sample	Randomness for PETS, R	Composition of triblock copolyesters (mol %)		
		PETS	PLLA	PET/PES/PLLA
PETS	1.033	100	0	1.27/1.00/0.00
40PETS-C	1.014	37.8	62.2	1.43/1.00/4.00
40PETS-A	1.091	20.4	79.6	1.14/1.00/8.34
60PETS-C	1.115	53.6	46.4	1.38/1.00/2.07
60PETS-A	1.099	38.2	61.8	1.16/1.00/3.50

The composition of PLLA in copolyester can be determined by proton integration intensity in 5.100 ppm (L1), and the content of PET and PES units obtained from the integration intensity at 8.100 (T) and 2.320 ppm (S1), respectively. The compositions of triblock copolyesters are collected in Table II. Since the interesterification may occur in PETS at elevated temperature during ring-opening polymerization, degree of randomness (R) for PETS is monitored by ^{1}H NMR spectra and also included in Table II for comparison.

Degree of randomness for PETS is 1.033 and indicates PETS is random copolyester. The values of R shows there is no significant variation for degree of randomness in PETS when copolymerized with PLLA.

Note that the percentages of PETS agree well with the feed ratio for samples soluble in chloroform, while for those with solubility in acetone, the content of PLLA is larger than in feed ratio. This gives a good explanation to the discrepancy of solubility for samples with same feed ratio, which indicates PLLA block length effect solubility of triblock copolyesters. The contents of PLLA units in acetone soluble samples are higher than that in adding materials, while PLLA compositions in chloroform soluble samples are lower than feed ratio. This seemingly implies the multi-disperse of copolyesters in molecular weight.

The molecular weight of triblock copolyesters can be estimated by ^{1}H-NMR spectra:

$$\overline{M}_{n,\text{PLLA-PETS-PLLA}} = \frac{4I_{L1}}{I_T} \times 13.44 \times 72 + 5074 \quad (2)$$

in which I_{L1} and I_T are corresponding integration intensity in ^{1}H NMR spectra of triblock copolyesters. The constant 13.44 is the original intensity ratio of protons attached to terephthalic (T) to the sum of protons in end groups (X5 and X6) in PETS ^{1}H NMR spectra. The value 72 is the molecular weight of PLLA unit and 5074 the average molecular weight of PETS detected by ^{1}H NMR.

The variation trend of molecular weight (Table III) calculated from ^{1}H NMR spectra ($\overline{M}_{n,\text{NMR}}$) is coincident with intrinsic viscosity and the calculated values from feed ratio ($\overline{M}_{n,\text{cal}}$).

Moreover, the molecular weight of PLLA block can be estimated if PLLA blocks in triblock copolyesters are the same in length. The results are also collected in Table III.

The estimated average molecular weight of PLLA blocks are in the range of 980–3550 for the analyses of ^{1}H NMR and 1660–3310 for the results of GPC.

Thermal properties of PLLA-PETS-PLLA triblock copolyesters

Figure 4(a) shows DSC thermograms. PETS displays a melting temperature peak at 156.4°C with a relatively lower melting enthalpy of 10.82 J/g.

The triblock copolyesters show blunt and broader endothermic peaks, which reveal that the crystallization of both PLLA and PETS are interfered partially by copolymerization. The incorporation of different block hinders the chain packing, resulting in decreased crystallinity (X_c). The decrease of X_c is usually due to the interactions between the blocks,[18] and implies that PLLA and PETS are partially miscible.

Though the melting temperatures are not obvious enough, we can make out that 60PETS consisting of more rigid aromatic units of PET display higher endothermic peaks than 40PETS. Furthermore, among the copolyesters with the same content of PETS, the melting peaks decrease in acetone soluble samples. In a typical example, the peak temperature [as indicated in Fig. 4(a)] of the 40PETS-A is about 25°C lower than that of the 40PETS-C (endothermic peak value appears at 137.1°C for 40PETS-C and 111.4°C for 40PETS-A). Similar result is observed in

TABLE III
Average Molecular Weight for Triblock Copolyesters and PLLA

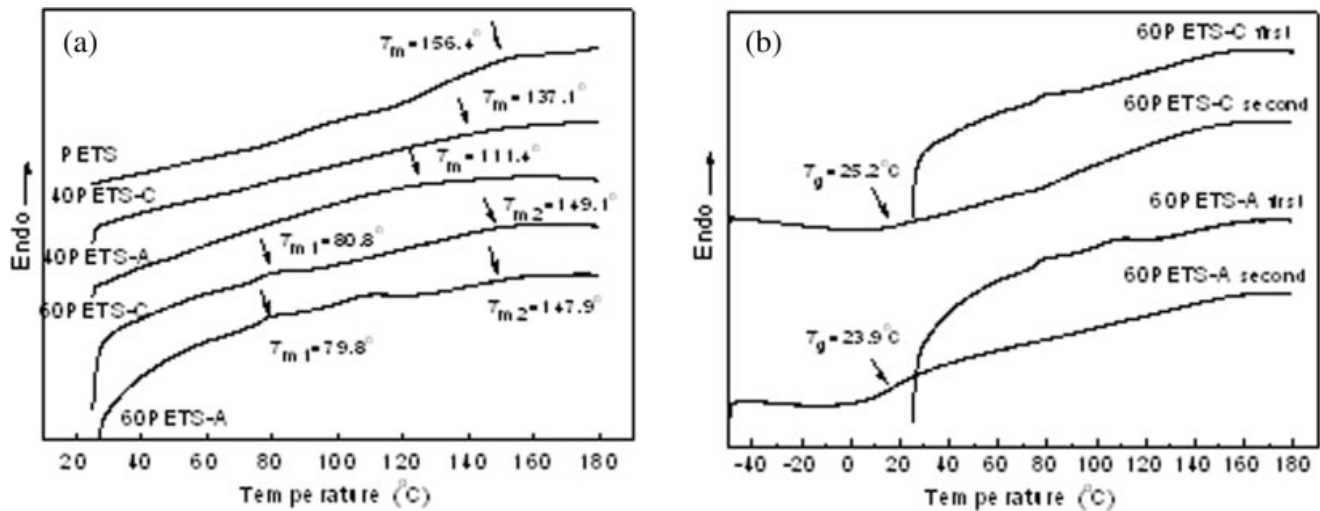| Sample	$\overline{M}_n$ (triblock copolyesters)				$\overline{M}_n$ (PLLA)	
	$\overline{M}_{n.\text{cal}}$	$\overline{M}_{n.\text{NMR}}$	$\overline{M}_{n.\text{GPC}}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_{n.\text{NMR}}$	$\overline{M}_{n.\text{GPC}}$
PETS	–	5074	7346	1.739	–	–
40PETS-C	12,706	7826	13,968	1.610	1376	3311
40PETS-A		12178	10,870	1.518	3552	1762
60PETS-C	8467	7037	10,678	1.799	981	1666
60PETS-A		8041	10,683	1.526	1483	1668

Figure 4 DSC curves of copolyesters: (a) first heating of PETS and triblock copolyesters; (b) first and second heating of 60PETS.

the 60PETS: T_m is 149.1°C for 60PETS-C and T_m is 147.9°C for 60PETS-A. This is because the earlier crystallization of the PETS blocks strongly restricted the crystallization of the PLLA blocks, leading to the decrease of endothermic peak. The trend is significant when the PLLA blocks are longer, and the difference magnitude between 40PETS-C and 40PET-A is larger than that between 60PETS-C and 60PETS-A.

Besides, we note that 60PETS series possesses multiendothermic peaks during first heating, and the melting peak appears at about 80°C, which is seemingly due to the crystallization of poly(ethylene sebacate) units. In the second melting heating run, the melting curves of 60PETS are different [Fig. 4(b)]. When the block copolyesters are cooled down after first melting process, PETS blocks containing rigid aromatic unit PET solidify and crystallize at higher temperatures, thus limiting the mobility of the flexible

PLLA segments. Consequently, the crystallization of PLLA is severely hindered by the already solidified PETS chains, and lead to diverse melting behavior.

Crystalline morphology of PLLA- PETS-PLLA triblock copolyesters

Only the specimen of 60PETS-C shows a visual morphology when crystallized slowly from the solution. As shown in Figure 5, an interesting feature is observed with rep-like patterns.

Microphase separation and confinement of crystallization are suggested. Ho et al. believe that crystallization of blocks within the microphase-separated lamellar microdomain in a block copolymer is carried out from hard confinement to soft confinement according to experimental temperature.[19]
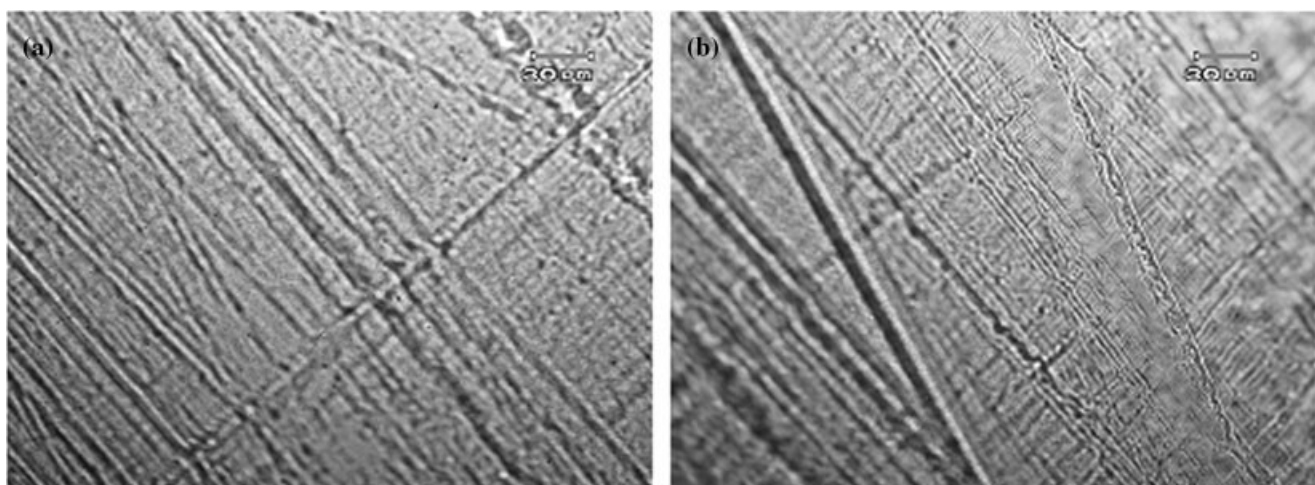

Figure 5 Polarized microcopy images of block copolyesters: (a) 60PETS-C (1) (b) 60PETS-C (2).

Block copolymers with multiple crystallizable blocks have attracted attention, and Li suggested that coupling and competition between crystallization and microphase separation as a similar underlying mechanism.[20,21] Phase separation between PLLA and PETS blocks takes place due to the crystallization process, since the two blocks are partially miscible. The existing feature formed at room temperature under which lamellar morphology is created, and the relatively weak restraint in crystallizable blocks at the connected junctions of the incompatible microdomains is likely to increase the mobility of the entire copolyester chain, resulting in a regularity of crystalline morphology.

Though the unique crystalline morphology of PLLA-PETS-PLLA triblock copolyester comprising crystalline PLLA domain and PETS domain is apparent, the mechanism of morphological evolution needs further investigation.

Tensile properties of PLLA-PETS-PLLA triblock copolymers

Figure 6 illustrates tensile curves of triblock copolyester, and mechanical properties such as Young's modulus, stress at break, and strain at break evaluated from the stress–strain curves are listed in Table IV.

It is obvious that the modulus and stress of 40PETS series decrease dramatically as compared with that of 60PETS series, since 60PETS are PET-rich samples with higher value of modulus, stress at yield and break.

As for copolyesters with the same PETS feed ratio, samples soluble in chloroform show higher modulus and stress values than those that are soluble in acetone. In detail, the modulus is about 26 MPa for 40PETS-C, but it exhibits about 20 MPa for 40PETS-A. The difference of modulus between 60PETS-C
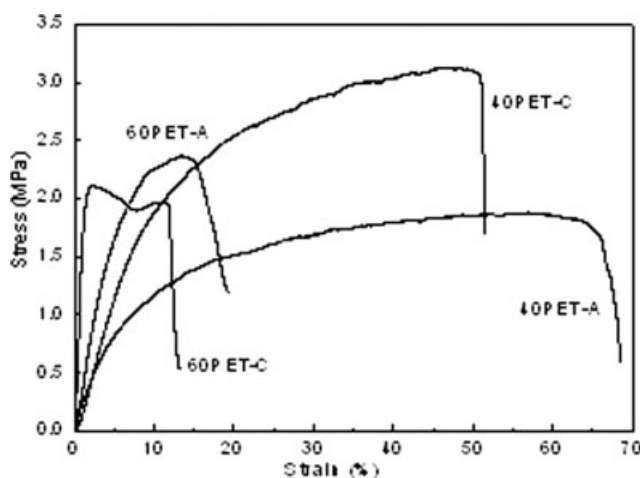
TABLE IV
Characteristic Data of Tensile Properties

Sample	Young's modulus (MPa)	Stress at break (MPa)	Strain at break (%)
40PETS-C	26.1 ± 0.8	3.0 ± 0.4	57.2 ± 8.1
40PETS-A	20.9 ± 4.9	1.8 ± 0.2	76.6 ± 8.2
60PETS-C	137.9 ± 18.6	1.9 ± 0.5	13.8 ± 1.7
60PETS-A	50.8 ± 5.3	2.3 ± 0.4	15.5 ± 1.2

and 60PETS-A is more significant. The results are also because that samples with solubility in chloroform possess relatively higher content of PETS, and the composition of aromatic units PET will lead to the larger values of both modulus and stress.

CONCLUSIONS

PLLA-PETS-PLLA triblock copolyesters have been successfully synthesized using random copolyester PETS as a macromonomer to initiate the ring-opening polymerization of poly(L-lactide). The block copolyesters show diverse solubility according to the PLLA content in the main chain. The composition and structure of block copolyester were obtained from the analyses of ^{1}H NMR spectra, and the molecular weight was confirmed by GPC. The crystalline morphology of triblock copolyester with 60PETS % (mol) showed special rep-like patterns, which is due to microphase separation and confinement of crystallization. The tensile properties of triblock copolyesters' solution-casting films illustrated typical features coincided with the composition. Copolyesters with more content of aromatic units of PET exhibited increased values in both of stress and modulus. As for the same feed ratio, flexibility was obtained as a result of the incorporation of PLLA.

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Figure 6 Tensile curves of block copolyesters.

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