

Synthesis and Characterization of Copolymeric Aliphatic-Aromatic Esters Derived from Terephthalic Acid, 1,4-Butanediol, and ϵ -Caprolactone by Physical, Thermal, and Mechanical Properties and NMR Measurements

Ching-Huang Wang,¹ Ping-Hsun Tsai,¹ Lou-Sing Kan,^{1,2} C. Will Chen¹

¹Department of Bioengineering, Tatung University, Taipei 10452, Taiwan, Republic of China

²Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan, Republic of China

Correspondence to: C. W. Chen (E-mail: will@ttu.edu.tw)

ABSTRACT: In this study, a series of aliphatic–aromatic poly(butylene terephthalate-*co*- ϵ -caprolactone) (PBTCL) copolyesters were synthesized from various monomeric compositions of terephthalic acid (TPA), 1,4-butanediol (BDO), and ϵ -caprolactone (CL) in the presence of tetrabutyl titanate (Ti(Obu)₄) and stannous octoate (Sn(Oct)₂) as catalysts through a combination of polycondensation and ring opening polymerization. A significant increase in the melting temperature (T_m) of copolyesters was observed by increasing the TPA/(CL+TPA) molar ratio, starting from the low end (T_m 66.2°C) of pure poly- ϵ -caprolactone PCL upward. We found that PBTCL-50, which has a TPA/(CL+TPA) 50% molar ratio and polycondensation at 260°C for 1.5 h, resulted in a proper T_m of 139.2°C that facilitates thermal extrusion from biomass or other biodegradable polymers of similar T_m . The number–average molecular weight (M_n) of 7.4×10^4 for PBTCL-50 was determined from the intrinsic viscosity $[\eta]$ by using the Berkowitz model of $M_n = 1.66 \times 10^5 [\eta]^{0.9}$. Good mechanical properties of PBTCL-50 have been shown by tensile stretching experiment that indicates tensile strength, elongation, and Young's modulus are 11.9 MPa, 132%, and 257 MPa, respectively. Polymers with aforementioned properties are suitable for manufacturing biodegradable plastic films for downstream agricultural applications or merely for trash bag. This article reveals that the PBTCL-50 contains all five monomers with different molar ratios and characteristic linkages between each other. The novel structure was furthermore analyzed by ¹H- and ¹³C-NMR spectroscopy. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: aliphatic–aromatic copolyester; poly(butylene terephthalate-*co*- ϵ -caprolactone); structure analysis; thermal properties; mechanical properties; ¹H- and ¹³C-NMR spectroscopy

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INTRODUCTION

Using biodegradable aliphatic–aromatic polyester as an alternative to conventional nonbiodegradable plastics could contribute to the solution of reducing pollutions originated from traditional plastic wastes. In recent years, there is a growing interest in the development of biodegradable aliphatic polyesters produced by ring opening polymerization (ROP) of either lactones or lactides, and from the polycondensation of diols and dicarboxylic acid.^{1–4} In some cases, potentially biodegradable aliphatic polyesters synthesized mainly by polycondensation processes without incorporating ROP mechanism are known to exhibit moderate mechanical properties and low melting temperatures and thus have limited commercial applications.^{5,6} On the other hand, traditional aromatic polyesters, such as poly

(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(propylene terephthalate) (PPT), show excellent thermal and mechanical performance, but lack biodegradability. However, by incorporating rigid aromatic structures into aliphatic polyesters, their overall mechanical, thermal properties, and biodegradability can be modified.^{7–9} Poly(ϵ -caprolactone) (PCL) is a highly flexible polyester with good biodegradable and mechanical properties.¹⁰ However, the application of PCL is limited by its low melting temperature ($\sim 67^\circ\text{C}$), which makes it difficult to process with biomass materials such as starch or cellulose.^{11–13} PCL had been copolymerized with poly(ethylene succinate) (PES), poly(butylene succinate) (PBS), or poly(propylene succinate) (PPSu), but the copolyesters still have low melting temperature.^{10,14,15} To remedy this, modifications of PCL have been attempted, such as introduction of aromatic

polyesters achieved by melt-blending PCL with PBT or PET.^{16–19} The poor miscibility of high molecular weight of PCL with aromatic polyesters resulted in low ester-interchange reaction and also poor elongation property of the resulting melt-blended polyesters. Other attempts include copolyesters of cyclic poly(butylene terephthalate) oligomers (*c*-PBT) and ϵ -caprolactone (CL) monomer reported by Tripathy et al.²⁰ Unfortunately, their *c*-PBT/CL (50/50) copolyesters are soft, with low Young's modulus and high elongation. Cheng et al.²¹ synthesized PBT/CL copolyesters from different molar ratios of dimethyl terephthalate (DMT), 1,4-butanediol (BDO), and CL and proposed that increasing the hard segment content of butylene terephthalate (BT) could improve the thermal properties of the copolyester. However, they did not investigate the mechanical properties of the copolyesters. In this study, we did a more detailed study of the poly(butylene terephthalate-*co*- ϵ -caprolactone) (PBTCCL) copolyesters constituted from TPA, BDO, and CL. We aimed to find the synthetic conditions with respect to monomer composition, polycondensation temperature, and reaction time by monitoring copolyesters' physical, thermal, and mechanical properties that are suitable for manufacturing biodegradable plastic films for agricultural applications or for trash bag. At the same time, we quantified a novel structure of different repeated linkages of monomers within the chain structure of PBTCCL.

EXPERIMENTAL METHODS

Materials

BDO, CL of analytical reagent grade and tetra-*n*-butyl titanate Ti(Obu)₄ were purchased from Acros Organics (USA). Stannous octoate (Sn(Oct)₂) was purchased from Fluka Chemical (Japan). TPA, benzyl alcohol, sodium hydroxide, and hydrochloric acid were purchased from Wako (Japan). Methanol, chloroform, and acetone were purchased from Merck Chemical (Germany).

Synthesis of PBTCCL Copolyesters

PBTCCL copolyesters were synthesized by melt polycondensation method in 500 mL glass batch reactor. The reactor was a four-neck flask equipped with a mechanical stirrer, nitrogen inlet, a condenser, and thermometer. In all cases, the total quantity of CL+TPA was kept at one mole, and catalysts Sn(Oct)₂ of 0.74 mmol per mole of CL+TPA, and Ti(Obu)₄ of 0.293 mmol per mole of CL+TPA were charged into the reactor. The quantity of TPA was varied from 0.2 to 0.8 mol in the synthesis of 20 to 80 mol % of TPA/(CL+TPA). The molar values of BDO were based on the specific molar ratio of BDO/TPA. As an example, the synthesis of copolyester with 50 mol % of TPA/(CL+TPA) and molar ratio of BDO/TPA = 1.4 mol/mol, i.e., PBTCCL-50, is described. The reaction mixture of TPA 0.5 mol, BDO 0.7 mol, and CL 0.5 mol were added in reactor. The reaction mixture was heated at 200°C under nitrogen atmosphere and stirred at a constant speed of 500 rpm. Water formed during the esterification reaction was distilled off completely to reach its theoretical value. The theoretical molar value of water formed was calculated from the molar value of the di-acid (TPA) that reacted with the excess molar value of diol (BDO). The reaction mixture was subsequently heated to the designed temperature under gradually reducing pressure to 2 mmHg and maintained for 0.5 h. In the polycondensation phase, the pressure of the reaction

chamber was reduced gradually to a final vacuum of less than 0.5 mmHg. The polycondensation is terminated when the mixer torque approached its maximum value.

Characterization

Intrinsic Viscosity and Molecular Weight Analysis. Intrinsic viscosities $[\eta]$ of the copolyesters were measured using an Ubbelohde viscometer with chloroform as solvent at 30°C. All copolyesters were dissolved at 30°C to make a final concentration of 0.5 g/dL. Viscosity of each sample solution was tested in triplicates. Intrinsic viscosity was calculated by using Solomon-Ciuta equation.²²

$$[\eta] = \frac{\sqrt{2\{(t/t_0) - \ln(t/t_0) - 1\}}}{C} \quad (1)$$

where C is concentration of the solution (g/dL), t is the flow time (s) of solution, and t_0 is the flow time (s) of pure solvent.

The molecular weights of copolyesters were measured on a Perkin–Elmer Series 200 gel permeation chromatography (GPC) equipped with a refractive index detector and a network chromatography interface NCI 900. Two PLgel 5 μ m mixed-D type of 300 \times 7.5 mm columns (Polymer Laboratories Ltd., UK) were applied in series, with chloroform as the eluent at 1.0 mL/min under 40°C. Polystyrene standards from Showa Denko Ltd. Japan were used to calibrate the elution traces.

End Group Analysis. The concentration of unreacted carboxyl end group of the copolyesters was determined by the Pohl method,²³ with minor modification. A total of 5 mL benzyl alcohol was added to about 0.1 g of copolyester and heated at 150°C in a test tube for 10 min. Quickly removed the test tube from hot plate and immersed in a 50°C water bath for 10 min. A total of 5 mL of chloroform was added until the precipitate dissolved completely. The mixture was titrated with 0.1N sodium hydroxide solution to the first discernible pink color of phenol red indicator that persisted for 10 s. A blank was run on the benzyl alcohol-chloroform (1 : 1 v/v) mixtures. Benzyl alcohol was chosen because of its good copolyester solubility at high temperature (150°C), stability with base, and low relative toxicity.²³

Thermal Properties Analysis. The melting temperature (T_m) and heat of fusion (ΔH_m) of PBTCCL were measured by a differential scanning calorimeter DSC 2910 (TA Company) with indium metal for calibration. Nitrogen gas was used as purging gas at a flow rate of 40 mL/min. About 5 mg of each polymer sample was encapsulated in an aluminum pan, and then was heated to about 20°C above the corresponding melting temperature at a heating rate of 10°C/min. After keeping for 3 min, the sample was cooled down to room temperature at 10°C/min rate. The process was repeated for a second scan on the same sample. The temperatures of crystal melting peaks in the second heating traces were taken as the melting points. The thermal decomposition temperature (T_d) was measured by thermal gravimetric analysis (TGA) on a TGA2950 analyzer. Thin films of 7.0 \pm 0.1 mg was isothermal at 35°C. After keeping for 5 min, the samples were heated from ambient temperature to

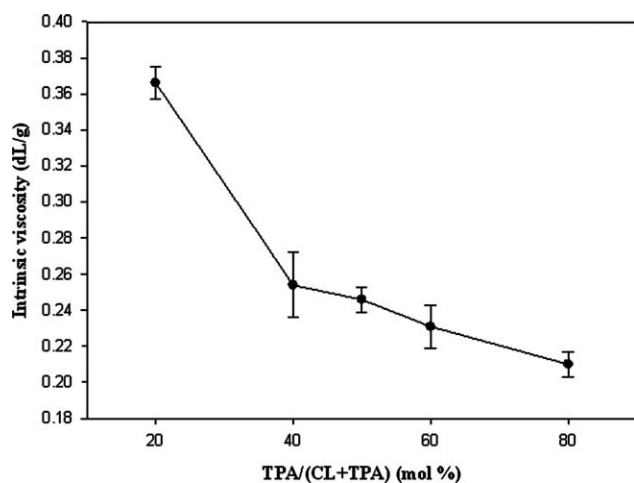


Figure 1. Intrinsic viscosity of PBTL in various molar percentage of TPA/(CL+TPA) (mol %) with molar ratios of BDO/TPA = 1.2 mol/mol. The polycondensation was performed at 250°C for 2 h.

550°C at a heating rate of 15°C/min under nitrogen atmosphere at 50 mL/min.

Mechanical Properties Analysis. The tensile strength, Young's modulus, and elongation at break were measured with an Instron model 4400R universal test machine (USA) in accordance with ASTM D638. Dumbbell-type specimens were used at a crosshead speed of 50 mm/min. All the reported mechanical properties presented are average values of three trials.

Nuclear Magnetic Resonance. The nuclear magnetic resonance (NMR) sample was prepared by dissolving the synthesized polymer (ca. 5 mg) in 500 μ L of chloroform-d. All NMR spectra were recorded using Bruker AVANCE 600, 500, and DRX 500 MHz spectrometers equipped with Bruker TXI and QNP probes (Bruker BioSpin AG, Fallallden, Switzerland) in room temperature.

RESULTS AND DISCUSSIONS

Effect of TPA on Physical and Thermal Properties

A series of PBTL copolyesters in various molar percentage of TPA were synthesized by polycondensation under high degree of vacuum (<0.5 mmHg) at 250°C and reaction time maintained for 2 h. All the synthesized PBTL were purified by dissolving in chloroform and precipitated into ice cold methanol to remove low-molecular oligomers as well as trace of the catalyst. The intrinsic viscosity [η] of PBTL are shown in Figure 1. The viscosities of the copolyesters [η] were decreased from 0.37 to 0.22 dL/g as TPA/(CL+TPA) molar percentage was increased from 20 to 80 mol %. As [η] relates to the synthesized molecular weight (Table I), we assume that the increasing ring structure of terephthalate segments in the linear structure of ϵ -caprolactone segments act as an impurity to interrupt the synthesis of polymer matrix. Papageorgiou et al.⁹ reported that increasing terephthalate molar percentage from 20 to 60 mol % also resulted in decreasing [η] of poly(propylene terephthalate-co-adipate) (PPTAd).

Figure 2 shows the DSC thermogram of a series of copolyesters with different molar percentage of TPA/(CL+TPA). It was observed that homopolymer and copolyester exhibited single

Table I. Thermal and Physical Properties Analysis of PCLBT in Various TPA/(CL+TPA) Compositions with Molar Ratios of BDO/TPA = 1.2 mol/mol

TPA/(CL+TPA) (mol %)	$M_n \times 10^{-4a}$ (Dalton)	T_m^b (°C)	T_d^c (°C)	ΔH_m (J/g)	X_c^d (%)
PCL ^e	-	66.2	304.2	88.1	63.1
20	6.7	92.1	327.5	6.3	4.5
40	4.8	96.3	351.1	13.2	9.4
50	4.7	129.1	360.6	17.9	12.8
60	4.4	155.9	364.2	19.7	13.6
80	4.1	193.3	368.3	29.8	20.6
PBT ^f	-	227.6	373.8	56.4	39.0

The polycondensation was performed at 250°C for 2 h, ^aNumber-average molecular weight determined by $M_n = 1.66 \times 10^5([\eta])^{0.9}$, ^bDSC at a heating rate of 10°C/min, ^cDecomposition temperature of the polyesters, namely the temperatures corresponding to polyester weight losses of 50% in nitrogen atmosphere, ^d X_c was calculated by dividing the observed heat of fusion from melting endotherm by the theoretical value 139.5 J/g for a 100% crystalline PCL (from TPA/(CL+TPA) of 0 to 50 mol %) and by the theoretical value 144.5 J/g for a 100% crystalline PBT (from TPA/(CL+TPA) of 60 to 100 mol %).^{8,15}, ^ePolycaprolactone (PCL) was prepared by ring opening polymerization at TPA/(CL+TPA) = 0 mol % at temperature 150°C for 2 h, ^fPoly(butylene terephthalate) (PBT) was prepared by polycondensation at TPA/(CL+TPA) = 100 mol % at temperature 250°C for 2 h.

peak in the DSC thermogram which indicates a uniform chemical structure of copolyesters without immiscibility between different structure segments. Table I shows the thermal properties of PBTL at various TPA/(CL+TPA) compositions. The melting point (T_m) of the homopolyesters PCL and PBT are 66.2 and 227.6°C, respectively. PBTL of TPA/(CL+TPA) from 20 to 80 mol % showed a tendency of T_m to increase from 92.1 to 193.3°C, the range of T_m 's of their component homopolyesters. The synthesized aliphatic or aromatic copolyesters, e.g., poly(-butylene succinate-co-propylene succinate) or c-PBT/CL, with T_m fell between their homopolymers' had been reported.^{4,20} The T_m of a copolyester is crucial in differentiating whether they are

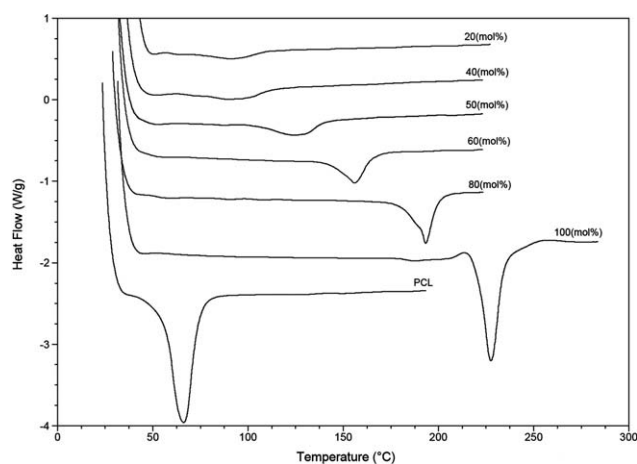


Figure 2. DSC thermogram of PBTL with different molar percentage of TPA/(CL+TPA) (mol %) with molar ratios of BDO/TPA = 1.2 mol/mol at heating rate of 10°C/min. The polycondensation was performed at 250°C for 2 h.

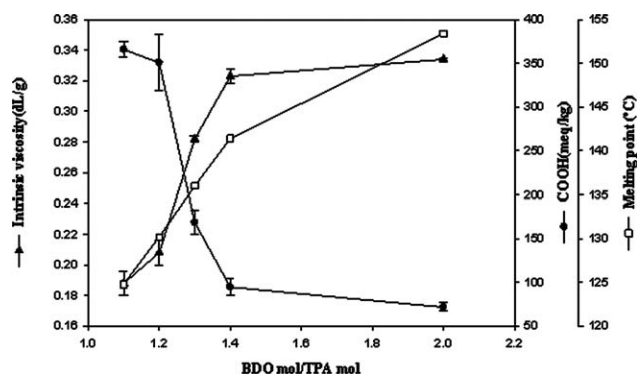


Figure 3. Intrinsic viscosity, melting point, and carboxyl end groups of PBTCCL in various molar ratio of BDO/TPA with TPA/(CL+TPA) = 50 mol %. The polycondensation was performed at 250°C for 2 h.

suitable for thermal blending with other biomass, e.g., starch or cellulose. The commercial aliphatic/aromatic copolyesters, such as poly(butylene adipate-*co*-terephthalate) or Ecoflex[®], have T_m 's in the range of 115 to 125°C, which is suitable for thermal blending with starch. Table I shows that TPA/(CL+TPA) of 40 to 50 mol % give T_m 's between 96 to 129°C, suitable for future commercial applications and warrants further study. The T_m of the synthesized *c*-PBT/CL copolyesters of 50 mol % of *c*-PBT is 119°C.²⁰ On the other hand, the synthesized PBT/CL copolyesters of butylene-terephthalate segments of 49 to 58 wt % had been reported a low T_m of 77 to 107°C.²⁴ Table I shows that the TPA composition effect on the decomposition temperature (T_d) of PBTCCL has a similar tendency as in T_m . The T_d of homopolyesters PCL and PBT are 304.2 and 373.8°C, respectively. The T_d of synthesized PBTCCL falls between their homopolymers'. It is noted that the T_d of TPA/(CL+TPA) 50 mol % is 360.6°C which is far away from its T_m , suitable to prevent its degradation during the thermal blending process. Hence, it is concluded that PCL copolymerized with the TPA composition can enhance its thermal properties favorably.

Storey and Sherman²⁵ reported that the functional group used as an initiator in the ROP of CL is a diol, e.g., BDO. In the presence of a catalyst, such as Sn(Oct)₂, the initiation is induced by the transfer of tin alkoxide (Sn-O-butane-OH) as an active intermediate. Therefore, we consider in polycondensation the TPA reacts with the hydroxyl group of BDO and with oligomers whose hydroxyl end groups of PCL previously initiated by BDO. From Figure 1, it is obvious that increasing TPA/(CL+TPA) mol %, with fixed TPA/BDO ratio at 1.2 mol/mol, resulted in decreasing $[\eta]$ and also decreasing molecular weight as shown in Table I. Therefore, TPA alone does not favor the polymerization. Note that it is more important to produce copolyesters that have proper physical properties for intended applications rather than to strive for maximum degree of polymerization. For example, proper melting point (T_m) is important when thermal extrusion with other biomass is desired; proper crystallinity and mechanical properties, e.g., elongation at break, are important factor when consider constructing films; or even proper molecular weight is the more important when biodegradability is of concern.

Crystallinity of PBTCCL Copolyesters

The crystallinity (X_c) values of the polymers can be readily evaluated by DSC based on the heat of fusion for perfect crystal.⁴ The X_c values of copolyesters are calculated by dividing the observed heat of fusion from melting endotherm by the theoretical value 139.5 J/g for a 100% crystalline PCL¹⁵ and by the theoretical value 144.5 J/g for a 100% crystalline PBT.⁸ Table I shows the measured heat of fusion (ΔH_m) of 88.1 J/g for synthesized PCL homopolyester, and 56.4 J/g for synthesized PBT giving X_c values of PCL and PBT 63.1% and 39%, respectively. The inclusion of TPA monomers, e.g., 20 mol % TPA/(CL+TPA), into PCL causes significant decrease of X_c values to 4.6%. It may be due to the incorporation of butane-diol-terephthalate segments into the polyester chain, which enhance chain or segmental mobility inside the amorphous region of copolyester that interrupt the crystalline regions.⁸ However, more TPA segments will enhance crystalline regions that slightly increase the X_c values of copolyesters from 4.6 to 20.6% for PBTCCL changing from 20 to 80 mol % of TPA/(CL+TPA). Li et al.⁸ reported that including DMT segments into PBS polymer matrix will also cause similar effect on crystallinity variation of PBST copolyesters.

Effect of BDO Ratio on the Synthesis of PBTCCL

The influence of the diol/diacid ratio on aliphatic or aromatic copolyesters in improving their $[\eta]$ values (or molecular weights) and the degree of polymerization of copolyesters has been pointed out previously.^{4,10,25,26} The measured viscosity, $[\eta]$, and the estimated amount of unreacted carboxyl end groups of PBTCCL with 50 mol % of TPA/(CL+TPA) in various molar ratio of BDO/TPA are shown in Figure 3. The $[\eta]$ of copolyesters increased linearly with increasing BDO until the BDO/TPA ratio reached 1.4 mol/mol. In the mean time, the carboxyl end groups (COOH) decreased gradually as polymerization neared completion.

The carboxyl end groups detected are ascribable to those being temporarily inactivated in the polycondensation reactions due to chemical degradation of the carboxylic chain ends; side reactions; or the reactive ends being unable to approach each other due to diffusion limitations.²⁷ The role of BDO in the ROP of CL has been mentioned before by Storey and Sherman²⁵ as an initiator and functional group. During initiation, it reacts with catalyst Sn(Oct)₂ to form an active intermediate and is thus key to polymerization. As shown in Figure 3, increasing the BDO/TPA ratio in the range of 1.1 to 1.4 mol/mol resulted in increasing $[\eta]$ or the molecular weight of PBTCCL. Therefore, proper ratio of BDO/TPA favors the polymerization.

Bikiaris and Achilias²⁸ proposed that higher diol/diacid molar feeding ratio drives reaction equilibrium toward esterification. Although slightly higher values of $[\eta]$ and lower carboxyl end groups of copolyesters were obtained when BDO/TPA molar feeding ratio is 2.0 mol/mol, it is not recommended due to the need to add extra BDO at the beginning and the removal of its excess at the end. It is not cost effective. In addition, it is less favorable for biomass thermal blending process as T_m reaches high temperature at 151°C when BDO/TPA is at 2.0 mol/mol. Therefore, 1.4 mol/mol of BDO/TPA was used in this study.

Effect of Temperature and Time Course of Polycondensation

A previous study shows that the polycondensation of copolyesters affected rarely by the polymerization temperature and

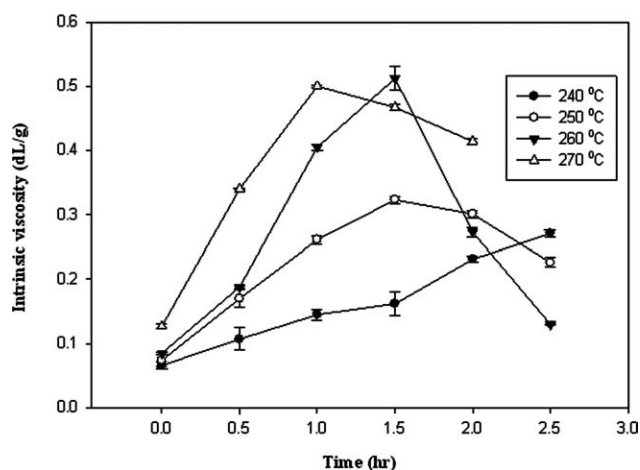


Figure 4. Reaction time course of PBTCCL at different polycondensation temperatures. Molar ratios of BDO/TPA = 1.4 mol/mol with TPA/(CL+TPA) = 50 mol %.

reaction time.²⁷ The time course of $[\eta]$ of PBTCCL with 50 mol % of TPA/(CL+TPA) at different polycondensation temperatures is shown in Figure 4. Reaction temperature below 250°C resulted in slow reaction to reach high values of $[\eta]$. A maximum $[\eta]$ of 0.51 dL/g was reached at 260°C for 1.5 h of reaction time. Bikiaris and Achilias²⁷ proposed that increasing temperature as well as higher diffusion rates of by-product were removed rapidly; the resulted fast condensation rate led to increased $[\eta]$, i.e., increasing molecular weight. Tripathy et al.²⁹ also reported that polymerization performed at higher temperatures would often cause parasitic reactions such as macrocyclic species formation and the formation of higher molecular weight polyester. Furthermore, high temperatures may also accelerate thermal and oxidative degradation during the polycondensation process.²⁷

Mechanical Properties of PBTCCL Copolyesters

The mechanical properties of synthesized PBTCCL are important factors governing their future applications. The mechanical properties were measured for samples synthesized under optimal polycondensation conditions at temperature of 260°C and at 1.4 mol/mol of BDO/TPA. Figure 5(a–c) show the tensile strength at break, elongation at break, and Young’s modulus of PBTCCL in various molar percentages of TPA/(CL+TPA). A small amount of embedded TPA and BDO, e.g., PBTCCL-20 (TPA/(CL+TPA) = 20 mol %), into the homopolymer PCL could dramatically change the physical structure of homopolymer PCL. By comparing the mechanical properties of homopolymer PCL with PBTCCL-20, we observed a drop in elongation at break as well as a decrease in the tensile strength and Young’s modulus as shown in Figure 5(a–c). The molar ratio of TPA/(CL+TPA) plays a major role to determine the mechanical and thermal properties of PBTCCL copolyesters. Although increasing the TPA/(CL+TPA) ratio from 20 to 80 mol % (PBTCCL-20 to PBTCCL-80) resulted in decreasing molecular weight of the copolyesters (Table II), the increasing aromatic unit (TPA) in the PBTCCL copolyesters from PBTCCL-20 to PBTCCL-40 could help to rebuild and strengthen the physical structure of polymer. Thus,

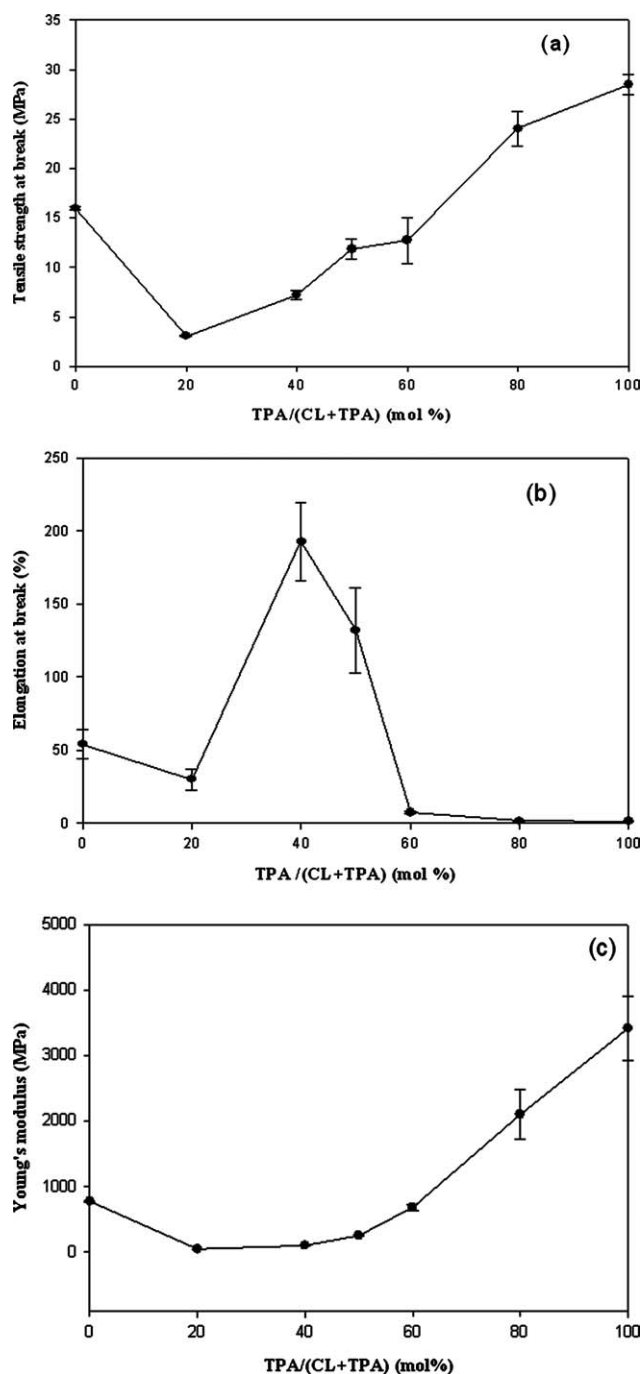


Figure 5. Mechanical properties of PBTCCL (PBTCCL-20 to PBTCCL-80) with different molar percentage of TPA/(CL+TPA) with molar ratios of BDO/TPA = 1.4 mol/mol. The polycondensation was performed at 260°C for 1.5 h: (a) tensile strength at break, (b) elongation at break, and (c) Young’s modulus.

we observed significant increase in its tensile strength as well as in elongation at break without significant changes in the Young’s modulus (or hardness) of the copolyesters. The enhancement of elongation at break without change in Young’s modulus for PBTCCL-20 to PBTCCL-40 may also be favored by the low crystallinity of copolyesters in such composition range (Table II). For copolyesters from PBTCCL-50 to PBTCCL-80, the increase in crystallinity (Table II) as well as the significant

Table II. Thermal and Physical Properties Analysis of PCLBT-20 to PCLBT-80 with Molar Ratios of BDO/TPA = 1.4 mol/mol

Copolyesters	TPA/ (CL+TPA) (mol %)	$M_n \times 10^{-4a}$ (Dalton)	T_m^b (°C)	ΔH_m (J/g)	X_c^c (%)
PCL ^d	0	–	66.2	88.1	65.0
PBTCL-20	20	7.8	103.3	20.1	14.4
PBTCL-40	40	7.1	126.2	14.1	10.1
PBTCL-50	50	7.4	139.2	14.4	10.3
PBTCL-60	60	6.4	169.3	21.9	15.2
PBTCL-80	80	5.2	195.2	38.9	26.9
PBT ^e	100	–	227.6	56.4	39.0

The polycondensation was performed at 260°C for 1.5 h, ^aNumber-average molecular weight determined by $M_n = 1.66 \times 10^5 ([\eta])^{0.9}$, ^bDSC at a heating rate of 10°C/min, ^c X_c was calculated by dividing the observed heat of fusion from melting endotherm by the theoretical value 139.5 J/g for a 100% crystalline PCL (from TPA/(CL+TPA) of 0 to 50 mol %) and by the theoretical value 144.5 J/g for a 100% crystalline PBT (from TPA/(CL+TPA) of 60 to 100 mol %).^{8,15} ^dPolycaprolactone (PCL) was prepared by ring opening polymerization at TPA/(CL+TPA) = 0 mol % at temperature 150°C for 2 h, ^ePoly(butylene terephthalate) (PBT) was prepared by polycondensation at TPA/(CL+TPA) = 100 mol % at temperature 250°C for 2 h.

increasing of Young's modulus [Figure 5(c)] resulted in significant decrease of elongation at break [Figure 5(b)].

The low elongation of homopolyesters of PCL (54.1% ± 10.2%) and PBT (1.5% ± 0.8%) restricted their application in some specific field, e.g., film type of products. Meanwhile, TPA/(CL+TPA) between 40 and 50 mol % (PBTCL-40 and PBTCL-50) showed a proper elongation at break between 192.7% and 132%. PBTCL-50 possesses tensile strengths

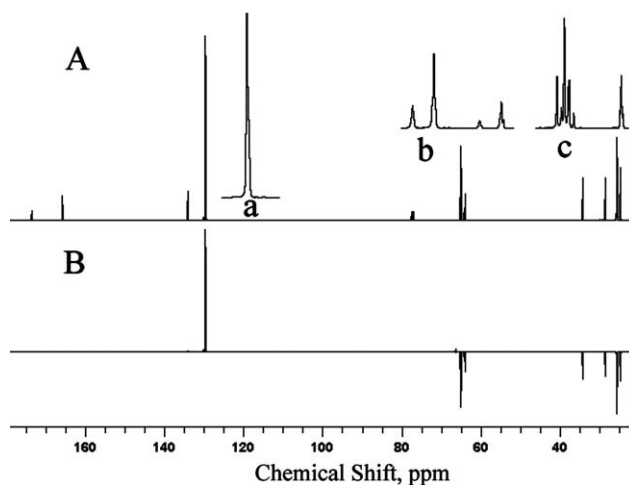


Figure 6. The 1D (A) and DEPT-135 (B) ¹³C-NMR spectra of PBTCL-50. The solvent carbon resonance is located at 77 ppm. The inserted spectra a, b, and c in (A) are expanded area of 129–130, 63.5–65.5, and 24–26 ppm, respectively. Singlets at 34.06 and 28.36 ppm are not expanded. The entire assignment is listed in Table III.

around 12 MPa which is appropriate for making film type products. Meanwhile the Young's modulus of PBTCL-40 and PBTCL-50 are 104.6 MPa and 257.3 MPa, respectively. Tripathy et al.²⁰ reported that synthesized c-PBT/CL of 50 mol % c-PBT had been reported to form a weak and soft copolyester with respect to its tensile stress (5.3 MPa), elongation at break (690%), and Young modulus (18 MPa). In summary, the mechanical properties of PBTCL-50 indicate that they are suitable for serving as film type materials in the biomass containing plastics.

Table III. Chemical Structure of Monomers in PBTCL-50 and Measured ¹³C Chemical Shift

Monomer	Abb.	Structure	Carbon	¹³ C Chemical shift (ppm)
Terephthalic acid (TPA)	T		T_α	165.5
			T_β	133.9
			T_{C1}	129.4
1,4-Butanediol (BDO)	B		B_{C1}	64.8
			B_{C2}	24.4
			B_{C3}	24.4
			B_{C4}	64.9
γ -Caprolactone (CL)	C		C_γ	173.4
			C_{C1}	63.5
			C_{C2}	28.5
			C_{C3}	24.7
			C_{C4}	25.8
			C_{C5}	34.1

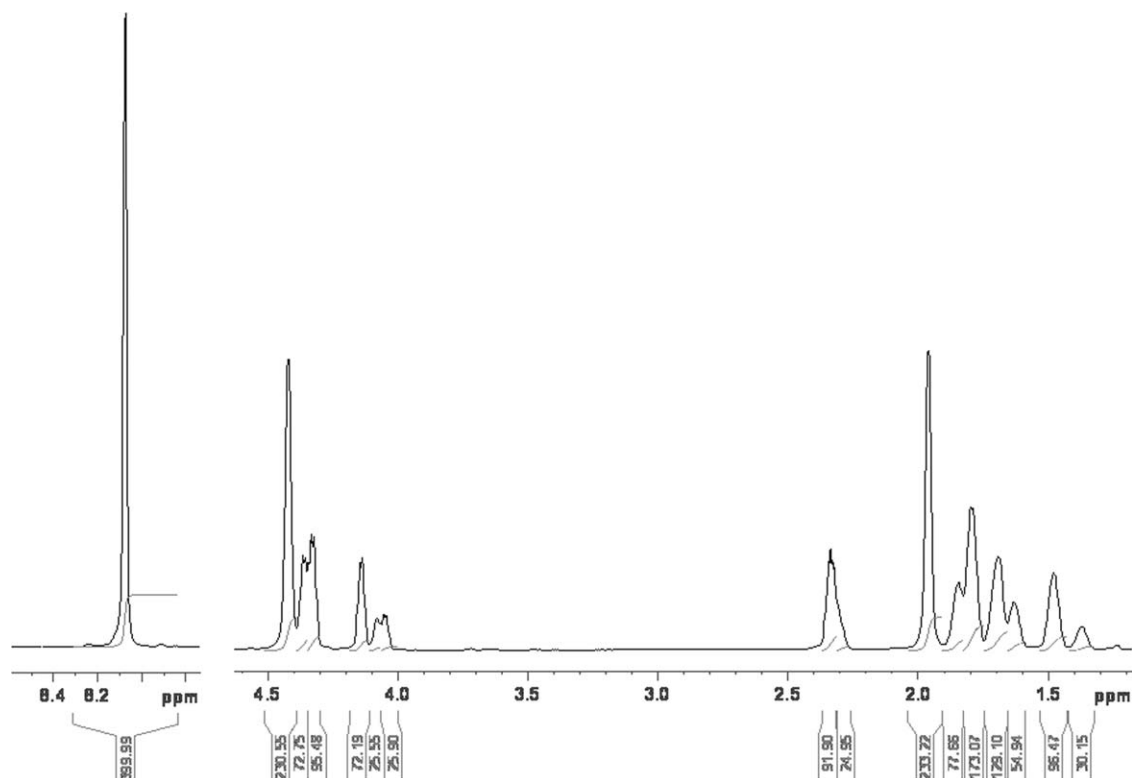


Figure 7. The proton (^1H)-NMR spectra of PBTCCL-50 in CDCl_3 . The values of integration are shown under each peak in bracket by assigning the TPA (T_1 protons at 8.01 ppm) the number 400, arbitrarily.

NMR Analysis and Chemical Structure of PBTCCL

The chemical structures of PBTCCL were analyzed with ^1H - and ^{13}C -NMR spectroscopy. As shown in Figure 6, the ^{13}C -NMR peaks of the three component monomers (TPA, BDO, and CL) of PBTCCL-50 can be seen, and their chemical shifts are listed in Table III. The ^{13}C -NMR spectrum of PBTCCL-50 and its corresponding DEPT-135 (distortionless enhancement by polarization transfer-135 spectroscopy)³⁰ are shown in Figure 6(A, B), respectively. The quaternary carbon, CH, and CH_2 can be assigned by no signal observed, positive signal, and negative signal, respectively, in Figure 6(B). This result is consistent to the assignment based on the ^1H assignment by the one-bond heteronuclear (C—H) shift correlation spectrum³¹ (spectrum not shown). Three downfield quaternary carbon resonances at 173.4, 165.5, and 133.9 ppm can be further identified as the carbonyl carbon in CL, carbonyl carbon, and benzyl carbons in TPA, respectively, by their characteristic chemical shift values. All detail assignment is listed in Table III.

The proton (^1H)-NMR spectra of PBTCCL-50 in CDCl_3 with peak area integration referred to TPA aromatic proton (at 8.01 ppm) intensity (400) as an arbitrary reference are shown in Figure 7. The difference of integrated peak areas is due to different compositions of the building blocks of CL (C), TPA (T), and BDO (B) in PBTCCL-50. Figure 8 shows the 2D-COSY spectrum of PBTCCL-50 in the region 1.3 to 4.6 ppm. These are used to identify the novel five different repeated linkages in polymer with different CL, TPA, and BDO compositions. Figure 9 shows the five types of linkages composed of

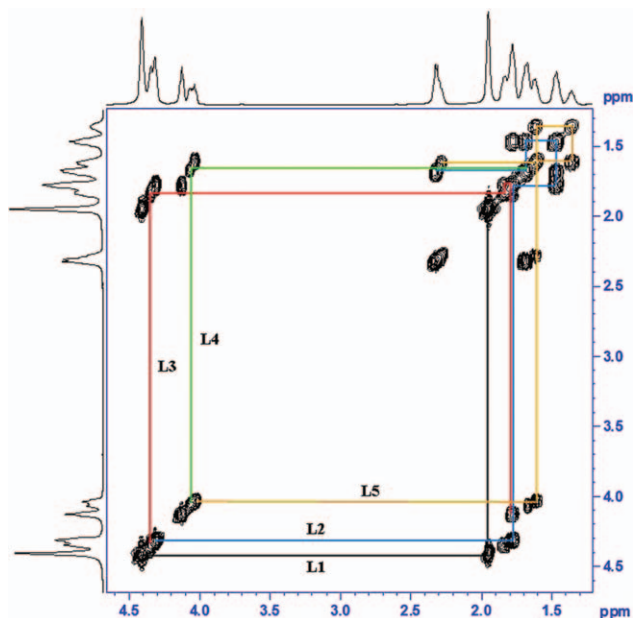


Figure 8. The five novel linkages in PBTCCL-50 can be revealed by 2D-COSY spectrum in the region 1.3 to 4.6 ppm. The connections are illustrated by different color lines for clarity: T-B-T (L_1)-black; T-B-C (L_2)-blue; T-C-C (L_3)-red; C-B-C (L_4)-green; and C-C-C (L_5)-brown. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

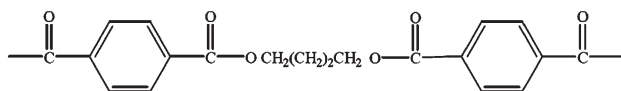
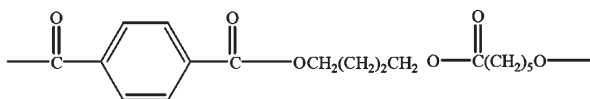
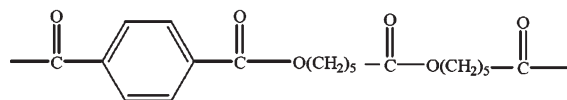
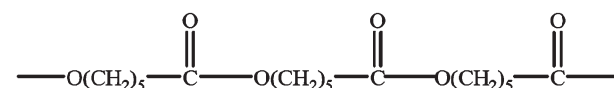
L₁: T-B-TL₂: T-B-CL₃: T-C-CL₄: C-B-CL₅: C-C-C

Figure 9. Identification of five novel structures in PBTCL-50 by NMR analysis.

different monomeric triplets (namely, X-Y-Z). The identified chemical shifts in each proton of the middle monomer (coded in bold) in each linkage, namely T-B-T (L₁), T-B-C (L₂), T-C-C (L₃), C-B-C (L₄), and C-C-C (L₅) are also shown in Table IV, and the integrated intensity (*I*) of each proton groups (based on 2H) are shown. Because of the interference of same chemical shift from different linkages, some of the intensity of proton group could not be measured accurately due to overlapping, e.g., intensities of chemical shifts at 1.68 and 1.78 ppm. However, for identical linkages, the intensities can be calculated accurately when they do overlap, e.g., intensity of chemical shifts at 4.41, 1.95, 4.06, and 1.62 ppm. The average intensities (*I*_{av}) for each linkage, calculated from the intensity of each proton group in the middle monomer (bold), are shown in Table III. We consider that *I*_{av} could be used to estimate the relative molar percentage (Mp) for each linkage. Mp (mol %) can be calculated as follows:

$$Mp_i = \frac{I_{avi}}{\sum_{i=1}^5 I_{avi}} \quad (2)$$

where *I*_{avi} denotes the average intensity of linkage type *i*, L_{*i*}.

Table IV. Chemical Structure of Different Linkages in the PBTCL-50 and Measured Intensity of 1H Resonances in the Middle Monomer of Each Linkage

Linkage	Structure	Chemical shift (in ppm) and intensities (in parentheses) of Proton resonances in the middle monomer (bold) of linkage										Mp ^b (mol %)
		B ₁ (2H)	B ₂ (2H)	B ₃ (2H)	B ₄ (2H)	C ₁ (2H)	C ₂ (2H)	C ₃ (2H)	C ₄ (2H)	C ₅ (2H)	<i>I</i> _{av} ^a	
L ₁	T-B-T	4.41 (<i>I</i> ^c = 231/2)	1.95 (<i>I</i> = 233/2)	1.95 (<i>I</i> = 233/2)	4.41 (<i>I</i> = 231/2)	-	-	-	-	-	116	36
L ₂	T-B-C	4.35 (<i>I</i> = 73)	1.84 (<i>I</i> = 78)	1.78 (-) ^d	4.13 (<i>I</i> = 72)	-	-	-	-	-	74	23
L ₃	T-C-C	-	-	-	-	4.32 (<i>I</i> = 95)	1.78 (-)	1.47 (<i>I</i> = 96)	1.68 (-)	2.32 (<i>I</i> = 92)	94	29
L ₄	C-B-C	4.06 (<i>I</i> = 26/2)	1.68 (-)	1.68 (-)	4.06 (<i>I</i> = 26/2)	-	-	-	-	-	13	4
L ₅	C-C-C	-	-	-	-	4.03 (<i>I</i> = 26)	1.62 (<i>I</i> = 55/2)	1.35 (<i>I</i> = 30)	1.62 (<i>I</i> = 55/2)	2.28 (<i>I</i> = 25)	27	8

^a*I*_{av} = average intensity (based on 2H) of each linkage calculated from the protons in the middle monomer of linkage, ^bMp = relative molar percentage of each linkage calculated from the *I*_{av}, divided by the sum of *I*_{av} from L₁ to L₅, ^c*I* = intensity of ¹H chemical shift based on intensity of T₁ protons (*I* = 400, arbitrarily) at 8.01 ppm, ^dCannot be measured accurately due to overlapping.

The molar percentages (Mp) of each linkage are shown in Table IV. It is obvious that linkages with TPA (Mp_1 to Mp_3) had much higher percentage than linkages without TPA (Mp_4 and Mp_5), namely 36 mol % of T-B-T, 23 mol % of T-B-C, 29 mol % of T-C-C, 4 mol % of C-B-C, and 8 mol % of C-C-C. Since the aromatic structure, e.g., TPA, is considered to contribute to the hard segment in the copolyester structure when compared with its soft segment counterpart of linear (aliphatic) structure,²⁴ it is worthwhile to lead further detailed investigations about the effects of various linkages on the physical or chemical properties of PBTCL.

We could also consider defining the relative molar intensity of TPA (MI_T) from the average intensity of linkages including TPA, e.g., L_1 to L_3 , and the relative molar intensity of CL (MI_C) from the average intensity of linkages L_2 to L_5 as follows:

$$MI_T = 2I_{av1} + I_{av2} + I_{av3} = 400$$
$$MI_C = I_{av2} + 2(I_{av3} + I_{av4}) + 3(I_{av5}) = 369$$

Therefore, the synthesized molar percentage of TPA/(CL+TPA) can be estimated from $MI_T/(MI_C + MI_T)$ as 52 mol % which is very close to the prepared molar feeding ratio (50 mol %) in preparing the PBTCL-50. The method proposed in this NMR study could be considered as an initial intramolecular quantification for the structure of copolyesters with multiple monomers. More detailed investigation on the key factors affecting the variation of molar percentages (Mp) of each linkage will be presented in the near future.

CONCLUSIONS

In conclusion, PBTCL copolyesters were synthesized from BDO, TPA, and CL through polycondensation, using $Ti(Obu)_4$ and $Sn(Oct)_2$ as catalysts. TPA/(CL+TPA) of 40 to 50 mol % (PBTCL-40 and PBTCL-50) possesses T_m between 96 to 129°C—within a temperature range suitable for thermal blending with biomass in many applications. Moreover, thermal properties characterized by DSC and TGA indicated that incorporation of TPA segments significantly hindered the crystallinity of the PCL matrix. Trends of increasing melting point and decomposition temperature with increasing TPA content in the PBTCL copolyesters were observed. The optimal reaction conditions in obtaining the highest $[\eta]$ for PBTCL-50 are found to be as follows: 260°C for polycondensation, 1.5 h and at 1.4 mol/mol of BDO/TPA. The molar ratio of TPA/(CL+TPA) played a major role in determining the mechanical and thermal properties of PBTCL copolyesters. Although increasing TPA/(CL+TPA) ratio from 20 to 80 mol % (PBTCL-20 to PBTCL-80) resulted in decreasing molecular weight of copolyesters (Table II), the tensile strength and melting points of the copolyesters increased nonetheless. However, we found only 40 to 50 mol % PBTCL's (PBTCL-40 to PBTCL-50) possess the best physical properties that are most suitable for making film type products from thermal extrusion with biomass. These properties include as follows: proper tensile strength (around 12 MPa), elongation at break (between 192.7% and 132%), Young's modulus (between 104.6 MPa and 257.3 MPa), and also melting points (between 126.2 and 139.2°C, Table II). Meanwhile the synthesized molar per-

centage of TPA/(CL+TPA) estimated from NMR analysis is 52 mol % which is very close to the prepared molar feeding ratio (50 mol %) in preparing the PBTCL-50. The chemical shifts obtained from 1H - and ^{13}C -NMR spectroscopy identify, unambiguously, five novel and different repeated linkages in PBTCL-50 with different CL (C), TPA (T), and BDO (B) compositions, namely 36 mol % of T-B-T, 23 mol % of T-B-C, 29 mol % of T-C-C, 4 mol % of C-B-C, and 8 mol % of C-C-C.

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