

A well-defined biodegradable 1,2,3-triazolium-functionalized PEG-*b*-PCL block copolymer: facile synthesis and its compatibilization for PLA/PCL blends

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Abstract A novel biodegradable 1,2,3-triazolium-functionalized PEG-*b*-PCL copolymer (TAPEC) was synthesized by the “click” coupling of methoxypolyethylene glycol azide and α -propargyl- ω -hydroxyl-poly(ϵ -caprolactone), followed by the quaternization of the 1,2,3-triazole moiety with iodomethane. All the intermediates and TAPEC were characterized by ¹H NMR, FT-IR, and gel permeation chromatography (GPC). Taking advantage of the characteristics of ionic liquid and block copolymer, this ion-containing diblock copolymer is expected to be used as a novel compatibilizer in mixed biopolyester for regulating the interface and crystallization behaviors. Hence, the TAPEC was evaluated as a compatibilizer and an interface emulsifier in the blends of polylactic acid (PLA) and poly(ϵ -caprolactone) (PCL). Non-isothermal crystallization experimental results showed that the TAPEC with the higher amount of ϵ -caprolactone units induces a plasticization and nucleate effect that increased the crystallization ability of the PLA phase; meanwhile, in the PCL phase, the agminated ionic cluster acting as a nucleating agent significantly increased the crystalline of PCL.

Keywords 1,2,3-Triazolium · Ion-containing compatibilizer · Click chemistry · Crystallization · PLA/PCL blends

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Introduction

Bio-based materials have shown great potential to gradually replace petroleum-based polymers on the account of sustainability and environmental friendliness. Among all bio-based polymers, polylactide (PLA) has occupied a pivotal position in both commercial applications and scientific research owing to its excellent biodegradability, biocompatibility, and renewable sources [1–3]. However, some shortcomings of PLA, for example, brittleness and rigidity, become the main obstacles for its broad commercialization. Therefore, to overcome these limitations, lots of ductile polymers, such as poly(butylene succinate) (PBS) [4, 5], poly(ethylene adipate) (PEA) [6], poly(3-hydroxybutyrate) (PHB) [7, 8], and poly(ϵ -caprolactone) (PCL) [9–11], were used to blend with PLA to improve the impact resistance and fracture toughness of PLA-based polymers. Among them, PLA/PCL blends offer more intriguing characteristics, such as all biodegradability and high mechanical strength [2]. However, due to the poor compatibility between PLA and PCL and the phase separation during the aging process, the PLA/PCL blends cannot maintain the modified mechanical properties over time. Hence, how to modify the interfacial interaction of PLA with PCL is the key factor to control the blends' properties. The modification can be performed in many ways, including compatibilization with premade or in situ-generated copolymers and the addition of compatibilizers. Generally, the latter plays an important role in the development of high-performance PLA/PCL blends [12].

Ionic liquids (ILs), as a type of organic/inorganic salts with a melting point lower than 100 °C, possess numerous merits like low volatility, excellent thermal stability, non-flammability, and large electrochemical window [13–15]. Introduction of ILs as plasticizers and/or additives into polymer matrix would be a promising way to improve the properties of

polymers and extend their corresponding applications. For example, Chen et al. reported that the incorporation of ILs as effective plasticizers into PLA matrix produced a modified PLA with high modulus and ductility [16]. Also, Dias and his co-workers covered that the phosphonium-based ILs can be potentially employed as a poly(vinyl chloride) modifier for biomedical applications [17]. In our previous work, ILs with low molecular weight can cause a significant phase separation and induce the polymer nucleation when added into PLA owing to the polarity difference of IL and PLA [18]. It is known that the block copolymer was often used as a compatibilizer to improve the compatibility of polymer blends; however, as far as we know, ion-containing block copolymer as a compatibilizer used in immiscible polymer blends has not been investigated.

Recently, 1,2,3-triazolium-containing polymers have received increasing attention owing to their broad structural variety enabled by the concept of click chemistry and the efficient *N*-alkylation reaction of 1,2,3-triazoles and their potential applications [19–21], such as electrochemical devices and fuel cells. Hence, in this work, we likely to explore the application of this 1,2,3-triazolium-containing copolymer, acting as a compatibilizer, to the field of polymer blends. A detailed investigation into the effect of 1,2,3-triazolium-functionalized PEG-*b*-PCL copolymer (TAPEC) on the morphology and crystallization behavior of immiscible 80:20 PLA/PCL blends was presented. Particular emphasis was made on spherulitic growth kinetics of the PLA phase, and the crystallization behavior of the PCL phase in the blends was included as well. The results obtained have allowed us to postulate a selective dissolution of the copolymer chains in both blend phases. Owing to the compatibilization effect of the TAPEC copolymer between the PLA and PCL interfaces and a nucleating effect of the PCL phase, a synergistic effect was obtained on the PLA and PCL crystallization rates. Furthermore, considering the benefits of IL and block copolymer, this ion-containing diblock copolymer would be utilized as a compatibilizer to control the interface and other properties of other immiscible biopolyester blends.

Experimental section

Materials

PLA was purchased from NatureWorks biopolymer PLA 4032D, with M_n of 120 kDa and polydispersity index of 1.78. PCL was purchased from Solvay Co. Ltd. (PCL 6800) with the M_n of 80 kDa. Poly(ethylene glycol) monomethyl ether (PEG-1000, average M_n 1000 g mol⁻¹), *p*-toluenesulfonyl chloride (TsCl), and sodium azide were purchased from Aladdin Chemistry Co., Ltd. and used as received without further purification. Diphenyl phosphate

(DPP, TCI, >99%) was used as received. Propargyl alcohol (PGA) and ϵ -caprolactone (ϵ -CL) were purchased from J&K and distilled over CaH₂ and then stored under nitrogen atmosphere. CuSO₄·5H₂O (99.0%) and ascorbate sodium (99.6%) were obtained from Guangzhou Xinbo Chemical Co. Ltd. and Aladdin Chemistry Co., Ltd., respectively, and both were recrystallized from water twice and dried under vacuum at room temperature for 24 h. Water was deionized with a Milli-Q SP reagent water system (Millipore) to a specific resistivity of 18.4 M Ω cm. Unless otherwise noted, the other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. without further purification.

Measurements

¹H NMR spectrum was recorded on a Bruker 600-MHz spectrometer, using CDCl₃ as solvent. Gel permeation chromatography (GPC) was performed on a Waters 1515 pump and a Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of linear Styragel HR1, HR2, and HR4 columns. Molecular weight and polydispersity data are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.3 mL min⁻¹. FT-IR spectra were recorded on a PerkinElmer Spectrum 100 IR spectrometer using KBr pellets at room temperature. The morphology of sample's fracture surfaces was observed by scanning electron microscopy (SEM) after gold coating under vacuum, using a Hitachi JSM-6490LV electron microscope, and the specimens were cryogenically fractured after 1 h of immersion in liquid nitrogen. Thermogravimetric analysis (TGA) measurement was performed in N₂ atmosphere at a heating rate of 10 °C min⁻¹ from 25 to 700 °C using a TA Q500 instrument. A differential scanning calorimeter (DSC TA Q2000, TA Instruments) was used to measure the melting temperatures of neat PLA and PLA/PCL blends. For all the DSC measurements, 5.0–8.0 mg of the samples was taken. For non-isothermal DSC measurements, the samples were heated from room temperature to 200 °C at a heating rate of 10 °C min⁻¹. After being held at 200 °C for 5 min, the samples were cooled to -50 °C at a cooling rate of 5 °C min⁻¹, while the corresponding cooling scans were recorded. Finally, the samples were reheated to 200 °C at the same rate to register the subsequent heating scans. In order to avoid degradation reactions, each sample was dried overnight at 60 °C under vacuum before DSC measurements, and it was not used for more than two non-isothermal experiments.

Synthesis of PEG-*b*-PCL (3a)

Methoxypolyethylene glycol azide (**1b**, the molecular weight calculated by ¹H NMR was 984 g mol⁻¹ and the ethylene glycol segment of about 22) and α -propargyl- ω -hydroxylpoly(ϵ -caprolactone) (**2a**) were synthesized according to the

reported literatures [22, 23], and the detailed synthesis procedures and characterization were described in the supporting information. The molecular weight of **2a** calculated by ^1H NMR was 6680 g mol^{-1} with the caprolactone segment of about 58, and the relative molecular mass measured by GPC was $14,700\text{ g mol}^{-1}$ with narrow molecular weight distribution (PDI = 1.18).

PEG-*b*-PCL was prepared using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ /sodium ascorbate as co-catalyst in THF/ H_2O mixed solvents, and the typical procedure was illustrated as follows: **2a** (1.0 g, 0.17 mmol), **1b** (0.171 g, 0.17 mmol), sodium ascorbate (6.6 mg, 0.033 mmol, about 20% mol to alkynyl group, dissolved in 1 mL of H_2O), and 35 mL THF were added into a Schlenk tube. After the mixture in the tube was degassed by three freeze-vacuum-thaw cycles, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (4.16 mg, 0.017 mmol, about 10% mol to alkynyl group, and dissolved in 1.0 mL of deionized water), which was also degassed by freeze-vacuum-thaw cycles in another tubes, was added into the system and initiated the azide-alkyne click reaction. After the polymerization proceeded for 24 h at room temperature, the reaction was quenched by exposure to air. The polymerization mixture was concentrated and diluted with dichloromethane (DCM) (50 mL), and the copper catalyst was removed by extraction with EDTA aqueous solution ($30\text{ mL} \times 4$). The colorless organic layer was combined and dried over anhydrous Na_2SO_4 , concentrated under reduced pressure, then dissolved in DCM (10 mL), and precipitated in cold ether (150 mL). After drying in vacuum, the polymer was obtained as a white powder with the yield of 87% (1.02 g).

^1H NMR (CDCl_3 , δ , ppm): 1.38 (m, 53.6 H, CH_2), 1.64 (m, 104.8 H, CH_2), 2.31 (t, 51.8 H, COCH_2), 3.38 (s, 3H, $-\text{OCH}_3$), 3.65 (m, 41.6 H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.89 (t, 2H, $-\text{CH}_2-$), 4.06 (t, 51.7 H, COOCH_2), 4.57 (t, 2H, $-\text{CH}_2-$), 5.23 (s, 2H, CH_2), 7.85 ppm (s, 1H, CH). FT-IR: C–H 2943, 2865, 1461; C=O 1733; C–O–C 1100 cm^{-1} . GPC results: $M_{n,\text{GPC}} = 15,200\text{ g mol}^{-1}$, PDI = 1.13. The molecular weight

calculated by ^1H NMR results was $M_{n,\text{PEG}} + M_{n,\text{PCL}} = 984 + 6680 = 7664\text{ g mol}^{-1}$, and the weight fractions of PEG and PCL blocks in PEG-*b*-PCL are 12.8 and 87.2 wt%, respectively.

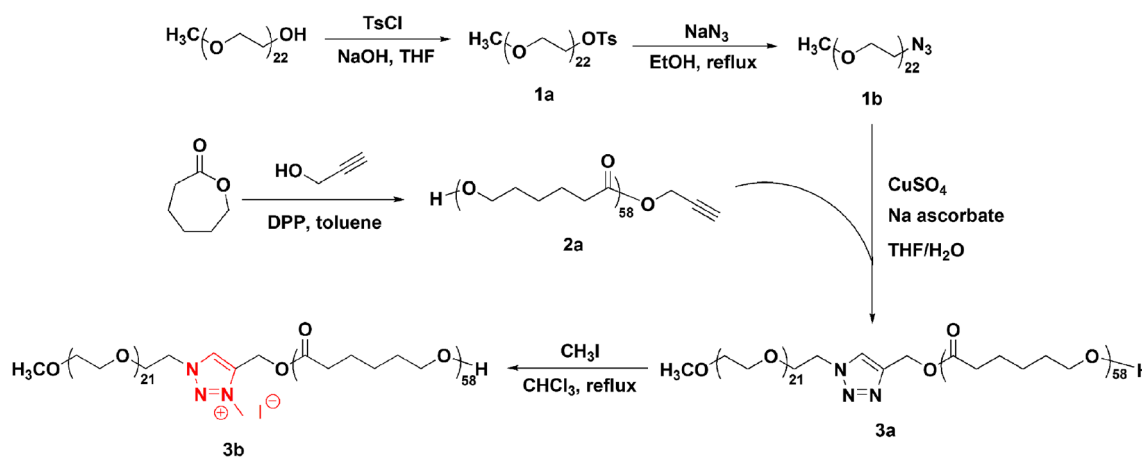
Synthesis of 1,2,3-triazolium-functionalized PEG-*b*-PCL (TAPEC, **3b**)

To a solution of PEG-*b*-PCL (0.50 g, 0.07 mmol) in dry CHCl_3 (20 mL), placed under ice-water bath, CH_3I (98.6 mg; 0.70 mmol) was added dropwise with a dropping funnel. After stirring at $0\text{ }^\circ\text{C}$ for 30 min, the mixture was stirred for another 72 h at $45\text{ }^\circ\text{C}$. The resulting homogenous solution was concentrated and then added dropwise to the excess amount of ether; the precipitate was filtered and washed thoroughly with ether and dried under vacuum at room temperature for 24 h to afford the white solid with the yield of 99%. Complete quaternization of the 1,2,3-triazole group was confirmed by the disappearance of its characteristic ^1H NMR signal at $\delta = 7.85\text{ ppm}$ and the appearance of the new signal at $\delta = 8.90\text{ ppm}$, which correspond to the proton of 1,2,3-triazolium (Scheme 1).

^1H NMR (CDCl_3 , δ , ppm): 1.38 (m, 54 H, CH_2), 1.64 (m, 103.3 H, CH_2), 2.31 (t, 49.5 H, COCH_2), 3.38 (s, 1.1 H, $-\text{OCH}_3$), 3.65 (m, 41.6 H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.71 (s, 0.71 H, $-\text{CH}_3$), 3.97 (t, 0.15 H, $-\text{CH}_2-$), 4.06 (t, 50 H, COOCH_2), 4.84 (m, 0.18 H, $-\text{CH}_2-$), 5.45 (s, 0.17 H, CH_2), 8.90 ppm (s, 0.10 H, CH).

Preparation of PLA/PCL/TAPEC blends

Prior to blending, all the materials were dried overnight in the vacuum oven: the PLA at $80\text{ }^\circ\text{C}$ and the PCL and TAPEC at $40\text{ }^\circ\text{C}$, respectively. In this work, a solution casting method was used to prepare PLA/PCL blends and the constant PLA/PCL weight ratio of 80:20 wt% was employed with chloroform as a mutual solvent. The final blend approximate ratio is shown in Table 1.



Scheme 1 Synthetic routes employed for the preparation of PEG-*b*-PCL (**3a**) and 1,2,3-triazolium-functionalized PEG-*b*-PCL (TAPEC, **3b**)

Table 1 Composition of the prepared blends

Sample	PLA (w/w %)	PCL (w/w %)	TAPEC (w/w %)
PLA	100	–	–
PCL	–	100	–
80PLA/20PCL	80.0	20.0	–
80PLA/20PCL/2TAPEC	78.4	19.6	2.0
80PLA/20PCL/5TAPEC	76.0	19.0	5.0

Results and discussion

Synthesis of PEG-*b*-PCL (**3a**) and TAPEC (**3b**)

PEG-*b*-PCL block copolymer was synthesized by coupling of α -propargyl- ω -hydroxyl-poly(ϵ -caprolactone) (**2a**) with methoxypolyethylene glycol azide (**1b**) via a click reaction. A mild condition with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ /sodium ascorbate as the catalyst and THF/ H_2O (v/v, 35:2) as mixed solvent was used, since the addition of a small amount of water can improve the efficiency of the “click” reaction [24–26]. Figure 1a shows the ^1H NMR spectrum of the polymer **3a** measured in CDCl_3 at room temperature. The resonances at 7.85 ppm (*d*) and 5.23 ppm (*e*), which should be assigned to the protons of the 1,2,3-triazole proton and the methylene protons of PCL adjacent to the 1,2,3-triazole ring, respectively, were observed, confirming that the click conjugation reaction proceeded successfully. Moreover, the molar ratio of PEG and PCL blocks in the proposed polymer **3a** can be deduced

by comparing the integral areas of signals *b* and *h* from PEG and PCL segments [27], respectively, and the results agree well with the theoretical value. Meanwhile, the GPC traces of polymer **3a** along with **1b** and **2a** are depicted in Fig. 2, which showed the monomodal GPC traces of the obtained PEG-*b*-PCL, indicating that the azide-terminated PEG and propargyl-terminated PCL were definitely coupled with each other. The M_n and M_w/M_n of **3a** were respectively estimated to be 15.2 kDa and 1.13 based on GPC analyses with equivalent to polystyrene standard. In addition, the FT-IR spectra of polymer **3a** and the precursors **1b** and **2a** are illustrated in Fig. S1, and the characteristic absorption peak of azide group at 2100 cm^{-1} in precursor **1b** and propargyl group at 3249 and 2238 cm^{-1} in precursor **2a** disappeared totally after click reaction. These results indicate that the copper-catalyzed click coupling of **1b** and **2a** proceeded efficiently without any side reactions.

Subsequently, 1,2,3-triazole moiety in copolymer **3a** was quaternized by CH_3I in CHCl_3 at $45\text{ }^\circ\text{C}$ affording the corresponding 1,2,3-triazolium-functionalized PEG-*b*-PCL (TAPEC, **3b**) [21, 28, 29]. Figure 1b displays the ^1H NMR spectrum of the obtained 1,2,3-triazolium-functionalized PEG-*b*-PCL. Complete quaternization was confirmed by the disappearance of the ^1H NMR signal at $\delta = 7.85\text{ ppm}$ of the proton of the 1,2,3-triazole group and the emergence of new signal of 8.90 ppm, which is assigned to the proton of 1,2,3-triazolium. Besides, the methylene protons of PCL conjoint to the 1,2,3-triazole ring were significantly shifted towards down field from 5.23 to 5.31 ppm, further confirming the successful quaternization.

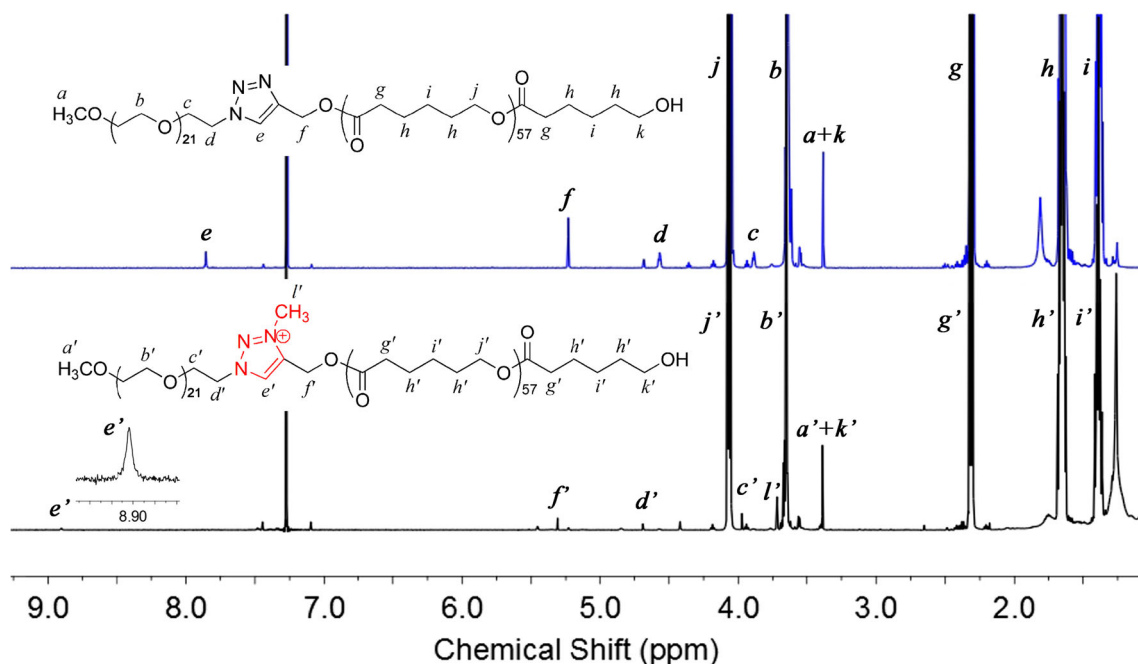


Fig. 1 ^1H NMR spectra of PEG-*b*-PCL (**a**) and TAPEC (**b**) in CDCl_3

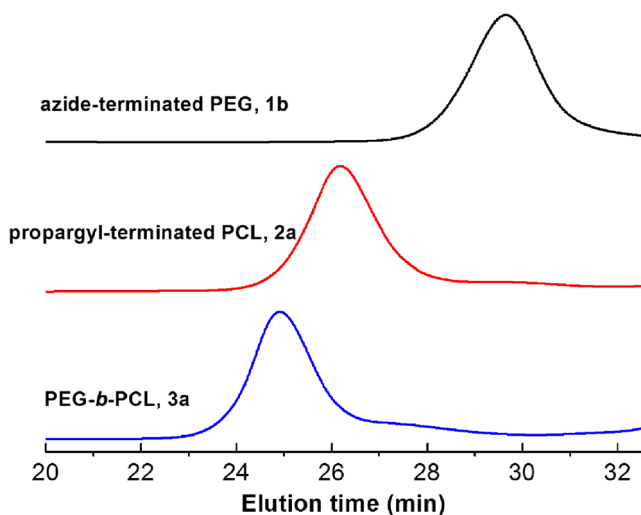


Fig. 2 GPC traces of the obtained PEG-*b*-PCL with the precursors propargyl-terminated PCL and azide-terminated PEG

Thermal properties

The thermal stability of the neutral 1,2,3-triazole coupling PEG-*b*-PCL (**3a**) and the quaternized 1,2,3-triazolium-functionalized PEG-*b*-PCL **3b** was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. Figure 3a shows the TGA curves of all the obtained polymers and exhibited a similar pattern of decomposition with no significant weight loss up to the temperature of 300 °C. In comparison with azide-terminated PEG and propargyl-terminated PCL with 5% weight loss temperatures ($T_{5\%}$) of 294 and 343 °C (Fig. S2), respectively, **3a** displayed higher stability ($T_{5\%} = 375$ °C) than the two precursors, and the decomposition behavior was similar with the previously reported results [30]. Owing to the low mass percentage of 1,2,3-triazole group in PEG-*b*-PCL, the quaternized 1,2,3-triazolium-functionalized PEG-*b*-PCL **3b** with $T_{5\%}$ of 366 °C showed slightly low thermal stability than **3a** (Fig. 3a), which is consistent with the previous results [21, 31]. Moreover, the onset temperature of **3b** is above 200 °C, which is higher than the degradation temperature of PLA, demonstrating the

sufficient thermal stability of TAPEC in further blending and machining process.

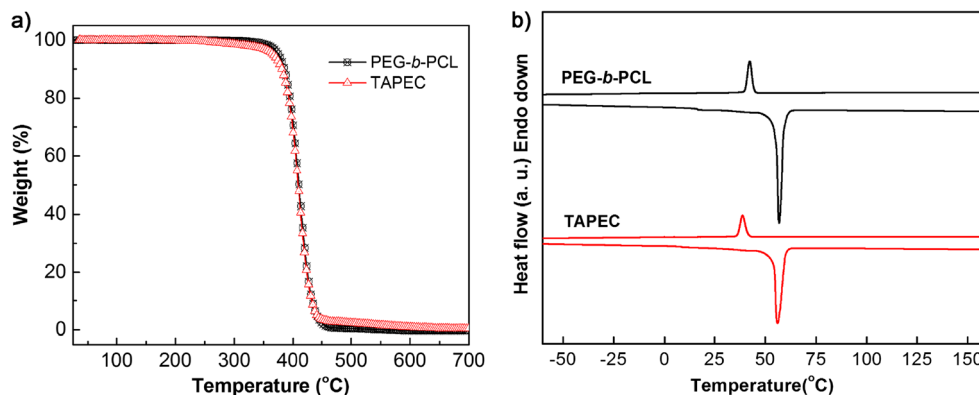
Differential scanning calorimetry (DSC) was further employed to investigate the thermal phase transition of bulk TAPEC, and its typical DSC thermograms are shown in Fig. 3b. DSC scan of the second heating process at a rate of 10 °C min⁻¹ showed that the TAPEC displayed two different signals: a crystallization peak at 39 °C and a melting peak at 56 °C, respectively. Compared with the thermal phase transition of PEG-*b*-PCL, the crystallization temperature of TAPEC decreased from 42 to 39 °C, a possible explanation is that the electrostatic interaction of the quaternized 1,2,3-triazole moieties may restrict aligning of the block IL to form an ordered structure [18].

SEM micrographs

Figure 4 illustrates the SEM micrographs for cryogenically fractured surfaces of 80PLA/20PCL, 80PLA/20PCL/2TAPEC, and 80PLA/20PCL/5TAPEC blends. In all cases, a sea-island morphology was observed, where the matrix formed by PLA and the PCL was well dispersed as droplets, corresponding to the typical structure of immiscible blends [32, 33]. For the neat PLA/PCL blends (Fig. 4a), a large number of cavities were observed as a result of interfacial debonding between PCL and PLA during cryogenic fracture. After the addition of TAPEC, debonding was reduced, and the number of cavities for 80PLA/20PCL/2TAPEC (Fig. 4b) and especially for 80PLA/20PCL/5TAPEC (Fig. 4c) was decreased. These differences can be correlated with the degree of crystallinity of the PLA matrix in the blends. When the PLA matrix crystallizes in the blend, it undergoes a larger volume contraction upon solidification compared to when it remains amorphous; therefore, the corresponding density increases upon crystallization. The droplets are then less likely to detach during cryogenic fracture.

From the SEM results, we could also found that the addition of TAPEC into the PLA/PCL blends let the particle size

Fig. 3 Thermal properties of PEG-*b*-PCL and TAPEC. **a** TGA. **b** DSC



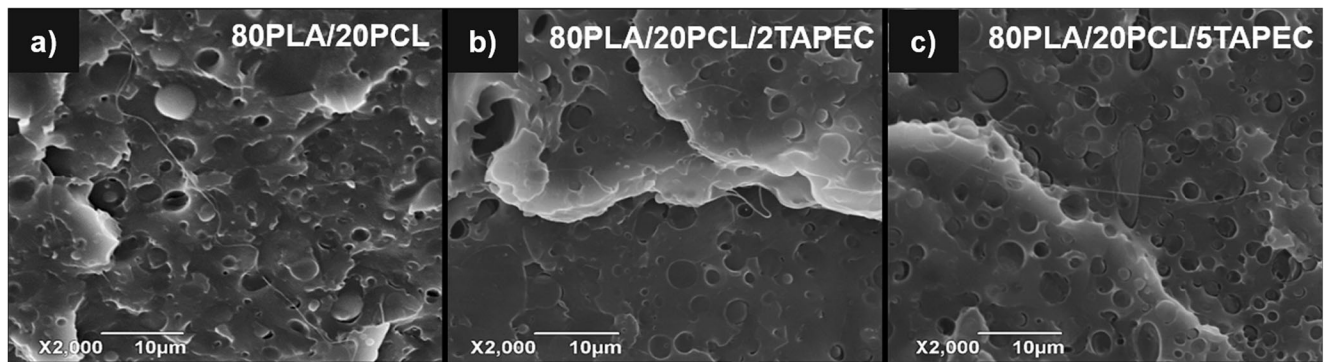


Fig. 4 SEM micrographs for the cryogenically fractured surfaces of **a** 80PLA/20PCL, **b** 80PLA/20PCL/2TAPEEC, and **c** 80PLA/20PCL/5TAPEEC

distributions of PCL droplets in the blends more uniformed, and with the content of the TAPEEC increasing, the PCL average particle size in the blends reduced from about $0.37 \mu\text{m}$ for PLA/PCL blends to $0.35 \mu\text{m}$ for 80PLA/20PCL/2TAPEEC and $0.31 \mu\text{m}$ for 80PLA/20PCL/5TAPEEC. This result indicates that the TAPEEC significantly reduces the interfacial tension between PCL and PLA since it can migrate to the interfacial regions between the two components. In the PCL phase, TAPEEC acts as a compatibilizer and an interface emulsifier, contributing to the enhancement of the compatibility between the dispersed PCL domains and the PLA matrix and reduced the particle size of PCL.

Non-isothermal DSC experiments

Figure 5 shows the DSC cooling thermograms from the melt and subsequent heating scans for all the investigated samples, and Table 2 lists the characteristic temperatures and enthalpies derived from the neat PLA and PCL and the blends. As can be seen in Fig. 5a, the neat PCL crystallized at 28°C with a sharp exothermic peak; however, when PCL dispersed as the form of droplets in PLA matrix (80PLA/20PCL blends, Fig. 4b), its crystallization was fractionated into two peaks at 17 and 3°C ,

respectively. Generally, fractionated crystallization was often observed in immiscible blends as the number of droplets of a crystallizable phase is larger or with the same order of active heterogeneities presenting in the bulk polymer [34]. In PLA/PCL blend system, the first crystallization exotherm was recorded at 17°C , corresponding to the crystallization of PCL droplets that have been nucleated by the PLA matrix. The second crystallization exotherm occurred at a low temperature of 3°C , which may be accounted for the rest of PCL droplets with less active heterogeneities [35].

Similarly, as for PLA/PCL/TAPEEC blends, the fractionated crystallization of PCL was also exhibited, and the TAPEEC did not significantly influence the crystallization behavior of PCL in the blends of 80PLA/20PCL/2TAPEEC. However, as the content of TAPEEC increased to 5 wt% in 80PLA/20PCL/5TAPEEC blends, the crystallization temperature of PCL droplets reached to 8 and 29°C , respectively, which are higher than those of PLA/PCL and 80PLA/20PCL/2TAPEEC blends. Interestingly, the degree of crystallinity of PCL in 80PLA/20PCL/5TAPEEC blends reached as high as 41.9%, which is much higher than that in 80PLA/20PCL/2TAPEEC blends (27.6%) and even higher than in neat PCL with the crystallinity degree of 36.0%, indicating that all PCL droplets could be crystallized sufficiently.

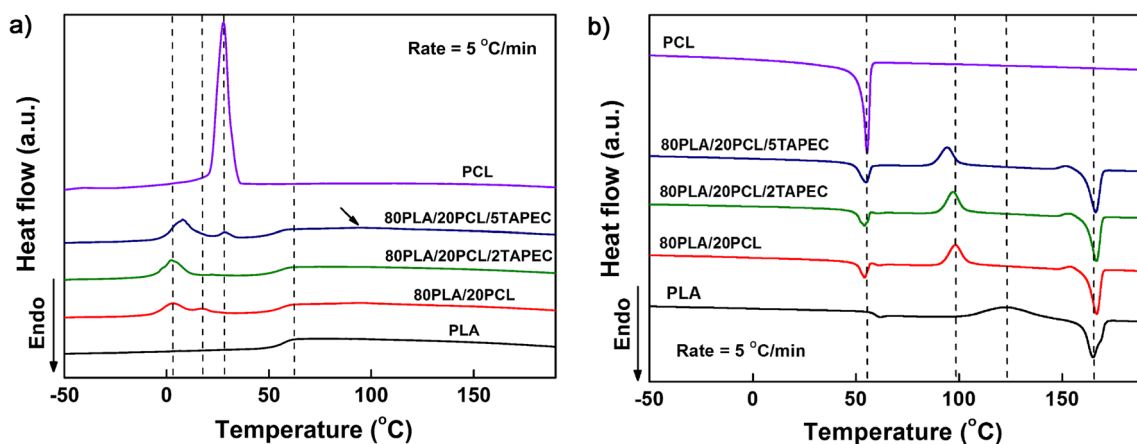


Fig. 5 Non-isothermal DSC experiments. Cooling curves **(a)** at 5°C min^{-1} from the melt state and the subsequent heating curves **(b)** at 5°C min^{-1} . The curves have been normalized by the weight of the samples

Table 2 Thermal properties obtained from non-isothermal DSC, cooling, and second heating curves

Samples	Cooling				2nd heating							
	$T_{c,PCL}$ (°C)	$\Delta H_{c,PCL}$ (J g ⁻¹)	$T_{c,PLA}$ (°C)	$\Delta H_{c,PLA}$ (J g ⁻¹)	$T_{m,PCL}$ (°C)	$\Delta H_{m,PCL}$ (J g ⁻¹)	$X_{c,PCL}$ (%)	$T_{cc,PLA}$ (°C)	$\Delta H_{cc,PLA}$ (J g ⁻¹)	$T_{m,PLA}$ (°C)	$\Delta H_{m,PLA}$ (J g ⁻¹)	$X_{c,PLA}$ (%)
PLA	–	–	–	–	–	–	–	122	33.7	165	34.2	0.9
PCL	28	56.5	–	–	55	56.5	36.0	–	–	–	–	–
80PLA/20PCL	3:17	7.4	96	0.1	54	8.3	26.4	98	20.1	167	34.7	19.5
80PLA/20PCL/2TAPEC	3:22	9.6:0.1	–	–	54	8.5	27.6	97	20.8	167	34.9	19.2
80PLA/20PCL/5TAPEC	8:29	14.4	95	0.2	55	12.5	41.9	94	18.2	166	36.2	25.3

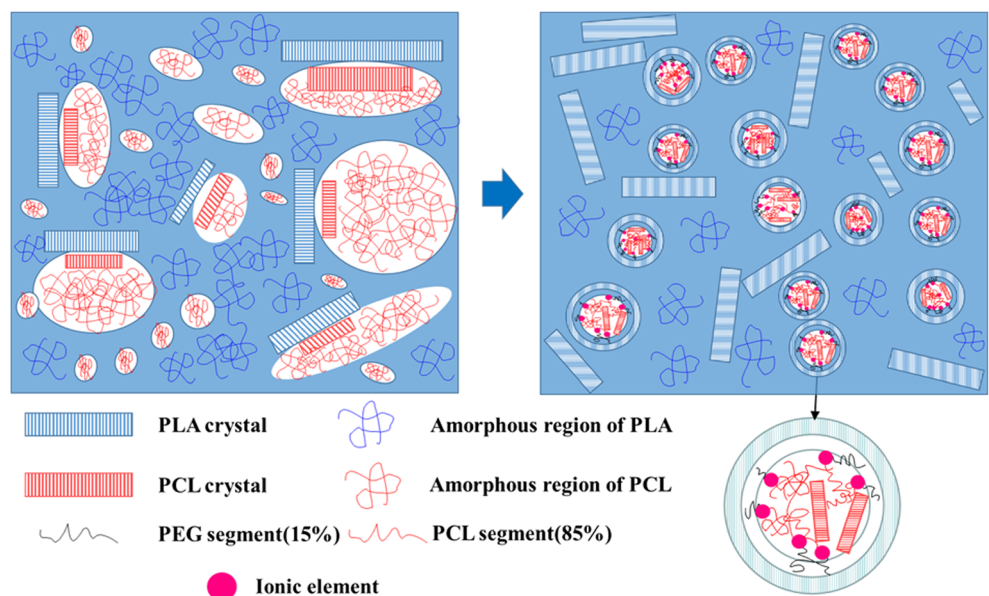
The enthalpies of crystallization and melting have been normalized by the weight fraction of the samples

On the other hand, according to Fig. 5a, neat PLA does not crystallize during the cooling stage employed at the scanning rate of 5 °C min⁻¹. The reason for this behavior is the D-LA isomer content of 1.2–1.6% present in commercial PLA 4032D [36]. Similar to the neat PLA, there was no obvious crystallized peak observed for PLA/PCL and 80PLA/20PCL/2TAPEC blends; however, a small exothermic peak could be observed (as indicated by arrow in Fig. 5a) in 80PLA/20PCL/5TAPEC samples with the X_c increased from 19.5% for PLA/PCL to 25.3% for 80PLA/20PCL/5TAPEC. Therefore, the presence of 5 wt% of TAPEC in PLA/PCL blends could enhance the crystallization capacity of PLA as PLA melt was cooled down at a cooling rate of 5 °C min⁻¹.

As indicated in Fig. 5b and Table 2, each PLA blend showed a strong exothermic peak in the subsequent heating scanning at a rate of 5 °C min⁻¹, attributing to the cold crystallization of PLA at the amorphous solid state. The corresponding crystallization peak was known as the cold crystallization temperature (T_{cc}). The enthalpy of cold crystallization of neat PLA as listed in Table 2 was almost identical to the melting enthalpy,

demonstrating that the neat PLA was amorphous. A broad exothermic peak at 122 °C was observed for neat PLA, and this exothermic peak was shifted to lower temperature at 98 to 97 °C for PLA/PCL and 80PLA/20PCL/2TAPEC samples. In the case of 80PLA/20PCL/5TAPEC blends, this peak was further shifted to even lower temperature of 94 °C, which indicated that the T_{cc} decreased with the increasing of TAPEC content. The improvement of cold crystallization ability of PLA can be attributed to the plasticizing effect of TAPEC, by enhancing the mobility of PLA segment, as incorporation of TAPEC resulted in larger free volume of PLA segment than neat PLA and PLA/PCL segments. As a consequence of this, during the second DSC scanning, the cold crystallization enthalpies for the PLA phase of the 80PLA/20PCL/5TAPEC blends are reduced, as compared to that of 80PLA/20PCL and 80PLA/20PCL/2TAPEC blends. This simultaneous enhancement of the crystallization ability of the PLA and PCL in PLA/PCL blends by the addition of compatibilizer has not been reported for similar systems [37]. The positive effect of the addition of ion-containing macromolecular compatibilizer to the blends on PLA crystallization under

Fig. 6 Illustration of the mechanism of the effect of incorporation of TAPEC into PLA/PCL blends



non-isothermal conditions will be further investigated in the future.

From the SEM and DSC results, we schemed that the compatibilizer TAPEC was mainly dispersed on the interfacial regions between the PLA and PCL components, acting as a compatibilizer and an interface emulsifier, and the schematic representation is shown in Fig. 6. But considering the TAPEC employed in this work containing 12.8 wt% PEG and 87.2 wt% PCL repeating units, the weight ratio of PCL was much higher than that of PLA in TAPEC; hence, we could conclude that during the mixing procedure, in addition to be dispersed on the interfacial regions between the PLA and PCL components, TAPEC is preferred to be dissolved in the PCL phase compared with the PLA phase. So, compared with the PLA/PCL blends, the PCL phase in PLA/PCL/TAPEC blends contained much more ionic cluster which could promote PCL nucleation, acting as heterogeneous nuclei; also in the PLA phase, the rarely dissolved TAPEC and the abundant PEG segments stayed on the interfacial regions, acting as a nucleating agent and a plasticizer, respectively, promoting the PLA phase crystallization, so the TAPEC could simultaneously enhance the crystallization ability of the PLA and PCL phases in the PLA/PCL blends.

Conclusion

A novel 1,2,3-triazolium-functionalized PEG-*b*-PCL copolymer (TAPEC) was synthesized by the combination of ring-opening polymerization and click reaction, and the structure was confirmed by NMR, FT-IR, and GPC. It was found that the addition of TAPEC to PLA/PCL blends can improve the compatibility between the dispersed PCL domains and the PLA matrix and reduce the particle size of PCL. The non-isothermal experiment demonstrated that the incorporation of TAPEC into the blends increased the crystallinity of the PLA phase, acting as a plasticizer. Meanwhile, the addition of TAPEC also significantly increased the crystallinity of the PCL, which can be accounted for the high amount of ϵ -CL units of TAPEC prone to aggregating in the PCL phase, acting as a nucleating agent. This simultaneous enhancement of the crystallization ability of the PLA and PCL in the PLA/PCL blends by the addition of compatibilizer has not been reported for similar systems. Such a novel ion-containing compatibilizer as well as the potential structure diversity enabled by the concept of click chemistry offers us an opportunity to better understanding of the crystalline morphology and crystallization behavior of the polymer blends.

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