



Thermosensitive poly(lactic-acid)-based networks



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ABSTRACT

Poly(lactic-acid)-based thermosensitive networks were prepared in a simple way through reversible Diels–Alder reaction. First, hydroxyl-telechelic PLA with well-controlled molar masses were synthesized by ring-opening polymerization of L-lactide using 1,4-butanediol/Sn(Oct)₂ as catalytic system in a solvent-free process. The molar ratio of lactide/initiator was fixed to control the number average molecular weight (M_n). Before the synthesis of the network, a second precursor which is the Diels–Alder adduct was prepared apart for a better control of the Diels–Alder conversion. The thermoreversible networks were then obtained by simultaneous coupling of the hydroxyl-telechelic PLA, Diels–Alder adduct, multi-alcohols such as glycerol and xylitol, and a diisocyanate (H₁₂MDI) through the alcoholysis reaction of isocyanate. The networks' properties were characterized. The cross-linking and de-cross-linking thermal dependence of PLA-based networks was shown by solubility tests at room and high temperatures and by thermo-mechanical analysis. The effect of the node concentration and steric hindrance on the networks' formation and properties was investigated. Low de-cross-linking temperatures were obtained for some materials.

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1. Introduction

Poly(lactic-acid) (PLA) is a biodegradable, biocompatible and bio-based polyester used for many applications: packaging [Auras et al., 2004], medicine (surgical sutures, scaffolds and tissue regeneration [Mainil-Varlet et al., 1997; Nostrum et al., 2004]), and agriculture (mulch films and controlled release matrices for fertilizers, pesticides and herbicides [Chang et al., 1996]) are the main three fields of use of PLA. PLA has suitable properties for such applications; nevertheless, many efforts have been made, during the last few years and especially after the fall of PLA prices [Dubois, 2002], to improve its properties and make the product more competitive against petroleum-based polymers. Particular efforts were made on the expansion of the PLA processing window and also to enhance its thermal stability in order to prevent thermal degradation and maintain molar masses and properties during processing. For this, polymer blends [Liu et al., 2011], block copolymerization [Min et al., 2005], composites [Faludi et al., 2013; Wu et al., 2013], stereocomplex formation between poly(L-lactic acid) (PLLA) and poly(D-lactic

acid) (PDLA) [Quynh et al., 2008] and cross-linking by radiation [Mitomo et al., 2006] have been investigated.

Among these methods, cross-linking seems to be a particularly good method to improve the thermal stability of PLA while maintaining its biodegradability [Quynh et al., 2007; Mitomo et al., 2006]. Nevertheless, the proposed cross-linking method does not allow the re-processability of the issued materials.

In order to cumulate the advantages due to the cross-linking while preserving the possibility of re-processing, dynamic reactions such as Diels–Alder reaction can be used for network formation [Gandini et al., 2010; Kavitha and Singha, 2007; Kirchhof et al., 2013; Aumsuwan and Urban, 2009; Wei et al., 2010; Gandini, 2013; Marref et al., 2013; Yamashiro et al., 2008; Inoue et al., 2009; Ikezaki et al., 2014].

This possibility was evaluated for PLA by Yamashiro et al. (2008) and Inoue et al. (2009); it was shown that in addition to the reversibility of the networks, the prepared materials had shape-memory behavior. Nevertheless, even though the prepared material is particularly interesting, the proposed multiple-step strategy seems very complicated to implement, making its use on an industrial scale not quite realistic.

In this paper, a one-step facile and efficient approach is used to prepare thermally-reversible PLA network. It consists in a simultaneous coupling of hydroxyl-telechelic PLA, a dihydroxy-Diels–Alder adduct and multi-alcohols with a diisocyanate. The

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Table 1
Synthesis of PLA-Diols – molar ratios.

PLA-Diols	L-lactide/butanediol	Sn(oct) ₂ /L-lactide
PLA-Diol 1	12	10 ⁻²
PLA-Diol 2	4	10 ⁻²
PLA-Diol 3	2	10 ⁻²

thermoreversibility in the proposed systems is provided by Diels–Alder reaction between furan and maleimide. Through this approach and after the synthesis of precursors (hydroxyl-telechelic PLA and dihydroxy-Diels–Alder adduct), networks were assembled. The parameters of the reaction, such as PLA molar masses, node density and hindrance effect were modulated to study their influence on the network. The cross-linking/de-cross-linking thermal dependence of the networks was highlighted by dynamic mechanical analyses and solubility tests.

2. Experimental

2.1. Reagents

L-Lactide was obtained from PURAC, PURASORB. 1,4-butanediol (99%), 4,4'-methylene bis(cyclohexylisocyanate) (H₁₂MDI, mixture of isomers, 90%), maleimide (98%), glycerol (99%), pentaerythritol ethoxylate (3/4 EO/OH) ($M_n = 270 \text{ g mol}^{-1}$), xylitol (99%), formaldehyde (solution, 37 wt.% in water), catalysts: tin(II)2-ethylhexanoate (stannous octoate–Sn(oct)₂) (95%), dibutyltin-dilaurate (95%) and different solvents, chloroform, dimethylformamide (DMF), and ethanol were purchased from SIGMA ALDRICH. The furfuryl alcohol (98%) was purchased from ACROS ORGANICS and solvents, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), petroleum ether and ethyl acetate from CARLO ERBA. Glycerol and DMF were dehydrated by molecular sieves 3 Å (rod shape, size 1/16 in., Fluka) for 48 h. All the other reagents were used as received.

2.2. Synthesis

2.2.1. Hydroxyl telechelic polylactic acid

Hydroxyl telechelic polylactic acids (PLAs-Diols) were prepared by ring opening polymerization using L-lactide dimer, 1,4-butanediol as initiator and stannous octoate (Sn(oct)₂) as catalyst. All reactions were carried out at 110 °C for 5 h under nitrogen flow with L-lactide/butanediol and Sn(oct)₂/L-lactide molar ratios given in Table 1.

The PLA-Diol 2 synthesis is given as an example. In a 150 mL round-bottom flask, 30 g (0.208 mol) of L-lactide were mixed with 4.69 g (0.052 mol) of 1,4-butanediol and Sn(oct)₂ 0.84 g (0.002 mol). The mixture was heated for 5 h at 110 °C under nitrogen flow.

Table 2
Networks synthesis.

	M_n (g mol ⁻¹)	Number of PLA arms		H ₁₂ MDI (mol)	Glycerol (mol)	PLA-Diol (mol)	HMM/FAI adduct (mol)
Run 1 ^a	2050	3		6	1	3	1.5
Run 2 ^a	810	3		6	1	3	1.5
Run 3	520	1		4	1	1	1.5
Run 4	520	2		5	1	2	1.5
Run 5 ^a	520	3		6	1	3	1.5
			H ₁₂ MDI (mol)	Pentaerythritol ethoxylate (mol)		PLA-Diol (mol)	HMM/FAI adduct (mol)
Run 6	520	4	8	1		4	2
			H ₁₂ MDI (mol)	Xylitol (mol)		PLA-Diol (mol)	HMM/FAI adduct (mol)
Run 7	520	5	10	1		5	2.5

^a Runs 1, 2 and 5 are defined in Scheme 3.

2.2.2. Bifunctional Diels–Alder adduct synthesis

The Diels–Alder adduct was obtained from an equimolar ratio of N-hydroxymethylmaleimide (HMM) and furfuryl alcohol (FAI). In a first step the HMM was synthesized according to Tawney et al.'s protocol [Tawney et al., 1961]. The bifunctional Diels–Alder adduct was then prepared as previously described [Okhay et al., 2013] with a 76% yield. The molecule's structure (exo form) was confirmed by ¹H NMR (*d*₆-DMSO): δ (ppm) 6.5 (2H₁₁, s); 6.3 (1H₆, t); 5.1 (1H₂, s); 4.9 (1H₈, t); 4.7 (2H₅, d); 3.7–4 (1H₇, m); 3.0 (1H₄, d); 2.9 (1H₃, d). $T_m(\text{DSC}) = T_{r\text{DA}} = 141 \text{ }^\circ\text{C}$ [Jegat and Mignard, 2008].

2.2.3. Polymer network formation

The formation of the reversible bio-based networks consists of an assembling of four compounds (PLA-Diol, Diels–Alder adduct, diisocyanate and a multialcohol) through the condensation reaction of isocyanate and alcohol functions. Networks were synthesized by coupling isocyanate with alcohol functions, in the presence of dibutyltin-dilaurate as catalyst ([dibutyltin-dilaurate]/[H₁₂MDI] = 10⁻²) molar formulations are given in Table 2. For the synthesis of run 1, H₁₂MDI (2.29 g, 0.0087 mol), glycerol (0.13 g, 0.0014 mol), PLA-Diol 1 (8 g, 0.0043 mol), Diels–Alder diol-adduct (0.51 g, 0.0022 mol), dibutyltin-dilaurate (0.05 g, 0.000087 mol) and 40 mL of dried DMF were introduced in a 100 mL glass reactor under nitrogen flow and mixed at 90 °C for 7 h. The viscous product obtained was then dried under vacuum at 40 °C for 72 h.

2.3. Characterizations

¹H NMR analyses were performed with a Bruker Avance II spectrometer (250 MHz) using deuterated chloroform (CDCl₃) as solvent for most of the products and deuterated dimethylsulfoxide (*d*₆-DMSO) for Diels–Alder bifunctional adduct and for N-hydroxymethylmaleimide (HMM). Tetramethylsilane (TMS) was used as internal reference.

The DSC thermal analyses were performed with a TA Instruments Q10 Differential Scanning Calorimeter DSC. All the samples were analyzed in hermetic sealed pans in a temperature range going from –60 °C to 160 °C with a heating and a cooling rate of 5 °C min⁻¹. Transition temperatures (T_g) were evaluated from the data recorded during the second cycle of heating by identifying the inflection points.

Size exclusion chromatography (SEC) was performed on a 515 WATERS system, equipped with a WATERS 2414 refractive index, a WYATT ViscoStar viscosimeter and a WYATT MiniDawn Treos light scattering detectors and WATERS Styragel HR 0.5, 1 and 3 columns. THF (Biosolve, GPCgrade) was used as the mobile phase at an elution rate of 1 mL min⁻¹.

FTIR absorption spectra were recorded on a Nicolet Nexus spectrometer (500–4000 cm⁻¹) using ATR technique.

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