

## Synthesis, structure and thermal properties of propylene oxide–carbon dioxide–L-lactide terpolymers

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Terpolymers with different L-lactic acid contents in the poly(propylene carbonate) chain were synthesized by the terpolymerization of carbon dioxide, propylene oxide and L-lactide, catalyzed by zinc adipate. The terpolymerization products were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, 2D {<sup>1</sup>H-<sup>13</sup>C} HMBC and FT-IR spectroscopy, DSC, TGA and GPC.

Poly(propylene carbonate) (PPC) is a sustainable polymer that undergoes complete ash-free incineration accompanied by the formation of CO<sub>2</sub> and H<sub>2</sub>O. PPC is prepared by the copolymerization of propylene oxide with CO<sub>2</sub>, and it exhibits attractive physical and mechanical properties responsible for its potential practical applications. It is known<sup>1,2</sup> that the introduction of ester units into a polymer chain increases its biodegradability.

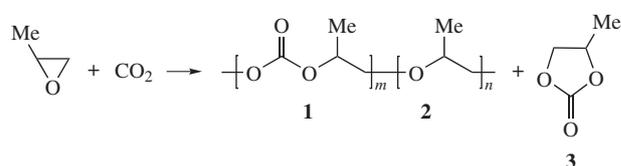
Here, we describe the synthesis and characterization of terpolymers sourced from propylene oxide (PO), CO<sub>2</sub> and L-lactide.<sup>†</sup>

The synthesis of PPC from CO<sub>2</sub> and PO proceeds by the anionic coordination mechanism according to Scheme 1.

The reaction yields a copolymer with a strictly alternating structure (**1**). Under certain conditions, cyclic propylene carbonate can be generated as a by-product (**3**). Ether bonds can be detected in the PPC chains as a result of the successive insertion of PO (**2**)

<sup>†</sup> CO<sub>2</sub> (>99.995%, JSC Linde Gaz Rus) and argon (>99.99%, JSC Linde Gaz Rus) were used without additional purification. PO (99.0%, Sigma-Aldrich) was pre-boiled over calcium hydride and distilled in argon. L-lactide (98.0%, Sigma-Aldrich) was triply recrystallized from dry ethyl acetate, dried *in vacuo* to constant weight and sealed in ampoules under dry argon. Adipic acid (99.0%, Sigma-Aldrich), zinc oxide (99.0%, Sigma-Aldrich) and solvents of analytical grade were used without additional purification.

**Synthetic procedure.** A 10 or 5 ml autoclave fitted with a magnetic stirrer was used to prepare poly[(propylene oxide)-co-(carbon dioxide)] (PPC) and poly[(propylene oxide)-co-(carbon dioxide)-co-(L-lactic acid)] (PPCLA). The zinc adipate catalyst (0.7×10<sup>-3</sup> or 0.35×10<sup>-3</sup> mol depending on the autoclave volume) and appropriate amounts of PO and L-lactide in dry argon were loaded in the autoclave, which was preliminarily dried *in vacuo* at 120 °C for 2 h and cooled to room temperature. After sealing, the autoclave was filled with CO<sub>2</sub> to the molar ratio PO:CO<sub>2</sub> = 1 : 1. Carbon dioxide was loaded in accordance with a calibration curve [CO<sub>2</sub> (mol) = *f*(*P*)] where *P* is the pressure (in MPa) in the autoclave<sup>3</sup> and kept in a thermostatic water bath at 70 °C with vigorous stirring. After a time interval, the autoclave (reactor) was cooled to room temperature and decompressed. The reaction mixture removed from the autoclave was dissolved in a proper volume of CH<sub>2</sub>Cl<sub>2</sub> and washed consequently with a 3% aqueous solution of HCl and distilled water. The product solution was concentrated using a rotary evaporator and precipitated out by pouring the concentrated solution into methanol under vigorous stirring. The product insoluble in MeOH was filtered off and dried *in vacuo* to constant weight. PPC was prepared by a similar procedure except for the addition of L-lactide to the reaction mixture. L-lactide was synthesized according to a published procedure.<sup>4</sup> Zinc adipate was prepared from ZnO and adipic acid according to a published procedure<sup>5</sup> and dried at 130 °C for 12 h *in vacuo* before use.



Scheme 1

into the polymer chain to entail a certain disruption of its structure regularity.<sup>7–9</sup>

The copolymerization of CO<sub>2</sub>, PO and L-lactide can also include the reactions of CO<sub>2</sub>, PO and L-lactide terpolymerization, L-lactide homopolymerization and PO and L-lactide copolymerization.<sup>10,11</sup>

Terpolymerization products (PPCLA) were analyzed by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see Figures S1–S7, Online Supplementary Materials).<sup>‡,§</sup>

The FT-IR spectra of both PPCLA and PPC prior their isolation from the reaction mixture exhibited strong absorption bands at 1750 cm<sup>-1</sup> (C=O). The absence of absorption bands in the region of 1800 cm<sup>-1</sup> indicates that by-product **3** is not produced.<sup>12</sup>

<sup>‡</sup> The molecular weight characteristics of the polymers were determined by gel permeation chromatography (GPC) in CHCl<sub>3</sub> at 35 °C on a Knauer liquid chromatograph equipped with an RI-2300 refractometer and three columns (Waters Styrogel HT-2, HT-4 and HT-6E). The elution rate was 1 ml min<sup>-1</sup>. A polystyrene standard (PL Polymer Laboratories) was used for calibration.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AM-300 and Bruker AV-600 spectrometers with CDCl<sub>3</sub> as a solvent.

The DSC measurements were performed on a Mettler DSC-822e differential scanning calorimeter at a heating rate of 20 K min<sup>-1</sup> in argon at the second scan on the samples previously heated in the DSC cell up to 180 °C and cooled at a rate of 20 K min<sup>-1</sup>. Indium and zinc standards were used for calibrating the temperature and enthalpy, respectively. The degree of crystallinity of terpolymers was calculated from their experimental heats of melting and that for poly-L-lactic acid with 100% crystallinity.<sup>6</sup> Thermogravimetric analysis (TGA) was performed on a Derivatograph-C (MOM, Hungary) in air at a heating rate of 10 K min<sup>-1</sup> with samples of about 10 mg.

The FT-IR spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer.

Optic activity [ $\alpha$ ]<sub>D</sub> was measured on a Perkin-Elmer 341 polarimeter at a wavelength of 589 nm in CHCl<sub>3</sub> at 25 °C; the polymer concentration was 1 g dl<sup>-1</sup>.

The  $^1\text{H}$  NMR spectrum of PPCLA precipitated with MeOH from a solution in  $\text{CHCl}_3$  shows signals with chemical shifts intrinsic to protons of the propylene carbonate units and signals at 1.58 [3H, MeCH (a')] and 5.16 ppm [1H, CH(CO<sub>2</sub>) (c')] that evidence L-lactide cycle opening.<sup>13</sup>

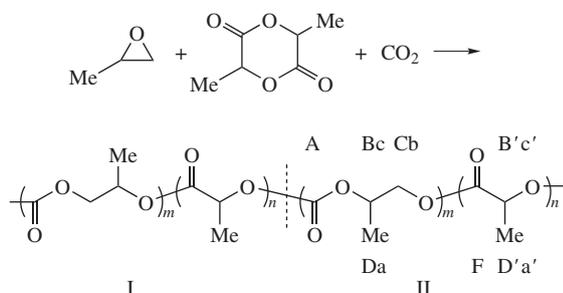
Weak signals at 3.5 ppm in the  $^1\text{H}$  NMR spectra of PPCLA, alike to PPC,<sup>14</sup> indicate a small amount of ether bonds contained in a polymer chain as the sequence of PO and CO<sub>2</sub> units.

The signals assigned to the carbon atom of the carbonyl group in PPCLA and PPC ( $\delta$  153.5–155.0 ppm) evidence that all possible additions of PO units to the copolymer chain: head-to-head (H-H), head-to-tail (H-T) and tail-to-tail (T-T), the head-to-tail type being predominant, are performed during polymerization in the presence of zinc adipate in both PPC and PPCLA, by analogy with other catalytic systems.<sup>15,16</sup>

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PPCLA contain minor signals at  $\delta$  4.2 ppm (CH<sub>2</sub>) for propylene carbonate units and at  $\delta$  169.7 ppm (CO<sub>2</sub>) for L-lactic acid units. To elucidate the origin of the signals, 2D  $\{^1\text{H}-^{13}\text{C}\}$ HMBC NMR spectroscopy was used. Cross-peaks corresponding to proton-carbon interactions of protons ( $\delta$  4.0–4.3 ppm) with carbon nuclei ( $\delta$  169.5–169.7 ppm) are observed in the spectrum, which indicates that L-lactic acid units directly bonded to propylene carbonate units are presented in the polymer chain.

The optic activity data for PPCLA and poly(L-lactic acid) are indicative of the retained configuration of L-lactide while entering the copolymer chain  $\{[\alpha]_{589}^{25} \text{PPCLA (45 wt\% LA)} = -70.4$ ;  $[\alpha]_{589}^{25} \text{PPCLA (28.4 wt\% LA)} = -44.8$ ;  $[\alpha]_{589}^{25} \text{poly-L-lactic acid} = -154.4\}$ . This gives the basis to conclude that L-lactide introduction into a polymer chain is performed by acyl–oxygen bond [C(O)–O] cleavage.

The combination of  $^1\text{H}$ ,  $^{13}\text{C}$ , and 2D  $\{^1\text{H}-^{13}\text{C}\}$ HMBC NMR data allows us to assume that the copolymerization of CO<sub>2</sub>, PO and L-lactide affords PPCLA terpolymers composed of propylene carbonate blocks combined with L-lactic acid blocks, and they can be depicted by structure segment II in Scheme 2.



Scheme 2

PPCLA with different abundances of L-lactic acid (PPCLA1, PPCLA2 and PPCLA3) were examined by DSC (Figure 1) and TGA (Figure S8) (Table 1).<sup>‡</sup>

We found that L-lactic acid block phase in PPCLA was capable to crystallize even with a very low L-lactide content. The exothermal effect regions related to cold crystallization of L-lactide repeat units phase and endothermal melting peaks were

<sup>‡</sup> Poly[(propylene oxide)-co-(carbon dioxide)-co-(L-lactic acid)] (PPCLA):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.3 [3H, Me (a)], 4.2 [2H, CH<sub>2</sub>(CO<sub>3</sub>) (b)], 5.0 [1H, CH(CO<sub>2</sub>) (c)], 1.58 [3H, Me(CH) (a')], 5.16 [1H, CH(CO<sub>2</sub>) (c')].  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 153.5–155.0 [CO<sub>3</sub> (A)], 72.3 [CH–O (B)] 69.1 [CH<sub>2</sub> (C)], 16.2–16.7 [Me (D, D')], 169.7 [CO<sub>2</sub> (F)], 69.0 [CH(CO<sub>2</sub>) (B')].

Poly[(propylene oxide)-co-(carbon dioxide)] (PPC):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.3 [3H, Me (a)], 4.2 [2H, CH<sub>2</sub>(CO<sub>3</sub>) (b)], 5.0 [1H, CH(CO<sub>3</sub>) (c)].  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 153.5–155.0 [CO<sub>3</sub> (A)], 72.3 [CHO (B)], 69.2 [CH<sub>2</sub> (C)], 16.2 [Me (D)].

Table 1 Thermal characteristics of PPCLA and mixtures of PPC and poly(L-lactic acid).<sup>a</sup>

Sample	L-lactic acid, molar fraction (%)	$M_w/10^3$	$M_w/M_n$	$T_g^{\text{PPC}} / (T_g^{\text{PL-LA}}) / ^\circ\text{C}$	$T_m / ^\circ\text{C}$	$X_c$ (%) <sup>b</sup>	$T_d^{5\%} / ^\circ\text{C}$
PPC	–	340	3.4	38 (–)	–	–	243
PPCLA1	15	356	7.0	34 (–)	144	1	248
PPCLA2	22	347	5.1	35 (45)	158	3	260
PPCLA3	37	244	9.4	39 (50)	159	17	270
Mixture1 <sup>c</sup>	13	–	–	38 (60)	175	1	260
Mixture2 <sup>c</sup>	37	–	–	39 (60)	175	17	270
Poly(L-lactic acid) <sup>d</sup>	–	154	2.8	– (60)	172	24	281

<sup>a</sup> Conditions: temperature 70 °C; molar ratio PO:CO<sub>2</sub> = 1:1, PO:L-lactide = 4:1 (for PPCLA1 and PPCLA2), and 1.5 (for PPCLA3); polymerization times are 3, 6, and 21 h, respectively; zinc adipate (cat.),  $0.7 \times 10^{-3}$  or  $0.35 \times 10^{-3}$  mol (depending on autoclave volume). <sup>b</sup>  $X_c$  is the degree of crystallinity. <sup>c</sup> Mixtures 1 and 2 are the mixtures of PPC and poly(L-lactic acid) (PL-LA). <sup>d</sup> Molar fraction of L-lactic acid in the PPCLA products was determined by  $^1\text{H}$  NMR.

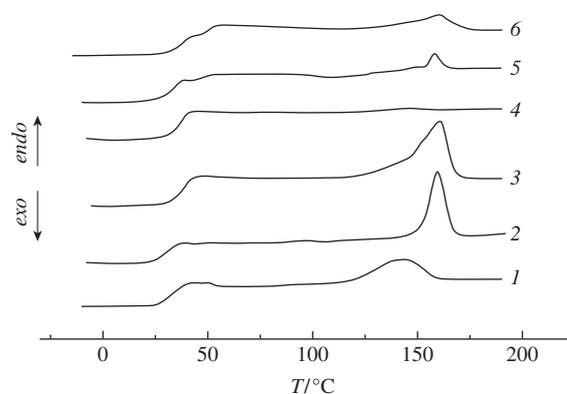


Figure 1 DSC curves for (1, 4) PPCLA1, (2, 5) PPCLA2, (3, 6) PPCLA3 at (1–3) first and (4–6) second heatings at a heating/cooling rate of  $\pm 20 \text{ K min}^{-1}$ .

presented in the DSC curves. Table 1 shows that the degree of crystallinity ( $X_c$ ) depends on the composition and increases with the L-lactic acid content of PPCLA. Note that L-lactic acid blocks phase melting temperature ( $T_m$ ) in PPCLA is lower than that in the mixtures of close composition.

According to the DSC data for PPCLA with the L-lactic acid content above 20%, there are two glass transition temperatures ( $T_g$ ) corresponding to the consecutive  $T_g$  of propylene carbonate and L-lactic acid block amorphous phases.  $T_g$  of L-lactic acid block phase rises as its content in PPCLA increases, though it does not run up to the value of the L-lactide homopolymer, whereas PPCLA1 retains the sole  $T_g$  value. This behaviour may be related to the fact that the propylene carbonate and L-lactic acid block phases in PPCLA are compatible to a limited extent in the amorphous state. A study on the thermal behaviour of mixtures of PPC and L-lactide homopolymer with a composition close to that of PPCLA shows the presence of two glass transition steps. At the same time,  $T_g$  of poly(L-lactic acid) in the mixtures is markedly higher than that for PPCLA under study and approaches the  $T_g$  of L-lactide homopolymer.

DSC method allows one to determine minor deviations in the thermal behaviour of both PPCLA synthesized and homopolymers with a reliable accuracy. In accordance with published data,<sup>17</sup> essential distinctions between both  $T_g$  and  $T_m$  observed for PPCLA and those obtained for homopolymers compositions give the basis to ascribe a block structure to PPCLA. DSC data proved to be in a good correlation with previously mentioned NMR results.

The TGA study of PPCLA and homopolymer compositions revealed that the onset degradation temperature ( $T_d$ ) for both

PPCLA and the mixtures increased with the L-lactic acid content (Table 1). However it should be noted that, whereas PPCLA3 and the mixture of the similar composition possess the same  $T_d$ , the situation is different for PPCLA1 and its composite analogue.  $T_d$  for the mixed composition is noticeably higher than the same parameter for the PPCLA1, probably owing to a different distribution of L-lactic acid and correspondingly to a different mode of oxygen diffusion towards degradation active species.

In summary, a series of partially crystalline high molecular weight  $-(\text{PO-alt-CO}_2)_m-(\text{L-lactic acid})_n-$  block terpolymers with different L-lactic acid content has been synthesized by the copolymerization of CO<sub>2</sub>, PO and L-lactide in the presence of zinc adipate. The terpolymers were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, 2D {<sup>1</sup>H-<sup>13</sup>C}HMBC and FT-IR spectroscopy, DSC, TGA and GPC.

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#### Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.06.017.

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