

# COORDINATIVE-IONIC COPOLYMERIZATION OF PROPYLENE OXIDE, CARBON DIOXIDE AND L-LACTIDE

**Ernest E. Said-Galiev**<sup>\*a b</sup>, **Zinaida N. Nysenko**<sup>a</sup>, **Alexey M. Sakharov**<sup>a</sup>, **Mikhail I. Buzin**,<sup>b</sup>  
**Yakov E. Belevtsev**,<sup>b</sup> **Sergei I. Dayneko**<sup>b</sup>, **Mikhail M. Ilyin**,<sup>b</sup> **Galina G. Nikiforova**<sup>b</sup>

<sup>a</sup> *N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 4142; e-mail: [as@zelinsky.ru](mailto:as@zelinsky.ru)*

<sup>b</sup> *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

## ABSTRACT

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

## INTRODUCTION

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

This paper discusses results of the synthesis, composition, structural studies and thermal properties of terpolymers sourced from propylene oxide (PO), CO<sub>2</sub> and L-lactide.

## MATERIALS AND METHODS

CO<sub>2</sub> (>99.995 %, JSC Linde Gaz Rus) and argon (>99.99 %, JSC Linde Gaz Rus) were used without extra purification. PO (99.0 %, Sigma-Aldrich) was pre-boiled over calcium hydride and distilled in argon. L-lactide (98.0 %, Sigma-Aldrich) was three-fold recrystallized from dry ethyl acetate, dried *in vacuo* until the constant weight and batched in ampoules in dry argon to be then kept in sealed ampoules. Adipic acid (99.0 %, Sigma-Aldrich) and zinc oxide (99.0 %, Sigma-Aldrich) were used without extra purification. Solvents were of analytical grade and used without further purification.

### *Preparation of copolymers and a catalyst*

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 catalyst – zinc adipate – in quantity  $0.7 \times 10^{-3}$  or  $0.35 \times 10^{-3}$  mol, depending on the autoclave volume, and appropriate PO and L-lactide amounts in dry argon were loaded in the autoclave that was preliminary dried *in vacuo* at 120 °C during 2 h and cooled down to a room temperature. After sealing, the autoclave was filled with CO<sub>2</sub> until the molar ratio PO : CO<sub>2</sub> = 1 reached. Carbon dioxide was loaded in accordance with the

calibration curve ( $\text{CO}_2$  (mol) =  $f(P)$  where  $P$  – pressure (in MPa) in the autoclave<sup>3</sup>) and kept on a thermostatic water bath at  $70^\circ\text{C}$  with vigorous stirring. After a certain time interval, the autoclave (reactor) was cooled down to a room temperature and decompressed. The reaction mixture removed from the autoclave was dissolved in a proper volume of  $\text{CH}_2\text{Cl}_2$  and washed consequently with 3% water solution of HCl and distilled water. Product solution was concentrated using rotary evaporator and precipitated out by pouring the concentrated solution into methanol under vigorous stirring. The product insoluble in  $\text{CH}_3\text{OH}$  was filtered off and dried *in vacuo* until the constant weight. PPC was prepared by a similar procedure except for the L-lactide addition to the reaction mixture. L-lactide was synthesized according to the procedure proposed in<sup>4</sup>. Zinc adipate was prepared from ZnO and adipic acid according to the procedure described in<sup>5</sup> and further dried at  $130^\circ\text{C}$  for 12 h *in vacuo* before being used.

### Characterization

The molecular weight characteristics of the polymers were determined using the gel permeation chromatography (GPC) method in  $\text{CHCl}_3$  at  $35^\circ\text{C}$  on a Knauer liquid chromatograph equipped with a refractometer RI-2300 and three columns (Waters Styrogel HT-2, HT-4, and HT-6E). The elution rate was 1 ml/min. The calibration was done using the polystyrene standard (PL Polymer Laboratories).

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Brüker AM-300 and Brüker AV-600 spectrometers with  $\text{CDCl}_3$  as a solvent.

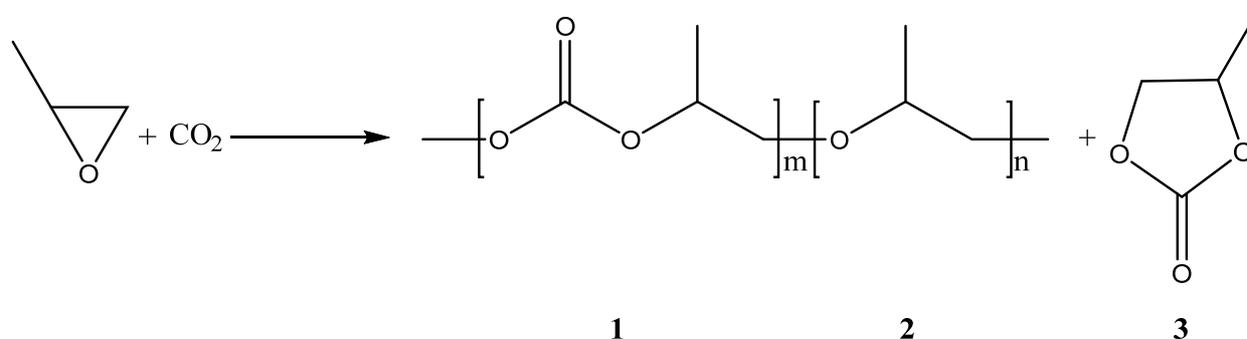
The DSC measurements were done in a Mettler DSC-822e differential scanning calorimeter at a heating rate  $20^\circ\text{C}/\text{min}$  in argon at the second scan on the samples previously heated in the DSC cell up to  $180^\circ\text{C}$  and cooled with the rate  $20^\circ\text{C}/\text{min}$ . The degree of crystallinity of terpolymers was calculated from experimental values of their heat of melting and that for poly-L-lactic acid with crystallinity 100 %<sup>6</sup>. A thermogravimetric analysis (TGA) was performed on a Derivatograph-C (MOM, Hungary) in air at a heating rate  $10^\circ\text{C}/\text{min}$  on samples of about 10 mg by weight.

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

Optic activity  $[\alpha]_D$  was measured in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ , the polymer concentration  $1\text{ g dl}^{-1}$  on a Perkin-Elmer 341 polarimeter at the wavelength 589 nm.

## RESULTS AND DISCUSSION

The synthesis of PPC from  $\text{CO}_2$  and PO proceeds by the anionic coordination mechanism according to the Scheme 1:



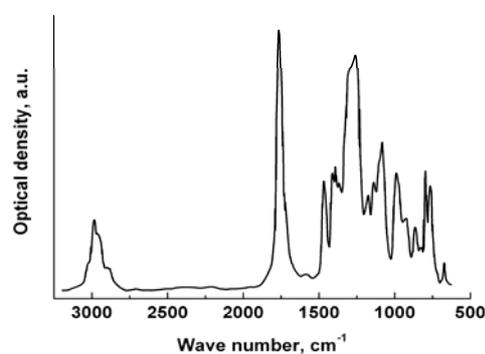
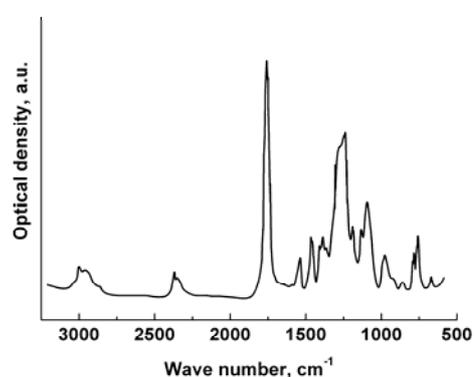
Scheme 1

The reaction yields a copolymer with a strictly alternating structure **1** (Scheme 1). Under certain conditions a byproduct **3**, *i.e.* cyclic propylene carbonate, can be generated. Also, ether bonds might be revealed in the PPC chains as a result of the successive insertion of PO (**2**) into the polymer chain to entail a certain disruption of its structure regularity<sup>7-9</sup>.

Copolymerization of CO<sub>2</sub>, PO and L-lactide apart from the aforesaid processes, can include reactions of CO<sub>2</sub>, PO and L-lactide terpolymerization, L-lactide homopolymerization, PO and L-lactide copolymerization<sup>10,11</sup>.

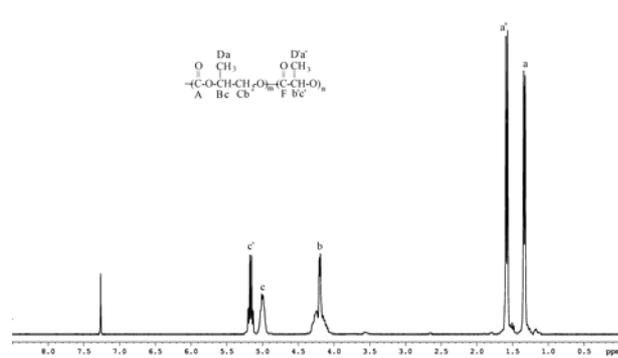
Terpolymerization products (PPCLA) were analyzed by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy methods.

The FT-IR spectra of both PPCLA (see Figure 1) and PPC (Figure 2) prior their isolation from reaction mixture feature strong absorption bands in the region of 1750 cm<sup>-1</sup> (C=O). The absence of absorption bands in the region of 1800 cm<sup>-1</sup> indicates that the byproduct, *i.e.* cyclic propylene carbonate **3** (Scheme 1), is lacking in the reaction products if this is the case<sup>12</sup>.

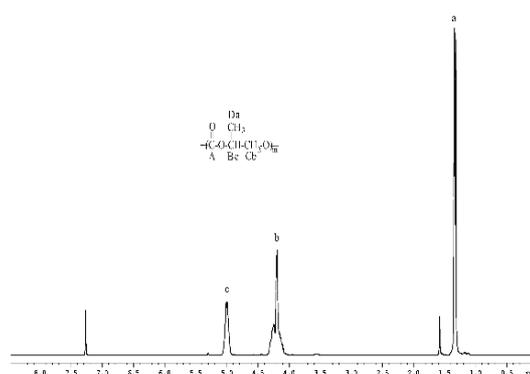


**Figure 1.** FT-IR spectrum of reaction mixture      **Figure 2.** FT-IR spectrum of PPC.

The <sup>1</sup>H NMR spectrum of PPCLA, insoluble in CH<sub>3</sub>OH (for <sup>1</sup>H NMR spectrum see Figure 3), show the signals with chemical shifts intrinsic to protons of the propylene carbonate units (CDC1<sub>3</sub>, δ, ppm): 1.3 [3H, CH<sub>3</sub> (a)], 4.2 [2H, CH<sub>2</sub>(CO<sub>3</sub>) (b)], and 5.0 [1H, CH(CO<sub>3</sub>) (c)] and the signals 1.58 [3H, CH<sub>3</sub>(CH) (a')] and 5.16 [1H, CH(CO<sub>2</sub>) (c')] that evidence L-lactide cycle opening<sup>13</sup>. <sup>1</sup>H NMR spectrum of PPC is represented (see Figure 4) for comparison.



**Figure 3.** <sup>1</sup>H NMR spectrum of PPCLA3

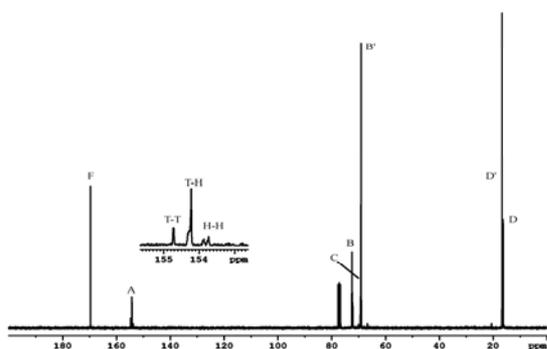


**Figure 4.** <sup>1</sup>H NMR spectrum of PPC

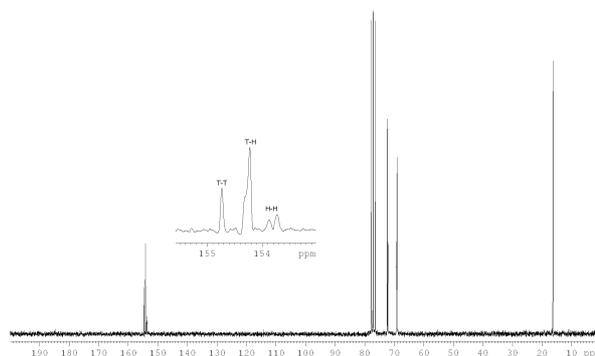
The presence of weak signals at 3.5 ppm in  $^1\text{H}$  NMR spectra of PPCLA, alike to PPC<sup>14</sup>, indicates to a small amount of ether bonds contained into a polymer chain that allows considering the sequence of PO and CO<sub>2</sub> units to be very similar to the strictly alternate one.

$^{13}\text{C}$  NMR spectrum of PPCLA (see Figure 5) (CDCl<sub>3</sub>,  $\delta$ , ppm): 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 [CH<sub>3</sub> (D,D')], 169.7 [CO<sub>2</sub> (F)], 69.0 [CH(CO<sub>2</sub>) (B')]. PPC signals (CDCl<sub>3</sub>,  $\delta$ , ppm): 153.5-155.0 [CO<sub>3</sub> (A)], 72.3 [CHO (B)], 69.2 [CH<sub>2</sub> (C)] and 16.2 [CH<sub>3</sub> (D)] (see Figure 6).

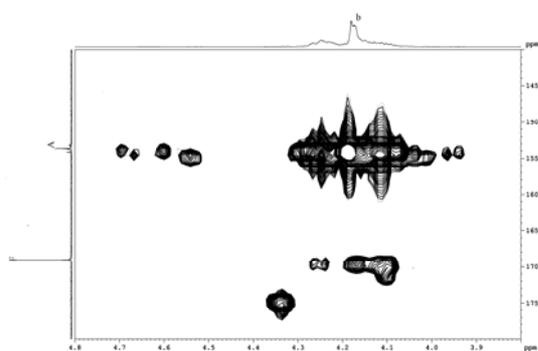
The signals assigned to carbon atom of the carbonyl group in PPCLA and PPC (see Figures 5 and 6:  $\delta$  153.5-155.0 ppm) evidence all possible additions of PO units to the copolymer chain: head-to-head (H-H), head-to-tail (H-T) and tail-to-tail (T-T), the head-to-tail type being predominant, are performed during polymerization in the presence of zinc adipate both in PPC and PPCLA, by analogy with other catalytic systems action<sup>15,16</sup>.



**Figure 5.**  $^{13}\text{C}$  NMR spectrum of PPCLA3



**Figure 6.**  $^{13}\text{C}$  NMR spectrum of PPC.



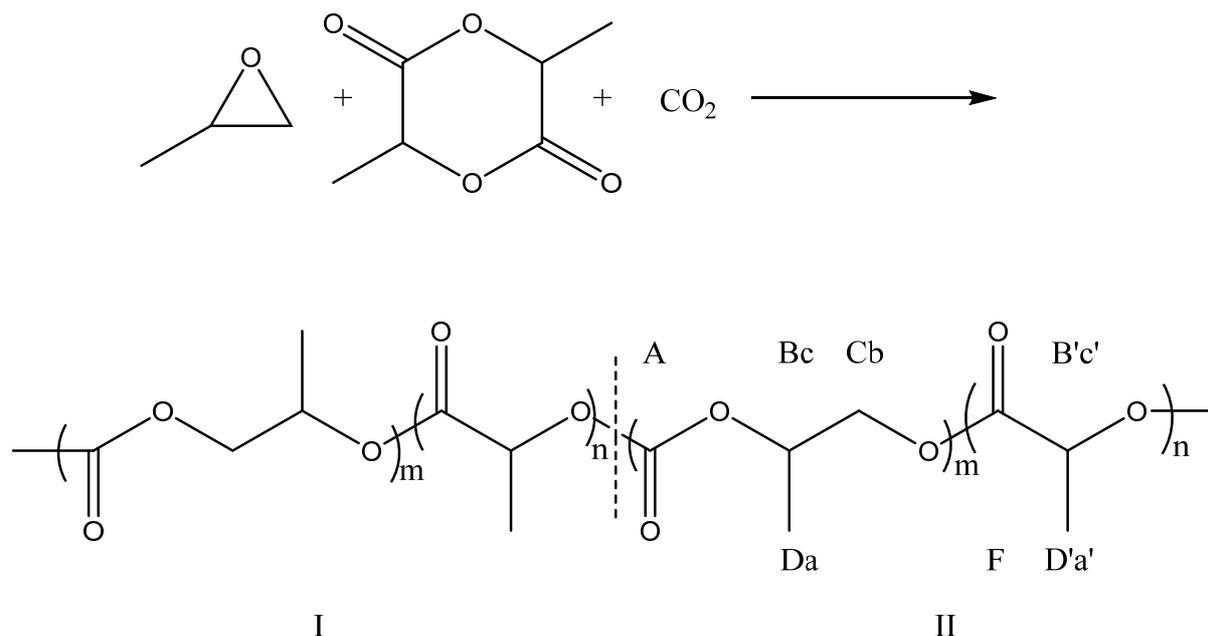
**Figure 7.** 2D  $\{^1\text{H}-^{13}\text{C}\}$  HMBC spectrum of PPCLA3

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PPCLA feature a number of additional 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 a 2D  $\{^1\text{H}-^{13}\text{C}\}$ HMBC NMR method 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 (see Figure 7) which indicates that L-lactic acid units directly bonded to propylene carbonate units are presented in the polymer chain.

The optic activity research results for PPCLA3 and poly(L-lactic acid) are

indicative of the retained configuration of L-lactide while entering the copolymer chain ( $[\alpha]_{589}^{25}$  PPCLA3 =  $-70.4^\circ$ ,  $[\alpha]_{589}^{25}$  poly-L-lactic acid =  $-154.4^\circ$ ). This gives the basis to conclude that L-lactide introduction into a polymer chain is performed by acyl-oxygen bond (–CO–O–) cleavage.

The combination of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $\{^1\text{H}-^{13}\text{C}\}$ HMBC NMR study results allows an assumption that copolymerization of CO<sub>2</sub>, PO and L-lactide yields to terpolymers PPCLA composed of propylene carbonate blocks combined with L-lactic acid blocks and may be depicted by segment II of structure represented onto Scheme 2.



**Scheme 2.** Reagents and conditions: 70 °C, molar ratio PO : CO<sub>2</sub> = 1, PO : L-lactide = 4 (for PPCLA1 and PPCLA2) and 1.5 (for PPCLA3), polymerization time is 3, 6, and 21 h accordingly, zinc adipate (cat) – 0.7×10<sup>-3</sup> and 0.35×10<sup>-3</sup> mol (depending on autoclave volume). PPCLA with a different abundance of L-lactic acid (PPCLA1, PPCLA2 and PPCLA3) were examined by the DSC (see Figure 8) and TGA (Figure 9) methods (Table 1).

**Table 1** Thermal characteristics of PPCLA and mixtures of PPC and poly(L-lactic acid)

Sample	L-lactic acid, molar fraction, (%)	M <sub>w</sub> ×10 <sup>-3</sup>	M <sub>w</sub> /M <sub>n</sub>	T <sub>g</sub> <sup>PPC</sup> /T <sub>g</sub> <sup>PL-LA</sup> , (°C)	T <sub>m</sub> , (°C)	α, (%)	T <sub>d</sub> <sup>5%</sup> , (°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	13	–	–	38/60	175	1	260
Mixture2	37	–	–	39/60	175	17	270
Poly(L-lactic acid)	–	154	2.8	–/60	172	24	281

Conditions: temperature: 70 °C; molar ratio PO : CO<sub>2</sub> = 1, PO : L-lactide = 4 (for PPCLA1 and PPCLA2) and 1.5 (for PPCLA3), polymerization time is 3, 6, and 21 h

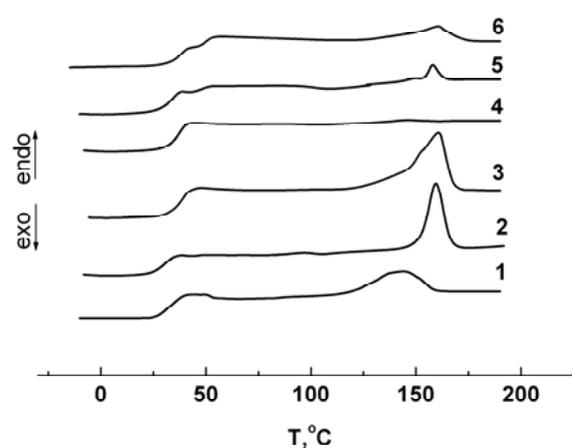
accordingly, zinc adipate (cat) –  $0.7 \times 10^{-3}$  and  $0.35 \times 10^{-3}$  mol (depending on autoclave volume).

Mixtures 1 and 2 – mixtures of PPC and poly(L-lactic acid) (PL-LA).

Molar fraction of L-lactic acid in the PPCLA products was determined by  $^1\text{H}$  NMR.

It was found that L-lactic acid blocks 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 presented on the DSC curves.

As seen from Table 1 the degree of crystallinity ( $\alpha$ ) depends on the composition and grows as the L-lactic acid content in PPCLA increases. It should be noted that L-lactic acid blocks phase melting temperature ( $T_m$ ) in PPCLA is lower than in the mixtures close by composition.

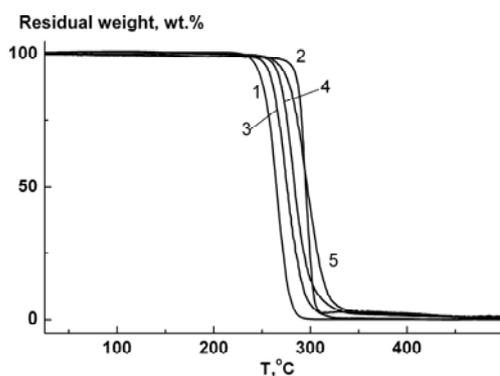


**Figure 8.** DSC curves for PPCLA1 (1, 4), PPCLA2 (2, 5), PPCLA3 (3, 6) at first (1, 2, 3) and second (4, 5, 6) heatings at a heating/cooling rate  $\pm 20$  °C/min.

markedly higher than that for PPCLA under study and approaches  $T_g$  of the L-lactide homopolymer.

DSC method allows determining minor deviations in thermal behavior of both PPCLA synthesized and homopolymers with a reliable accuracy. In accordance with literature 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 aforesaid NMR study results.

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 glass transition of propylene carbonate and L-lactic acid blocks amorphous phases.  $T_g$  of L-lactic acid blocks 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 behavior may be related to that the propylene carbonate and L-lactic acid blocks phases in PPCLA are compatible to a limited extent in the amorphous state. A study on the thermal behavior of mixtures of PPC and L-lactide homopolymer with a composition close to PPCLA shows a presence of two glass transition steps. At the same time,  $T_g$  of poly(L-lactic acid) in the mixtures is



**Figure 9.** TGA curves for PPC (1), poly(L-lactic acid) (2) and terpolymers: PPCLA1 (3), PPCLA2 (4), PPCLA3 (5) at a heating rate 10 °C/min

–[(PO-alt-CO<sub>2</sub>)<sub>m</sub>–(L-lactic acid)<sub>n</sub>] with different L-lactic acid content has been synthesized by means of CO<sub>2</sub>, PO, and L-lactide copolymerization in the presence of zinc adipate. The terpolymers obtained were characterized by methods of <sup>1</sup>H and <sup>13</sup>C NMR, 2D {<sup>1</sup>H-<sup>13</sup>C}HMBC, DSC, TGA, FT-IR spectroscopy, and GPC. L-Lactic acid content increase was shown to be accompanied with elevation of terpolymers melting temperature and onset degradation temperature values.

The research was supported by the Russian Ministry of Education and Science (Contract No. 14.513.11.0139).

## References

- [1] HWANG, Y., KIM, H., REE, M. *Macromol. Symp.*, Vol. 224, **2005**, p. 227.
- [2] YASUDA, H., ALUDIN, M-S, KITAMURA, N., TANABE M., SIRAHAMA, H., *Macromolecules*, **1999**, Vol.32, p. 6047
- [3] RAKHIMOV, T., SAID-GALIEV, E., IL'IN, V., NYSENKO, Z., SAKHAROV, A., *Russ. Khim. Zh.*, Vol.48, **2004**, p. 124
- [4] DUDA, A., PENCZEK, S., KOWALSKI A., LIBISZOWSKI, J., *Macromol. Symp.*, Vol. 153, **2000**, p. 41
- [5] KUTZTOWA, S., EMMAUS, T., ALBURTIS, A., STEIN S., FOGELSVILLE, B., *US Patent 5, 026, 676*, **1991** (*Chem. Abstr.*, Vol.115, **1991**, p. 93209)
- [6] JAMSHIDI, K., NYON S-H., IKADA, Y., *Polymer*, Vol.29, **1988**, p. 229
- [7] CHEN, X., SHEN Z., ZHANG, Y., *Macromolecules*, Vol.24, **1991**, p. 5305
- [8] ALLEN, S., MOORE, D., LOBKOVSKY, E., *J. Am. Chem. Sci.*, Vol. 124, **2002**, p. 14284
- [9] DARENSBOURG, D., WILDESON, J., YARBROUGH, J., *J. Am. Chem. Soc.*, Vol.122, **2000**, p., 2487
- [10] LIU, S., WANG, J., HUANG, K., LIU, Y., WU, W. *Polym. Bull.*, Vol.66, **2011**, p. 327
- [11]. GU, L., QIN, Y., GAO, Y., WANG, X., WANG, F. *Chin. J. Chem.*, Vol.30, **2012**, p. 2121

The TGA study of PPCLA and homopolymer compositions revealed that the onset degradation temperature ( $T_d$ ) both for PPCLA and for the mixtures increased as the L-lactic acid content was elevating (Table 1). However it should be noted that, whereas PPCLA3 and the mixture of the similar composition have the same  $T_d$ , the situation is different for PPCLA1 and its composite analog.  $T_d$  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 high molecular weight partially crystalline block terpolymers

- [12] Rokicki A., Kuran, W. J. *Macromol. Sci. Rev. Macromol. Chem.*, Vol. 21, **1981**, 135
- [13] Yang, D.M., Lu, Q.I., Fan, Z.Y. , Li, S.M., Tu J.J., Wang, W. *J. Appl. Polym. Sci.*, 118, **2010**, p. 2304
- [14] Chisholm M., Navarro-Liobet, D. *Macromolecules*, Vol. 35, **2002**, p. 2389
- [15] Lednor P.W., Rol, N.C. *J. Chem. Soc. Chem. Commun.*, Vol. 9, **1985**, p. 598
- [16] Li, H., Niu, Y. , *React. Funct. Polym.*, Vol. 71, **2011**, p. 121
- [17] Noshay, A., McGrath , J.E. , *Block Copolymers*, Academic Press, New York, San Francisco, London, **1977**.