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Novel copolymers for fibers based on cyclocarbonates and lactide

Milana U. Agaeva,[a] Anna K. Berkovich,[a] Polina A. Ledneva,[a] Valeriia A. Serova,[a] Artem E. Zhirnov,[a] Artem N. Fakhrutdinov,[b] Badma N. Mankaev[a] and Sergey S. Karlov*[a]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: s.s.karlov@chemistry.msu.ru*
[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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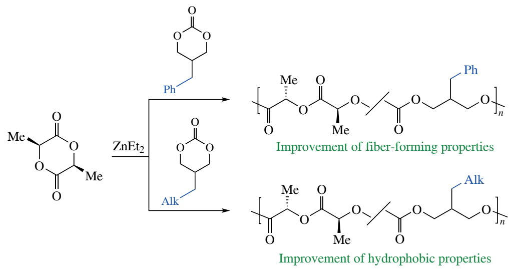
Three cyclocarbonates, namely 1,3-dioxan-2-ones bearing 5-positioned ethyl, butyl and benzyl substituents, were synthesized by the cyclization of ethyl chloroformate with the corresponding propane-1,3-diols. Homopolymers of these cyclocarbonates as well as their copolymers with L-lactide were obtained by ring-opening polymerization using $ZnEt_2$ as the initiator. The prepared homo- and copolymers were found suitable for the production of composite polylactide fibers with tunable hydrophobicity.



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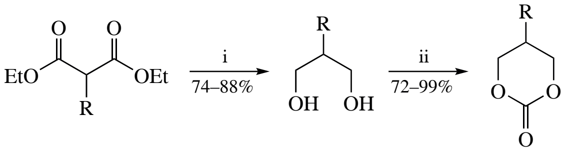
Over the past few decades, biodegradable polymers have attracted increased attention, mainly due to the environmental agenda. About 40 percent of the produced polymers are used for packaging.[1,2] Replacing ‘traditional’ polymers with biodegradable ones, at least in this area, should significantly reduce environmental impact. On the other hand, many known biodegradable polymers are also degradable *in vivo*, biocompatible and thus suite for biomedical applications. Among several known types of biodegradable polymers, polyesters are most promising in the field of engineered tissues, medical devices, and drug delivery systems.[3,4] The most commonly used polyester is polylactide available on the market as polymers with different molecular weights. At the same time, copolymers of lactide and other substituted cyclic derivatives, for example, cyclic carbonates (‘cyclocarbonates’, CCs), show promising values of degradation rate and hydrophobicity, as well as potential for post-modification.[5,6] In the meantime, the introduction of hydroxy,[7–9] carboxy[10–12] and amino[13–16] groups into trimethylene carbonate unit can effectively tune the hydrophilic properties. However, to our knowledge, there is no information on preparation of copolymers of lactide and alkyl (or benzyl) substituted trimethylene carbonate, whereas the introduction of such units into the polymer chain can increase the hydrophobicity of the polymer depending on the number of substituted carbonate units.

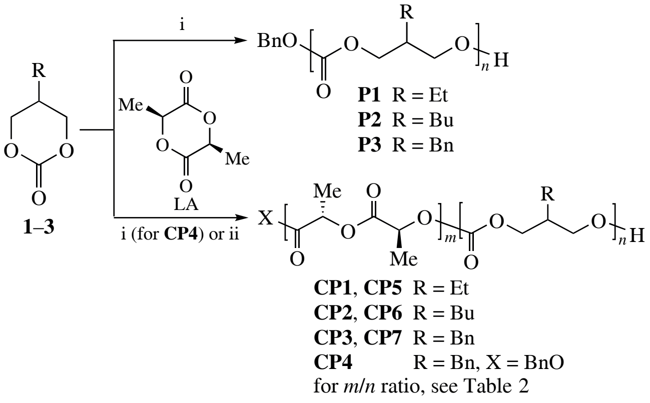
Polylactide-based fibers can be used for suture threads or scaffolds in tissue engineering. Requirements for mechanical and functional properties under specific conditions of using are imposed on designing materials of this kind.[17] In this case, one of the comonomers is primary, the other is a modifier. We chose L-lactide (LA) as a primary comonomer due to prevalence of polylactide materials. The modifier comonomer should be easily accessible and be versatile in its ability to carry functional groups, and should be readily involved in copolymerization with primary comonomer. So, we synthesized a series of CCs (5-substitued 1,3-dioxan-2-ones) to use them as easily modified comonomers. This paper features three members of this series, namely, 5-ethyl- (**1**),[18] 5-butyl- (**2**)[19] and 5-benzyl-1,3-dioxan-2-one (**3**) (for the synthesis, see Scheme 1, compound **3** is new). The introduction of such substituents is aimed primarily at reducing the degree of crystallinity of the copolymer, which could help to tailor the thermomechanical properties of fibers engineered from these copolymers. Another feature of such fibers should be their increased adhesive ability.

The thus obtained CCs **1**–**3** were subjected to homopolymerization and copolymerization with LA *via* the ring-opening polymerization using $ZnEt_2$ as initiator (Scheme 2), with the CC monomers having been transformed into trimethylene carbonate (TMC) units. The $ZnEt_2$ initiator previously showed good efficiency both in lactide and CC polymerization.[20] The key moment of the reaction, which can only be verified experimentally, is the rate of polymerization of a particular monomer with a particular initiator. It is of note that sometimes a less active monomer in homopolymerization (for example, lactide) reacted faster in the course of copolymerization than a more active monomer (for example, caprolactone).[21–23] Herein, homopolymerization of CCs **1**–**3** under standard industrial conditions (100–130 °C, bulk polymerization) with $ZnEt_2$ in the presence of an external nucleophile (BnOH) was studied (see Scheme 2 and Scheme S1 of Online Supplementary Materials) to afford homopolymers **P1**–**P3** with sufficiently high molecular weights (Table 1). Benzyl-substituted CC **3** reacted faster than CCs **1**, **2** with alkyl groups, while the molecular



1 R = Et
2 R = Bu
3 R = Bn

Scheme 1 *Reagents and conditions*: i, $LiAlH_4$, THF; ii, ClC(O)OEt, Et_3N.



Scheme 2 *Reagents and conditions*: i, $ZnEt_2$ (0.2 mol%), BnOH (0.2 mol%), 100 °C, 3–90 h; ii, the same, without BnOH.

Table 1 Homopolymerization of cyclic carbonates (CCs) **1**–**3**.

Entry	CC	[CC] : $[ZnEt_2]$: : [BnOH] ratio	*t*/h	Conversion (%)^a	Homo-polymer	$M_n{}^b$/ g mol^{-1}	$M_w/M_n{}^b$
1	**1**	500 : 1 : 1	48	92	**P1**	33770	1.5
2	**2**	500 : 1 : 1	48	88	**P2**	63750	1.5
3	**3**	500 : 1 : 1	3	>99	**P3**	43750	1.6

^{a}From ^{1}H NMR data. ^{b}From SEC data.

weight of the resulted **P3** was lower than that of **P2** obtained from CC **2**.

Copolymerization of CCs **1**–**3** with LA was performed using the ratios LA : CC = 1 : 1 and 10 : 1 with $ZnEt_2$ (as 1 M solution in hexane) as the initiator (Table 2). The experiments were carried out in the absence of an external nucleophile (with the use of BnOH as the external nucleophile, a significant decrease in the polymer weight was observed, see Table 2, entry 4). The molecular weights of copolymers **CP1**–**CP7** turned to be *ca*. 10 times lower than those of homopolymers **P1**–**P3**. It should be noted that benzyltrimethylene carbonate units enter faster in the copolymerization with LA than those wih aliphatic Et and Bu groupings (24 *vs*. 90 h required for consumption of CC). In copolymers **CP5**–**CP7** (see Table 2, entries 5–7), the ratios of the corresponding monomer units are essentially different from the initial ratios despite high conversions of both monomers. We assume that CCs undergo parallel oligomerization, which consequently reduces the carbonate content in the copolymers.

Microstructure of copolymer **CP7** with novel cyclocarbonate **3** and LA (see Table 2, entry 7) was studied by ^{13}C NMR (see Online Supplementary Materials, Figure S1). Spectrum of homo-poly-L-lactide coincides with literature data.[24] The spectrum of copolymer **CP7** contains all signals that were observed in the homopolymers and reveals both types of homodyads such as LA–LA and TMC–TMC (TMC designates here only benzyltrimethylene carbonate unit). The signal 169.8 ppm was attributed to the TMC–LA–LA or LA–LA–TMC triads. The peak at 154.24 ppm was assigned to the LA–TMC–TMC and LA–TMC–LA triads, whereas the peak at 154.86 ppm was assigned to TMC–TMC–TMC and TMC–TMC–LA triads.[25] The peak at 154.24 has greater intensity than that at 154.86 ppm; the real ratio of LA and TMC units in copolymer **CP7** was 75 : 25. Peaks at 66.62–69.36 were attributed to dyads as LA–TMC, TMC–TMC, LA–LA.

Copolymer **CP7** (LA/TMC units ratio = 75 : 25) was also characterized by DOSY NMR to control the efficiency of the copolymerization.[26] Based on the data obtained (see Online Supplementary Materials, Figure S13 and Table S2), it is evident that the correlation spots related to the proton signals of polylactide and polycarbonate are characterized by the same diffusion coefficient ($D = 8.011 \times 10^{-11}$ m^2 s^{-1}), which confirms the formation of a copolymer rather than a mixture of two homopolymers. The relative signal intensity of the heterodyads is lower than that of the homodyads, but still significant. Hence, product **CP7** is a random copolymer, but one with relatively long blocks of each monomer unit.

Ability to form fibers depends on crystallinity of the polymer, so the thermal properties of homopolymers **P1**–**P3** and copolymers **CP1**–**CP7** were studied. The DSC thermograms for a series of homo-polylactide, homo-(polybenzyltrimethylene carbonate) and their 75 : 25 copolymer **CP7** are shown in Figure S2 (see Online Supplementary Materials). It should be noted that the Bn-containing TMC unit in **P3** homopolymer provides its capability for crystallization (mp 95 °C). As for copolymer **CP7**, a melting peak is also observed which most likely corresponds to the melting of defective polylactide crystallites. Therefore, polylactide chains in the copolymer are long enough to form crystallite.

In the cases of CCs with aliphatic ethyl or butyl substituents **1**, **2**, neither homopolymers **P1**, **P2** nor copolymers **CP1**, **CP2**, **CP5**, **CP6** with LA of equivalent composition crystallized. Crystallization of polylactide in such copolymers is possible only when LA unit content approaches 90% (Figure S3). Consequently, homopolymers and copolymers with a high content of ethyl- and butyl-substituted TMC units, depending on the molecular weight, are elastomers or even viscous liquids and are not suitable for the fiber production.

Therefore, we decided to test the obtained materials as additives to homopolylactide. This approach was not chosen by chance, since one of the most common and effective plasticizers for polylactide is oligomeric lactide, which allows one to effectively reduce the glass transition temperature of a polylactide material without leaching or exudation from it, resulting in significant increase in the material's plasticity.[27] To implement this approach, first of all, the possibility of obtaining homogeneous compositions based on mixtures of new polymers and a commercial sample of poly(L-lactide) grade 6252D was tested. To obtain mixed compositions, homo- (**P1**, **P3**) and copolymers (**CP5**, **CP7**) were selected (see Online

Table 2 Copolymerization of cyclic carbonates (CCs) **1**–**3** with L-lactide (LA) at 100 °C.

Entry	CC	[LA] : [CC] : $[ZnEt_2]$: [BnOH] ratio	*t*/h	Conversion of LA/CC^a (%)	Copolymer obtained	Ratio of LA/TMC units in copolymer^a	$M_n{}^b$/g mol^{-1}	$M_w/M_n{}^b$
1	**1**	500 : 50 : 1 : 0	90	95/97	**CP1**	92 : 8	6790	1.5
2	**2**	500 : 50 : 1 : 0	90	77/33	**CP2**	91 : 9	3768	1.3
3	**3**	500 : 50 : 1 : 0	24	71/99	**CP3**	88 : 12	4590	1.5
4	**3**	500 : 50 : 1 : 1	90	98/90	**CP4**	93 : 7	1590	1.6
5	**1**	500 : 500 : 1 : 0	90	88/90	**CP5**	80 : 20	3265	1.5
6	**2**	500 : 500 : 1 : 0	90	86/99	**CP6**	60 : 40	3220	1.5
7	**3**	500 : 500 : 1 : 0	24	66/99	**CP7**	75 : 25	5407	1.6

^{a} ^{1}H NMR data. ^{b} SEC data.

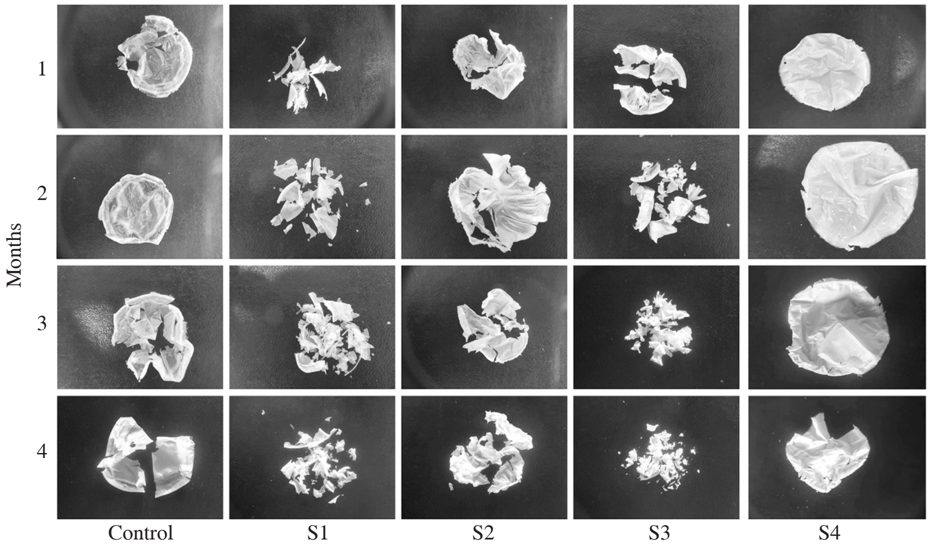


Figure 1 The behavior of films of compositions based on mixtures of new polymers and a commercial sample of poly(L-lactide) grade 6252D (control) when kept in water at 40 °C for 1–4 months. The samples are composed from 90% control and 10% substances as follows: sample S1 contains copolymer **CP5**; sample S2 contains homopolymer **P1**; sample S3 contains copolymer **CP7**; sample S4 contains homopolymer **P3**. For more details, see Table S1.

Supplementary Materials, Table S1 and Figure S3 as well as note to Figure 1). The fibers obtained from these compositions were too thin to study their mechanical properties. To analyze the mechanical properties and hydrolysis kinetics of mixed compositions, we used isotropic films obtained from a solution of polymer in chloroform. All samples showed tension with the formation of a neck, and the strength characteristics did not fundamentally change when the additive was introduced (see Table S1). This is a prospective approach to obtain fibers with functionalized polytrimethylenecarbonate units without loss of its mechanical properties.

The similar samples were used to study the kinetics of hydrolysis of mixed samples. The hydrolysis was carried out in distilled water at 40 °C (Figure 1). A noticeable weight loss ceased after 1 month, which may be due to the intense hydrolysis of the low molecular weight copolymer additive. Further hydrolysis proceeds much more slowly but leads to embrittlement of the samples. The most pronounced effect is observed in the case of the addition of copolymers containing substituted trimethylene carbonates (Table S1, samples S1 and S3), which is apparently associated with a more uniform distribution throughout the sample volume of the carbonate units, which are more susceptible to hydrolysis (see Figure 1). It is also of note that addition of copolymers (**CP5** and **CP7**) has more pronounced effect on polylactide mechanical properties than addition of homo-polycarbonates (S2 and S4). Both the hydrolytic and mechanical effects can be attributed, at least partially, to a more pronounced disruption of the supramolecular (crystalline) structure of polylactide upon the introduction of the copolymer.

To conclude, three cyclocarbonates bearing Et, Bu and Bn substituents in the trimethylene units were synthesized. These substances were polymerized or copolymerized with L-lactide in the presence of $ZnEt_2$ to form homo- or copolymers. The produced homopolymers possess high molecular weights while the copolymers have relatively low molecular weights. The copolymer of L-lactide with the benzyl-substituted cyclocarbonate (1 : 1) as well as the homopolymer of the benzyl-substituted cyclocarbonate can be used as fiber-forming materials due to their crystallization ability. All copolymers seem promising as hydrophobizing additives to polylactide-containing materials and accelerate the rate of hydrolysis of polylactide as additives to a greater extent compared to the additives of homopolymers of the studied cyclocarbonates. The polymeric materials obtained should be biodegradable.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7897.

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