Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2020, **30**, 46–48

Mendeleev Communications

Poly(ε-caprolactone-*co*-ω-pentadecalactone) electrospun fibers

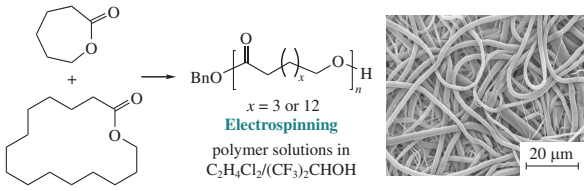
Ilya E. Nifant'ev,*[a,b] Maxim A. Kosarev,[a] Andrey V. Shlyakhtin,[a] Alexander N. Tavtorkin,[a,b] Mikhail E. Minyaev[b] and Pavel V. Ivchenko[a,b]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: inif@org.chem.msu.ru*

[b] *A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2020.01.015

Electrospun fibers with appropriate morphology have been prepared from ω-pentadecalactone/ε-caprolactone random copolymers when polymer solutions in 1,2-dichloroethane/ hexafluoroisopropanol media were used for molding.



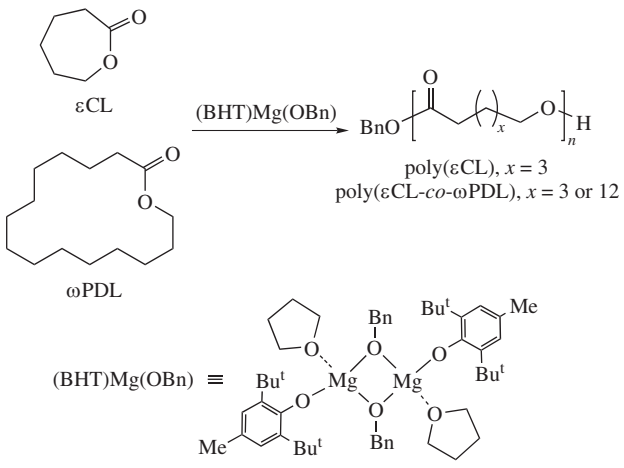
Keywords: biodegradable polymers, ε-caprolactone, copolymerization, electrospinning, fiber, ω-pentadecalactone, ring-opening polymerization.

Ring-opening polymerization (ROP) of knowingly non-toxic monomers is widely used in the synthesis of prospective polymers.[1–4] Among lactones, ω-pentadecalactone (ωPDL, pentadecanolide, a famous musk-odoured fragrance) draws attention due to the presence of extended linear hydrocarbon chains. This allows one to consider ωPDL-based polymers (Scheme 1) as a kind of the bridge between polyolefins and polyesters. Due to promising mechanical characteristics, relatively slow resorbability, and applicability of wet-spinning,[5,6] ωPDL polymers represent prospective materials for industrial and biomedical use.[7–14]

Synthesis of ωPDL polymers has been extensively described. Homopolymerization of ωPDL was carried out in the presence of organocatalysts,[15,16] metal complexes[17–22] and enzymes.[23,24] Block copolymers of ωPDL with L-lactide[25] and lactones[25,26] were also prepared, however random ωPDL copolymers look more promising due to homogeneity of physical characteristics. To date, random copolymers of ωPDL with different cyclic esters have been synthesized and characterized.[27–31] Copolymers with εCL are of particular interest because poly(εCL)/poly(ωPDL) materials demonstrate shape memory effect.[32–35]

Electrospun (ES) fibers are highly attractive for biomedical purposes due to specific morphology resembling extracellular matrix and providing the possibility of using the ES materials in surgery, tissue and neural engineering. Up to now, ES fibers were prepared from ωPDL homopolymers[5] and copolymers of ωPDL with L-lactide.[36] Poly(ωPDL) ES scaffolds are not cytotoxic and support cell proliferation.[5] Some problems remain unsolved in morphology and mechanical properties of ES fibers based on ωPDL.[5,36] These problems are caused by heterogeneity of the ROP products, gel formation and uneven evaporation of the solvents.[5]

Here, we report on the preparation of ES fibers based on random ωPDL/εCL copolymers, and comparison of the morphology and mechanical characteristics of these materials with ES fibers based on poly(ωPDL). In the synthesis of homo- and copolymers, we used highly active and non-toxic BHT-Mg catalyst[17,37] (see



Scheme 1

Table 1 Polymerization experiments.

Run	ωPDL[a]	εCL[a]	$M_n \times 10^3$ theory	$M_n \times 10^3$ (NMR)[b]	$M_n \times 10^3$ (SEC)[c]	$Đ_M$ (SEC)[c]	DSC peak / °C	
							1st heat	2nd heat
1	100	0	24.1	27.8	57.6	2.05	99.27	96.31
2	150	0	36.2	36.8	76.5	2.29	98.91	97.64
3	200	0	48.2	43.6	96.4	2.12	99.81	98.89
4	300	0	72.2	79.4	117.1	2.26	99.68	99.22
5	150	50	41.9	37.4	83.8	2.18	87.26	86.09
6	100	100	35.6	29.7	74.8	2.19	81.06	79.24

[a] Monomer/[Mg] molar ratio. [b] Calclulated by the formula M_n (NMR) = $= 108.14 + P_n (x M_{ωPDL} + y M_{εCL})$, where 108.14 is MW of BnOH, P_n is degree of polymerization determined as a ratio of integrals in ^{1}H NMR spectra of the signals of polymer OCH_2 fragments and CH_2OH end-groups, x and y are normalized molar fractions of ωPDL and εCL, respectively, for poly(ωPDL) $x = 1$, for poly(εCL) $y = 1$, for poly(εCL-*co*-ωPDL) $x + y = 1$. [c] Determined by SEC in 1,2,4-trichlorobenzene at 50 °C *vs.* polystyrene standards.

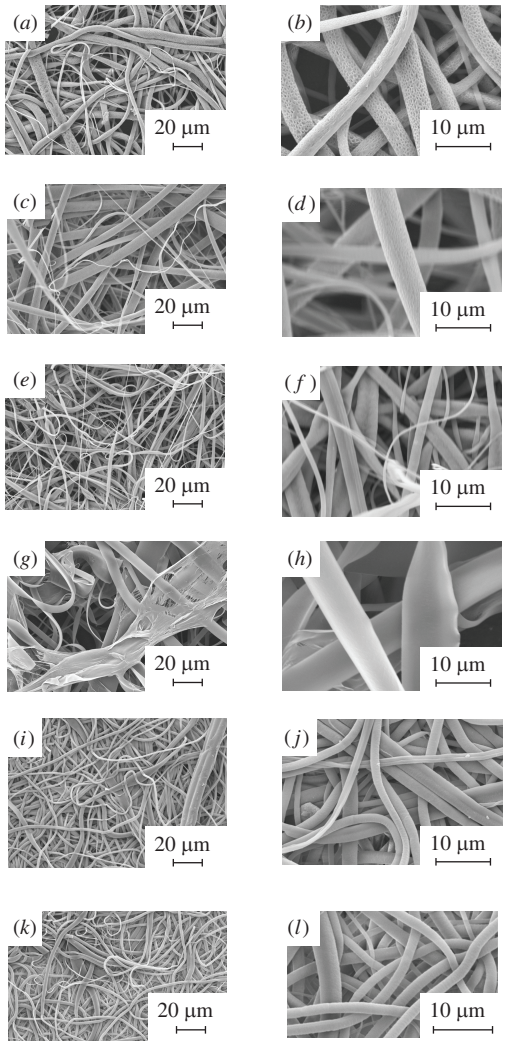


Figure 1 SEM images of electrospun fibers molded from poly(εCL-*co*-ωPDL) [Table S1, runs: (*a*,*b*) – 1, (*c*,*d*) – 2, (*e*,*f*) – 3, (*g*,*h*) – 4, (*i*,*j*) – 5, (*k*,*l*) – 6, see Online Supplementary Materials].

Scheme 1). Polymerization experiments were conducted at 100 °C in molten comonomer mixtures† (Table 1). The polymers obtained have slightly broadened $Đ_M$ due to diversification of the catalyst *via* the formation of more active mononuclear catalytic species in the course of reaction.[17,37,38] A noticeable difference in molecular weight (MW) values determined by NMR and by SEC could be attributed to the need to take into account the correction factor for polyester analysis using the PS standard; for εCL, the value of this factor is 0.56. The presence of single sharp peaks in DSC of poly(εCL-*co*-ωPDL) samples confirmed statistical nature of copolymers. Depending on the comonomer ratios, these peaks were shifted towards lower temperatures relative to DSC peak of poly(ωPDL) samples (see Table 1).

As was found earlier, $CHCl_3$ is the only good solvent for poly(ωPDL), however nanofibers obtained from solutions in pure $CHCl_3$ exhibit 'bead' defects.[5] We optimized the parameters of ES laboratory device, and studied electrospinning of 10 wt% solutions of poly(εCL-*co*-ωPDL) (comonomer ratio 150 : 50, see Table 1, run 5) in various media (for details, see Table S1 in the Online Supplementary Materials). When $CHCl_3$/EtOH was used, the fibers 1–4 μm in diameter with highly porous surface were obtained [Figure 1(*a*),(*b*)]. These defects almost disappeared when

† Visually, under these conditions polymerization finished after 5–10 min, the reaction mixtures were kept for additional 40 min. For experimental details and NMR spectra, see Online Supplementary Materials.

Table 2 Mechanical properties of electrospun mats obtained.

Run	ωPDL/εCL[a]	$M_n \times 10^3$ (NMR)	E^b/MPa	$\sigma_p{}^c$/MPa	$\varepsilon_p{}^d$ (%)
1	150/50	37.4	11 ± 2	5.9 ± 1.0	336 ± 20
2	100/100	29.7	8 ± 2	4.2 ± 0.8	305 ± 18
3	100/0	27.8	10 ± 3	2.4 ± 0.5	175 ± 14
4	150/0	36.2	11 ± 2	5.1 ± 1.1	344 ± 21

[a] Comonomer molar ratio relative to mole of Mg. [b] Young's modulus. [c] Tensile strength. [d] Elongation at break.

$CHCl_3$ was replaced by higher boiling point solvent, *e.g.*, with 1,2-dichloroethane [Figure 1(*c*),(*d*)]. However, both samples included significant amounts of ultra-thin threads. The addition of minimal amount of formic acid resulted in lowering the fiber diameter to 0.5–3 μm [Figure 1(*e*),(*f*)], but some ribbon-like structures were detected. We got the idea to use hexafluoroisopropanol (HFIP) instead of EtOH from the positive impact of the presence of acid. Electrospinning of polymer solution in HFIP [Figure 1(*g*),(*h*)] has yielded highly porous mats containing flat polymeric segments. Nevertheless, when 1,2-dichloroethane/HFIP mixture was used, we obtained fibers with desired homogeneous morphology, the main part of the fibers had a diameter of 2–4 μm without ultra-thin threads and ribbons. The optimal $C_2H_4Cl_2$/HFIP ratio was found to be 4 : 1 [Figure 1(*i*)–(*l*)]. We also studied electrospinning of poly(ωPDL) samples with different MW (see Table S1, runs 7–10) and found that for 10 wt% polymer solutions the optimum P_n value for the formation of homogeneous fibers was ~200 (Figure S5). The results of the mechanical test (Table 2)‡ of the fibrous mats obtained in ES (see Table S1, runs 5–8) demonstrate close characteristics for poly(ωPDL) and poly(εCL-*co*-ωPDL) ES materials.

In summary, we managed to get electrospun mats from poly(ωPDL) and random poly(εCL-*co*-ωPDL) with uniform morphology. These results were achieved by the application of 1,2-dichloroethane/HFIP system as the solvent. Poly(ωPDL) ES fibers are close to poly(εCL-*co*-ωPDL)-based fibers by morphology and mechanical characteristics. In this way, copolymers of ωPDL with lower MW lactones hold promise in the development of fibrous materials with regulated hydrophilicity. The studies of biocompatibility and biodegradation of new fibrous poly(εCL-*co*-ωPDL)-based materials are ongoing in our laboratory.

This work was supported by the Russian Science Foundation (grant no. 16-13-10344-P, in part of polymer synthesis and formation) and was carried out within the State Program of TIPS RAS (in part of polymer analysis).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.015.

References

1 P. Lecomte and C. Jérôme, *Adv. Polym. Sci.*, 2012, **245**, 173.
2 M. A. Hillmyer and W. B. Tolman, *Acc. Chem. Res.*, 2014, **47**, 2390.
3 R. P. Brannigan and A. P. Dove, *Biomater. Sci.*, 2017, **5**, 9.
4 A. S. Carlini, L. Adamiak and N. C. Gianneschi, *Macromolecules*, 2016, **49**, 4379.
5 M. L. Focarete, C. Gualandi, M. Scandola, M. Govoni, E. Giordano, L. Foroni, S. Valente, G. Pasquinelli, W. Gao and R. A. Gross, *J. Biomater. Sci., Polym. Ed.*, 2010, **21**, 1283.
6 M. A. F. Delgove, J. Luchies, I. Wauters, G. G. P. Deroover, S. M. A. De Wildeman and K. V. Bernaerts, *Polym. Chem.*, 2017, **8**, 4696.
7 D. McGinty, C. S. Letizia and A. M. Api, *Food Chem. Toxicol.*, 2011, **49**, S193.

‡ Mechanical tests were carried out on a TiraTest-2200 tensile machine (movement speed: 5 mm min^{-1}, the sample geometry was 10 × 3 × 0.03 mm).

8 I. van der Meulen, M. de Geus, H. Antheunis, R. Deumens, E. A. J. Joosten, C. E. Koning and A. Heise, *Biomacromolecules*, 2008, **9**, 3404.
9 M. de Geus, I. van der Meulen, B. Goderis, K. van Hecke, M. Dorschu, H. van der Werff, C. E. Koning and A. Heise, *Polym. Chem.*, 2010, **1**, 525.
10 S. Rutkowski, A. Zych, M. Przybysz, M. Bouyahyi, P. Sowinski, R. Koevoets, J. Haponiuk, R. Graf, M. R. Hansen, L. Jasinska-Walc and R. Duchateau, *Macromolecules*, 2017, **50**, 107.
11 H.-M. Ye and S.-F. Yao, *Ind. Eng. Chem. Res.*, 2017, **56**, 13725.
12 C. H. R. M. Wilsens, M. P. F. Pepels, A. B. Spoelstra, G. Portale, D. Auhl, Y. S. Deshmukh and J. A. W. Harings, *Macromolecules*, 2016, **49**, 2228.
13 A. Sorrentino, G. Gorrasi, V. Bugatti, T. Fuoco and D. Pappalardo, *Mater. Today Commun.*, 2018, **17**, 380.
14 J. A. Wilson, Z. Ates, R. L. Pflughaupt, A. P. Dove and A. Heise, *Prog. Polym. Sci.*, 2019, **91**, 29.
15 V. Ladelta, P. Bilalis, Y. Gnanoub and N. Hadjichristidis, *Polym. Chem.*, 2017, **8**, 511.
16 B. Wang, L. Pan, Z. Ma and Y. Li, *Macromolecules*, 2018, **51**, 836.
17 I. E. Nifant'ev, A. V. Shlyakhtin, A. N. Tavtorkin, P. V. Ivchenko, R. S. Borisov and A. V. Churakov, *Catal. Commun.*, 2016, **87**, 106.
18 J. A. Wilson, S. A. Hopkins, P. M. Wright and A. P. Dove, *Polym. Chem.*, 2014, **5**, 2691.
19 D. Myers, T. Witt, A. Cyriac, M. Bown, S. Mecking and C. K. Williams, *Polym. Chem.*, 2017, **8**, 5780.
20 S. Naumann, P. B. V. Scholten, J. A. Wilson and A. P. Dove, *J. Am. Chem. Soc.*, 2015, **137**, 14439.
21 H.-C. Huang, B. Wang, X.-L. Chen, L. Pan and Y.-S. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2019, **57**, 973.
22 C. B. Durr and C. K. Williams, *Inorg. Chem.*, 2018, **57**, 14240.
23 A. E. Polloni, J. G. Veneral, E. A. Rebelatto, D. de Oliveira, J. V. Oliveira, P. H. H. Araújo and C. Sayer, *J. Supercrit. Fluids*, 2017, **119**, 221.
24 A. E. Polloni, E. A. Rebelatto, J. G. Veneral, D. de Olivera, J. V. Olivera, P. H. H. Araújo and C. Sayer, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 1219.
25 N. Zhao, C. Ren, Y. Shen, S. Liu and Z. Li, *Macromolecules*, 2019, **52**, 1083.
26 V. Ladelta, J. D. Kim, P. Bilalis, Y. Gnanou and N. Hadjichristidis, *Macromolecules*, 2018, **51**, 2428.
27 P. Walther and S. Naumann, *Macromolecules*, 2017, **50**, 8406.
28 J.-H Bai, X.-Q. Wang, J.-H. Wang and L.-F. Zhang, *J. Polym. Sci., Part A: Polym. Chem.*, 2019, **57**, 1189.
29 J. A. Wilson, S. A. Hopkins, P. M. Wright and A. P. Dove, *Macromolecules*, 2015, **48**, 950.
30 M. Bouyahy and R. Duchateau, *Macromolecules*, 2014, **47**, 517.
31 J. Fernández, A. Etxeberria, A. Larrañag and V. J.-R. Sarasua, *Polymer*, 2015, **81**, 12.
32 K. Wang, Y.-G. Jia and X. X. Zhu, *Macromolecules*, 2017, **50**, 8570.
33 A. Arnebold and A. Hartwig, *Polymer*, 2016, **83**, 40.
34 H. Song, Z. Fang, B. Jin, P. Pan, Q. Zhao and T. Xie, *ACS Macro Lett.*, 2019, **8**, 682.
35 F. Pilate, G. Stoclet, R. Mincheva, P. Dubois and J.-M. Raquez, *Macromol. Chem. Phys.*, 2018, **219**, 1700345.
36 A. M. Ziemba, K. P. Lane, I. M. San Segundo, A. R. D'Amato, A. K. Mason, R. J. Sexton, H. Casajus, R. A. Gross, D. T. Corr and R. J. Gilbert, *ACS Biomater. Sci. Eng.*, 2018, **4**, 1491.
37 I. E. Nifant'ev, A. V. Shlyakhtin, V. V. Bagrov, M. E. Minyaev, A. V. Churakov, S. G. Karchevsky, K. P. Birin and P. V. Ivchenko, *Dalton Trans.*, 2017, **46**, 12132.
38 P. V. Ivchenko, A. V. Shlyakhtin and I. E. Nifant'ev, *Mendeleev Commun.*, 2017, **27**, 278.

Received: 12th July 2019; Com. 19/5984