Preparation and mechanical properties of PCL-based polyurethanes as potential biomaterials for short-term applications

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Abstract: A series of polyurethanes (PURs) were prepared by metal-free method, containing polycaprolactone (PCL) as the soft segment with molecular weights of 1600, 2400 and 2600. PCL was obtained by the ring-opening polymerization of ϵ -caprolactone in the presence L-alanine and L-phenylalanine. The structure of synthesized oligoesters and PURs were spectroscopically confirmed. The molecular weights, mechanical and thermal properties of the obtained materials were reported.

Introduction

Polyurethanes (PURs) are very interesting materials which characterize unique combination of biological, chemical and physical properties. They have good mechanical properties, good biocompatibility, biostability and antithrombogenicity. PURs have been used as biomaterials in various applications (e.g. aortic grafts, endotracheal tubes, vascular tubing, heart valves, heart assist devices, catheters, pacemaker wire insulation, transcutaneous access sets, restorative and preventative dental materials, components of hemodialysis units). [1-8]

The commercial PURs are obtained on the polyaddition process which involves diisocyanates and bi-functional or multi-functional polyols (polyethers, polyesters, polycarbonates) with hydroxyl terminal group. The catalytic activity in the reaction of isocyanates with polyols is shown by organometallic compounds (Sn, Pb and Fe). [9]

Linear poly(ϵ -caprolactone) (PCL) is often used in the biomedical PURs production processes. They are usually prepared by ring-opening polymerization (ROP) in the presence of alkaline, Lewis acids, enzymes and coordination catalysts [10-19]. The coordinating catalysts are very effective in ROP of ϵ -caprolactone (CL) but most of them are toxic for humans. Recently, we found that amino acids and creatinine, are satisfactory natural initiators for ROP of cyclic esters [20-21].

Our objective in this study was to synthesize and characterize a group of PURs based on PCL. We describe method of the synthesis of PURs without using metal-catalysts. The preliminary studies on their mechanical properties were shown. We believe that the obtained polyurethanes can find practical applications as

biomaterials for short-term applications (e.g. catheters, cardiovascular, wound dressing, transdermal patches).

Results and discussion

Synthesis of PCL

Recent investigation shows that natural amino acids are satisfactory initiators for ROP of cyclic esters [20]. So, we decided to carry out more detailed investigation of that reaction initiated by L-alanine and L-phenylalanine. The purpose of this work was to obtain the oligomers with respect to their applications as soft segments in biomedical polyurethanes.

The polymerization reactions of CL were carried out at 140 °C for 2-72 h (Scheme 1). The molar ratio of amino acids to a given monomer was 1:25, 1:50 or 1:100. Reaction conditions, yields, intrinsic viscosity and average molecular weight of polyesters are collected in Table 1.

R – Ala or Phe unit

Scheme 1. Synthesis of PCL.

The chemical structures of the obtained oligoesters were confirmed by ^{13}C , ^1H -NMR and IR studies (see experimental section). Insertion of the amino acids fragment into the polymer chain was confirmed by the proton NMR spectral analysis. The peaks at 5.8 - 6.2 ppm were observed in all products obtained by polymerization of CL. The formation of the –NHCO- group indicates that the amino group of the amino acids was incorporated into PCL chain [20]. The peaks characteristic for amino acids fragment were not observed in the spectra of purified polymerization products (after precipitated from cold methanol with diluted hydrochloric acid). The disappearance of the peaks at 5.8 - 6.2 ppm indicated that the amide group in the polymers was removed completely before purification process.

The MALDI-TOF spectra of PCL comprise three of peaks. The most prominent series of peaks is characterized by a mass increment of 114 Da, which is equal to the mass of the repeating unit in the PCL. It is assigned to PCL terminated with a hydroxyl group (residual mass: 41 Da, Na^+ adduct). The second series of peaks also corresponded to PCL, terminated with a hydroxyl group (residual mass: 57 Da, K^+ adduct). In addition, the mass spectrum contains a low-intensity series of peaks corresponding to cyclic molecules (residual mass: 23 Da, Na^+ adduct). The content of macrocycles was estimated on the basis of the intensity ratio of the peaks for linear

and cyclic polymer. MALDI-TOF spectrum shows the formation of cyclic species, as a consequence of backbiting degradation. This feature is observed for all amino acids studied [20].

Tab. 1. Polymerization of CL initiated by L-Ala and L-Phe at 140 °C.

Code	I	M/I	Time (h)	Yield (%)	M_n^a (Da)	M_w/M_n^a	M_n^b (Da)	M_w/M_n^b	MC (mol %)	η_{inh}^c (dl·g ⁻¹)	M_n^d (Da)
PCL-1	L-Ala	25:1	24	76	-	-	-	-	-	0.06	-
PCL-2	L-Ala	25:1	48	82	1900	1.2	1800	1.1	9	0.06	1600
PCL-3	L-Ala	50:1	2	traces	-	-	-	-	-	-	-
PCL-4	L-Ala	50:1	24	74	-	-	2200	1.1	5	0.11	-
PCL-5	L-Ala	50:1	48	80	3300	1.2	2400	1.2	8	0.12	2600
PCL-6	L-Ala	50:1	72	82	-	-	2500	1.2	21	0.12	-
PCL-7	L-Ala	100:1	24	79	4400	1.3	-	-	-	0.21	-
PCL-8	L-Ala	100:1	48	90	-	-	-	-	-	0.23	-
PCL-9	L-Phe	25:1	24	84	-	-	-	-	-	0.07	-
PCL-10	L-Phe	25:1	48	88	-	-	-	-	-	0.07	-
PCL-11	L-Phe	50:1	24	81	-	-	-	-	-	0.12	-
PCL-12	L-Phe	50:1	48	85	2900	1.2	2000	1.2	6	0.13	2400
PCL-13	L-Phe	100:1	24	89	-	-	-	-	-	0.27	-
PCL-14	L-Phe	100:1	48	88	3800	1.3	-	-	-	0.24	-

I – initiator, M/I – ratio of monomer to initiator,

M_n^a , M_w/M_n^a – molecular mass and polydispersity of oligomers determined by GPC;

M_n^b , M_w/M_n^b – molecular mass and polydispersity of oligomers determined by MALDI;

MC – macrocycles content (determined by MALDI-TOF)

^c measured at 30 °C in DMF;

^d M_n calculated from L_{OH}

Spectroscopy and spectrometry studies have been in agreement with earlier findings [20].

The average molecular mass values of PCL determined by the MALDI-TOF method are in the 1800–2500 Da range (polydispersity indexes 1.1–1.2).

The effects of reaction conditions such as time and ratio of monomer to initiator are described below.

Tab. 2. Synthesis of PURs.

Code	Reagents/catalyst	Molar ratio	η_{inh}^a (dL/g)	T_g^b [°C]	T_m^c [°C]
PUR-1	MDI-1,4-BD -OEAD-PCL-2/DABCO	2.5 : 1.5 : 0.6 : 0.4 : 0.01	1.81	-12	74
PUR-2	MDI-1,4-BD -OEAD-PCL-5/DABCO	2.5 : 1.5 : 0.6 : 0.4 : 0.01	2.24	-14	68
PUR-3	MDI-1,4-BD -OEAD-PCL-5/DABCO	2.5 : 1.0 : 0.8 : 0.7 : 0.01	2.04	-17	55
PUR-4	MDI-1,4-BD -OEAD-PCL-5/DABCO	2.5 : 0.7 : 1 : 0.8 : 0.01	1.93	-18	42
PUR-5	MDI-1,4-BD -OEAD-PCL-12/DABCO	2.5 : 1.5 : 0.6 : 0.4 : 0.01	1.98	-15	68
PUR-6	MDI-1,4-BD -OEAD-PCL-12/DABCO	2.5 : 0.7 : 1 : 0.8 : 0.01	2.03	-19	44

^a measured at 30°C in DMF;

^b glass transition temperature determined from DCS (the second heating)

^c melting point determined from DSC

Polymerization yields were similar and practically independent of the nature of the amino acid and ratio of monomer to initiator (see Tab. 1). The reaction yield was determined by the weight method. For PCL-2, PCL-5, PCL-8, PCL-10, PCL-12 and PCL-14 the corresponding monomer yield values were 82%, 80%, 90%, 88%, 85% and 88%, respectively. Similarly, the yield values for PCL-1, PCL-4, PCL-7, PCL-9, PCL-11 and PCL-13 were 76%, 74%, 79%, 84%, 81% and 89%, respectively.

Table 1 shows the yield of polymerization of CL versus time. After 2 h of conducting the polymerization of CL, traces of the product were only obtained. However, after 24, 48 and 72 h the reaction yield was 74, 80 and 82%, respectively. The decrease in polymerization rate as the polymerization proceeds is consistent with slowed diffusion of monomer and propagating chain ends with increased reaction viscosity, probably.

Fig. 1. The ¹H-NMR spectrum of the PCL-based PUR (in DMSO-d₆).

However, significant differences were observed between the intrinsic viscosities (see Tab. 1). As shown in Table 1, the PCL products were obtained with the intrinsic

viscosity of 0.06, 0.12, 0.23, 0.07, 0.13 and 0.24 dl·g⁻¹ for PCL-2, PCL-5, PCL-8, PCL-10, PCL-12 and PCL-14, respectively.

The average molecular mass values of PCL determined by the GPC method are in the 1900–4400 Da range. The polydispersity shows only small variations (between 1.2 and 1.3). As shown, the molecular mass of PCL is dependent on the monomer/amino acid molar ratio.

Synthesis of polyurethanes

Polyurethanes (PURs) were synthesized using PCL and OEAD as a soft segment and MDI and BD as components of the hard segment. DABCO was the polyaddition catalysts. A one-step melt polymerization procedure was employed (at the molar ratio of NCO/OH = 1). The reaction conditions and η_{inh} of the products obtained are listed in Table 2.

Fig. 2. The ¹³C-NMR spectrum of the PCL-based PUR (in DMSO-d₆).

The chemical structure of PURs was characterized by ^1H , ^{13}C NMR and FT-IR (Figs. 1 and 2). The data was shown in the experimental section. It was found that all the characteristic peaks and absorption bands belonging to MDI, BD, PCL and OADE existed in the spectra of PURs. It indicated the reactions were complete and PURs were formed.

DSC results for the PURs during the second heating run are summarized in Table 2. The T_g values lie in the -12 to -19 °C. Next, the melting point of crystalline phase values lie in the 42 to 74 °C.

Tab. 3. Mechanical properties of the obtained PURs based on PCL.

Code	Se _f [MPa]	Se ₁₀₀ [MPa]	Se ₂₀₀ [MPa]	Se ₃₀₀ [MPa]	E _b [%]	[oIRH]
PUR-1	27.0±1.1	6.7±0.2	7.0±0.1	10.1±0.3	318±8	51±2
PUR-2	29.0±1.0	6.5±0.2	7.2±0.2	10.3±0.4	301±7	53±2
PUR-3	20.3±0.8	7.4±0.2	8.8±0.2	12.7±0.4	435±8	42±2
PUR-4	18.3±0.7	7.7±0.2	9.1±0.2	13.1±0.4	455±10	39±1
PUR-5	26.1±0.8	6.6±0.1	7.9±0.2	11.4±0.3	329±7	48±2
PUR-6	20.1±0.6	7.9±0.1	8.9±0.2	14.1±0.3	477±11	40±2

Se_f - fail stress, Se₁₀₀ – stress at 100% elongation, Se₂₀₀ – stress at 200% elongation, Se₃₀₀ – stress at 300% elongation, E_b – elongation at break, oIRH – hardness

Mechanical properties of PURs are more important than any other properties with respect to practical applications. So, some mechanical properties like fail stress (Se_f), stress at 100% elongation (Se₁₀₀), stress at 200% elongation (Se₂₀₀), stress at 300% elongation (Se₃₀₀), hardness (oIRH) and stress at 100% elongation at break (E_b) of PURs obtained are determined. The data on the tensile analysis of PURs with various soft segment contents were listed in Table 3. It can be seen that the PURs have high fail stress and hardness, and their elongation at break can be greater than 300%. The elongation at break decreases with a significant decrease in the soft segment. It was found that PUR-4 and PUR-3 have better elongations with more than 400% while PUR-2 showed an elongation of about 300%. Similarly, E_b for PUR-6 and PUR-5 was 477% and 329 %, respectively. The fail stress showed an opposite trend. For example, Se_f for PUR-2, PUR-3 and PUR-4 was 29 and 20 and 18 MPa, respectively. Similarly, PUR-5 has better fail stress than PUR-6.

It is seen that the fail stress and the hardness increase with increasing the hard-segment content, and the elongation at break has the opposite trend.

The toxicity of obtained PCL-based PURs is still under study and will be presented in the next paper.

Conclusions

Series of oligoesters have been synthesized by ring-opening polymerization of CL in the presence of L-Ala and L-Phe with high yields (about 90 %). The oligoesters were reacted with 4,4'-methylenebis(phenyl isocyanate) in the presence of 1,4-butanediol as the chain extender to obtain PURs. The polyaddition process was catalyzed by DABCO. Obtained materials characterized good mechanical properties (fail stress, hardness and elongation at break). Values between 16 and 30 MPa, 39 and 53, 300 and 400% were found for these properties, respectively. PURs showed elastomeric

properties. The study of the toxicity and the blood compatibility of obtained PURs are further carried out. The free-metal method of the synthesis of oligomerols and PURs is very promising in the synthesis of polymers intended for biomedical applications.

Experimental part

Materials

ϵ -Caprolactone (2-Oxepanone, 99%, CL) was purchased from Aldrich. Before use, it was dried and distilled over CaH_2 at reduced pressure. Amino acids (99%, Aldrich) (L-alanine – L-Ala, L-phenylalanine – L-Phe), dichloromethane (POCh), dimethyl sulfoxide (DMSO, 99%, Aldrich), N,N-dimethylformamide (DMF, 99%, Aldrich), methanol (POCh) were used as received. 4,4'-methylenebis(phenyl isocyanate) (MDI, 98%, Aldrich), dihydroxy(polyethylene adipate) (OEAD, $M_n = 1000$ Da, Aldrich), 1,4-butanediol (BD, 98%, Fluka), 1,4-diazabicyclo[2.2.2]octane (DABCO, 99%, Aldrich) were used without further purification.

Synthesis of PCL

CL and amino acids (L-Ala, L-Phe) were placed in glass ampoules under argon atmosphere. The reaction vessels were then left standing in a thermostated oil bath for the required temperature and time. When the reaction was completed (Table 1), the cold product was dissolved in dichloromethane, precipitated from cold methanol with diluted hydrochloric acid (5% aqueous solution) and dried in vacuum for 72 h to isolate a powdery polymer.

PCL:

^1H NMR (CDCl_3 , δ , ppm): 4.03 (2H, t, $-\text{CH}_2\text{CH}_2\text{OC(O)}-$), 3.70 (2H, t, $-\text{CH}_2\text{CH}_2\text{OH}$, end group), 2.27 (2H, t, $-\text{CH}_2\text{CH}_2\text{COO}-$), 1.61 (4H, m, $-\text{CH}_2\text{CH}_2\text{COO}-$), 1.36 (2H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$); ^{13}C NMR (CDCl_3 , δ , ppm): 173.3 ($-\text{C(O)O}-$), 63.9 ($-\text{CH}_2\text{CH}_2\text{OC(O)}-$), 33.8 ($-\text{CH}_2\text{CH}_2\text{COO}-$), 28.1 ($-\text{CH}_2\text{CH}_2\text{OC(O)}-$), 25.4 ($-\text{CH}_2\text{CH}_2\text{COO}-$), 24.4 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$); FTIR (KBr, cm^{-1}): 2950 ($\nu_{\text{as}}\text{CH}_2$), 2865 ($\nu_{\text{s}}\text{CH}_2$), 1730 ($\nu_{\text{C=O}}$), 1240 ($\nu_{\text{as}}\text{COC}$), 1190 ($\nu_{\text{OC-O}}$), 1170 ($\nu_{\text{s}}\text{COC}$).

Synthesis of PURs

All the PURs were synthesized by a one-step melt polymerization. Before reaction all reactants e.g. MDI, OEAD, BD and PCL were dried in vacuum for 1 h at 70 °C. Then the polyesters (OEAD and PCL), BD and DABCO were mixed at 100 °C in a 250-ml three-necked flask equipped with a stirrer and thermometer. After 1 h MDI was progressively added into the reactor and content of the flask was vigorously stirred. The synthesis of PUR was carried out under argon atmosphere at the NCO/OH molar ratio of 1. After the reaction was complete, the product was conditioned in a steel mould under vacuum at 35 °C for 2 h. The PURs were dissolved in DMSO and then isolated from the solution by pouring into water. Then, they were kept under vacuum at 70 °C for one week.

PURs:

^1H NMR (DMSO, δ , ppm): 9.50 ($-\text{O(O)CNHArCH}_2\text{ArNHC(O)O}-$), 8.51 ($-(\text{O)CNHAr}-$), 7.31 (hydrogen atoms attached to aromatic carbon), 7.04 (hydrogen atoms attached to aromatic carbon), 4.15 ($-\text{OC(O)CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C(O)OCH}_2\text{CH}_2\text{OC(O)NHAr}-$), ($-\text{OC(O)NHAr-OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C(O)O}-$), ($-\text{ArHNC(O)OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OC(O)NH}$

Ar–), (–OCH₂CH₂CH₂CH₂CH₂C(O)O–), 3.78 (–O(O)CNHArCH₂ArNHC(O)O–), 2.35 (–OCH₂CH₂CH₂CH₂CH₂C(O)O–), 1.81 (–ArHN(O)COCH₂CH₂CH₂CH₂OC(O)NHAr–), 1.54 (–OCH₂CH₂CH₂CH₂CH₂C(O)O–), 1.34 (–OCH₂CH₂CH₂CH₂CH₂C(O)O–); ¹³C NMR (CDCl₃, δ, ppm): 172.5–170.0 (–OC(O)–), 154.6 (–OCH₂CH₂CH₂CH₂OC(O)NHAr–), 153.3 (–OC(O)CH₂CH₂CH₂CH₂C(O)OCH₂CH₂OC(O)NHAr–), 137.1 (aromatic carbon atoms - bonded with the methylene group), 135.4 (aromatic carbon atoms - bonded with the urethane group), 128.8 (aromatic carbon atoms), 118.3 (aromatic carbon atoms), 63.0 (–OCH₂CH₂CH₂CH₂CH₂OC(O)NHAr–) (–ArNHC(O)OCH₂CH₂CH₂CH₂OC(O)NHAr–), 61.8 (–OCH₂CH₂CH₂CH₂C(O)OCH₂CH₂O C(O)NHAr–), 32.9 (–OCH₂CH₂CH₂CH₂CH₂C(O)O–), 25.3 (–OCH₂CH₂CH₂CH₂CH₂C(O)O–), 23.7 (–OCH₂CH₂CH₂CH₂CH₂C(O)O–) (–ArNHC(O)OCH₂CH₂CH₂CH₂O C(O)NHAr–), 22.5 (–OCH₂CH₂CH₂CH₂CH₂C(O)O–), 17.6 (–OCH(CH₃)C(O)O–); FTIR (KBr, cm^{–1}): 3340 (N–H in urethane group), 2990–2945 (C–H in –CH₂– group), 2880–2860 (C–H in –CH₃ and –CH– group), 1750–1690 (C=O in urethane group), 1720 (C=O in ester group), 1600 (C–H in –C₆H₄), 1250 (C–O in –C(O)O– group).

Measurements

The polymerization products were characterized by means of ¹H and ¹³C-NMR (Varian 300 MHz), and FT-IR spectroscopy (Perkin-Elmer). The NMR spectra were recorded in CDCl₃. The IR spectra were measured from KBr pellets. Relative molecular mass and molecular mass distributions were determined by MALDI-TOF and gel permeation chromatography (GPC) techniques. MALDI-TOF spectra were measured in the linear mode on a Kompact MALDI 4 Kratos analytical spectrometer using a nitrogen gas laser and 2[(4hydroxyphenyl)diazenyl] benzoic acid (HABA) as a matrix. Molecular weight and molecular weight distributions of polymers were determined at 308 K on Lab Alliance gel permeation chromatography equipped with JordiGelDVBMixed Bed (250 mm A10 mm) columns and refractive detector, and THF or chloroform as eluent (1 cm³/min). The molecular weights were calibrated with polystyrene standards. Polymer viscosity was measured in N,N-dimethylformamide (at 30 °C) using a Ubbelohde viscometer (on Stabinger Viscometer SVM 3000).

DSC studies were performed in the temperature range from -60 °C to +120 °C using a Perkin Elmer Pyris 1 calorimeter at a heating rate of 20 °C/min for samples of 10–25 mg mass.

The obtained polyurethanes were extruded in the shape of threads (by Brabender extrusion machine). Fail stress (Se_f), stress at 100% elongation (Se₁₀₀), stress at 200% elongation (Se₂₀₀), stress at 300% elongation (Se₃₀₀), elongation at break (E_b), elongation (E), hardness (oIRH) of the samples were measured using an Zwick model 1445 tester. Se_f, Se₁₀₀, Se₂₀₀, Se₃₀₀, E_b were determined according to national standard PN-ISO 37:98. E and oIRH were determined by IPG “Stomil” methods.

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