Bioresorbable poly(ester-ether urethane)s from L-lysine diisocyanate and triblock copolymers with different hydrophilic character

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Received 2 May 2005; revised 4 July 2005; accepted 11 July 2005
Published online 29 November 2005 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/jbm.a.30540

Abstract: Bioresorbable linear poly(ester-ether urethane)s with different hydrophilic character were synthesized from block copolymers of poly(ϵ-caprolactone)-poly(ethylene oxide)-poly(ϵ-caprolactone) (PCL-PEO-PCL) as macrodiols, and L-lysine diisocyanate (LDI). A series of PCL-PEO-PCL triblock copolymers with different PEO and PCL chain length was obtained by reacting PEO with ϵ-caprolactone. Polyurethanes were synthesized by reacting the triblock copolymers with LDI in solution using stannous 2-ethylhexanoate as catalyst. The prepared triblock copolymers and polyurethanes were fully characterized by proton nuclear magnetic resonance spectroscopy, size exclusion chromatography, differential scanning calorimetry, and wide-angle X-ray diffraction. Water uptake, hydrolytic stability, and tensile properties of polyurethanes with different composition were evaluated and discussed in terms of the chain length and molecular weight of the polymers and its block components. Water uptake seems to depend on the ethylene oxide unit content of the polyurethane regardless of the triblock structure. Mechanical properties of the synthesized polymers were strongly affected by the molecular weight achieved during polymerization. The use of triblock macrodiols with different hydrophilicity allowed the preparation of a series of polyurethanes having a broad range of properties. © 2005 Wiley Periodicals, Inc. J Biomed Mater Res 76A: 729–736, 2006

Key words: bioresorbable polyurethanes; lysine diisocyanate; triblock copolymers; poly(ethylene oxide); poly(ϵ-caprolactone)

INTRODUCTION

Polyurethanes are considered excellent biomedical materials because of their good mechanical properties and blood compatibility. They are used in numerous intra- and extracorporeal biomedical devices.[1] Many research efforts in synthetic biomedical polyurethanes have been directed toward the synthesis and modification of segmented polyurethanes with improved biostability[2,3] for long-term implanted devices, such as left ventricular assist devices, vascular prostheses, and other cardiovascular applications.

In recent years, however, there is an increasing interest in the design of biodegradable polyurethanes for specialized applications. Depending on their mechanical properties, chemical composition, surface chemistry, morphology, and a number of other aspects, biodegradable polyurethanes can be used for cardiovascular grafts, cancellous bone grafts, adhesives, controlled drug delivery systems, or other nontoxic implanted devices. Moreover, biodegradable polymers may act as temporary scaffolds (artificial extracellular matrices) that facilitate tissue regeneration or replacement in the field of tissue engineering.[4]

Degradable polyurethanes may be produced through the introduction of labile moieties susceptible to hydrolysis in the polymer structure, such as polylactides and poly(ϵ-caprolactone) (PCL). Biodegradable poly(ester urethane)s have been widely used in biomedical devices, but these materials produce toxic byproducts (suspected carcinogens) which have limited their *in vivo* applications. For example, 4,4′-methylenediphenyl diisocyanate (MDI) hydrolyzes after degradation *in vivo* into 4,4′-methylenedianiline producing hepatitis in humans.[5] Cycloaliphatic diisocyanates such as hydrogenated MDI or hexamethylene diisocyanate have also been used, but the derived diamines also resulted to be more or less toxic.

To avoid the use of monomers that yield toxic compounds when degraded, other precursors based on L-lysine, as well as other amino acids, have been developed.[6–8] Bruin et al.[6] reported that the synthesis of biodegradable poly(ester-urethane)s using ethyl 2,6-

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diisocyanatohexanoate (LDI), a L-lysine-derived diisocyanate, did not produce adverse tissue reactions.[9] Other researchers used LDI, but not significant toxic or tumorigenic responses to the materials upon implantation were found.[4]

PCL is a very well known biodegradable aliphatic polyester widely investigated in the biomedical field. PCL was used as matrix for long-term delivery, wound-covering materials, matrix for tissue engineering,[10] and a number of medical and drug delivery devices with the Food and Drug Administration approval. PCL has a hydrophobic character (because of the presence of five nonpolar methylene groups and a single relatively polar ester group), a semicrystalline structure, and a hydrolytic biodegradability at long term. The combination of its crystallinity and high olefinic character, determines a low biodegradation rate.

The use of poly(ethylene oxide) (PEO) in the formulation of biomedical polyurethanes as well as in surface modification treatments, has been widely reported. PEO presents outstanding physicochemical and biological properties, including hydrophilicity, solubility in water, lack of toxicity, absence of antigenicity, and immunogenicity. It is established that PEO exhibits a good biocompatibility and even satisfactory blood compatibility. Polyurethanes based on PEO have low platelet retention factor, which is further reduced when the molecular weight of the polyol is increased.[11,12]

PCL-PEO-PCL triblock copolymers have been described in the literature,[13–15] and several works propose their use for biomedical applications. Moreover, multiblock copolymers offer the possibility of combining the hydrophilicity of the central PEO block with the degradability of PCL.[16,17] These solid polymeric materials, which show bulk degradation and further resorb *in vivo* through natural pathways, either because of simple filtration of degradation byproducts or after their metabolization, are called bioresorbable.

This article focuses on the synthesis and complete characterization of polyurethanes formulated with PCL-PEO-PCL triblock copolymers with different hydrophilic-to-hydrophobic ratio and LDI. The use of triblocks with different PCL and PEO chain lengths allows the preparation of materials with different hydrophilicity having a broad range of properties such as swelling, degradation rate, thermal, and mechanical behavior. This work can be considered as a preliminary effort in the study of segmented polyurethane-ureas extended with amino acids.[18,19]

MATERIALS AND METHODS

Materials

ϵ-Caprolactone (ϵ-CL) (Merck-Schuchardt) was used as received. PEO number-average molecular weight (M_n) = 900, 2000, and 4000 (Aldrich) were vacuum dried at 90°C for at least 6 h on a rotary evaporator. Polycaprolactone diol M_n = 2000 was obtained from Aldrich and used as model macrodiol. To remove traces of water, the PCL diol was dissolved in the reaction flask in toluene and the solvent was exhaustively distilled off. L-Lysine-diisocyanate (methyl 2,6-diisocyanatohexanoate) (LDI) was kindly donated by Kyowa Hakko Kogyo Co. (Japan). Stannous 2-ethylhexanoate (Aldrich) was used as catalyst without purification and 1,2-dichloroethane (DCE) (Scharlau) was distilled over phosphorous pentoxide before use.

Synthesis of poly(ester-ether-ester) macrodiols

The synthesis of block copolymers by using an active-hydrogen compound as initiator in ring-opening polymerization of ϵ-CL has been widely investigated. Triblock copolymers consisting of PCL-PEO-PCL with different hydrophilic-to-hydrophobic ratios were synthesized. Polymerization mixtures were prepared by charging a predetermined volume of ϵ-CL into a three-necked flask containing a preweighed amount of dried PEO. Catalyst (0.1% weight respect to the monomer weight) was then added. The reaction was performed in bulk for 24 h under magnetic stirring at 130°C. Afterward, the macrodiol was exhaustively dried under high vacuum (10^{-3} mm Hg) while cooling during 24 h at room temperature. The reaction yield was found to be higher than 95%. Table I shows the series of synthesized materials. The nine synthesized triblock copolymers were identified as quoted in Table I, where the code indicates the molecular weight of the central block (PEO) and the [ϵ-CL]/[PEO] initial molar ratio. Thus, for example, C900-10 indicates the copolymer having a PEO central block of 900 Da and a [ϵ-CL]/[PEO] molar ratio in the feed of 10 (which corresponds to a theoretical PCL chain length of 5 units in each block). Scheme 1 shows the chemical structure of triblock copolymers and LDI.

Synthesis of poly(ester-ether urethane)s

To properly control the polymer molecular weight, the monomer concentration was adjusted so that they were slightly nonstoichiometric. The stoichiometric imbalance of the two bifunctional monomers was investigated by reacting LDI with a commercial PCL diol (M_n = 2000) as low-molecular-weight macrodiol model. In this way, the diisocyanate/macrodiol molar ratio which led to higher molecular weight was 1.05:1. All the reactions were performed by using this reactant ratio.

Each macrodiol was dissolved in toluene and the solution was azeotropically dried. Polymerization was performed in DCE solution (0.39*M*) at 85°C under magnetic stirring and nitrogen flow. The molar concentration was selected in order to have less than 100% total w/v. A catalyst concentration of 0.2% w/w was used. The reaction was completed when the infrared band corresponding to the isocyanate group at 2260 cm^{-1} was not observed anymore. The resulting polymer was exhaustively dried under vacuum for complete solvent removal. The nine polyurethanes were identified using the same code that

TABLE I
Average PCL Chain Length, PEO Content, and Average Number (M_n) and Average Weight (M_w) Molecular Weights of the Synthesized Triblock Copolymers

Triblock Copolymer	PCL Chain Length[a]	PEO (% w/w)[b]	Triblock Species (%)	M_n[c]	M_n[d]	M_w[d]	P.I.[d]
C900-10	4.8	44.9	71.7	2005	2990	4870	1.63
C900-20	10.0	28.3	81.5	3180	6720	9610	1.43
C900-40	20.0	16.5	89.8	5470	13610	18060	1.33
C2000-10	4.1	68.3	68.4	2930	5420	6300	1.16
C2000-20	10.0	46.6	94.8	4290	8660	9730	1.12
C2000-40	20.5	29.9	89.1	6680	13420	18470	1.38
C4000-50	23.5	42.7	95.6	9370	16960	19230	1.13
C4000-100	34.2	33.8	100	11820	21550	23000	1.10
C4000-200	80.1	17.9	100	22290	23960	33180	1.38

[a]Average number of repeating units of ε-CL of each PCL block as determined by ^{1}H NMR.
[b]PEO content (% w/w) as measurement of the hydrophilicity.
[c]Values determined by ^{1}H NMR.
[d]Values determined by SEC. P.I.: polydispersity index: M_w/M_n.

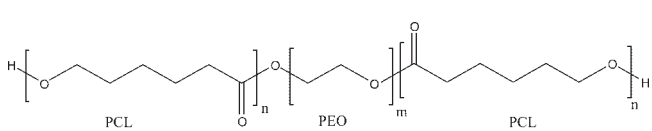
was used for the triblock copolymer with an initial letter P (i.e., P900-10).

Methods used for triblock copolymers and polyurethanes characterization

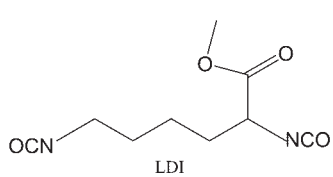
Proton nuclear magnetic resonance (^{1}H NMR) spectra were performed in a Varian XLR-300 NMR spectrometer operating at 300 MHz. The^{1}H NMR spectra were obtained from 5% w/v $CDCl_3$ solutions at room temperature.

Average molecular weight and molecular weight distributions were determined by size exclusion chromatography (SEC) using a PerkinElmer gel permeation chromatograph equipped with a refractive index detector series 200. A set of 10^4 Å, 10^3 Å, and 500 Å PL-gel columns conditioned at 25°C was used to elute the samples of 10 mg mL^{-1} concentration at 1 mL min^{-1} high-performance liquid chromatography-grade chloroform flow rate. A set of polystyrene standards (Polymer Laboratories) was used for calibration.

Attenuated total internal reflectance-Fourier transform infrared (ATR-FTIR) analysis was performed using a PerkinElmer Spectrum One infrared spectrometer equipped with an ATR accessory. The absorbance of each functional group was normalized by using the absorbance of the carbonyl group.



PCL-PEO-PCL triblock copolymers



Scheme 1. Chemical structure of the triblock copolymers and LDI.

Wide-angle X-ray diffraction (WAXD) patterns were obtained by means of a Philips PW 1130 diffractometer (Cu Kα radiation), at a scan rate of 2° min^{-1} over the 5–40 2θ range.

Differential scanning calorimetry (DSC) experiments were carried out in a Mettler Toledo (DSC822e) calorimeter. Sample weights, which ranged from 5 to 15 mg, were sealed in aluminum pans. Two scans were performed by using a 10°C min^{-1} heating rate and the fastest cooling rate of the instrument between runs. Thermograms were obtained in the range −90° to 80°C under nitrogen purge. The glass transition temperature (T_g) of the polymer systems was determined at the onset of the transition of DSC traces.

Tensile properties were measured according to ISO 37. Plaques with 0.6–0.7 mm in thickness for tensile specimens were obtained by compression molding. Dumbbell test specimens were prepared by cutting plaques using a sharp die with Type 3 dimensions; that is, 2 ± 0.1 mm in width of the narrow parallel portion and 35 mm in length. Tests were conducted at room temperature (23° ± 2°C) in an MTS universal testing machine model 4467, with a 100 N cell at a crosshead displacement rate of 5 mm/min. True stress-deformation curves were obtained by dividing the load by the original cross-sectional area and converting it into true stress, assuming constant volume deformation. The deformation was calculated directly from the crosshead speed.

Swelling behavior and hydrolytic stability experiments

The water sorption measurements were obtained from dried discs of known weights that were immersed in phosphate-buffered saline (PBS) solution at pH = 7.4 and incubated at 37°C. At appropriate times, the samples were removed, blotted quickly with absorbent paper to remove the water attached on its surface, and weighed. The water uptake percentage of the samples was calculated from the following relation:

$$\text{Water uptake (\%)} = [(W_m - W_o)/W_o] \times 100$$

where W_m is the maximum weight of swollen specimen and W_o is the initial weight of the specimen.

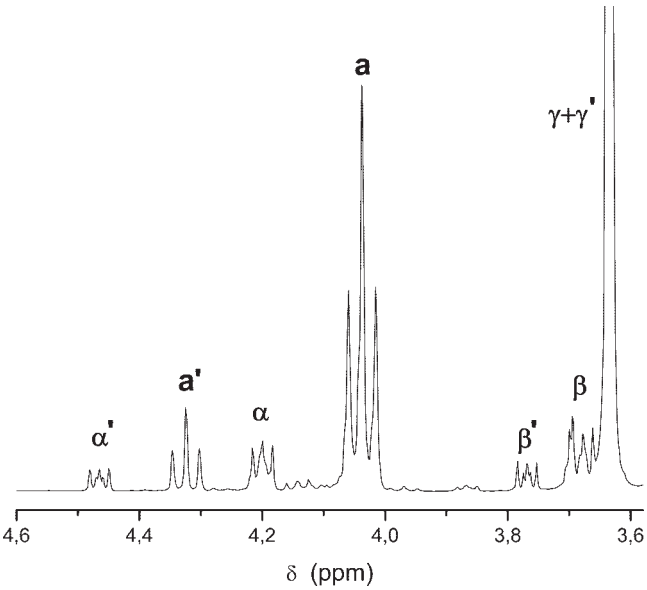


Figure 1. NMR spectrum of C900-90 after derivatization with trifluoroacetic anhydride.

In vitro degradation studies were performed by placing the discs in PBS at 37°C. Weight loss was gravimetrically monitored at various time intervals. In all the experiments, a minimum of three samples was measured and averaged. At appropriate times, the samples were removed, exhaustively dried under vacuum, and weighed. The weight loss percentage was calculated from the following relation:

$$\text{Weight loss (\%)} = [(W_o - W_t)/W_o] \times 100$$

where W_t is the weight of dried specimen at time t.

RESULTS AND DISCUSSION

Triblock copolymer characterization

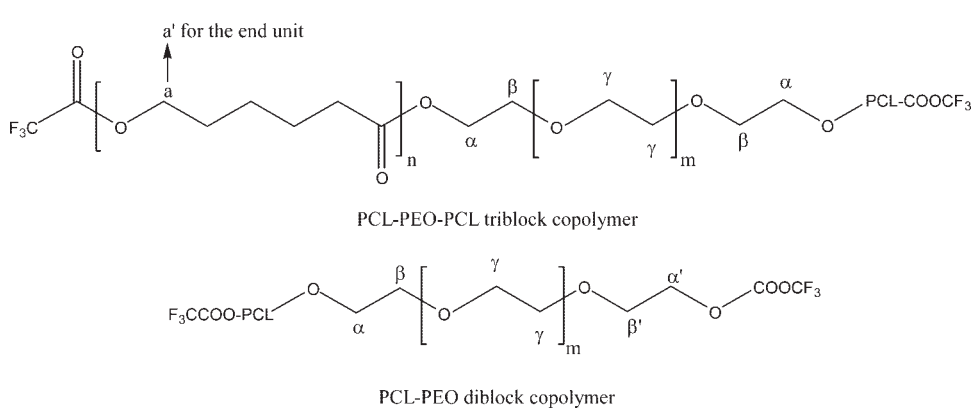
A series of PCL-PEO-PCL copolymers having different block chain lengths was successfully synthesized. The PEO content of the prepared copolymers ranged from 16.5 to 68.6%, indicating systems with different degrees of hydrophilicity. Moreover, copolymers having the same PEO content (close to 30 and 45%) and different PEO molecular weight (900, 2000, and 4000 Da) were also obtained.

The block copolymer structure was characterized by ^{1}H NMR and SEC. The CH_2-OH end-group signal appeared as a triplet at 3.62 ppm totally overlapped with the PEO signals. To determine the PCL chain length and the molecular weight of the copolymer, the triblock was derivatized with trifluoroacetic anhydride. This allowed the separation of the PCL end-group which was shifted downfield to 4.3 ppm. Figure 1 shows a typical NMR spectrum of a PCL-PEO-PCL triblock copolymer. PCL-PEO diblock copolymers were observed to be present in all formulations except for C4000-100 and C4000-200 which only had triblock copolymers. Scheme 2 shows the NMR assignments for di- and triblock copolymers.

The PCL chain length was determined by integrating the signals of the methylene groups of the repeating unit indicated as **a** and the end-group signal indicated as **a**′. They were rationed against the signals of PEO ($\alpha + \alpha' + \beta + \beta' + \gamma + \gamma'$) supposing the nominal weights of 900, 2000, and 4000 for PEO. The relative amount of diblock and triblocks could be quantified by NMR analysis through the ratio of signals $\alpha/(\alpha + \alpha')$. Table I summarizes the results obtained for the synthesized copolymers.

For C900 and C2000 macrodiols, the molecular weight values were close to theoretical values, whereas, for C4000 series, the achieved M_n values were only close to theoretical ones in C4000-50. In the case of C900 series, C2000 series, and C4000-50, the PCL block length was between 5 and 25, and the reaction condition seemed to be enough for completion, whereas, for C4000-100 and C4000-200, because of the longer PEO chain and a more diluted reaction medium, the reaction conditions were not enough to reach completion. Probably longer reaction times would have led to completion.

SEC measurements with polystyrene standards calibration render overestimated values for M_n, as al-



Scheme 2. NMR assignments for di- and triblock copolymers.

TABLE II
Melting Enthalpy (ΔH_m) (DSC), Peak Temperatures (DSC), and Crystalline Species Present at Room Temperature (WAXD) for Triblock Copolymers

Triblock Sample	First Scan		Second Scan		Crystalline Species at T_{amb}
	ΔH_m (J/g)	Peak T (°C)	ΔH_m (J/g)	Peak T (°C)	
C900-10	67.44	25,33, 48	62.17	25, 32, 42	Residual PCL
C900-20	67.14	42, 58	46.67	43, 51	PCL
C900-40	67.29	62	54.23	49, 54	PCL
C2000-10	102.06	51	83.15	43	PEO
C2000-20	87.04	26, 44, 52	82.57	35, 44	PCL + PEO
C2000-40	71.33	18, 41, 59	46.90	18, 32, 50, 54	PCL
C4000-50	106.73	48, 58	92.21	44, 50, 53	PCL + PEO
C4000-100	77.31	44, 58	53.51	32, 49, 53	PCL + PEO
C4000-200	84.75	44, 62	55.28	20, 53, 56	PCL

ready reported for PCL,[20] and therefore are useless for a precise molecular-weight determination.

The triblock copolymers displayed endothermal melting traces, some of them exhibiting several peaks. Table II summarizes the results of DSC measurements. The analysis of these systems became complex because both components, PEO and PCL, are semicrystalline polymers which show melting endotherms in the same temperature range. In some cases those endotherms appeared partially overlapped, making a conclusive morphological analysis based only on DSC information very difficult to reach.

X-ray measurements determined the crystalline species present in the copolymer (Table II). For C900 series, only PCL was able to crystallize at all CL contents (peaks at 21.5 and 23.8° for pure PCL). Crystallinity increased with CL content increase in coincidence with DSC results (X-ray spectra compared with DSC first scan above 20°C). Melting enthalpy increased in the same way. The small PEO crystallinity found in PEO 900 was completely lost in the triblocks. For C4000 series, PCL crystals were always present, and for the triblocks of low CL content, PEO was able to crystallize (peaks at 19.4–19.5° and 23.6–23.7° for pure PEO). In this series, the increase in CL content reduced PEO crystallinity until total suppression. The intermediate series displayed a similar behavior (Fig. 2). In this manner, when 10 CL units were attached to PEO, only PEO crystallized. Increasing CL content up to 20 units, both PEO and PCL crystallized, although PEO did it in a very small amount. When 40 CL units were attached, only PCL crystallized. Therefore, an increase in CL content from 10 to 40 units produces an increase in PCL crystallization and a reduction in PEO crystallization until complete suppression.

Although melting of samples changed the endotherm shape in the second run, the crystallized species were the same. X-ray patterns of a melted and recrystallized sample were identical to those of the same sample before melting.

Polyurethane characterization

During synthesis, increase in solution viscosity showed molecular weight build-up of polyurethanes. As already shown for triblocks, polystyrene standards were not adequate for precise molecular-weight determination of the polymers, but at least the SEC-derived values allowed for comparison.

In Table III, SEC-determined values are shown. It is clear that P900 series have the highest molecular-weight values, whereas P2000 series seems to have the lower chain growth. From our experience, we believe that the M_n values calculated from ^{1}H NMR spectra are overvalued, but, in this case, they are quite far from real values for some triblocks, leading to a deficient evolution of M_n in the corresponding polyurethanes. Repetition of the synthesis of P2000 and P4000 series with M_n supposed 5% above and below the value calculated by ^{1}H NMR did not improve polyurethane molecular weight.

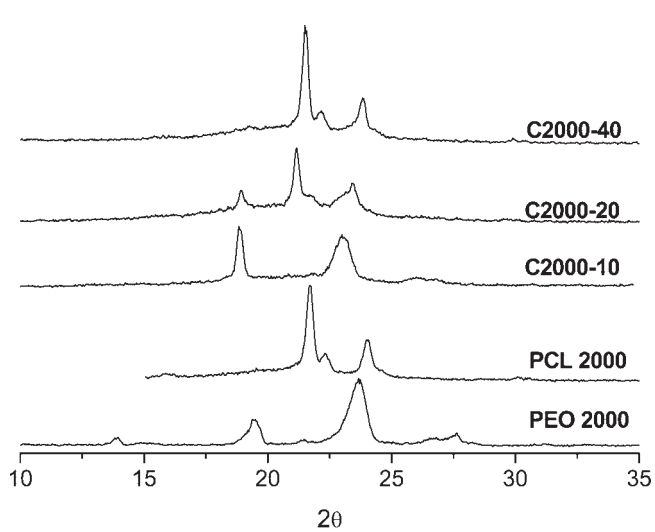


Figure 2. X-ray diffractograms of PEO 2000, PCL 2000, and the triblocks C2000-10, C2000-20, and C2000-40.

TABLE III
Average Molecular Weights (SEC), Melting Enthalpy (ΔH_m) (DSC), Peak Temperatures (DSC), and Crystalline Species Present at Room Temperature (WAXD) for Polyurethanes

Polyurethane Sample	PEO (%)	M_n	M_w	First Scan ΔH_m (J/g)	First Scan Peak T (°C)	Second Scan ΔH_m (J/g)	Second Scan Peak T (°C)	Crystalline Species at T_{amb}
P900-10	40.4	36,000	53,800	34.82	11, 41	34.31	5, 35	PCL
P900-20	26.4	55,800	71,100	44.00	54	36.13	47	PCL
P900-40	15.9	112,900	145,730	57.52	59	43.76	51	PCL
P2000-10	63.5	23,130	32,240	61.60	25, 44	48.89	36	PEO
P2000-20	44.3	31,100	38,400	61.04	24, 38, 49	50.25	24, 37	PCL
P2000-40	28.9	26,560	36,630	64.45	21, 61	52.83	19, 54	PCL
P4000-50	41.7	29,750	36,730	78.72	46, 50, 61	64.01	38, 51	PCL + PEO
P4000-100	33.2	37,900	44,760	76.42	27, 59	62.87	26, 51	PCL
P4000-200	17.7	49,900	70,900	77.99	22, 63	66.99	17, 55	PCL

Also in Table III, DSC and X-ray-determined values are listed. It is clear from X-ray spectra that PEO ability to crystallize is further reduced when triblocks react with LDI; thus, P2000-20 and P4000-100 do not show PEO crystals. For the remainder of polymers, the crystalline species are the same as for triblocks. When comparing triblocks with polyurethanes, X-ray spectra show that CL crystallizes slightly less for polyurethanes, with reduction being higher for shorter CL chains. In any case, the reduction is not very significant, not even for the worst case. One exception to this behavior is P900-10. For this particular case, an increase in CL crystallinity is observed, going from an almost amorphous polymer to a very slightly crystalline one (Fig. 3).

Swelling and *in vitro* hydrolytic stability

Figure 4 shows the results of water uptake measurements. For all the studied formulations, the time to reach equilibrium water uptake was approximately 10 min. After that time the values remained almost constant for the next 10 h. The results clearly show that the equilibrium values decrease with increasing PCL content. In other words, it is expected that materials with high PEO content, highly hydrophilic, display high equilibrium water contents. Thus, P2000-10 and P900-40, which have different hydrophilic characteristics (PEO content 63.5 and 15.9% w/w, respectively), exhibited the higher and lower water uptake values: 377% and 16.6%, respectively. In fact, there is a dependence between ethylene oxide (EO) unit content and water uptake regardless of triblock structure itself. The value of P900-10 turned out to be an exception because of the fact that, when having the 40.4% EO unit content, it should have had a water uptake value above that of P4000-100. This could be related to the abnormal behavior found by DSC, which demonstrated the presence of more crystallized CL than in the corresponding triblock, contrary to the remainder of the polymers. Crystalline CL units will not swell in water, whereas amorphous CL units will in a much

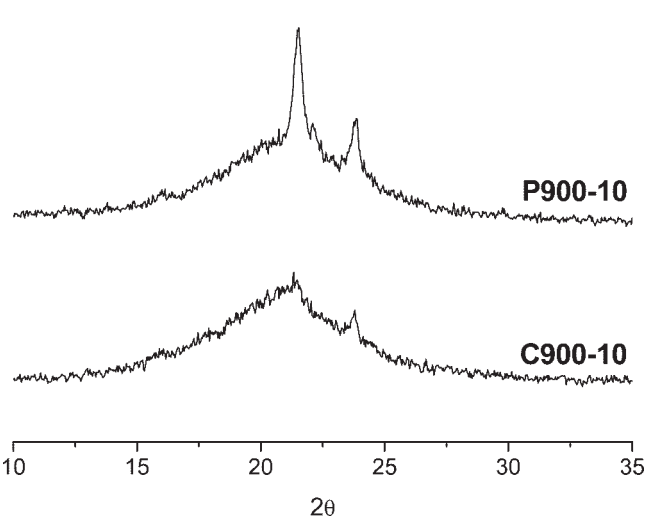


Figure 3. X-ray patterns of C900-10 and P900-10 samples.

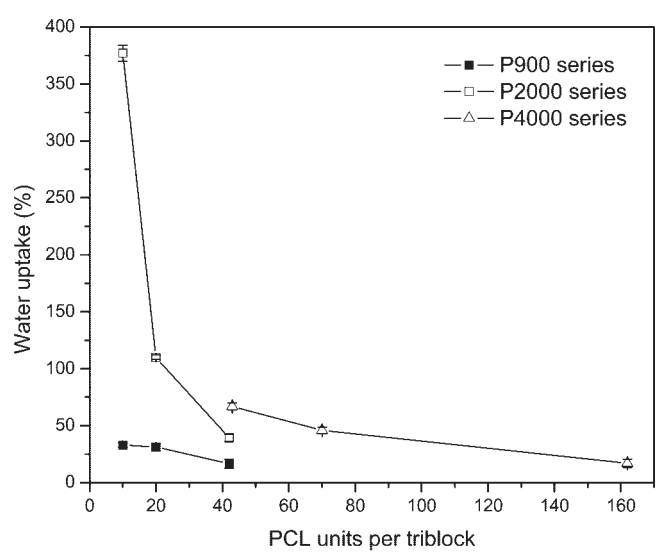


Figure 4. Water uptake percentages as a function of PCL units per triblock copolymer.

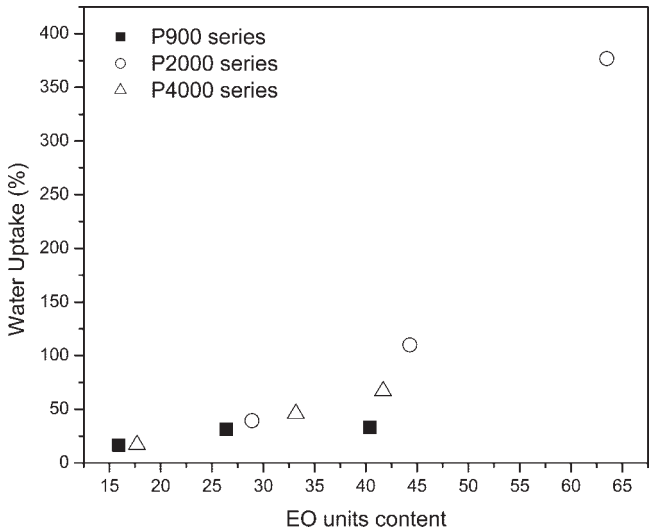


Figure 5. Water uptake percentages as a function of EO unit content present in the triblock copolymer.

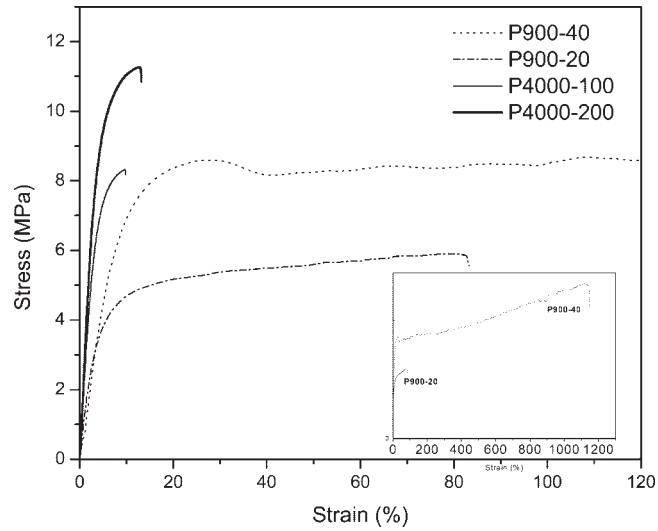


Figure 6. Tensile properties of some polyurethane films.

less extent than EO units, because of its hydrophobic character.

For the same PEO chain length, the major variation was observed in P2000 series. This series is the only one with EO unit content values above 42%. It seems that above this value, water uptake increases much more with the increase in EO unit content (Fig. 5). However, because of the complex crystalline behavior of these block structures, it would be necessary to synthesize more polymers in order to check if this dependence is a rule and P900-10 is really the exception.

The immersion of samples in PBS for determined periods of time allowed the study of the hydrolytic stability. Weight-loss measurements were very difficult to obtain because the hydrophilic nature of PEO segment avoided the complete drying of samples. P2000-10, P2000-40, and P4000-44 were severely affected and appeared disintegrated after 7 days of immersion.

Weight loss could only be monitored during 1 month for P900 series. After that time, P900-10 retained around a 35% of its initial weight, whereas P900-20 and P900-40 degraded more slowly, retaining approximately 88 and 98% of the initial weight, respectively. There is therefore a dependence between hydrophilicity and hydrolytic stability: the higher the EO unit content, the lower the hydrolytic stability.

Mechanical properties

In Table IV, tensile test results are displayed along with SEC molecular-weight values. From the data, it is clear that the mechanical properties are strongly influenced by molecular weight although SEC does not render absolute values. Samples of M_n below 30,000 were too fragile and broke when we tried to take them out of the clamp. A case apart was sample 900-10, too soft and weak to give reliable values.

TABLE IV
Average Molecular Weights (SEC) and Tensile Test Results of Polyurethanes

Polyurethane Sample	M_n	M_w	σ_u (MPa) [±SD]	ε (%) [±SD]	E (GPa) [±SD]
P900-10	36,000	53,800	n.d.	n.d.	n.d.
P900-20	55,800	71,100	5.26 [±0.26]	70 [±5.50]	0.12 [±0.01]
P900-40	112,900	145,730	13.46 [±1.07]	1142 [±84.40]	0.10 [±0.01]
P2000-10	23,130	32,240	n.d.	n.d.	n.d.
P2000-20	31,100	38,400	1.30 [±0.15]	10.3 [±3.6]	0.03 [±0.004]
P2000-40	26,560	36,630	n.d.	n.d.	n.d.
P4000-50	29,750	36,730	n.d.	n.d.	n.d.
P4000-100	37,900	44,760	8.24 [±0.05]	9.3 [±0.01]	0.23 [±0.01]
P4000-200	49,900	70,900	11.20 [±0.2]	13.8 [±2.50]	0.30 [±0.01]

If we look at the tensile curves (Fig. 6), all tested polymers behaved as ductile plastics, showing a yield point. Only two polymers with M_n above 50,000 did not break after reaching the yield point. The strain at break was much higher for the polymer with higher M_n, P900-40. Within a series, the higher the CL content was, the higher the tensile properties turned out to be. If we compare polymers with similar EO unit content (P900-20 versus P4000-100 and P900-40 versus P4000-200), it can be observed that stress at yielding is higher for polymers with longer chain segments.

Obviously, with these results, most of these polymers are ruled out for tissue engineering scaffolds, but they could be useful in some other biomedical applications that do not demand specific mechanical properties.

CONCLUSIONS

A new family of bioreabsorbable poly(ester-ether urethane)s based on PEO, PCL, and LDI with nontoxic byproducts and different hydrophilicity have been prepared and characterized. In starting triblocks, depending on the length of PEO and PCL moieties, PEO segments can crystallize. A PEO with molecular weight above 900 was necessary to achieve PEO crystallization. When PCL content increased, PEO crystallization was reduced until it vanished. In addition, when triblock copolymers reacted with LDI, PEO crystallization was further reduced. PCL crystallization was present in all triblocks and polyurethanes, except for P2000-10. Overall crystallization was reduced from triblock copolymers to polyurethanes, the effect being more important when the triblock molecular weight was lower, except for P900-10.

Water uptake seems to depend on the EO unit content of the polyurethane regardless of the triblock structure, again P900-10 being an exception. A high swelling is observed above 45% EO units.

Mechanical properties of the synthesized polymers were strongly affected by the molecular weight achieved during polymerization. Tested polyurethanes behave as ductile plastics showing yielding strength values. While in a series the yield strength was higher as the amount of CL units in the polymer increased, between series, the yield strength was higher when the segments were longer.

Current works address the introduction of amino acids as chain extenders in order to improve the mechanical properties of polyurethanes to make them suitable for tissue engineering applications.

The authors thank Alicia Martin Rodriguez and Hernan Romeo for their assistance in experimental tasks and Mr. Alberto Fernández for DSC measurements. The donation of LDI from Kyowa Hakko Kogyo Co. Ltd (Japan), the partial support of MAT2001/1634 project, Fundación ANTORCHAS and CONICET (Argentina) are gratefully acknowledged.

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