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Synthesis of poly(l-lactide-*co*-serine) and its graft copolymers with poly(ethylene glycol)

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A new monomer, phenylmethyl [2-(6-methyl-2,5-dioxo-3-morpholinyl)] ethyl ether (monomer **1**), was synthesised and used to prepare copolymers with L-lactide. Different feed ratios of monomer **1** to L-lactide (6 and 20 mol%) were used. The copolymers (PLS2) have ester and amide functional groups in the backbone, as well as pendant free hydroxy functional groups. The presence of free hydroxy groups was further confirmed by reacting with diisocyanate-terminated poly(ethylene glycol) (DIPEG). The copolymers of PLS2 with DIPEG were crosslinked to varying degrees, depending on the amount of free hydroxy groups in PLS2. The addition of poly(ethylene glycol) decreased the T_g or increased the amorphous property of the polylactide drastically. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: functionalized polyactide; serine; polyethylene glycol)

INTRODUCTION

Aliphatic polyesters are one of the most widely utilised classes of biodegradable polymers in medicine. Among these, the lactide/glycolide polymers are among the few degradable polymers used clinically in wound closure[1,2], tissue repair and regeneration[3], and drug delivery[4]. The introduction of functional groups in polylactide for the modification of its properties has been investigated. Veld *et al.* reported the synthesis of a series of biodegradable polyesteramides with pendant functional groups[5]. Barrera *et al.* synthesised a copolymer poly(L-lactic acid-*co*-lysine) containing about 2 mol% of lysine residues[6,7]. Further reaction of pendant lysine with N^{ε}-(carbobenzoxy)-L-lysine *N*-carboxyanhydride provided up to a 35-fold increase in the lysine residue[8]. The free amino group in the lysine residue was used to chemically attach a biologically active peptide GRGDY[6]. There are several other potentially degradable polyesters containing side chains with functional groups that have been synthesised[9–12], but biomedical applications have not been studied.

Our objective is to synthesise biodegradable polymers containing nucleation sites for inorganic phases such as hydroxyapatite (HAP), calcium phosphate and calcium carbonate. Thus copolymers of lactide and the amino acid, serine, were synthesised. These copolymers have free hydroxy groups pendant to the ester backbone. Some natural polymers, including cellulose and chitosan, with functional groups such as hydroxy groups have been modified using phosphoric acid to make polymer–HAP composites[13]. The use of serine is also important because of the role of phosphoserine in phosphoryn, which is a calcium ion binding protein in biological systems[14].

EXPERIMENTAL

Materials

O-Benzyl-L-serine was purchased from Advanced Chemtech. D-Alanine, palladium chloride and triethylsilane were obtained from Acros. L-Lactide was provided by Golden-Tech. Co., USA. Stannous octoate ($SnOct_2$) was obtained from Sigma. The above chemicals were used without further purification. Hexamethylene diisocyanate (Acros) was redistilled under reduced pressure. Poly(ethylene glycol) (average molecular weight = 200, Polysciences Inc.) was dried under vacuum. Methylene chloride and 1,2-dichloro ethane were redistilled at atmospheric pressure. Triethyl amine and *N*-diisopropyl ethyl amine were dried in CaH_2 under reflux and redistilled. All other chemicals were purchased from Acros and used as received.

Characterisation

The ^1H and ^{13}C n.m.r. spectra were obtained on a Bruker AF-400 spectrometer. *FT*i.r. spectra were obtained on a Nicolet 60SX spectrometer. The molecular weights and molecular weight distributions of the polymers were determined using gel permeation chromatography (g.p.c.). The g.p.c. analysis was conducted in THF with a Waters 150-C ALC/GPC equipped with μ-Styragel HT columns of 10^5, 10^5, 10^3 and 10^3 Å pore size at 35°C and a flow rate of 1 ml/min. Narrow molecular weight polystyrene standards were used for calibration. Differential scanning calorimetery (d.s.c.) of the polymers was performed using a TA Instrument, DSC 2920, in N_2 at a heating rate of 10°C/min. T_g and T_m values of the polymers were obtained from the second run of d.s.c. thermograms. Elemental analysis was performed by Onedia Research Services Inc., NY. Fab-Mass analysis was performed in a high resolution, double focusing, magnetic sector, Kratos MS50RSA mass spectrometer.

Synthesis of monomer **1**: phenylmethyl 2-(6-methyl-2,5-dioxo-3-morpholinyl) ethyl ether. The synthesis method of the monomer **1** is similar to that of Barrera *et al.*[7], except that the amino acid used was the protected serine, *O*-benzyl-L-serine not the protected lysine, N^{ε}-(carbonyl-benzoxy)-L-lysine. Also, in the last step of the preparation of the monomer, CH_2ClCH_2Cl was used as the solvent instead of CH_3Cl.

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^{1}H n.m.r. ($CDCl_3$, ppm): 1.55, 1.58 (d, J = 7.0 Hz, 3H, CH_3), 3.80, 3.90 (t, 2H, J = 3.5 Hz, $C\underline{H}_2OCH_2Ph$), 4.30, 4.36 (t, J = 3.5, 1H, $NHC\underline{H}CH_2$), 4.55 (m, 2H, $OC\underline{H}_2Ph$), 4.85, 5.03 (q, J = 7.0 Hz, 1H, $OC\underline{H}CH_3$), 7.05, 7.20 (1H, NH), 7.30 (m, 5H, aromatic protons).

^{13}C n.m.r. ($CDCl_3$, ppm): 17.10, 17.36 (CH_3), 53.60, 55.08 (CHNH), 68.98, 71.41 ($\underline{C}H_2OCH_2Ph$), 73.68, 74.88 ($\underline{C}HCH_3$), 127.68–128.56 (aromatic carbons), 136.66 ($OCH_2\underline{P}h$), 165.73, 166.32, 168.25, 169.31 (carbonyl carbons).

I.r. (KBr, cm^{-1}): 3380 (amide NH), 1751 (C=O, ester), 1658 (amide I), 1545 (amide II)

Elemental analysis calculated for $C_{13}H_{15}O_4N$: C, 62.65; H, 6.02; N, 5.62. Found: C, 62.50; H, 5.94; N, 5.59.

Fab-MS of $C_{13}H_{15}O_4N$: found (M + 1), 250; calculated (M), 249.

Synthesis of polymers

Poly(L-lactide) (PLac) and protected poly(L-lactide-co-serine) (PLS1). A pressure tube was dried at 300°C overnight and then transferred into a nitrogen-filled glove box. All the chemicals were added in the glove box. For the synthesis of poly(L-lactide), 10 mmol (1.44 g) of L-lactide (monomer **2**) was placed in the pressure tube. For the synthesis of protected poly(L-lactide-*co*-serine), 6 and 20% molar ratios of monomer **1** to monomer **2** were used. Thus, 0.6 mmol (0.15 g) (6%) or 2 mmol (0.50 g) (20%) of monomer **1** and 10 mmol (1.44 g) of monomer **2** were added into a pressure tube and mixed, then 0.8 or 1.0 μl (0.06 wt.%) of stannous octoate initiator was added. After being taken out from the glove box, the pressure tube was heated at 110°C in an oil bath for 24 h. Next, 20 ml of methylene chloride was added to dissolve the polymer and then poured into a beaker. After evaporating half the volume of the CH_2Cl_2, 100 ml of methanol was added to the solution to precipitate the polymer. The white precipitate was filtered and dried in a vacuum oven overnight, giving 1.28 g PLac (89%), 1.30 g (82%) of PLS1(a) and 1.51 g (78%) of PLS1(b), respectively.

^{1}H n.m.r. (PLac, $CDCl_3$, ppm): 1.54 (d, J = 7.1 Hz, 3H, CH_3), 5.14 (q, J = 7.1 Hz, 1H, CH).

^{13}C n.m.r. (PLac, $CDCl_3$, ppm): 16.83 (CH_3), 69.20 (CH), 169.80 (C=O).

^{1}H n.m.r. (PLS1, CD_2Cl_2, ppm): 1.54 (d, J = 7.1 Hz, 3H, CH_3), 5.14 (q, J = 7.1 Hz, 1H, CH), 7.31 (m, aromatic carbons). Other small peaks are from monomer **1**.

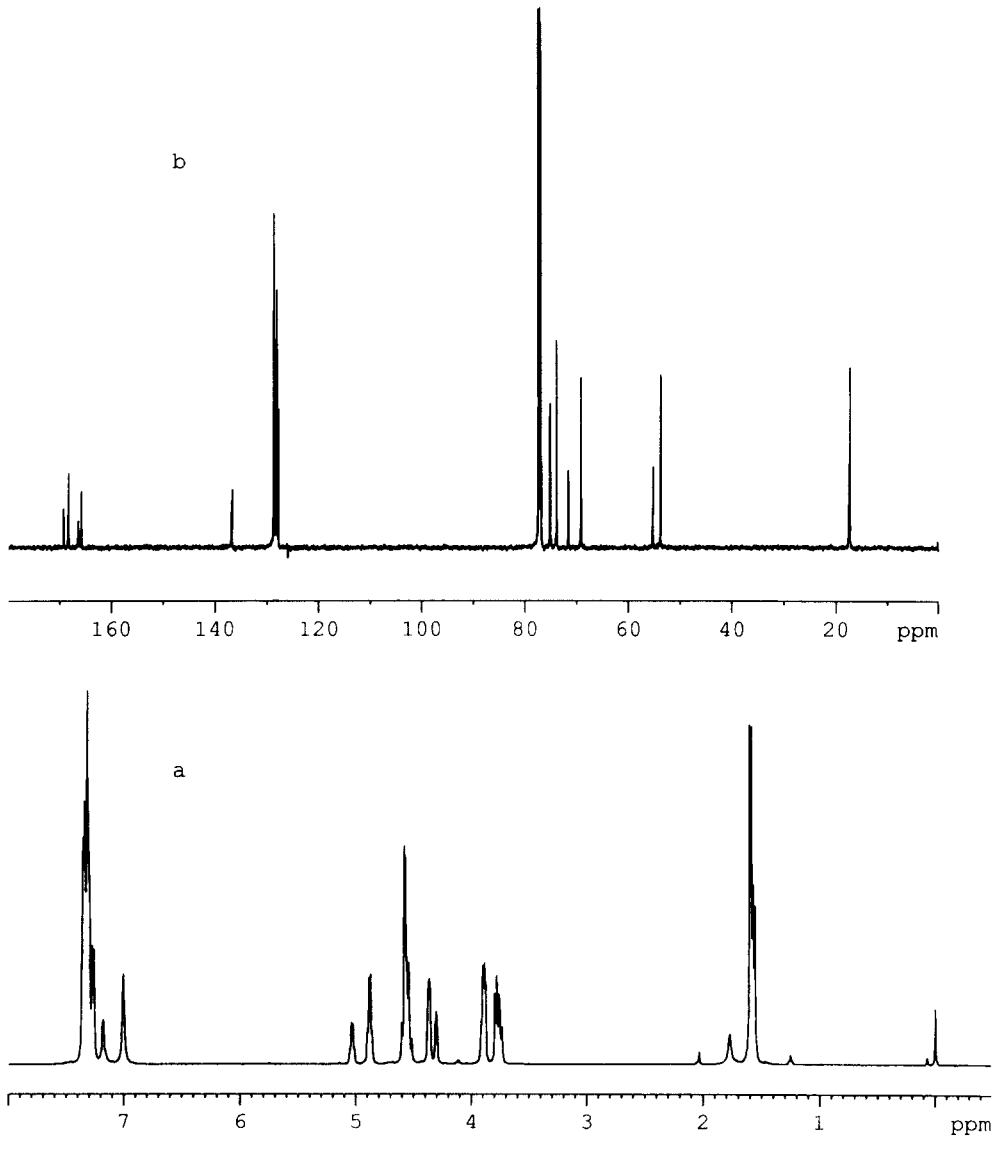


Figure 1 N.m.r. spectra of monomer **1** ($CDCl_3$): (a) ^{1}H n.m.r. and (b) ^{13}C n.m.r.

^{13}C n.m.r. (PLS1, $CDCl_3$, ppm): 16.83 (CH_3, monomer **2**), 17.86 (CH_3, monomer **1**), 52.26, 52.37 (CHNH), 69.20, 69.51 (CH, monomer **2**,) 71.46, 71.52 ($\underline{C}H_2OCH_2Ph$), 73.50, 73.57 ($\underline{C}HCH_3$, monomer **1**), 127.90–128.57 (aromatic carbons), 136.66 ($OCH_2\underline{Ph}$), 168.85, 169.45. 169.91 (carbonyl carbons, monomer **1**) 169.80 (C=O, monomer **2**).

I.r. (cast film, cm^{-1}): 1760 (C=O, ester).

Deprotected poly(L-lactide-co-serine) (PLS2). In the glove box, 1 g of polymer was added into a pressure tube. Twenty ml of methylene chloride were added to dissolve the polymer. Then 5 ml of triethyl silane was added, followed by 0.1 ml of triethyl amine and 0.15 g of $PdCl_2$. The pressure tube was removed from the glove box and maintained at room temperature for 72 h. After the reaction was completed, $PdCl_2$ was removed by filtration and 5 ml of methanol was added to react with the extra triethyl silane. After removing the solvent, more methanol was added to precipitate the polymer, followed by drying in a vacuum oven; 0.9 g (90%) of the deprotected polymer was obtained. The ^1H n.m.r. spectra showed a smaller peak at 7.31 ppm (aromatic protons of protecting group). The i.r. spectra were similar to that of the protected copolymers.

Diisocyanate-terminated poly(ethylene glycol) (DIPEG). Poly(ethylene glycol) (PEG) 0.01 mol (2.00 g) and 0.02 mol (3.36 g) of hexamethylene diisocyanate (HDI) were charged into a flask under N_2, then a catalytic amount of Et_3N (0.1 ml) was added to the flask. The reaction was stirred for 24 h, and then subsequently under vacuum, Et_3N and probably some unreacted HDI were removed. The product was slurry like and used without any further purification.

^1H n.m.r. ($CDCl_3$, ppm): 1.31–1.64 (m, 16H, $(CH_2)_4$ in HDI), 3.14 (m, 4H, CH_2NCO), 3.30 (q, 4H, $C\underline{H}_2NHCOO$), 3.64–3.67 (b, about 20H, $(OCH_2\underline{CH}_2)_5$), 4.19 (b, 4H, $C\underline{H}_2OCONH$), 4.95 (b, 2H, NH)

I.r. (neat, cm^{-1}): 2281 (–N=C=O stretching), 1720 (–NHCOO–), 1128 (C–O stretching).

Poly(L-lactide-*co*-serine)-*co*-poly(ethylene glycol) (PLSPEG). Under the protection of N_2, 0.2 g of PLS2

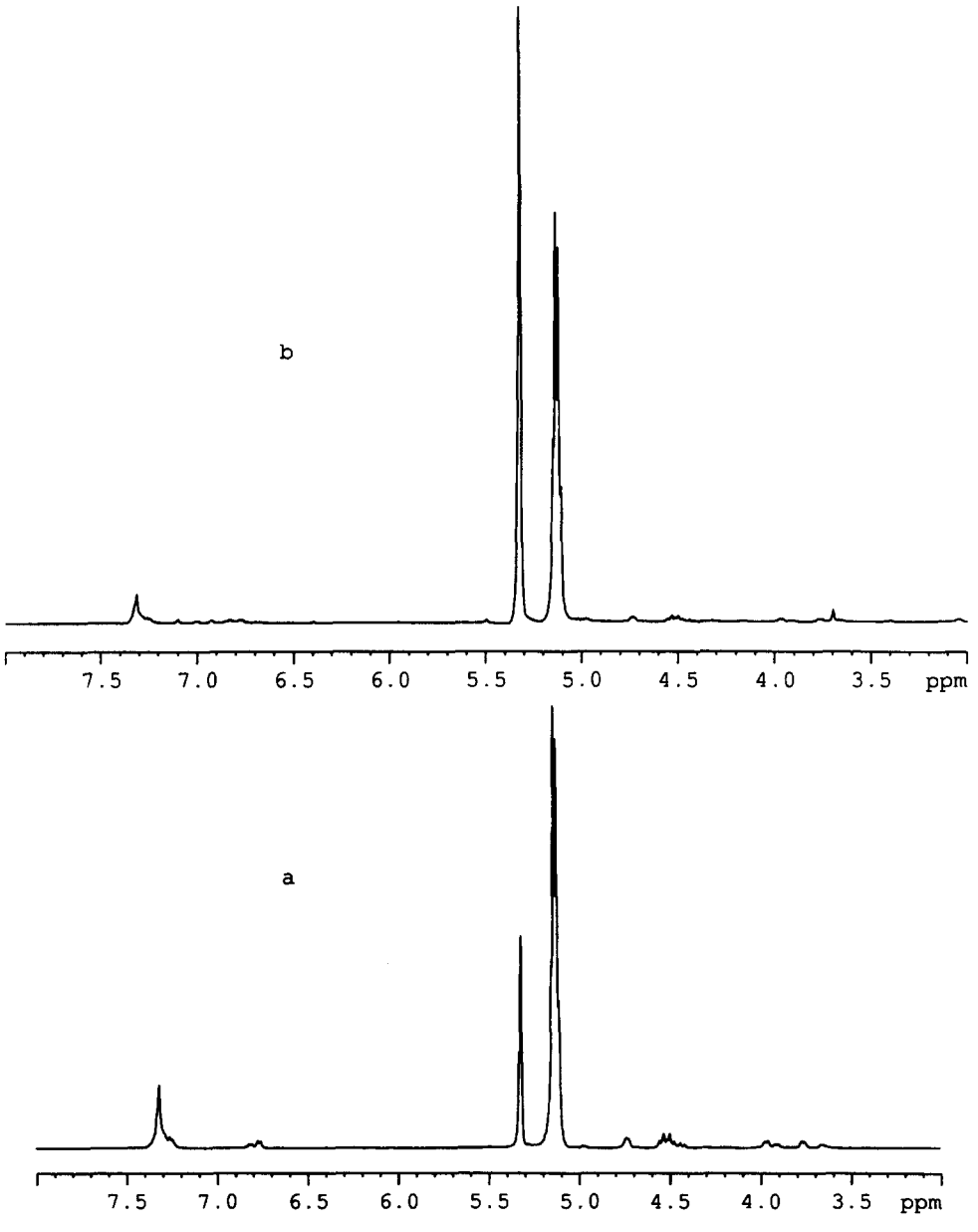
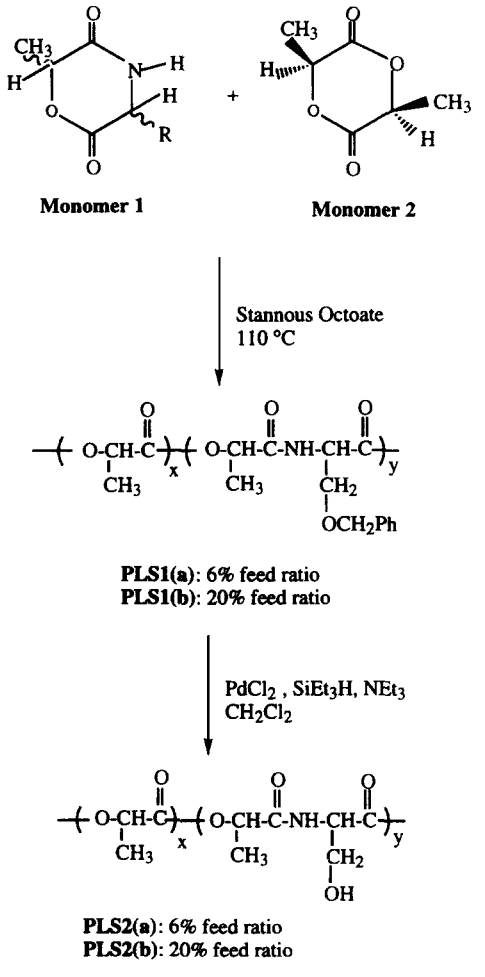


Figure 2 ^1H n.m.r. spectra of the copolymer PLS (CD_2Cl_2): (a) PLS1(a) and (b) PLS2(a)

was added into a 25-ml flask, and 2 ml of CH_2Cl_2 was added to dissolve the polymer. Then an excess (0.05 g) of DIPEG was added to the mixture, followed by the addition of a catalytic amount (0.02 ml) of Et_3N. The mixture was stirred for 24 h, and then the reaction was quenched by the addition of methanol. For PLS2(a), the polymer PLSPEG(a) was soluble in CH_2Cl_2. Methanol was added to precipitate the polymer. The polymer was washed several times with methanol and then dried under vacuum, giving 0.18 g of the product. For PLS2(b), the polymer PLSPEG(b) was not soluble in CH_2Cl_2 and any other common solvents, indicating the formation of a crosslinked polymer. The polymer PLSPEG(b) was filtered, washed with more CH_2Cl_2 and dried, giving 0.17 g of the product. This polymer was fibrous and tough.

^{1}H n.m.r. (PLSPEG(a), $CDCl_3$, ppm): 1.3–1.6 (b, $(CH_2)_4$ in DIPEG) 1.58 (d, $J = 7.1$ Hz, 3H, CH_3), 3.10–3.2 (b, 4H, $C\underline{H}_2NHCOO$), 3.60–3.64 (b, $OCH_2C\underline{H}_2$), 4.1–4.2 (b, $C\underline{H}_2OCONH$), 4.99 (b, 2H, NH), 5.15 (q, $J = 7.1$ Hz, 1H, CH).



Scheme 1

Table 1 Molar percentage of serine residues in the copolymers

	Copolymer			
	PLS1(a)	PLS1(b)	PLS2(a)	PLS2(b)
Benzyl (mol%)	2.9	8.5	1.1	2.4

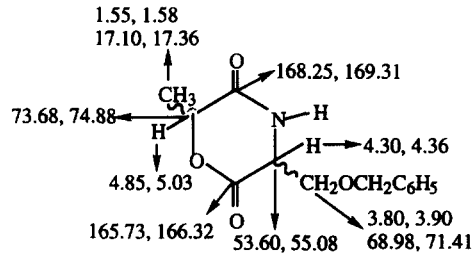
I.r. (PLSPEG(a), (cast film, cm^{-1}): 1760 (C=O ester). 1751 (urethane).

I.r. (PLSPEG(b), (microscope, cm^{-1}): 1757 (C=O ester), 1711, 1691, 1631 (urethane).

RESULTS AND DISCUSSION

Synthesis of monomer

Monomer **1** was synthesised as reported by Barrera *et al.*[7]. All the analyses of monomer **1**, including ^{1}H and ^{13}C n.m.r., i.r. and Fab-MS spectra, and elemental analyses proved the structure of monomer **1**. Monomer **1** has two chiral carbons next to the two carbonyl groups. The formation of the ring structure was not stereospecific, and the resulting isomers were discernible from the ^{1}H and ^{13}C n.m.r. spectra (*Figure 1*). All the protons and carbons have two different stereo structures, showing two close peaks in the ^{1}H and ^{13}C n.m.r. spectra for each set of protons, as shown in the following structure, except the CH_2 next to the benzene ring and the aromatic protons and carbons.

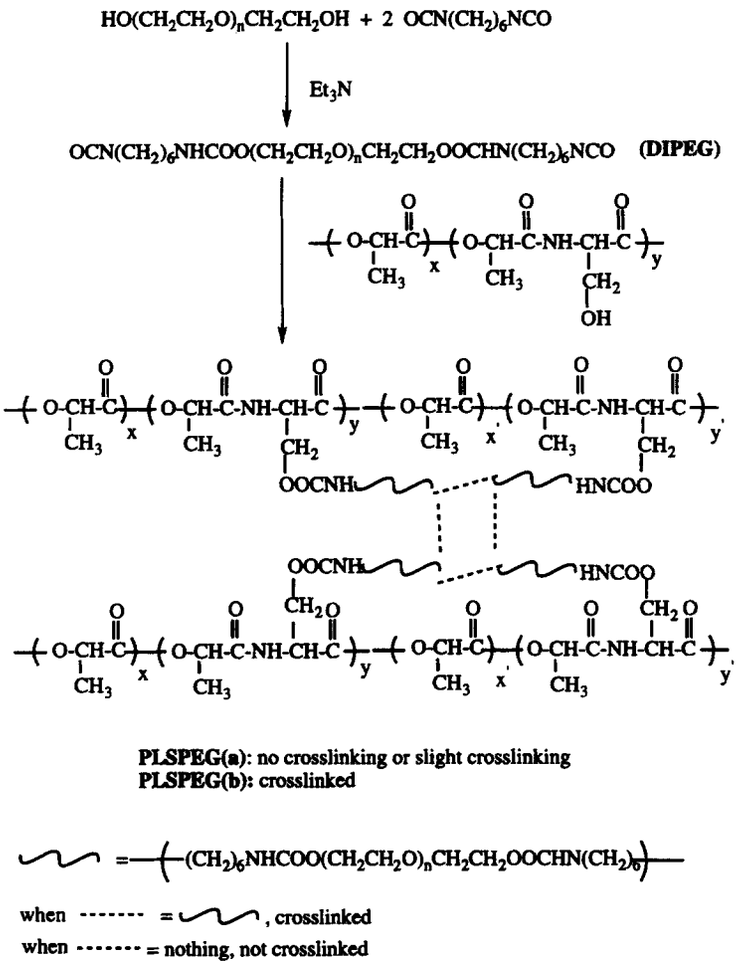


Monomer 1

Synthesis of polymers

The synthesis of the polymers are shown in *Scheme 1* and *Scheme 2*. The feed ratios of monomer **1** to monomer **2**, L-lactide, were 6 and 20%, respectively. The formation of the copolymers was confirmed by their ^{1}H n.m.r. spectra. The copolymer PLS1(a) (*Figure 2a*) showed the aromatic protons (7.31 ppm) from monomer **1**. Other peaks from monomer **1** (1.5, 1.7, CH_3; 3.6, 3.8, $C\underline{H}_2OCH_2Ph$; 3.9, 4.1, $NHC\underline{H}CH_2$; 4.5, $OC\underline{H}_2Ph$; 4.8, $OC\underline{H}CH_3$) were also evident in *Figure 2a*. The removal of the protecting phenylether group from PLS1 was attempted several times using some common methods reported[15], but the deprotection was not complete. The use of $PdCl_2/SiEt_3H$ enabled the deprotection to proceed smoothly. The removal of phenylether can also be observed from the ^{1}H n.m.r. spectrum (*Figure 2b*). The aromatic peak around 7.31 ppm was smaller than that of the protected one.

The sequence distribution of the copolymer PLS1 can be assessed from the ^{13}C n.m.r. spectrum (*Figure 3*). All the absorptions from monomer **1** and monomer **2** were observed in the ^{13}C n.m.r. spectrum of PLS1(b) (peak assignments are provided in the Section Section 2). Furthermore, the C signal of $OC^*H(CH_3)CO$ in monomer L-lactide (69.20 ppm) showed a shoulder in the ^{13}C n.m.r. spectrum (enlarged in *Figure 3*), while that of the homopolymer PLac did not. This corresponds to the two possible distributions of monomer **2** unit in the copolymer (*Scheme 3*). Assuming that monomer **2** unit is A, and monomer **1** unit is B, C* in $OC^*H(CH_3)CO$ in the two distributions: A–A–A and B–A–B has different chemical environments, which results in different chemical shifts. The presence of a shoulder (from B–A–B) in the absorption at 69.20 ppm (from A–A–A)

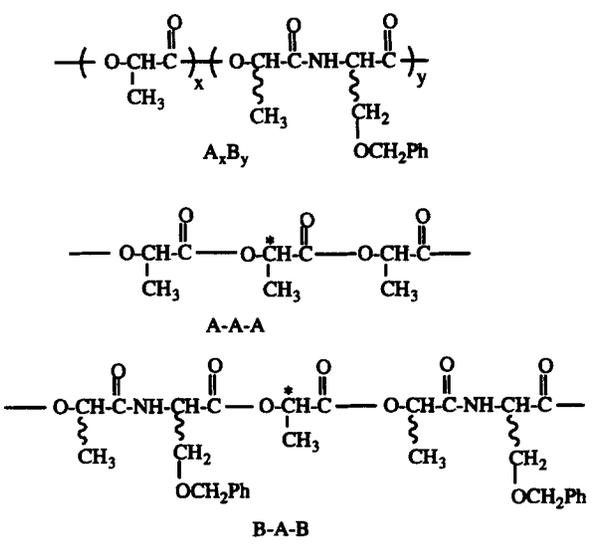


Scheme 2

indicated that these two distributions exist, i.e. they contribute to the randomness of the copolymer. Unit B has two chiral centers originating from monomer **1**. The carbon absorptions in B were complicated by the racemisation, thus were not used to determine the comonomer distribution. All other C signals were not effected by the comonomer distributions.

The molar percentage of free hydroxy groups in the copolymer was calculated from the ^{1}H n.m.r. spectra of the protected and deprotected copolymers. By the difference of the integrals of aromatic protons in the protected and deprotected polymer, along with the CH proton in the lactide, the molar percentage of the free hydroxy groups in the copolymer was calculated (*Table 1*). The theoretical percentage of serine in the copolymer is 3 and 10% for 6 and 20% feed ratio, respectively, considering that monomer **1** is composed of one lactide and one serine residue. The calculated molar percentage of free hydroxy groups are about 2 and 6%, respectively. The presence of free hydroxy groups can also be confirmed by reacting with diisocyanate. The use of diisocyanate-terminated poly(ethylene glycol) was also aimed at modifying the crystallinity of the lactide polymer. Increasing the amorphous property is very important for poly(L-lactide) applications[16–19].

The copolymer, PLSPEG(a) formed from DIPEG and PLS2(a), was soluble, as were its precursors, and could be cast into films. The polymer was softer than its PLS2(a) precursor, due to the incorporation of flexible PEO segments. The addition of DIPEG to PLS was indicated by i.r. and ^{1}H n.m.r. spectra. In the i.r. spectrum (*Figure 4d*), there is a new peak at 1752 cm^{-1}, indicating the formation of a new urethane functional group. Also in *Figure 5*, those peaks from ^{1}H n.m.r. spectrum of DIPEG (*Figure 5a*, 1.31–1.64, $(CH_2)4$ in HDI; 3.14, CH_2NCO; 3.30, $C\underline{H}_2NHCOO$; 3.64–3.67, $(OCH_2CH_2)_5$; 4.19 $C\underline{H}_2OCONH$) are shown in



Scheme 3

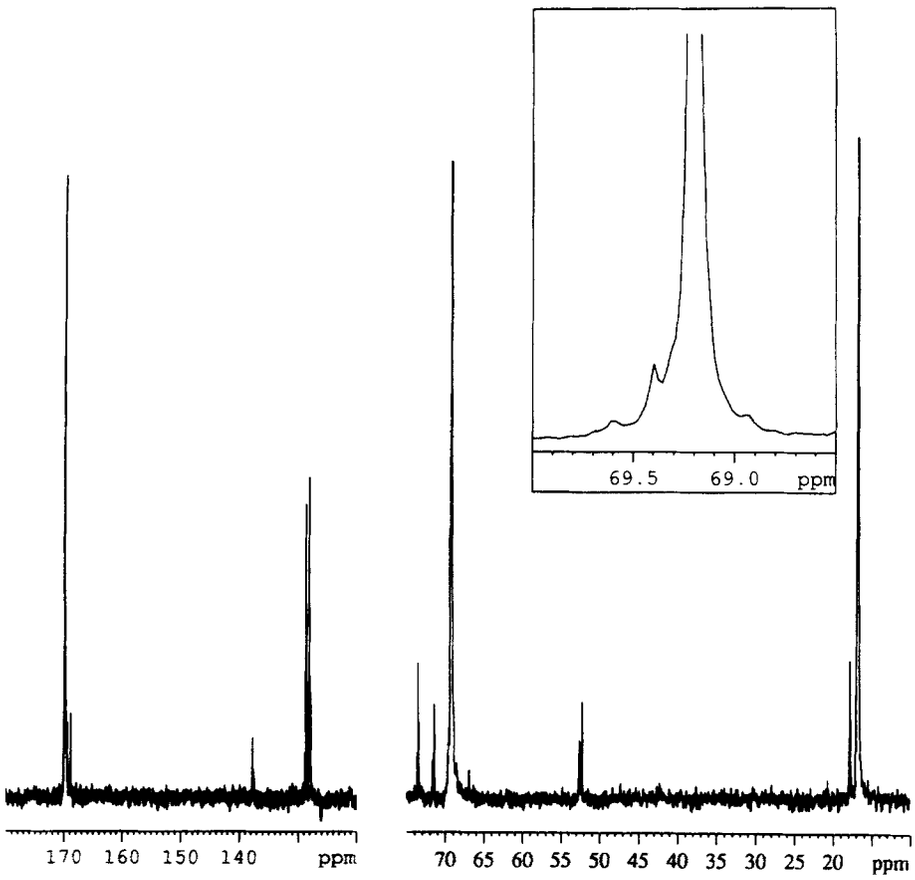


Figure 3 ^{13}C n.m.r. spectrum of copolymer PLS1(b) ($CDCl_3$)

Table 2 Molecular weight and thermal analysis of polymers

Polymer	M_w	M_n	T_g (°C)	T_m (°C)
PLac	102000	93000	64	179
PLS1(a)	85000	47000	59	165
PLS1(b)	42000	24000	60	167
PLS2(a)	88000	49000	63	168
PLS2(b)	45000	31000	60	157
PLSPEG(a)	92000	62000	5	166
PLSPEG(b)	—	—	4	—

the ^1H n.m.r. spectrum of the copolymer PLSPEG(a) (*Figure 5b*, 1.31–1.64, $(CH_2)_4$ in HDI, overlapping with 1.58, CH_3, lactide; 3.05, CH_2NHCOO; 3.64–3.67, $(OCH_2CH_2)_5$; 4.19 $C\underline{H}_2OCONH$)). There is no strong crosslinking, since the copolymer is still soluble in $CHCl_3$ and THF. This is probably due to the small percentage of OH groups, and these OH functional groups are randomly distributed. The molar percentage of OCH_2CH_2 units incorporated in the copolymer PLSPEG(a) was about 4%. This was obtained from the n.m.r. spectrum (*Figure 5b*) by comparing the integrals of CH proton (5.16 ppm) with OCH_2CH_2 protons (3.65 ppm). The copolymer PLSPEG(b) was not soluble in $CHCl_3$, indicating the formation of a crosslinked polymer. The n.m.r. spectrum was not obtained because of the insolubility of the polymer in most common solvents. The i.r. spectrum showed several urethane peaks as a result of the addition of DIPEG.

The molecular weights of all soluble polymers (PLac, PLS1, PLS2 and PLSPEG(a)) are listed in *Table 2*. Thermal analysis data (T_g and T_m) of each polymer are also shown in *Table 2*. The molecular weight of PLS1 is lower than that of

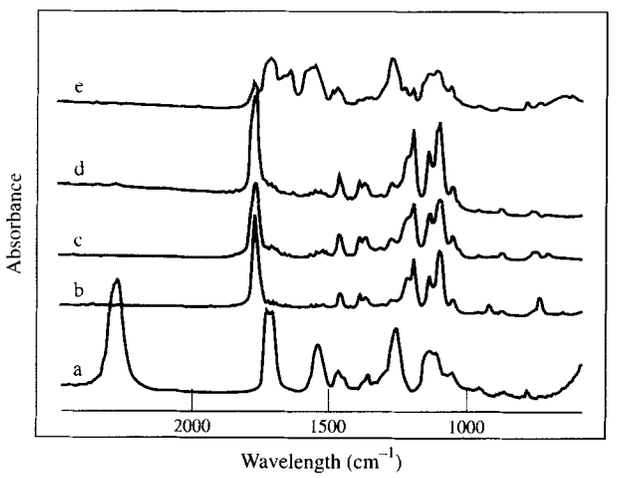


Figure 4 I.r. spectra of polymers: (a) DIPEG, (b) PLS1(a), (c) PLS1(b), (d) PLSPEG(a) and (e) PLSPEG(b)

PLac, and also the molecular weight of PLS1(b) is lower than that of PLS1(a), showing the tendency of decreasing molecular weights with the addition and increasing content of the serine monomer. The molecular weight of PSL1(a) and PLS2(a) are almost the same, indicating that no degradation occurred during the deprotection step. The molecular weight of PLSPEG(a) is larger than that of PLS2(a). This also confirms the addition of DIPEG to PLS. The measured molecular weight of the deprotected polymer, PLS2(b), was slightly larger than that of the undeprotected one, PLS1(b). This could be explained by the presence of

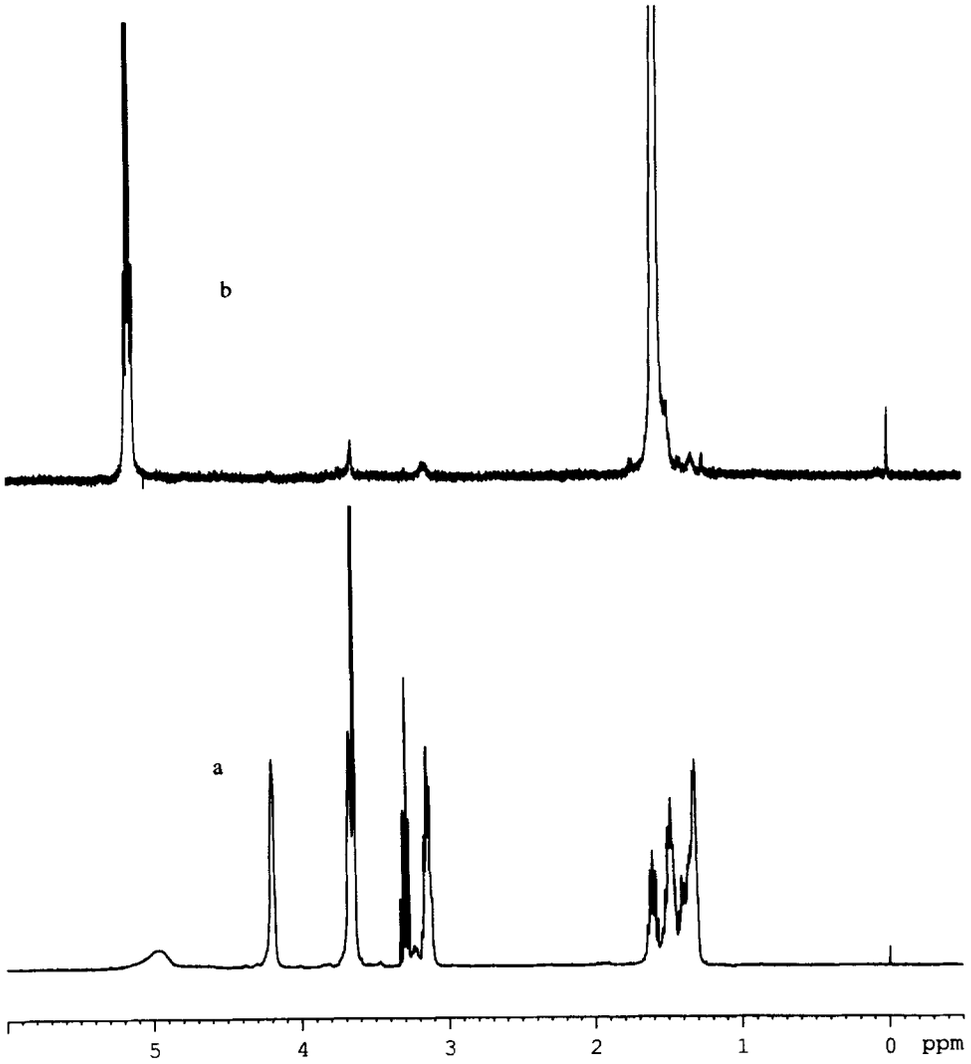


Figure 5 ^{1}H n.m.r. spectra of copolymers ($CDCl_3$): (a) DIPEG and (b) PLSPEG(a)

free hydroxy groups in the deprotected polymer. There are about 6 mol% of hydroxy groups in PLS2(b) which has an ester backbone. The possible hydrogen bonding between hydroxy and carbonyl groups could lead to an aggregation of the polymer chains, which in turn will lead to a larger hydrodynamic volume, and thus the molecular weight. For the polymer PLS2(a), since the mol% of hydroxy groups is about 2%, the interaction is smaller and aggregation should not occur to any appreciable extent. Due to the insolubility of PLSPEG(b), the molecular weight of this polymer was not measured.

The addition of the serine monomer into the lactide backbone lowers both the T_g and T_m values of the copolymers compared to that of the poly(L-lactide) homopolymer, which has a T_g of 64°C and a T_m of 179°C. The addition of a flexible chain, poly(ethylene glycol), decreases T_g drastically down to 5°C. All the d.s.c. profiles of the copolymers showed only one T_g and T_m, respectively, for each copolymer, indicating that the addition of the serine monomer into the lactide backbone was random.

CONCLUSION

A cyclic monomer from D-alanine and L-serine was successfully synthesised and used to make copolymers with L-lactide. The copolymers are expected to be biodegradable and have free hydroxy groups. The latter provide reaction sites to modify the polylactide. Flexible diisocyanate-terminated polyethylene glycol was added into the polylactide copolymer, and it increased the amorphous property of the polylactide. The free hydroxy groups, pendant to the polymer backbone, will be used to make polymeric–inorganic composites.

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