

# Methacrylate-endcapped poly(D,L-lactide-co-trimethylene carbonate) oligomers. Network formation by thermal free-radical curing

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A series of 3-arm, methacrylate-endcapped poly(D,L-lactide-co-trimethylene carbonate) prepolymers was synthesized using D,L-lactide:trimethylene carbonate (DLL:TMC) molar feed ratios of 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100. Number average molecular weights were in the range  $(2.3-2.6) \times 10^3 \text{ g mol}^{-1}$ . The prepolymers were free-radically crosslinked in the absence of reactive diluents to give amorphous, bioabsorbable networks with a broad range of thermal, mechanical, and degradative properties. Extraction studies indicated that sol-contents ranged from 2.89%–6.17%. Tensile modulus, ultimate strength, and  $T_g$  increased with increasing D,L-lactide content. Networks containing higher contents of D,L-lactide, 100:0, 80:20, and 60:40 (DLL:TMC), were strong and fairly rigid, but failed catastrophically at the yield point; networks containing lower contents of D,L-lactide, 20:80 and 0:100, showed a higher elongation to break, failing catastrophically at the yield point. A 40:60 DLL:TMC network fit perfectly within the series of compositions with regard to modulus and tensile strength; however, it showed a yield point, followed by a regime of plastic flow prior to break. Hydrolytic degradation experiments revealed that the network based on poly(D,L-lactide) homopolymer degraded fastest owing to its hydrophilicity. Hydrolytic degradation in the copolymer networks was controlled by two opposing effects which occurred as the trimethylene carbonate was increased:  $T_g$  depression, which increased water uptake, and increased hydrophobicity, which decreased water uptake. Increasing trimethylene carbonate in the 80:20 and 60:40 DLL:TMC copolymer networks caused a decrease in the water uptake and the degradation rate since these networks are both glassy at the degradation temperature of 37°C. The observed increase in degradation rate in the 40:60 copolymer network was due to increased water uptake caused by depression of the  $T_g$  to a value below the test temperature of 37°C. The 20:80 and 0:100 DLL:TMC networks were the slowest to degrade owing to their hydrophobicity. © 1997 Elsevier Science Ltd.

(Keywords: network formation; free-radical curing)

## INTRODUCTION

The recent development of totally biodegradable composites for medical and dental applications has stimulated research to develop matrix resins for these composite systems<sup>1,2</sup>. The semi-crystalline, thermoplastic fibres, poly(glycolide), poly(lactide), and poly( $\epsilon$ -caprolactone) are successfully used for sutures and surgical meshes since they degrade into naturally occurring metabolites; however, the semi-crystalline morphology of these materials leads to heterogeneous degradation rates whereby the amorphous regions degrade faster than the crystalline regions<sup>3-5</sup>. The result is a non-linear loss of strength with respect to mass loss and a material which remains in the body devoid of any useful physical properties<sup>6-8</sup>. Consequently, there has been recent interest in amorphous, degradable polymers, particularly for applications which require a monolithic rather than fibre-like geometry<sup>9-11</sup>. Particularly interesting are biodegradable composite systems

composed of an amorphous biodegradable matrix that is produced by crosslinking a liquid prepolymer, in conjunction with semi-crystalline fibres for added strength. Compositionally, aliphatic polyesters are suitable for both components of such a composite, and the use of liquid prepolymers greatly facilitates composite fabrication.

Recent studies involving low molecular weight fumarate-based polyesters show how these materials can be used as matrix resins in biodegradable composites; however, the low reactivity of 1,2-disubstituted olefinic groups requires the presence of reactive diluents during free-radical curing reactions, to increase the degree of crosslinking<sup>9-11</sup>. Storey et al. have shown that low molecular weight, methacrylate-terminated D,L-lactide based polyesters, cured in the absence of reactive diluents, give networks with glass transition temperatures, ultimate strengths, and tensile moduli higher than those cured with reactive diluents; however, the networks are brittle<sup>12</sup>.

Maxon<sup>®</sup>, a bioabsorbable suture material, is formed by the copolymerization of glycolide with approximately 32.5 mol% of the softer trimethylene carbonate<sup>13</sup>. Addition of trimethylene carbonate decreases the brittleness of pure

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**Table 1** Polymerization recipes for poly(D,L-lactide-co-trimethylene carbonate) triols

DLL:TMC	DLL (mol)	TMC (mol)	TMP (mol)	Sn(oct) <sub>2</sub> (g)
100:0	0.324	—	0.0250	0.202
80:20	0.275	0.0688	0.0250	0.202
60:40	0.353	0.236	0.0402	0.325
40:60	0.157	0.236	0.0250	0.202
20:80	0.0844	0.338	0.0250	0.202
0:100	—	0.457	0.0250	0.202

poly(glycolide); hence, it would be expected to yield the same effect with D,L-lactide and could be used to alleviate the brittleness in the aforementioned D,L-lactide-based networks. Also, *in vitro* and *in vivo* hydrolytic degradation studies have shown that Maxon<sup>®</sup> retains its strength longer, degrades less rapidly, and induces less tissue reaction than multifilament sutures that were previously available<sup>14</sup>. This type of degradation behaviour would most likely apply to the D,L-lactide/trimethylene carbonate copolymer system.

The objectives of this research were to synthesize reactive, low molecular weight copolymers, with various compositions of D,L-lactide and trimethylene carbonate monomers, and subsequently react these prepolymers to obtain crosslinked networks with potential applicability as bioabsorbable composite matrices. Addition of trimethylene carbonate into the backbone was expected to increase chain mobility, thus eliminating brittleness and matrix failure. It was also expected to decrease the rate of degradation, since it is a more hydrophobic monomer.

## EXPERIMENTAL DETAILS

### Materials

All reagents were used from the supplier without further purification unless specified otherwise. 2-Butanone peroxide (30 wt.% solution in dimethyl phthalate), calcium hydride (95%, ground into a fine powder), chloroform-*d* (99.8 at.%, containing 0.03% v/v TMS), 1,2-dichloroethane (DCE, anhydrous, 99 + %, distilled from calcium hydride), diethyl carbonate (99%), D,L-lactide (DLL), magnesium sulfate (anhydrous, 99%), methacryloyl chloride (tech. 90%, distilled prior to use), 4-methoxyphenol (99%), 1,3-propanediol (98%), triethylamine (99 + %), and trimethylolpropane (TMP, 99 + %) were purchased from Aldrich Chemical Co. Hexanes, hydrochloric acid (37%), methylene chloride, potassium hydroxide, and tetrahydrofuran (THF, distilled from calcium hydride) were all ACS Reagent Grade, purchased from Fisher Scientific Co. Stannous octoate (95%) and phosphate-buffered saline (dry powder blend, pH 7.4) were purchased from the Sigma Chemical Co. Cobalt(II) naphthenate (8 wt.%) was purchased from Fluka Chemicals. Fluorocarbon release agent (MS-145) was purchased from Miller-Stephenson Chemical Co., Inc. Trimethylene carbonate (TMC) was synthesized by reacting 1,3-propanediol with diethyl carbonate as previously described<sup>15</sup>.

### Synthesis of homopolymer and copolymer triols

A series of poly(D,L-lactide-co-trimethylene carbonate) triols was prepared by the ring opening polymerization of D,L-lactide (DLL) and trimethylene carbonate (TMC) using trimethylolpropane (TMP) as initiator and stannous octoate as a catalyst ( $2.0 \times 10^{-2}$  mol per mole of initiator). Reactant feed compositions for each polymerization are listed in Table 1; the target number average molecular weight was  $2000 \text{ g mol}^{-1}$  in all cases.

A representative procedure to form a 40:60 (DLL:TMC) copolymer was as follows. A 250 ml round bottom flask equipped with a magnetic stirrer was charged with 22.6 g (0.157 mol) D,L-lactide, 24.0 g trimethylene carbonate (0.236 mol), and 3.35 g (25.0 mmol) trimethylolpropane and heated to 115°C. Upon achieving homogeneity, 0.202 g ( $5.00 \times 10^{-3}$  mol) of stannous octoate was added and the reaction was allowed to run for 24 h. Subsequently, the polymer was dissolved in approximately 250 ml of methylene chloride, and the solution was added dropwise to 3.5 l of stirred hexanes. Upon decanting off the hexanes, the polymer was redissolved in 250 ml of methylene chloride and again precipitated into 3.5 l of hexanes. The polymer was then redissolved in methylene chloride, placed in a crystallization dish, and dried *in vacuo* for 24 h at 60°C.

### Methacrylate-endcapping of homopolymer and copolymer triols

All of the triol prepolymers were endcapped using excess methacryloyl chloride in the presence of triethylamine to give the corresponding 3-arm methacrylate-endcapped oligomer. A representative procedure was as follows. A 2000 ml three-necked flask was charged with 15.2 g (0.150 mol) freshly distilled methacryloyl chloride dissolved in 100 ml methylene chloride. This solution was added dropwise to the flask, and reaction was allowed to proceed for 48 h at ambient temperature. The triethylamine hydrochloride produced from the reaction was removed by filtration. The remaining solution was extracted repeatedly with 1% aqueous HCl until the aqueous layer remained colourless. The methylene chloride layer was collected, dried with magnesium sulfate, and filtered. The polymer solution was then inhibited with 10 ppm 4-methoxyphenol, and the majority of the solvent was removed under vacuum. The remaining polymer solution was transferred to a 500 ml screw cap erlenmeyer flask and excess solvent was removed by a nitrogen purge until the desired viscosity was obtained. To determine the wt.% of the polymer in solution, a small aliquot was removed and vacuum dried at 60°C until a constant weight was obtained. The percentage solids of the remaining polymer solutions are given in Table 2.

### Prepolymer characterization

Gel permeation chromatography (g.p.c.) was performed on the prepolymers using a previously described system<sup>15</sup>. The g.p.c. data were collected and analysed using Polymer Laboratories PL caliber software, to determine molecular weights and molecular weight distributions ( $M_w/M_n$ ) relative to polystyrene standards (Polysciences Corp.). The instrument was also very helpful in monitoring the depletion of the monomers in the copolymerization of D,L-lactide and trimethylene carbonate.

I.r. spectra were acquired on a Perkin-Elmer 1600 Series FTi.r. spectrometer using NaCl cells. Polymer samples were prepared by solution casting thin films onto a NaCl cell and drying under vacuum to remove the solvent.

<sup>13</sup>C n.m.r. spectra were acquired using a Bruker model AC-200 or AC-300 spectrometer operating at a frequency of 50.32 or 75.48 MHz, respectively, for carbon. For quantitative data, a recycle delay of 10 s was used; in addition, the proton decoupler was used only during actual data acquisition, and was gated off during the recycle period in order to suppress NOE effects (gated decoupling). Samples were analysed in CDCl<sub>3</sub> solutions with TMS (0.03% w/w) as internal reference.

### Network formation

A fraction (20–30 g) of each of the 3-arm methacrylate-encapped homopolymer and copolymer resin solutions was placed in a test tube, and the desired amounts of cobalt naphthenate solution ( $3.2 \times 10^{-4}$  g elemental cobalt per g resin solids) and 2-butanone peroxide solution (1 mol% 2-butanone peroxide relative to olefinic unsaturation in the prepolymer) were added using a micro-syringe. The solutions were stirred and then poured into aluminium pans that had been pre-coated with mould release agent. Solvent evaporation and polymerization were carried out under nitrogen at 60°C for 48 h and then 90°C for 24 h. The recipes for the six network reactions are shown in Table 2.

### Network extraction and equilibrium swelling

Extraction and swelling studies were carried out on all films using anhydrous 1,2-dichloroethane. The extraction procedure was as follows. A circular sample ( $d = 12.7$  mm) of a crosslinked film was analytically weighed and placed in a 60 ml jar containing 50 ml of 1,2-dichloroethane. After 24 h the sample was removed from the solvent, the solvent was discarded, and 50 ml of fresh solvent was added. This procedure was repeated four times, after which time the network was brought to a constant weight in a vacuum oven at 80°C.

Equilibrium swelling studies were also carried out on all films using anhydrous 1,2-dichloroethane as follows. A circular sample of a previously extracted, crosslinked film was analytically weighed, and the dimensions of the sample were measured to determine sample volume. The sample was heated to 60°C and placed in a 60 ml jar containing 50 ml 1,2-dichloroethane at 60°C. The level of the dichloroethane was maintained for 24 h at which time the sample was patted dry and weighed, the solvent was discarded, and 50 ml of fresh solvent was added. This procedure was repeated for 7 days and an equilibrium weight uptake was calculated.

### Mechanical testing

Mechanical properties of the networks were measured using an MTS model 810 Universal Test Machine equipped with a 100 lb load cell and a 100 lb load cartridge. Network samples were cut into micro-dumbbell shapes which provided a gauge length of 11.2 mm, widths between 1.4–1.7 mm, and sample thicknesses between 0.8–1.5 mm. Samples were pulled at a continuous strain rate of  $0.1 \text{ mm s}^{-1}$ .

### Thermal analysis

Differential scanning calorimetry (d.s.c.) was performed using a Mettler model 30 DSC with a heating rate of  $20^\circ\text{C min}^{-1}$  under constant nitrogen purge. Samples were dried in vacuo prior to sealing in aluminium pans.

### Hydrolytic degradation analysis

Tared network samples, cut into the shape of a micro-dumbbell, were placed into individual 20 ml vials containing phosphate buffered saline (pH 7.4, no bactericide) and placed in an incubator at 37°C. At incubation times of 7, 22, 40, 69 and 119 days, the following procedure was carried out. Three or more samples were removed, patted dry, and weighed to estimate weight gain due to water uptake during degradation. The tensile strength was determined by pulling the hydrated samples at a continuous strain rate of  $0.1 \text{ mm s}^{-1}$  until break. The broken pieces were then dried

under high vacuum at room temperature for seven days or until a constant weight was reached to determine mass loss over time.

## RESULTS AND DISCUSSION

### Network synthesis and characterization

A series of low molecular weight homopolymer and copolymer triols, based upon D,L-lactide and trimethylene carbonate monomers, was synthesized by the trimethylolpropane-initiated ring-opening polymerization of D,L-lactide and trimethylene carbonate in the presence of stannous octoate catalyst, as shown in Figure 1. G.p.c. molecular weight data for the isolated copolymers, relative to polystyrene standards, are listed in Table 3; in all cases the measured number average molecular weight  $M_n$  was slightly higher than the theoretical value of  $2000 \text{ g mol}^{-1}$  based on the monomer-to-initiator ratio. In addition, the molecular weight distribution was observed to increase systematically with the proportion of TMC in the copolymer. G.p.c. analysis of copolymerization reactions at intermediate conversions indicated that most of the D,L-lactide is consumed early in the reaction, followed by reaction of trimethylene carbonate; however, gated decoupling  $^{13}\text{C}$  n.m.r. analysis indicated that a disproportionately large number of the hydroxyl end groups were contained in terminal D,L-lactide residues. This may be clearly seen in the expanded spectrum shown in Figure 2, by comparing the relative peak heights of the methyl groups of internal (a) (16.2 ppm) and terminal (b) (19.8 ppm) D,L-lactide repeat units, versus the  $\beta$ -carbons of internal (c) (27.5 ppm) and terminal (d) (31.1 ppm) trimethylene carbonate repeat units, i.e. it may be noted that in terms of peak areas,  $b/(a + b) > d/(c + d)$ . This apparent incongruity was rationalized by assuming that D,L-lactide is the more reactive monomer and is in fact consumed first; however, the occurrence of transesterification tends to accumulate D,L-lactide units at the chain ends because primary hydroxyl groups derived from trimethylene carbonate units are more reactive in transesterification and thus become depleted. Integration of all gated decoupling  $^{13}\text{C}$  n.m.r. copolymer spectra showed that the composition of D,L-lactide and trimethylene carbonate in the copolymers was approximately equal to the feed ratio of the monomers. This was expected since the monomer conversions for the polymerizations were in all cases nearly quantitative.

All triols were subsequently encapped with methacryloyl chloride in the presence of triethylamine to yield free-radically-reactive prepolymers. The essentially complete reaction of all the hydroxyl endgroups of the triols was confirmed by the loss of the OH stretches at  $3200\text{--}3600 \text{ cm}^{-1}$  in the i.r. spectra. The methacrylate-terminated prepolymers were next crosslinked using 2-butanone peroxide (1 mol% relative to prepolymer unsaturation) to give a series of biodegradable networks. Extraction studies performed on the networks indicated sol-contents (percent extractables) ranging from 2.89%–6.17%, as listed in Table 4.

The sol-contents were directly related to the degree of crosslinking using the following two assumptions: (1) all extractables are unreacted prepolymers, and (2) all reactive prepolymers are trifunctional. Then, the number fraction of totally unreacted chains can be expressed by  $(1 - p)^3$ , where  $p$  is conversion of the double bonds during free-radical curing. Thus, the sol-contents ranging from 2.89%–6.17% represent double bond conversions ranging from 0.60–0.69.

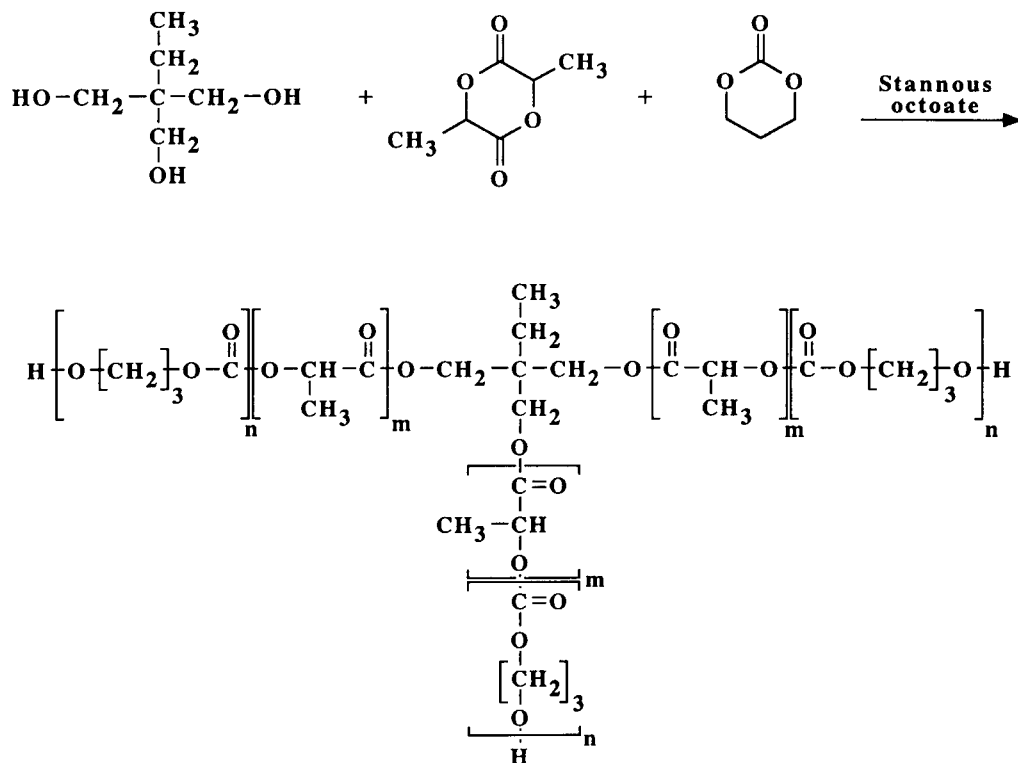


Figure 1 Synthesis of poly(D,L-lactide), poly(D,L-lactide-co-trimethylene carbonate) and poly(trimethylene carbonate) triols

Table 2 Formulations for network reactions

DLL:TMC	Resin (g)	Polymer (%)	Polymer (g)	Promoter <sup>a</sup> (μl)	Init. <sup>b</sup> (μl)
100:0	22.05	61.49	13.56	57.09	31.29
80:20	21.45	62.13	13.33	56.10	30.75
60:40	21.94	62.64	13.74	57.87	31.72
40:60	21.32	62.65	13.36	56.24	30.82
20:80	22.83	59.53	13.59	57.20	31.36
0:100	26.67	50.65	13.51	56.90	31.17

<sup>a</sup>Cobalt naphenate solution (8 wt.% elemental cobalt; solution density 0.95 g ml<sup>-1</sup>)

<sup>b</sup>2-Butanone peroxide in DMP (30 wt.% 2-butanone peroxide; solution density 1.17 g ml<sup>-1</sup>)

Table 3 G.p.c. analysis of poly(D,L-lactide-co-trimethylene carbonate) triols

DLL:TMC	$M_n \times 10^{-3}$ (g mol <sup>-1</sup> )	$M_w/M_n$
100:0	—	—
80:20	2.6	1.3
60:40	2.4	1.4
40:60	2.3	1.5
20:80	2.5	1.9
0:100	—	—

In actual fact, the measured sol-contents are probably not due totally to unreacted prepolymers; each network may have contained a small amount of residual dimethyl phthalate (DMP), which was the solvent used to introduce the 2-butanone peroxide initiator. However, even in the unlikely event that none of the DMP volatilized during curing, this would produce only a 5% inaccuracy in the measured sol-contents, on average.

Equilibrium swelling was used as a qualitative tool for comparing crosslink density. The equilibrium volume fractions of polymer  $V_2$ , and solvent  $V_1$ , in the swollen network are shown in Table 4.  $V_2$  was calculated

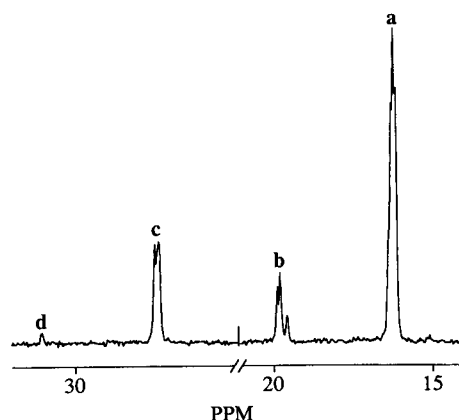
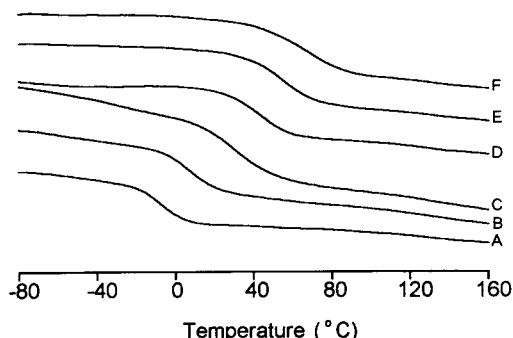


Figure 2 Expanded, gated-decoupling <sup>13</sup>C n.m.r. spectrum of poly(D,L-lactide-co-trimethylene carbonate) triol (DLL:TMC = 60:40) showing the methyl carbon of (a) internal and (b) terminal D,L-lactide repeat units, and the β-carbon of (c) internal and (d) terminal trimethylene carbonate repeat units

**Table 4** Extraction and equilibrium swelling data for network films

DLL:TMC	Sol-content (%)	Network density (g cm <sup>-3</sup> )	Weight gain (%)	V <sub>1</sub>	V <sub>2</sub>
100:0	5.33	1.213	83.56	0.447	0.553
80:20	2.39	1.211	85.15	0.425	0.575
60:40	3.53	1.205	86.58	0.454	0.546
40:60	3.12	1.259	88.37	0.470	0.530
20:80	2.90	1.348	88.68	0.488	0.512
0:100	2.89	1.378	104.82	0.535	0.465


**Figure 3** D.s.c. thermograms of 3-arm methacrylate-encapped poly(D,L-lactide), poly(trimethylene carbonate), and poly(D,L-lactide-co-trimethylene carbonate)-based thermally cured networks: DLL:TMC (A) 0:100, (B) 20:80, (C) 40:60, (D) 60:40, (E) 80:20, and (F) 100:0

according to

$$V_2 = \frac{w_0}{V_{\text{equil}} \rho_2} \quad (1)$$

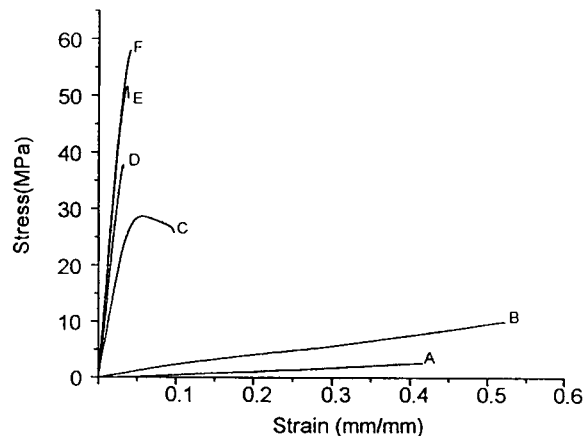
where  $w_0$  is the initial weight of the network,  $\rho_2$  is the network density, and  $V_{\text{equil}}$  is the equilibrium volume of the network, which is defined in equation (2)

$$V_{\text{equil}} = \frac{w_0}{\rho_2} + \frac{w_s - w_0}{\rho_1} \quad (2)$$

where  $w_s$  is the weight of the swollen network, and  $\rho_1$  is the density of 1,2-dichloroethane. At first glance, the  $V_2$  values seem to increase systematically with increasing D,L-lactide content, except for the network formed from 80% lactide and 20% trimethylene carbonate; however, equilibrium swelling data obtained on u.v.-cured prepolymers<sup>16</sup> show scatter in the  $V_2$  values, indicating that the apparent trend in the  $V_2$  value for the thermally cured networks may be coincidental and that the values may simply fall within a narrow range (0.465–0.553) of experimental error. Likewise, the percentage weight gain values seem to decrease systematically with increasing D,L-lactide content; however the weight gain data obtained on u.v.-cured prepolymers show scatter in the percentage weight gain values, indicating that the trend in the values for the thermally cured networks may also be coincidental.

Thermal analysis of the networks, shown in Figure 3, reveals the  $T_g$  of the 3-arm methacrylate-encapped poly(trimethylene carbonate)-based network to be  $-7.8^\circ\text{C}$ . It is quite evident that as the amount of D,L-lactide in the polymer was increased, the  $T_g$  increased up to  $68^\circ\text{C}$  for the 3-arm methacrylate-encapped poly(D,L-lactide)-based network. These results indicate that the glass transition temperatures of the networks can be controlled by the monomer feed ratio in the triol prepolymer synthesis.

The stress-strain curves, shown in Figure 4, are the median curve for a number of pulls made with each


**Figure 4** Stress-strain curves of thermally cured network films: DLL:TMC (A) 0:100, (B) 20:80, (C) 40:60, (D) 60:40, (E) 80:20, and (F) 100:0

network, and they indicate that the tensile modulus and ultimate strength increased with increasing D,L-lactide content. The networks containing a higher content of D,L-lactide, 100%, 80% and 60%, were strong and fairly rigid, but failed catastrophically at the yield point; while the networks containing a lower content of D,L-lactide, 20% and 0%, showed a much higher elongation to break before failing catastrophically at the yield point. The network containing 40% D,L-lactide and 60% trimethylene carbonate displayed a fairly extensive Hookean regime, followed by a regime of plastic yield; however, there was no indication of strain toughening beyond the yield point.

#### Network degradation

Hydrolytic degradation of the networks was studied by subjecting micro-dumbbell samples to phosphate buffered saline (pH 7.4) for extended periods of time at  $37^\circ\text{C}$  and monitoring water uptake, mass loss, and tensile strength loss. The data are collected in Table 5. Networks based on poly(D,L-lactide) homopolymer exhibited the fastest hydrolytic degradation rates; the data show that they swelled slightly (3.9%) over a period of 22 days during which time the mass and tensile strength had decreased 2.0% and 19% respectively. After 69 days, substantial degradation had occurred; a 41% gain in mass due to water uptake had facilitated hydrolysis of the network resulting in a 73% strength loss and a 21% mass loss. After 119 days the networks showed a 98% strength loss and a 55% mass loss. The poly(D,L-lactide) homopolymer-based networks also displayed a general phenomenon that was observed for almost all of the networks, and especially all of the glassy networks, namely, a slight increase in tensile strength at short immersion times, when the degree of water uptake was low and very little degradation had yet occurred. This was ascribed to the well known phenomenon of anti-plasticization<sup>17</sup>, which appears to occur in these systems when the level of imbibed water is low, e.g.  $\leq 2.5$  wt.%.

The copolymer-based networks with DLL:TMC = 80:20 and 60:40 exhibited much slower hydrolytic degradation rates compared with the poly(D,L-lactide) homopolymer-based networks. After 69 days the 80:20 and 60:40 copolymers had absorbed only very small amounts of water, 7.3% and 6.2% respectively, and the strength losses were negligible, 2% and 0% respectively. However, after 119 days the networks had swelled to 20% and 19% respectively, at which time the strengths had decreased by

**Table 5** Network degradation in phosphate buffered saline

Time (days)	DLL:TMC 100:0	DLL:TMC 80:20	DLL:TMC 60:40	DLL:TMC 40:60	DLL:TMC 20:80	DLL:TMC 0:100
	Mass gain due to water uptake % (s.d. <sup>a</sup> )					
7	2.5 (0.2)	1.3 (0.1)	1.4 (0.2)	1.9 (0.1)	1.7 (0.2)	1.1 (0.2)
22	3.9 (0.7)	3.2 (0.2)	2.2 (0.5)	3.8 (0.5)	2.6 (0.1)	1.0 (0.3)
40	11 (0.9)	3.5 (0.2)	2.8 (0.4)	5.8 (0.4)	2.9 (0.2)	1.2 (0.1)
69	41 (3.5)	7.3 (6.5)	6.2 (1.3)	13 (1.5)	4.6 (0.4)	1.0 (0.3)
119	-25 (4.1)	20 (0.9)	19 (5.7)	-5.3 (2.6)	8.5 (1.0)	0.83 (0.56)
	Mass loss <sup>b</sup> (s.d.)					
7	1.5 (0.2)	1.1 (0.05)	1.1 (0.2)	0.20 (0.04)	1.5 (0.4)	2.0 (0.1)
22	2.0 (0.4)	2.1 (0.4)	2.0 (0.2)	0.44 (0.10)	1.8 (0.1)	2.6 (0.5)
40	3.6 (0.4)	3.4 (0.2)	2.9 (0.3)	0.55 (0.16)	2.8 (0.5)	3.1 (0.3)
69	21 (3.5)	2.7 (0.4)	4.4 (1.4)	1.5 (0.4)	6.1 (0.9)	5.5 (1.0)
119	55 (3.9)	2.8 (0.8)	5.9 (0.6)	3.9 (0.4)	6.0 (0.5)	3.4 (0.3)
	Tensile strength <sup>c</sup> Mpa (% decrease <sup>d</sup> )					
0	56 (0)	52 (0)	40 (0)	26 (0)	9.8 (0)	2.8 (0)
7	60 (-7)	58 (-11)	43 (-8)	24 (8)	11 (-12)	4.4 (-57)
22	45 (20)	39 (25)	33 (18)	19 (27)	9.7 (1.0)	3.9 (-39)
40	44 (21)	50 (4)	36 (10)	15 (42)	9.9 (-1.0)	4.1 (-46)
69	15 (73)	51 (2)	40 (0)	10 (62)	7.8 (20)	3.9 (-39)
119	1.2 (98)	31 (40)	37 (8)	2.9 (89)	8.1 (17)	5.2 (-86)

<sup>a</sup>Standard deviation<sup>b</sup>Of vacuum-dried network after degradation, relative to original sample<sup>c</sup>Of swollen network<sup>d</sup>Relative to original, undegraded sample

40% and 7.4% respectively. These two networks also displayed the antiplasticization effect when they were examined after 7 days.

The poly(D,L-lactide-*co*-trimethylene carbonate)-based network (DLL:TMC = 40:60) exhibited the most uniform hydrolytic degradation rate, as measured in terms of strength loss. By this criterion, its degradation rate was comparable with that of the poly(D,L-lactide) homopolymer-based network; although it did not lose mass nearly as quickly or to as great an extent. The uptake of water into the 40:60 (DLL:TMC) copolymer network occurred at a faster rate than for the 80:20 or 60:40 copolymer networks; thus, degradation was also faster. These results can be rationalized in view of the thermal properties of the networks shown in Figure 3. The glass transition temperatures of the 80:20, 60:40 and 40:60 copolymer networks were 53°C, 43°C, and 27°C respectively. Since the degradation experiments were done in phosphate buffered saline at 37°C, both the 80:20 and 60:40 copolymer networks were below their glass transitions, making them less permeable to water; however, the 40:60 copolymer network was above its glass transition temperature, making it imbibe water and degrade at a faster rate.

The poly(D,L-lactide-*co*-trimethylene-carbonate)-based network (DLL:TMC = 20:80) and the poly(trimethylene carbonate)-based network, exhibited the slowest hydrolytic degradation rates. The 20:80 copolymer network showed a 4.6% water gain after 69 days which was accompanied by a 20% strength loss, and an 8.5% water gain after 119 days with no further loss in strength. The poly(trimethylene carbonate)-based network gained very small amounts of water after 119 days (approximately 1%) and appeared to exhibit antiplasticization throughout the experiment.

In summary, it appears that the copolymer network degradation behaviour can be explained by the balance of two opposing effects. D,L-lactide repeat units yield a more hydrophilic network with inherently more easily hydrolysable linkages, but cause a higher glass transition temperature which hinders the entry of water. TMC yields hydrophobic repeat units but also lowers  $T_g$ . Thus, the poly(D,L-lactide)-based network degraded the fastest owing to the hydrophilic nature of the network, even though it is

glassy at 37°C. Incorporation of only small amounts of the hydrophobic TMC, e.g. in the 80:20 and 60:40 copolymer networks, was insufficient to depress the  $T_g$  below 37°C, and thus the only effect was decreased hydrophilicity, and hence, decreased degradation rate. However, additional TMC in the 40:60 copolymer produced a rubbery network at 37°C, and there was observed an increase in water uptake and degradation rate in spite of the increase in hydrophobicity. The 20:80 copolymer network and the poly(trimethylene carbonate) network are so hydrophobic that they were the slowest degrading networks regardless of their very low  $T_g$  values.

## CONCLUSIONS

Polyester, polycarbonate, and poly(ester-carbonate) prepolymers were synthesized by the ring opening polymerization of D,L-lactide, trimethylene carbonate, and varied ratios of the two monomers respectively. The prepolymers were endcapped with methacrylate groups yielding unsaturated prepolymers with a higher reactivity than conventional bioabsorbable unsaturated polyesters. Free-radical cross-linking yielded a novel class of bioabsorbable thermosets with a broad range of thermal, mechanical, and degradative properties. Fundamental structure/property relationships were established including the effect of composition on the thermal, mechanical and degradative behaviour of the networks.

Thermal analysis indicated that the  $T_g$  of the networks can be controlled by the monomer feed ratio in the triol prepolymer synthesis. The  $T_g$  was increased or decreased by increasing the amounts of D,L-lactide and trimethylene carbonate in the prepolymer synthesis respectively.

The stress-strain data illustrated that the ultimate network strength was increased by increasing the amount of D,L-lactide in the network, whereas toughness was imparted by the presence of trimethylene carbonate units. The properties of the 40:60 (DLL:TMC) network suggested that it could be a viable matrix resin for composite fabrication. This network displayed a fairly high tensile strength, owing to the D,L-lactide content, but it also showed a yield point, followed by a regime of plastic deformation.

Hydrolytic degradation analysis of the thermally cured networks revealed that the degradation rate was dependant on the rate of water uptake and both rates were dependent on the glass transition and chemical composition of the network. The poly(D,L-lactide)-based networks degraded most rapidly owing to the hydrophilic nature of D,L-lactide. The poly(D,L-lactide-co-trimethylene carbonate)-based networks (DLL:TMC = 80:20 and 60:40) degraded more slowly because they are glassy at 37°C and hydrophobic due to the incorporation of trimethylene carbonate. The poly(D,L-lactide-co-trimethylene carbonate)-based network (DLL:TMC = 40:60) gave the most uniform degradation rate, in terms of strength loss, because at 37°C it is above  $T_g$ , and thus more permeable to water, yet still contains enough of the hydrophilic D,L-lactide to degrade relatively rapidly. The poly(D,L-lactide-co-trimethylene-carbonate)-based network (DLL:TMC = 20:80) and the poly(trimethylene carbonate) based network showed very little water uptake and slow degradation simply owing to the hydrophobic nature of the polymer.

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#### REFERENCES

1. Christel, P., Chabot, F., Leray, J.L., Morin, C. and Vert, M. in *Advances in Biomaterials: Biomaterials*, Vol. 3, ed. D.G. Winter, D.F. Gibbons and J. Plench Jr. Wiley, New York, 1982, pp. 271–280.
2. Vert, M., Garreau, H., Audion, M., Chabot, F. and Cristel, P., *Trans. Soc. Biomater.*, 1985, **8**, 218.
3. Frazza, E.J. and Schmitt, E.E., *J. Biomed. Mater. Res. Symp.*, 1971, **1**, 43.
4. US Patent 1,332,505, assigned to Ethicon, Inc., New Jersey, 1973.
5. Kricheldorf, H., Mang, T. and Jonte, J., *Macromolecules*, 1984, **17**, 2173.
6. Pitt, C.G., Hendren, R.W. and Schindler, A., *J. Controlled Rel.*, 1984, **1**, 3.
7. Baier, R.E., Meyer, A.F., Natiella, J.R. and Carter, J.M., *J. Biomed. Mater. Res.*, 1984, **18**, 3370.
8. Stokes, K. and Cobian, K., *Biomaterials*, 1982, **3**, 225.
9. Huang, S.J., Yang-Kyoo, H. and Edelman, P.G., *J. Macromol. Sci. Chem.*, 1988, **25**, 847.
10. Domb, A.J., Mathiowitz, E., Ron, E., Giannos, S. and Langer, R., *J. Polym. Sci. A: Polym. Chem.*, 1991, **29**, 571.
11. Storey, R.F. and Wiggins, J.S., *Soc. Plast. Eng. Tech. Pap.*, 1992, **38**, 734.
12. Storey, R.F., Warren, S.C., Allison, C.J., Wiggins, J.S. and Puckett, A.D., *Polymer*, 1993, **34**, 4365.
13. Katz, A.R., Mukherjee, D.P., Kagonov, A.L. and Gordon, S.A., *Surg. Gynecol. Obstet.*, 1985, **161**, 213.
14. Rodeheaver, G.T., Powell, T.A., Thacker, J.G. and Edlich, R.F., *Am. J. Surg.*, 1987, **154**, 544.
15. Storey, R.F. and Hickey, T.P., *Polymer*, 1994, **35**(4), 830.
16. Storey, R.F. and Warren, S.C., Unpublished results.
17. Sears, J.K. and Darby, J.R., *The Technology of Plasticizers*. Wiley, New York, 1982, pp. 54–55.