

# Synthesis of bioabsorbable networks from methacrylate-endcapped polyesters

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A low-molecular-weight poly( $\epsilon$ -caprolactone) triol ( $M_n = 540$ ) was reacted with an excess of methacryloyl chloride to give a 3-arm methacrylate-endcapped polyester. The loss of the hydroxyl endgroups, which are capable of hydrogen bonding, lowered the viscosity of the polymer, thus enabling the formation of networks without solvent processing. The prepolymer was free radically homopolymerized, and copolymerized with methyl methacrylate, styrene, and 2-methylene-1,3-dioxepane to give a series of twelve biodegradable networks. Extraction studies indicated substantial network formation for all of the networks except those in which 2-methylene-1,3-dioxepane was used as the reactive diluent. A series of three low-molecular-weight poly(D,L-lactide) triols ( $M_n < 10\,000$ ) was synthesized by the trimethylolpropane-initiated ring-opening polymerization of D,L-lactide. Number-average molecular weights of the triols were estimated to be 2300, 5100, and 8700, by using gel permeation chromatography (g.p.c.), calibrated with polystyrene standards. The triols were reacted with excess methacryloyl chloride to produce a series of low-molecular-weight 3-arm methacrylate-endcapped polyesters. These prepolymers were free radically homopolymerized, and copolymerized with methyl methacrylate and styrene to give a series of twenty-seven biodegradable networks. Extraction studies indicated substantial network formation for all of these systems. The  $T_g$  values of each of the three homopolymer networks were higher than the corresponding  $T_g$  values of either of their respective copolymer networks, thus illustrating substantial network formation in the absence of reactive diluents. The ultimate strengths and tensile moduli of the homopolymer networks synthesized from the higher-molecular-weight prepolymers ( $M_n = 5100$  and 8700) were higher than those measured for corresponding copolymer networks.

(Keywords: networks; endcapped polyesters; bioabsorbable polymers)

## INTRODUCTION

The demand for materials for surgical applications such as sutures, artificial skin, and tissue scaffolding has stimulated the development of a variety of bioabsorbable polymer systems. The commercially available poly(glycolide), poly(lactide) and poly( $\epsilon$ -caprolactone) have been studied extensively for these applications<sup>1-3</sup>; however, they still possess some inherent limitations. The semi-crystalline, thermoplastic nature and high molecular weights of these polymers renders them only marginally useful as matrix resins for the fabrication of bioabsorbable composites.

Recent work involving the free-radical addition polymerization of unsaturated prepolymers to produce crosslinked networks shows great potential for the fabrication of bioabsorbable composites<sup>4-6</sup>. Storey *et al.* have fabricated composites using poly(glycolide) surgical mesh (DEXON) with matrix resins of poly(lactide-co-glycolic acid) fumarate<sup>7</sup> and poly( $\epsilon$ -caprolactone-

co-D,L-lactide) fumarate<sup>6</sup> and have shown that they exhibit excellent physical properties; however, the low reactivity of the 1,2-disubstituted olefinic groups in these resins requires the use of reactive diluents during the crosslinking reactions in order to increase the degree of crosslinking.

The primary focus of this research was to develop bioabsorbable polymers containing more reactive olefinic groups through the synthesis of a series of 3-arm methacrylate-endcapped polyesters (3, 7). The high reactivity of the terminal double bonds in these prepolymers was expected to enable free-radical crosslinking reactions during composite fabrication without the addition of monomeric reactive diluents.

For all of the unsaturated systems thus far mentioned<sup>4-6</sup>, hydrolysis of ester and anhydride linkages leads to free acids and free alcohols which are easily absorbed; however, non-biodegradable, hydrocarbon polymer chains resulting from free-radical crosslinking reactions of olefinic groups are still present and these may be difficult or impossible to absorb. Until recently, this issue had not been addressed; however, recent work has illustrated that the copolymerization of cyclic ketene

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acetals with unsaturated polyester prepolymers can lead to completely bioabsorbable networks, if the reactivity ratios of the cyclic ketene acetal and the olefinic groups on the polymer are close to unity<sup>8</sup>. Bailey *et al.* have shown that the ketene acetal, 2-methylene-1,3-dioxepane, copolymerizes reasonably well with methyl methacrylate<sup>9</sup>. Hence, our secondary objective was to copolymerize the newly formed 3-arm methacrylate-endcapped polyesters (3, 7) with 2-methylene-1,3-dioxepane to give a completely biodegradable network.

Initially, a low-molecular-weight 3-arm methacrylate-endcapped poly( $\epsilon$ -caprolactone) (PC-MA) (3) was synthesized by reacting the poly( $\epsilon$ -caprolactone) triol (1) with an excess of methacryloyl chloride (2). The prepolymer was then homopolymerized, and copolymerized using styrene, methyl methacrylate (MMA), and 2-methylene-1,3-dioxepane as comonomers. Upon successfully endcapping the triol and incorporating the prepolymer into biodegradable networks, our focus was turned to endcapping materials with higher glass transition temperatures, which would in turn yield networks with enhanced physical properties (ultimate strength, tensile modulus, glass transition temperature, etc.).

A series of three low-molecular-weight ( $M_n < 10\,000$ ) polyester triols (6) was synthesized by initiating various compositions of D,L-lactide (5) with trimethylolpropane (4). The polyester triols were then reacted with an excess of methacryloyl chloride (2) to produce a series of 3-arm methacrylate-endcapped poly(D,L-lactide) prepolymers (PL-MA) (7). These prepolymers were then free radically homopolymerized and copolymerized, using methyl methacrylate and styrene as comonomers, to give a series of biodegradable networks.

## EXPERIMENTAL

### Poly( $\epsilon$ -caprolactone)-based networks

**Synthesis of 3-arm methacrylate-endcapped poly( $\epsilon$ -caprolactone) (PC-MA) (3).** A three-necked flask was charged with 72.65 g (0.135 mol) of TONE<sup>®</sup> 0305 high-performance poly( $\epsilon$ -caprolactone) triol (1) ( $M_n = 540$ , from Union Carbide) dissolved in 600 ml of methylene chloride and 51.15 g (0.505 mol) of triethylamine (Aldrich Chemical Company). An addition funnel was charged with 52.85 g (0.505 mol) of freshly distilled methacryloyl chloride (2) (Aldrich Chemical Company) dissolved in 100 ml of methylene chloride. This solution was added dropwise to the flask, and the reaction was allowed to proceed for 8 h at 0°C, after which time the triethylamine hydrochloride produced from the reaction was removed by filtration. The remaining solution was repeatedly extracted with 1% aqueous HCl solution until the aqueous layer remained colourless. The methylene chloride layer was collected and repeatedly extracted with 3% aqueous KOH solution until the aqueous layer remained colourless. The methylene chloride layer was then collected, dried with anhydrous magnesium sulfate, and filtered. The excess solvent was removed and the polymer was vacuum dried.

**Network formation.** Four resin mixtures based on the PC-MA prepolymer (3), designated as mixtures 1–4, were prepared in glass test tubes (16 × 150 mm), equipped with rubber septa; these were composed of 10 g prepolymer, 7.05 g of prepolymer/2.95 g of styrene,

7.12 g of prepolymer/2.88 g of methyl methacrylate, and 6.85 g of prepolymer/3.15 g of 2-methylene-1,3-dioxepane, respectively. All four tubes were charged with 0.4 wt% cobalt naphthenate (promoter), mixed thoroughly, and placed under nitrogen. A series of twelve network polymerization reactions were performed in mould-release-lined aluminium pans, under nitrogen at 60°C for 60 h, using the prepromoted resins with 2-butanone peroxide as a free-radical initiator. Specific reaction conditions for each polymerization are listed in Table 1. It should also be noted that the molar ratio of the prepolymer double bonds to the comonomer double bonds was 1:1 in systems 2–4.

**Extraction studies.** Extraction studies were carried out using anhydrous 1,2-dichloroethane. The extraction procedure was as follows: a crosslinked polymer film (0.2–0.3 g) was accurately weighed and placed in a 120 ml jar containing 20 ml of 1,2-dichloroethane. After 24 h the sample was removed from the solvent, the solvent was discarded, and 20 ml of fresh solvent was added. This procedure was repeated four times, after which time the network was brought to a constant weight by heating in a vacuum oven at 80°C.

### Poly(D,L-lactide)-based networks

**Synthesis of poly(D,L-lactide) triols (6).** A series of three low-molecular-weight poly(D,L-lactide) triols (6) was synthesized by the ring-opening polymerization of D,L-lactide (5) using trimethylolpropane (4) as the initiator and stannous octoate as a catalyst (0.4 wt% based upon the weight of initiator). The molecular weights of the three polyester triols were determined using g.p.c., calibrated with polystyrene standards (Polysciences Corporation). A representative procedure (e.g. to produce a polymer with  $M_n = 2300$ ) was as follows: a 1000 ml round-bottomed flask, equipped with a magnetic stirrer, was charged with 101.30 g (0.7028 mol) of D,L-lactide, 6.287 g (0.04686 mol) of trimethylolpropane (TMP), and 0.025 g of stannous octoate. The reaction was allowed to

**Table 1** Reaction conditions for the network homopolymerizations and copolymerizations of 3-arm methacrylate-endcapped poly( $\epsilon$ -caprolactone) prepolymer (PC-MA) (3)<sup>a</sup>

Sample	Resin <sup>b</sup>	Amount of initiator <sup>c</sup>	
		( $\mu$ l)	(mol%)
1	1	12.4	1
2	1	24.8	2
3	1	37.2	3
4	2	26.2	1
5	2	52.4	2
6	2	78.7	3
7	3	26.5	1
8	3	53.1	2
9	3	79.6	3
10	4	25.5	1
11	4	51.0	2
12	4	76.5	3

<sup>a</sup> All reactions carried out at 60°C for 60 h

<sup>b</sup> 3 g of resin used in every case: resin 1 = 100 wt% PC-MA; resin 2 = 70.5 wt% PC-MA, 29.5 wt% styrene; resin 3 = 71.2 wt% PC-MA, 28.8 wt% methyl methacrylate; resin 4 = 68.5 wt% PC-MA, 31.5 wt% 2-methylene-1,3-dioxepane

<sup>c</sup> 2-Butanone peroxide

proceed for 24 h at 135°C. The resulting polymer was dissolved in 1000 ml of methylene chloride and then precipitated by adding to a stirred mixture of hexanes (71). Upon decanting off the hexanes, the polymer was then redissolved in 1000 ml of methylene chloride and the precipitation process was repeated. The polymer was then redissolved in methylene chloride, placed in a crystallizing dish and finally dried *in vacuo* for 24 h at 60°C. The remaining two triols were synthesized using the same procedure, except that the charges of monomer and initiator were varied as shown in Table 2.

**Synthesis of 3-arm methacrylate-encapped poly(D,L-lactide) (PL-MA) (7).** A series of three, 3-arm methacrylate-encapped poly(D,L-lactide) prepolymers (7) was synthesized by reacting the three poly(D,L-lactide) triols (6) with excess methacryloyl chloride (2) in the presence of triethylamine. Since these polymers are glassy at ambient temperature, polymer solutions were prepared in 1,2-dichloroethane for all of the crosslinking reactions. A representative procedure was as follows: a three-necked flask was charged with 98.00 g of D,L-lactide triol ( $M_n=2300$ ) dissolved in 1000 ml of methylene chloride and 25.87 g (0.2557 mol) of triethylamine (Aldrich Chemical Company). An addition funnel was charged with 26.72 g (0.2556 mol) of freshly distilled methacryloyl chloride (Aldrich Chemical Company) dissolved in 100 ml of methylene chloride. This solution was added dropwise to the flask and the reaction was allowed to proceed for 48 h at ambient temperature. The triethylamine hydrochloride produced from the reaction was removed by filtration, and the remaining solution was repeatedly extracted with 1% aqueous HCl solution until the aqueous layer remained colourless. The methylene chloride layer was collected and repeatedly extracted with 3% aqueous KOH solution 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 260 ml bell jar and vacuum dried at room temperature. A 60.56 wt% solution of this polymer in 1,2-dichloroethane was then prepared. The remaining two triols were encapped using the same procedure, except that the charges of the triols were varied as shown in Table 3, and the prepared solution concentrations (wt%) of the  $M_n=5100$  and  $M_n=8700$  prepolymers in 1,2-dichloroethane were 62.55% and 58.84%, respectively.

**Network formation.** Nine resin mixtures, designated as mixtures 1–9, were prepared, as shown in Table 4, in glass test tubes (16 × 150 mm) equipped with rubber septa.

**Table 2** Synthesis of 3-arm poly(D,L-lactide) triols (6)<sup>a</sup>

Triol ( $M_n$ )	Reagents used		
	D,L-lactide (mol)	TMP (mol)	Sn(oct) <sub>2</sub> (g)
2300	0.703	0.0469	0.025
5100	0.700	0.0233	0.013
8700	0.703	0.0156	0.008

<sup>a</sup> All reactions carried out at 135°C for 24 h

**Table 3** Synthesis of 3-arm methacrylate-encapped poly(D,L-lactide) (PL-MA) prepolymers (7)

Triol ( $M_n$ )	Reagents used			
	Triol (g)	Et <sub>3</sub> N (mol)	RCI (mol)	Time (h)
2300	98.00	0.2557	0.2556	48
5100	86.53	0.2036	0.2057	48
8700	95.90	0.1704	0.1703	72

**Table 4** Formulation of resins based on 3-arm methacrylate-encapped poly(D,L-lactide) (PL-MA) prepolymers (7)

Resin	Components			
	PL-MA ( $M_n$ )	PL-MA (g)	MMA (g)	Styrene (g)
1	2300	20.45	1.615	–
2	2300	20.34	–	1.680
3	2300	23.12	–	–
4	5100	21.14	0.788	–
5	5100	21.09	–	0.809
6	5100	22.38	–	–
7	8700	23.00	0.467	–
8	8700	22.97	–	0.485
9	8700	23.97	–	–

All tubes were charged with 0.4 wt% cobalt naphthenate (promoter) and mixed thoroughly. Twenty-seven network polymerization reactions were performed in aluminium pans under nitrogen, first at ambient temperature for 12 h and then at 60°C for a further 48 h, using the prepromoted resins, with 2-butanone peroxide as a free-radical initiator. The specific reaction conditions for each of these polymerizations are listed in Table 5. It should also be noted that the molar ratio of the prepolymer double bonds to the comonomer double bonds was 1:1 for all of the copolymerizations, based upon molecular weights as determined by g.p.c.

**Extraction studies.** Extraction studies were carried out using anhydrous 1,2-dichloroethane. The extraction procedure was as follows: a crosslinked polymer film (0.1–0.2 g) was accurately weighed and placed in a 120 ml bell 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 by heating in a vacuum oven at 80°C.

#### Mechanical testing

Stress–strain curves for the networks initiated with 1 mol% 2-butanone peroxide were recorded on an MTS Model 810 universal test machine using a 50 lb load cell with a pulling rate of 0.10 mm s<sup>-1</sup>. All tensile data were acquired and analysed using MTS Testworks software.

#### Characterization

The resulting polymers/products for both the caprolactone and D,L-lactide systems were characterized by <sup>13</sup>C n.m.r., FTi.r., d.s.c., g.p.c. and other techniques.

**Table 5** Reaction conditions for the network homopolymerizations and copolymerizations of 3-arm methacrylate-encapped poly(D,L-lactide) (PL-MA) prepolymers (7)<sup>a</sup>

Sample	Resin	Components used		
		Resin (g)	Initiator <sup>b</sup>	
			( $\mu$ l)	(mol%)
1	1	6.30	14.2	1
2	1	6.30	28.4	2
3	1	6.30	42.6	3
4	2	6.29	14.2	1
5	2	6.29	28.4	2
6	2	6.29	42.6	3
7	3	6.61	8.0	1
8	3	6.61	16.1	2
9	3	6.61	24.1	3
10	4	6.26	6.8	1
11	4	6.26	13.7	2
12	4	6.26	20.5	3
13	5	6.26	6.7	1
14	5	6.26	13.7	2
15	5	6.26	20.5	3
16	6	6.39	3.6	1
17	6	6.39	7.2	2
18	6	6.39	10.9	3
19	7	6.71	4.1	1
20	7	6.71	8.2	2
21	7	6.71	12.3	3
22	8	6.70	4.1	1
23	8	6.70	8.2	2
24	8	6.70	12.3	3
25	9	6.80	2.1	1
26	9	6.80	4.3	2
27	9	6.80	6.4	3

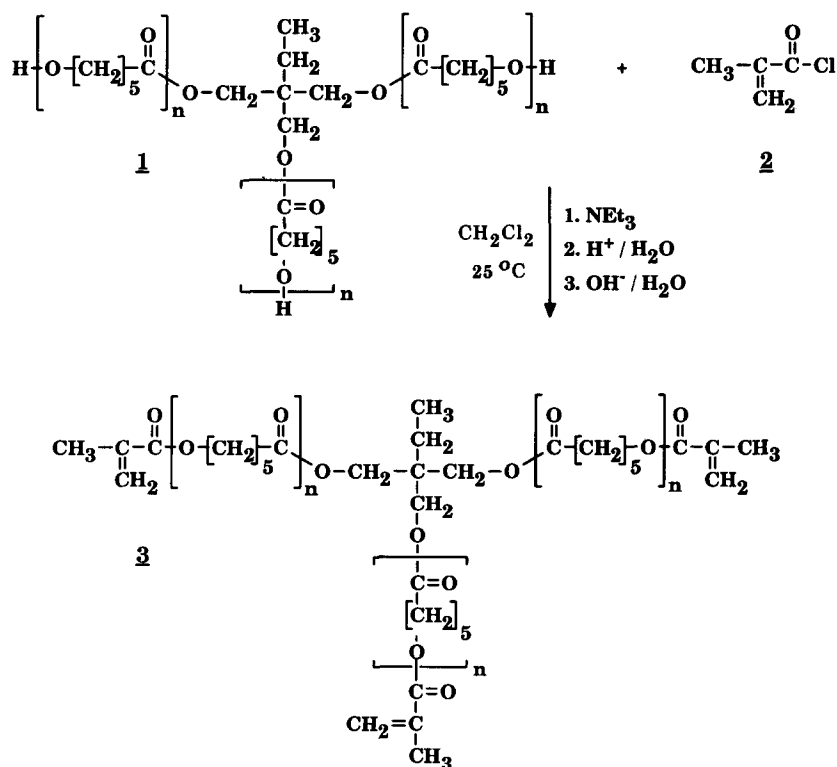
<sup>a</sup> All reactions carried out under nitrogen, at 25°C for 12 h and then at 60°C for a further 48 h

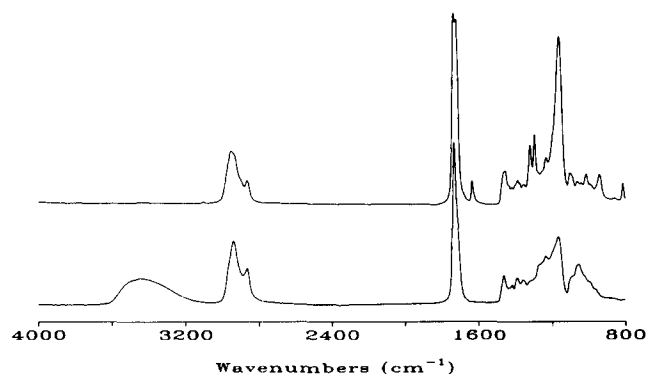
<sup>b</sup> 2-Butanone peroxide

## DISCUSSION

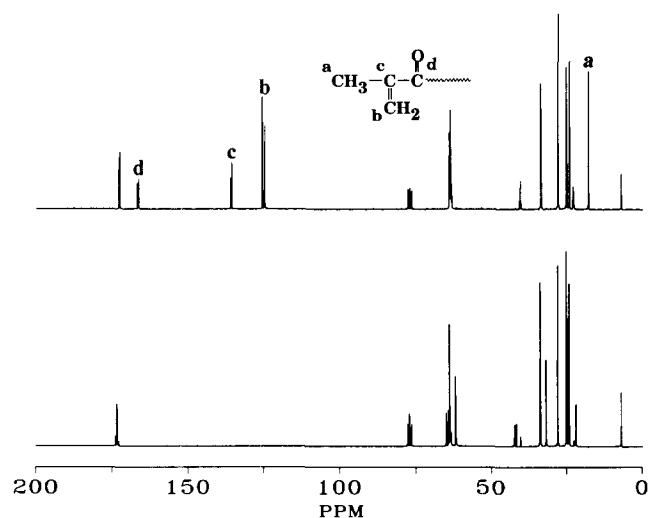
A low-molecular-weight 3-arm methacrylate-encapped poly( $\epsilon$ -caprolactone) (**3**) was synthesized (*Figure 1*) and characterized. The complete reaction of all of the hydroxyl endgroups of the poly( $\epsilon$ -caprolactone) triol (**1**) was confirmed by the loss of the OH stretching vibration at 3200–3600  $\text{cm}^{-1}$  in the infra-red spectrum (see *Figure 2*, upper trace) by using a Perkin-Elmer Model 1600 spectrophotometer. The loss of these hydroxyl groups, which are capable of hydrogen bonding, lowers the viscosity of the polymer, thus enabling the formation of networks without solvent processing. The  $^{13}\text{C}$  n.m.r. spectra, shown in *Figure 3*, were run on a Bruker MSL 200 spectrometer in  $\text{CDCl}_3$  and show the poly( $\epsilon$ -caprolactone) triol precursor (**1**) (lower trace), and the methacrylate encapped poly( $\epsilon$ -caprolactone) (**3**) (upper trace). The  $^{13}\text{C}$  chemical shifts show four new peaks arising from the methacrylate endgroups, namely the carbonyl carbon at 166 ppm, vinyl carbons at 125 and 136 ppm, and the methyl carbon at 18 ppm. The fact that each of these peaks is composed of at least two distinct peaks is doubtless due to the very low degree of polymerization of each arm of the poly( $\epsilon$ -caprolactone) prepolymer; the methacrylate unit is in a distinctively different chemical environment depending on whether it is separated from the central hub by one or two repeat units.  $^{13}\text{C}$  integration of the carbonyl carbons of caprolactone and methacrylate from the gated decoupling programme shows a ratio of caprolactone units to methacrylate units of 1.9 in the 3-arm methacrylate-encapped polymer. This is somewhat higher than the theoretical value, indicating that some of the arms failed to become functionalized, or that the lower fractions of the molecular-weight distribution were lost during polymer purification and work-up.

The methacrylate-terminated poly( $\epsilon$ -caprolactone)


**Figure 1** Synthesis of 3-arm methacrylate-encapped poly( $\epsilon$ -caprolactone) (**3**)



**Figure 2** Infra-red spectra of poly( $\epsilon$ -caprolactone) triol (1) (lower trace), and 3-arm methacrylate-endcapped poly( $\epsilon$ -caprolactone) (3) (upper trace)

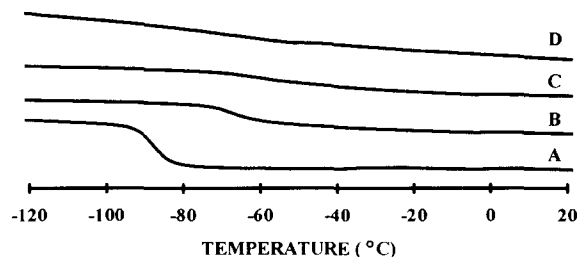


**Figure 3**  $^{13}\text{C}$  n.m.r. spectra of poly( $\epsilon$ -caprolactone) triol (1) (lower trace), and 3-arm methacrylate-endcapped poly( $\epsilon$ -caprolactone) (3) (upper trace)

polymer (3) was then successfully incorporated into a series of twelve biodegradable networks. Extraction studies indicated a high degree of crosslinking in all of the networks, except for those networks incorporating the reactive comonomer, 2-methylene-1,3-dioxepane. The extraction studies showed that the homopolymer networks had 6–7% sol contents. The styrene and MMA copolymer networks had sol contents ranging from 1 to 8%, and in both cases the sol contents increased with increasing initiator concentration. The 2-methylene-1,3-dioxepane copolymer networks had 23–27% sol contents, suggesting that the prepolymer and the cyclic ketene acetal did not copolymerize well under these conditions.

The glass transitions of the networks were very broad and difficult to characterize. In order to observe the evolution of the glass transition temperature, a neat, uninitiated prepolymer was thermally cured *in situ* using a Mettler Model 30 differential scanning calorimeter. The thermograms shown in Figure 4 illustrate how the glass transition is well defined at  $-89^\circ\text{C}$  in the prepolymer (cycle 1) and gradually increases and broadens with the degree of cure (cycle 7 and cycle 12). The top trace in Figure 4 shows that it is hard to discern the glass transition temperature of a fully cured sample.

Upon determining the proper conditions for methacrylate end-capping and successfully synthesizing caprolactone-



**Figure 4** D.s.c. thermograms of thermally cured networks based on 3-arm methacrylate-endcapped poly( $\epsilon$ -caprolactone) (3), illustrating the evolution of the glass transition temperature: (A) cycle 1; (B) cycle 7; (C) cycle 12 and; (D) curing initiated with 0.6% 2-butanone peroxide

based networks, the focus was turned to synthesizing prepolymers which would in turn lead to networks with better physical properties. A series of three low-molecular-weight poly(D,L-lactide) triols (6) was synthesized by the trimethylolpropane (4)-initiated ring-opening polymerization of D,L-lactide (5) in the presence of stannous octoate catalyst, as shown in Figure 5. G.p.c. chromatograms of the three poly(D,L-lactide) triols (6) are shown in Figure 6; these were run on a Waters Associates gel permeation chromatograph equipped with a Rheodyne injector, a Waters 510 solvent delivery system (THF), two PL-GEL  $3\mu$  Mixed-E-3-62 @ 300 mm  $\times$  7.5 mm (length/i.d.) columns (Polymer Laboratories) and a Waters 410 differential refractometer. Here it may be seen that the prepolymer triols are clean and very uniform with respect to their molecular-weight distributions; polydispersity indices estimated from g.p.c. were in the range 1.05–1.10. These polymers were endcapped with methacrylate groups (see Figure 7) using the previously established procedure, and the virtually complete reaction of all of the hydroxyl endgroups was confirmed by the loss of the OH stretching vibration at  $3200\text{--}3600\text{ cm}^{-1}$  in the infra-red spectra of all three polymers. This is illustrated by the infra-red spectrum of the prepolymer with  $M_n = 2300$ , which is shown in Figure 8.

The methacrylate-terminated poly(D,L-lactide) polymers (7) were then successfully incorporated into a series of twenty-seven biodegradable networks. The extraction studies indicated a high extent of crosslinking in all of the networks, with sol contents in all cases  $< 10\%$ .

In general, the glass transition temperatures of the networks appeared to increase slightly as the  $M_n$  of the corresponding prepolymer increased; for the homopolymer networks this suggested that the network  $T_g$  is more dependent on the  $T_g$  of the D,L-lactide prepolymer than on the molecular weight between crosslinks in the network. For the copolymers, however, interpretation of this result was more complicated because the mass fraction of prepolymer in the networks increased as the  $M_n$  of the prepolymer increased. Thus, compositional differences, as well as differences in crosslink density and prepolymer  $T_g$ , all contributed to the observed network  $T_g$ .

The  $T_g$  values of the homopolymer networks synthesized from all three prepolymers (7) were higher than the  $T_g$  values of the copolymer networks. This was illustrated clearly from the d.s.c. thermograms of the networks (see Figure 9) which were prepared from the prepolymer with  $M_n = 5100$ .

The stress-strain data (see Figures 10–12) for the poly(D,L-lactide)-methacrylate networks show that these

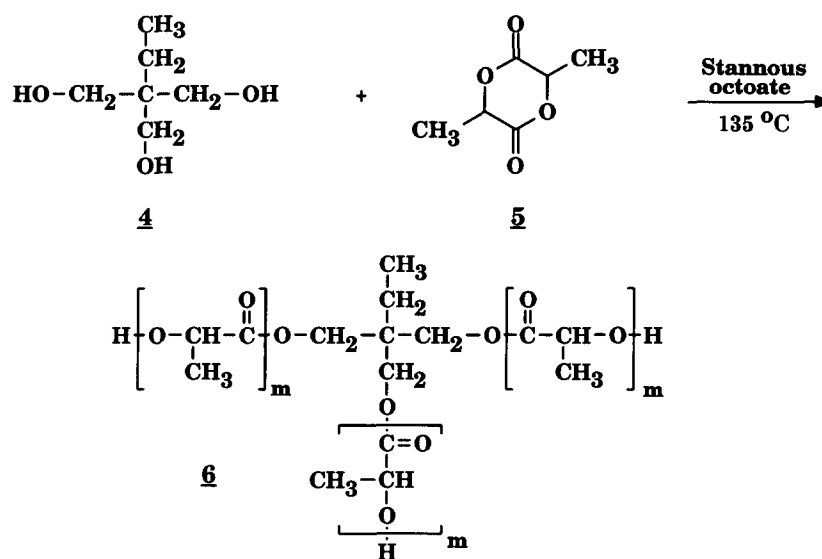


Figure 5 Synthesis of poly(D,L-lactide) triols (6)

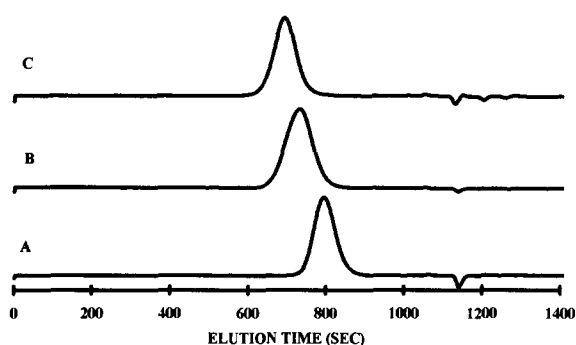


Figure 6 G.p.c. chromatograms of poly(D,L-lactide) triols (6): (A)  $M_n = 2300$ ; (B)  $M_n = 5100$  and; (C)  $M_n = 8700$

materials are quite strong and fairly rigid, and that their strength properties tend to increase with increasing molecular weight of the corresponding prepolymer. The stress-strain curves display a general shape which is characterized by a fairly extensive Hookean regime, followed by a broad yield point that also represents the ultimate strength attained. The two copolymer networks derived from the highest-molecular-weight prepolymer broke at the yield point, but for all of the other networks the yield was followed by a viscous 'pull-away' which was particularly extended for the neat networks. In none of the cases was there any indication of strain toughening beyond the yield point. It is significant that the (neat) homopolymer networks were in every case tougher,

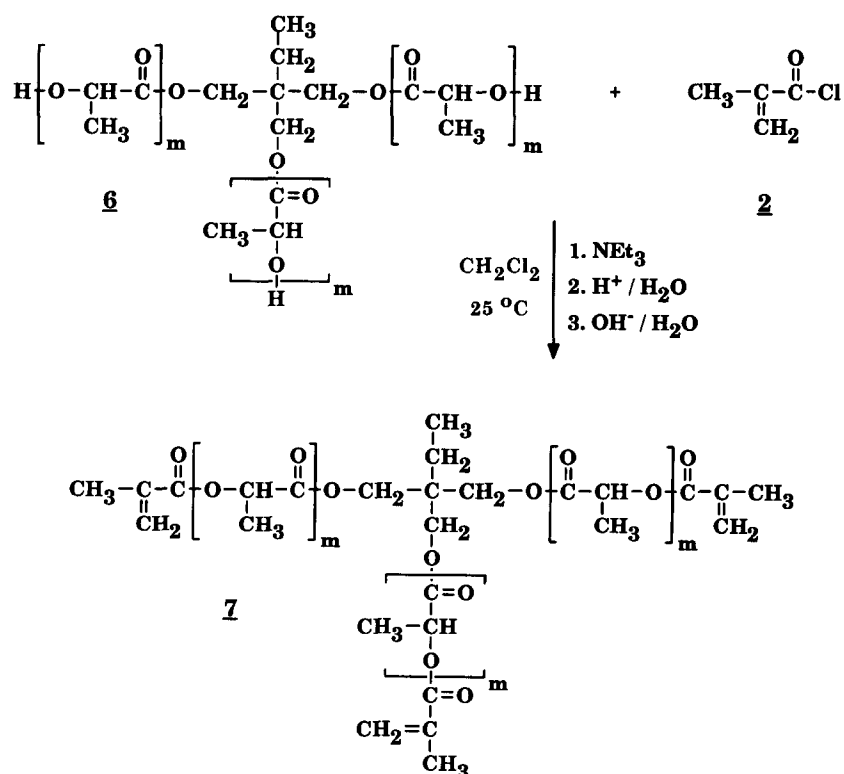
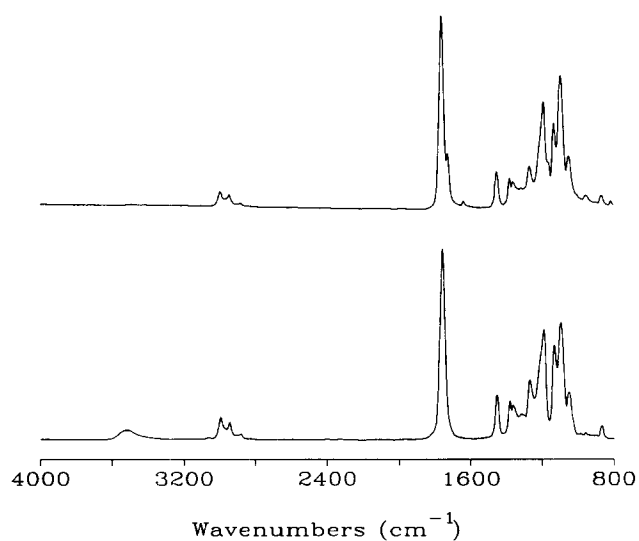
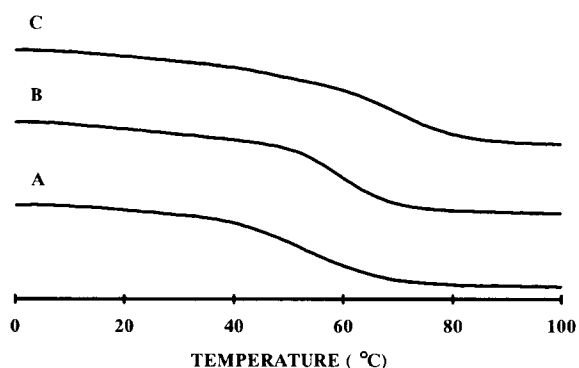


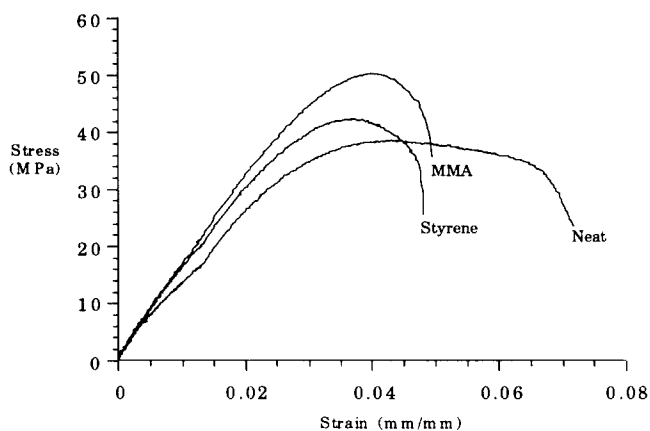
Figure 7 Synthesis of 3-arm methacrylate-endcapped poly(D,L-lactide) (7)



**Figure 8** Infra-red spectra of poly(D,L-lactide) triol (6) (lower trace) and 3-arm methacrylate-endcapped poly(D,L-lactide) (7) (upper trace)

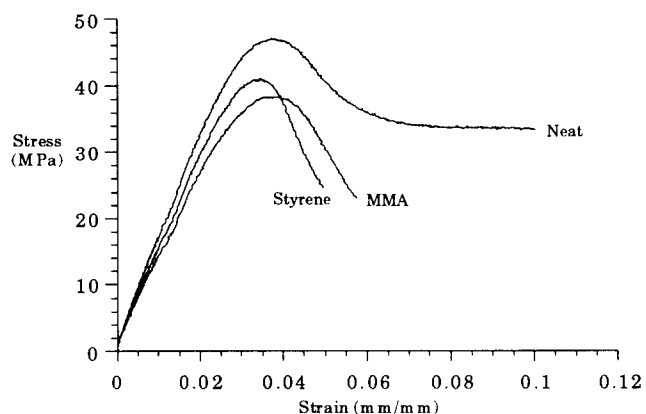


**Figure 9** D.s.c. thermograms of networks based on 3-arm methacrylate-endcapped poly(D,L-lactide) (7) ( $M_n=5100$ ), initiated with 1% 2-butanone peroxide: (A) MMA copolymer; (B) styrene copolymer and; (C) homopolymer

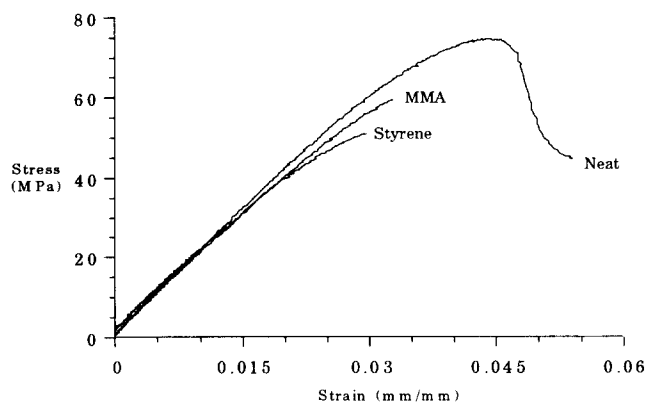


**Figure 10** Stress-strain curves of homopolymer (7) ( $M_n=2300$ ) and copolymer networks initiated with 1% 2-butanone peroxide

and for the networks based on the two higher-molecular-weight prepolymers, were also higher in tensile strength and modulus than the corresponding copolymer networks. Thus a reactive, monomeric diluent is neither necessary nor desirable for the processing of networks and/or composites from these prepolymers, and this is a tremendous advantage if we consider the obvious risks otherwise posed by the presence of unreacted, residual



**Figure 11** Stress-strain curves of homopolymer (7) ( $M_n=5100$ ) and copolymer networks initiated with 1% 2-butanone peroxide



**Figure 12** Stress-strain curves of homopolymer (7) ( $M_n=8700$ ) and copolymer networks initiated with 1% 2-butanone peroxide

monomers in polymer networks that are designed for implantation.

## CONCLUSIONS

It has been shown that methacrylate-terminated polyesters (3, 7) are viable intermediates in the formation of biodegradable networks. In the caprolactone-based prepolymer (3) the methacrylate groups reduced the hydrogen bonding, thus lowering the viscosity. This lowered viscosity enabled networks to be prepared without the use of organic solvents; this should allow for the synthesis of higher-molecular-weight prepolymers, and offers potential for the fabrication of bioabsorbable composites. The presence of the more reactive methacrylate group in the prepolymer, as opposed to materials containing the less reactive fumarate-based double bonds, which have been described previously<sup>4-6</sup>, allowed substantial crosslinking in all of the networks without the use of reactive diluents.

The extraction studies showed that the networks produced with styrene and methyl methacrylate copolymerized reasonably well; however, surprisingly the networks made with 2-methylene-1,3-dioxepane did not. Bailey *et al.*<sup>9</sup> have shown that 2-methylene-1,3-dioxepane copolymerizes better with methyl methacrylate at higher cure temperatures (120°C); thus our system could possibly be improved by using higher cure temperatures.

In the lactide-based homopolymer (7) networks, increased glass transition temperatures, ultimate strengths, and tensile moduli, when compared to the results obtained for the corresponding copolymer networks,

illustrated that a higher degree of crosslinking may be achieved, *without reactive comonomers*, through the incorporation of terminal methacrylate groups in the prepolymer. This is a tremendous advantage since it eliminates the risks otherwise posed by the presence of residual olefinic monomers in polymer networks that are designed for implantation. These results were further confirmed by the low sol contents (3–8%) of the networks, which were obtained from the extraction studies.

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