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Synthesis, characterization and crosslinking of functional star-shaped poly(ε-caprolactone)

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Abstract: Star-shaped low molecular weight poly(ε-caprolactone)s (PCLs) were synthesized and functionalized with crosslinkable terminal groups for subsequent crosslinking. The ε-caprolactone (CL) prepolymers were polymerized by ring-opening in the presence of polyglycerine (PGL) as an initiator (1, 3 and 5 mol%) and Sn(II)2-ethylhexanoate as a catalyst. Characterization of the prepolymer by $^{13}C/^{1}H$ nuclear magnetic resonance (NMR) spectroscopy, size exclusion chromatography (SEC), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) revealed a six-armed star-shaped structure for the prepolymer with the molecular weight controlled by the ratio of PGL and CL. Functionalization of the hydroxyl-terminated prepolymer was carried out with maleic or itaconic anhydride. In both cases, the characterization of the functionalized prepolymer showed that the hydroxyl groups were completely substituted. The functionalized PCLs were successfully crosslinked through the reaction of double bonds. The crosslinking was induced either thermally with organic peroxide or photochemically with a photosensitive initiator. Characterization of the crosslinked PCLs by Soxhlet extraction, DSC and FTIR showed that the itaconic double bond was much more reactive in thermal crosslinking than the maleic double bond. Thus, the crosslinked prepolymers that were functionalized with itaconic double bonds achieved a gel content of about 90%. A gel content of 100% was achieved with several compositions where crosslinking agents were employed.

Keywords: poly(ε-caprolactone); polyglycerine; crosslinking; itaconic anhydride; maleic anhydride

INTRODUCTION

Poly(ε-caprolactone) (PCL) and poly(L-lactide) (PLLA) have been under extensive study since they were introduced as potential biodegradable polymers. Most of the polymerization studies have dealt with the synthesis of linear[1–5] and branched[6–11] polymers. Crosslinking of these polymers has received less attention, but is of great interest because it would expand the possible applications.[12–16] Among other things, the rate and mechanism of degradation are then changed, leading to a longer and steadier degradation.[17,18] Steadily degrading polymer matrix material is advantageous in many controlled drug-release applications as a means of preventing dose dumping.[19] Other applications[13,14,20–23] for crosslinked biopolymers include hydrogels and slowly degrading orthopaedic implants, which are gradually replaced by human bone during the healing process.

Direct polycondensation can be applied to introduce a large amount of crosslinkable double bonds along the polymer chain. Fumaric acid for instance, or some other biocompatible Kreb's cycle intermediate acid[23] can be used in polycondensation of biopolymers.[18] There are some drawbacks, however. By-products are formed, the reaction time tends to be long and the reaction rarely reaches full conversion.[24] Moreover, it has been shown that the terminal double bonds are more reactive than those introduced along the polymer chain[25] by direct polycondensation. An alternative method to direct polycondensation is to prepare a prepolymer and functionalize its end-groups. Hydroxyl-terminated poly(ε-caprolactone), poly(lactic acid)s (PLAs) and poly(glycolide) have been functionalized in this way with maleic anhydride,[18] fumaric acid,[18] acrylates[26] and (3-isocyanatopropyl)triethoxysilane.[27] In addition, the patent literature mentions the possible use of itaconic acid anhydride.[28]

Previously, we have used methacrylic anhydride[29] and (3-isocyanatopropyl)triethoxysilane[30] to obtain crosslinkable functionalization in polylactides. We have also used succinic anhydride in the replacement of hydroxyl end-groups of PCL with carboxyl groups.[31] It was of interest, therefore, to find out if cyclic unsaturated anhydrides could be used in a similar way to succinic anhydride to introduce a crosslinkable functionality into the polymer. With this

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end in view, we synthesised star-shaped poly(ε-caprolactone) and functionalized it with maleic or itaconic anhydride. The functionalized polymers were then crosslinked in reactions induced either thermally or photochemically.

EXPERIMENTAL

Materials

The ε-caprolactone (CL, Solvay) was dried in the presence of molecular sieves. The polymerization catalyst, Sn(II)2-ethylhexanoate ($SnOct_2$), was supplied by Sigma. The polymerization initiator was polyglycerine-06 (PGL, Daicel Chemical Industries Ltd) and it was used as received. According to the manufacturer, the initiator contained an average of eight hydroxyl groups. Maleic (MA) and itaconic (IA) anhydrides were obtained from Fluka and hydroquinone was from Riedel-de Haën. *N*-Vinyl-2-pyrrolidone (NVP, Fluka), 2-hydroxyethyl methacrylate (HEMA, Fluka) and styrene (ST, Acros) were used as crosslinking agents. HEMA (300 ppm) and ST (15 ppm) contained hydroquinone monoethylether as an inhibitor against premature reaction of the double bonds. The crosslinking agents were used as received. 2-Butanone peroxide (MEKP), cobalt naphthenate (8% solution), camphore quinone (CQ) and ethyl-4-*N*,*N*′-dimethylaminobenzoate (4EDMAB) were supplied by Fluka.

Polymerization of prepolymer and functionalization procedure

Polymerizations were carried out in a 2.5 dm^3 batch reactor under nitrogen atmosphere. ε-Caprolactone, polyglycerine (1, 3 and 5 mol%) and $SnOct_2$ (0.02 mol%) were fed simultaneously into the preheated (150 °C) reactor. The reaction time was 5 h and the batch sizes were 0.6–1.0 kg. The functionalization of the prepolymer was carried out in a 0.15 dm^3 batch reactor under nitrogen atmosphere. Prepolymer and an equimolar amount of anhydride in relation to the hydroxyl groups were fed simultaneously into the preheated reactor (120 °C). No catalyst was used. After 1 h the temperature was raised to 140 °C for 30 min to ensure complete conversion of the reactants. Hydroquinone (100 ppm) was added during the cooling of the batch to prevent premature crosslinking during storage.

Crosslinking procedure

The thermal crosslinking experiments were carried out in glass test tubes at 50 °C for 24 h. The functionalized prepolymer was melted and the crosslinking agent (if used) was added and mixed. Peroxide (1.0 wt% with respect to the total weight of the reaction mixture) was carefully mixed into the reaction mixture before addition of the accelerator (Co-napth, 0.15 wt%), because the two form an explosive compound if added simultaneously. The batch sizes in the thermal crosslinking were 3.0–4.5 g. Tests were done in normal atmosphere. The photochemical crosslinking experiments were carried out at room temperature. Functionalized prepolymer, crosslinking agent (if used), CQ (0.2 wt%) and 4EDMAB (0.8 wt%) were mixed all at the same time and the reaction mixture was poured onto a metal sheet to a thickness of approximately 1 mm. This film was exposed to visible light (400–500 nm) for 5 min. The maximum exposure intensity was 800 mW cm^{-2}.

Characterization

The ^1H NMR measurements were recorded on a Varian XL-300 NMR spectrometer working at 300.032 MHz. The samples were dissolved in $CDCl_3$ in 10 mm NMR tubes at room temperature. The sample concentration was about 1% by weight for proton. Proton decoupled ^{13}C NMR spectra were obtained with the Varian XL-300 NMR spectrometer working at 75.452 MHz. The sample concentration in 10 mm tubes was 10% by weight in $CDCl_3$.

The molecular weights ($\overline{M}_n$ and $\overline{M}_w$) and the molecular weight distributions (MWD) were determined by room temperature size exclusion chromatography (SEC) (Waters System Interface module, Waters 510 HPLC pump, Waters 410 differential refractometer, Waters 700 satellite wisp and four PL gel columns (10^4, 10^5, 10^3 and 100 Å) connected in series). Chloroform (Riedel-de Haën) was used as solvent and eluent. The injected volume was 200 µl and the flow rate was 1 ml min^{-1}. Monodisperse polystyrene standards were used for primary calibration.

The thermal properties were determined with a Mettler Toledo Star DSC821 differential scanning calorimeter (DSC) in the temperature range −100 to 100 °C for the prepolymers and −100 to 210 °C for the crosslinked samples, at the heating and cooling rate of 10 °C min^{-1}. The residual reactivities of the crosslinked samples were observed from the first heating scan, during which the double bonds were expected to react completely. The glass transition temperatures were recorded during the second heating scan.

Fourier transform infrared spectroscopy was performed on a Nicolet Magna-FTIR 750 spectrometer. The prepolymer samples were film cast onto a potassium bromide plate from 1 wt% chloroform solutions. The crosslinked samples were analysed from thin films (about 0.5 mm), which were cut from the cured samples.

The gel content (ie the degree of crosslinking) of the polymers was measured by extracting the soluble phase into acetone in a Soxhlet apparatus for 20 h (ASTM D2765). The gel content was determined as the portion (in per cent) of the non-extractable material divided by the total weight of the original sample.

The mechanical properties were measured for five parallel specimens that had been preconditioned for 72 h at 23 °C and 50% relative humidity. An Instron 4204 testing machine was used to determine the

values, adapting the standards ISO 527-1993(E) on tensile, ISO 178-1998(E) on flexural and ASTM F451-86 on compression tests. The crosshead speed was $1\,mm\,min^{-1}$. The test samples for tensile and flexural tests were cut from the film casting, which was 4 mm in thickness. The test samples for the compression tests were prepared in a glass test tube, cured and cut to the required length. All the samples prepared for mechanical testing had been crosslinked thermally.

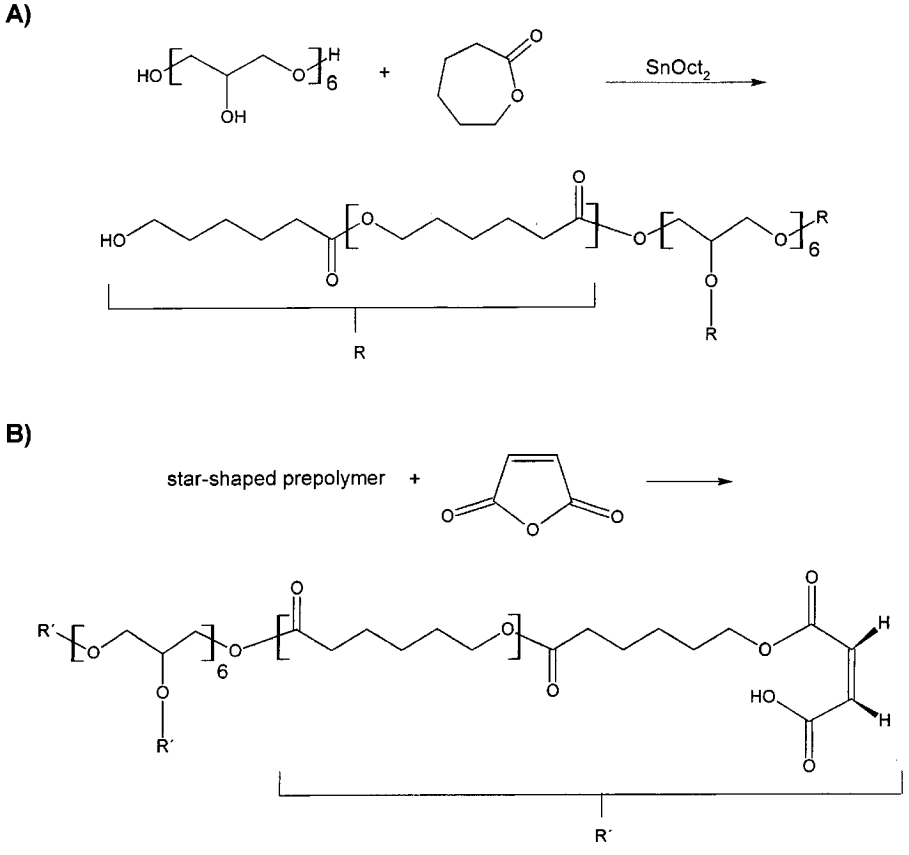
RESULTS AND DISCUSSION

The ε-caprolactone prepolymers were polymerized by ring-opening with different ratios of polyglycerine initiator, which produced branched OH-terminated polyesters with tailored molecular weight. The substitution of the hydroxyl terminal groups of the prepolymer was made with a double bond bearing anhydride (maleic or itaconic). The synthesis of the prepolymer and the reaction of cyclic anhydride (maleic anhydride) is shown in Scheme 1. Crosslinking through double bonds of the functionalized prepolymers was induced either thermally with the use of an organic peroxide initiator or photochemically with visible light by using a photosensitive initiator. Crosslinking agents were also used to increase the crosslinking density.

Polymerization of hydroxyterminated prepolymers

The SEC results showed that the molecular weight of the ε-caprolactone prepolymer could be tailored, as expected,[6] by varying the proportion of polyglycerine-06 (Table 1). The SEC instrument was calibrated with narrow polystyrene standards, and therefore SEC results were used only as a qualitative tool to check the peak shape and size distribution of the different polymers. The SEC curves of the prepolymers were symmetrical and unimodal, and no trace of unreacted ε-caprolactone was detected. In addition, the molecular weight distributions were quite narrow. Thus, the tailoring of the prepolymer structure was controlled and the conversion was shown to be high.

^{13}C NMR and ^{1}H NMR spectra of the prepolymer are shown in Figs 1(c) and 2(c), respectively. The conversion of the ε-caprolactone was shown, on the basis of the ^{1}H NMR analysis, to be close to 100% because there was no resonance of the monomer (—CH_2—COO—) at the chemical shift of 2.63 ppm. The number of arms of the star-shaped prepolymer was determined from the ^{13}C NMR spectrum. In the case of the PCL5 prepolymer, the average number of CL units per arm was 3.2. This was calculated from the ratio of the integrals at the chemical shifts of 173.8 and 173.6 ppm, assigned to carbons '17' and '23', respectively, in Fig 1(c). The number of CL (95 mol%) units per PGL unit (5 mol%) in the feed was theoretically 19, which indicated the presence of a six-armed (19/3.2 = 5.9) star-shaped polymer. In other words, approximately six of the eight hydroxyl groups of the PGL were capable of initiating the ring-opening polymerization. The ^{1}H NMR spectrum of the star-shaped prepolymer could not be used for determina-



Scheme 1. Reaction schemes showing (A) polymerization of the prepolymer and (B) functionalization with maleic anhydride.

	DSC		SEC			
Polymer[a,b]	T_g (°C)	T_m (°C)	$\overline{M}_w$ (g mol^{-1})	$\overline{M}_n$ (g mol^{-1})	MWD	$\overline{M}_n$[c] (g mol^{-1})
PCL1	−64	46	20800	17500	1,2	11800
PCL3	−59	24, 34	7200	5700	1,2	4200
PCL5	−57	8, 22	4500	3200	1,4	2600
PCL1+MA	−48	42, 49	13100	7200	1,8	12400
PCL1+IA	−55	39, 47	17800	9200	1,9	12400
PCL3+MA	−52	30	5800	3800	1,5	4800
PCL3+IA	−50	29	7600	3600	2,1	4800
PCL5+MA	−47	–	5500	2500	2,2	3200
PCL5+IA	−46	8	5300	3000	1,8	3300

[a] The number refers to the mol% of PGL used in the polymerization.
[b] MA and IA refer, respectively, to maleic and itaconic anhydride.
[c] Calculated as [CL]/[PGL] × M(CL) + M(PGL) + 8 × M(anhydride).

Table 1. Properties of the prepolymers and functionalized prepolymers

tion of the number of the initiating hydroxyl groups because of overlapping of the PGL resonances with the resonance of protons '7' and '8' of PCL (see Fig 2c).

Functionalization of the prepolymer

The SEC analyses showed a slight decrease of the molecular weight after functionalization, and a distinct widening of the MWD. The decrease of molecular

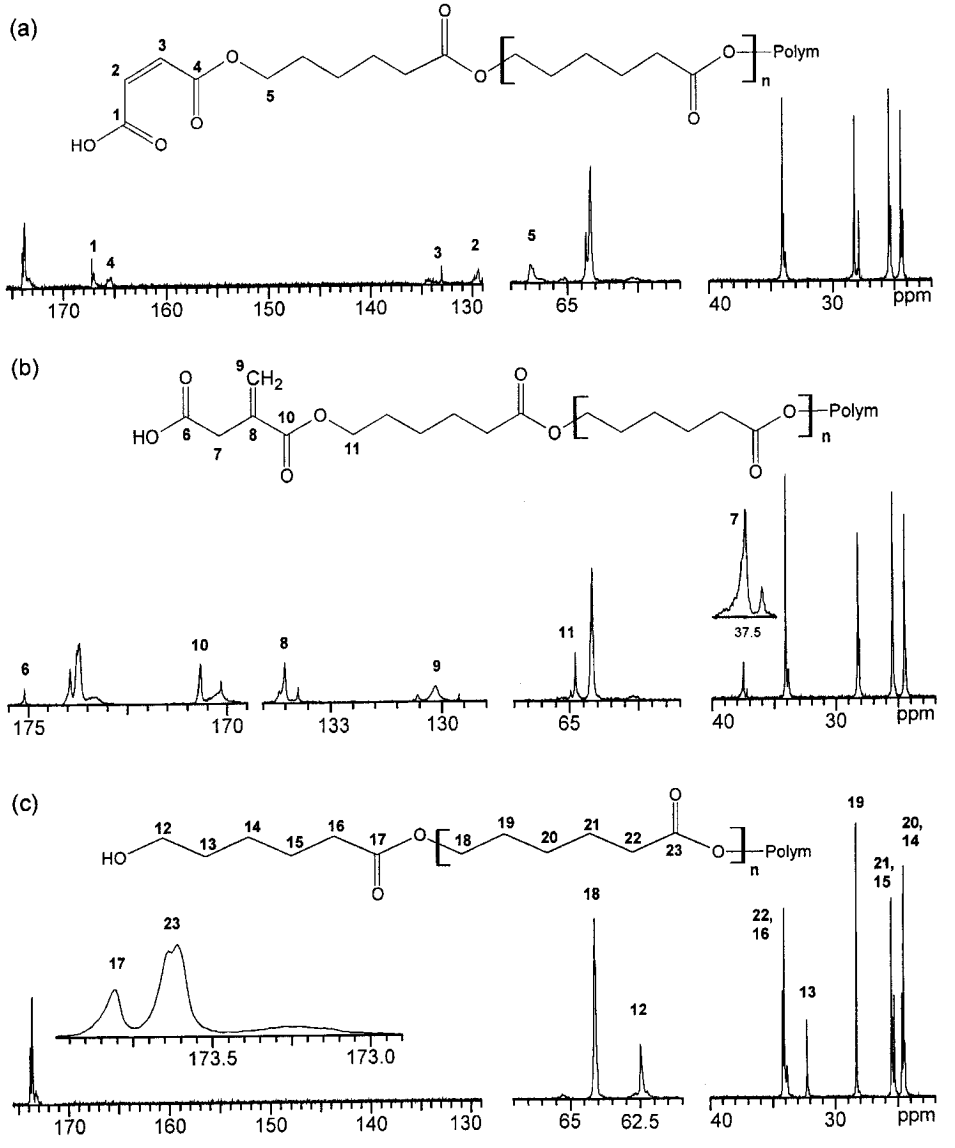


Figure 1. ^{13}C NMR spectra of (a) maleic double bond functionalized prepolymer, (b) itaconic double bond functionalized prepolymer and (c) PCL prepolymer.

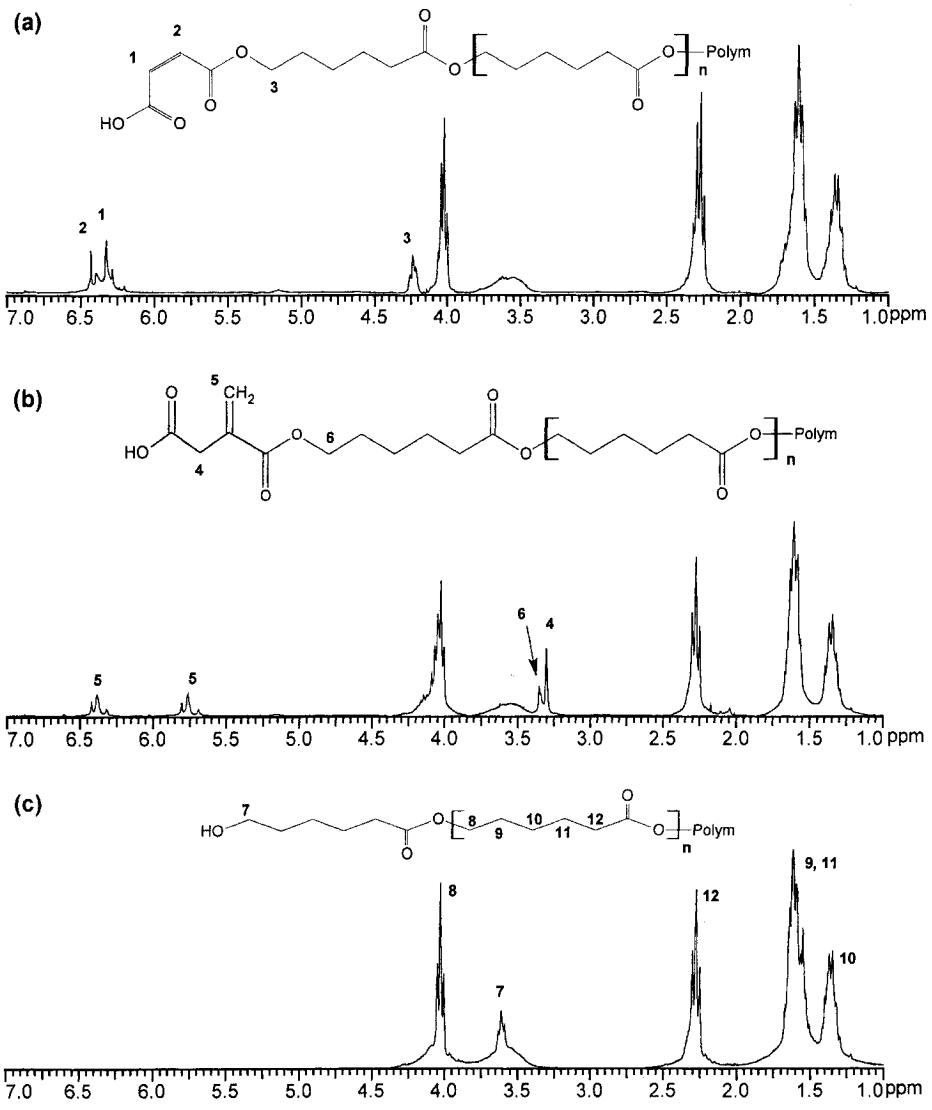


Figure 2. ^{1}H NMR spectra of (a) maleic double bond functionalized prepolymer, (b) itaconic double bond functionalized prepolymer and (c) PCL prepolymer.

weight after functionalization could be explained by the change in the polymer hydrodynamic volume in the SEC analyses,[9] but the simultaneous widening of the MWD indicates some side reactions. Side reactions that can widen the MWD include intramolecular and intermolecular transesterifications. Possibly the side reactions were enhanced by the formation of carboxylic end-groups in the functionalization phase.

The degree of substitution in the functionalization was nearly 100% with both maleic and itaconic anhydride because there was no sign of unreacted anhydride monomer in the ^{1}H NMR spectra at 7.46 ppm for δ(MA) (—C<u>H</u>=C<u>H</u>—COO—) or at 5.89 ppm for δ(IA) (C<u>H</u>$_2$=). It was further observed that the peaks for the hydroxymethylene resonances (^{1}H NMR δ = 3.61 ppm and ^{13}C NMR δ = 62.5 ppm) disappeared after functionalization. Although this observation was somewhat disturbed by the PGL resonances that overlapped with the hydroxyl group peak of the prepolymer, it was confirmed by the complete disappearance of the end-group methylene '13' (Fig 1) during functionalization.

Possible side reactions occurring during functionalization include double bond saturation induced by oxygen or hydroxyl group *via* electrophilic addition, and *cis–trans* isomerization of maleic acid to fumaric acid.[32] However, no chemical shifts were found for saturated MA at δ = 2.8–3.1 ppm[13] (Fig 2a) or for IA (Fig 2(b), no unexpected peaks). Isomerization of MA[13] was detected instead (^{1}H NMR δ = 6.83 ppm) but at a level lower than 1%. A higher degree of isomerization could be expected to increase the crosslinking density in the subsequent crosslinking phase because the fumaric double bond is more reactive in the crosslinking than the maleic bond.

The FTIR analyses confirmed the functionalization, because the hydroxyl absorption (3510 cm^{-1}) of the prepolymer changed to carboxyl absorption (3200 cm^{-1}) (Fig 3). Also, the appearance of carbon–carbon double bond absorption was detected at 1640 cm^{-1}. Because no unreacted monomer was detected in the NMR analyses, the double bond absorption must originate from the double bonds linked to the prepolymer.

The synthesized PCL prepolymers were semicrystalline. As the molecular weight of the prepolymer increased (see Table 1) the thermal properties approached those of linear high-molecular-weight

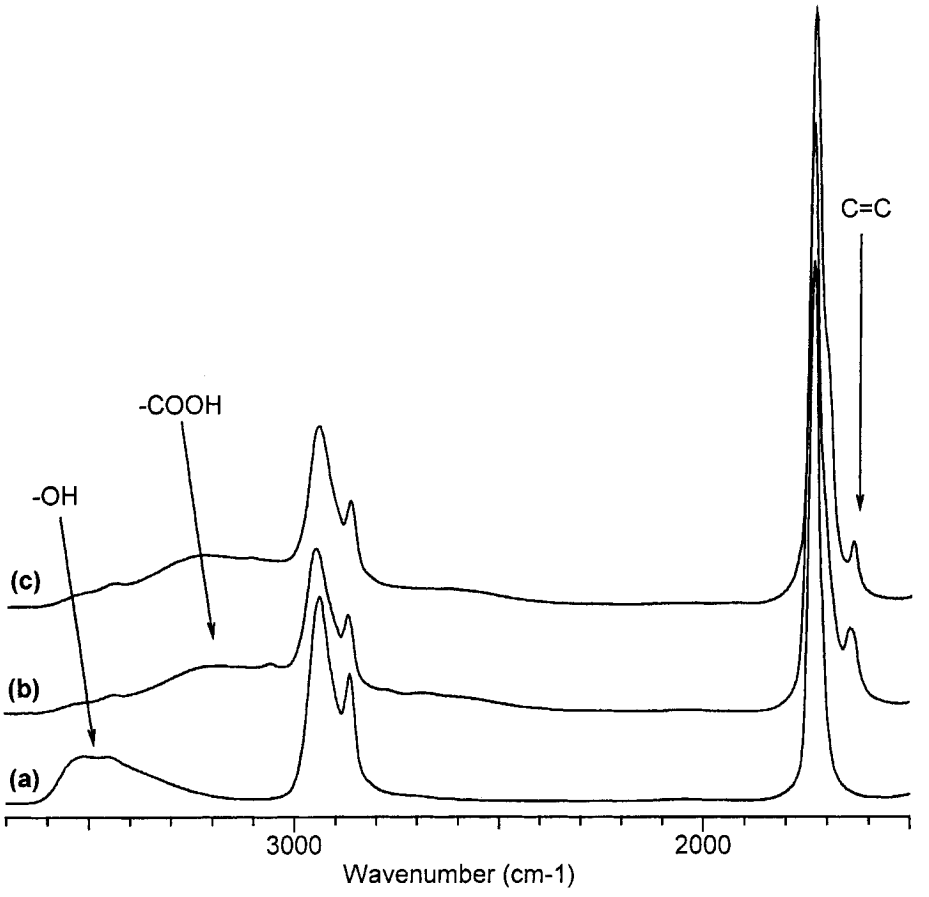


Figure 3. FTIR spectra of (a) PCL prepolymer, (b) maleic double bond functionalized prepolymer and (c) itaconic double bond functionalized prepolymer.

PCL (T_g −60 °C, T_m 60 °C).[33] The DSC analyses showed the glass transition temperature to increase with substitution of the terminal groups of the prepolymer. Both PCL3 and PCL5 exhibited two melting endotherms, while PCL1 exhibited one endotherm with a shoulder. Multiple melting endotherms are generally observed for branched polymers,[9,11,34] although the phenomenon has not been unambiguously explained. Functionalization of PCL1 caused the melting endotherm to split into two (Fig 4). However, when the length of the polymer chain was shorter, the functionalization prevented crystallisation, as can be seen in the absence of a melting endotherm for sample PCL5+MA.

Crosslinking of functionalized prepolymers

Prepolymers of three different molecular weights were synthesized to study the effect of crosslinking density. Furthermore, the crosslinkability was improved with three different crosslinking agents: styrene (ST), *N*-vinyl-2-pyrrolidone (NVP) and 2-hydroxylethyl methacrylate (HEMA). The crosslinkability was analysed with use of Soxhlet extraction as the primary method and with DSC and FTIR as additional methods.

Effect of structure of the functionalized prepolymer on crosslinkability

The Soxhlet extractions showed the itaconic double bond to be more reactive than the maleic one. This is seen in Fig 5 in terms of the much higher gel contents

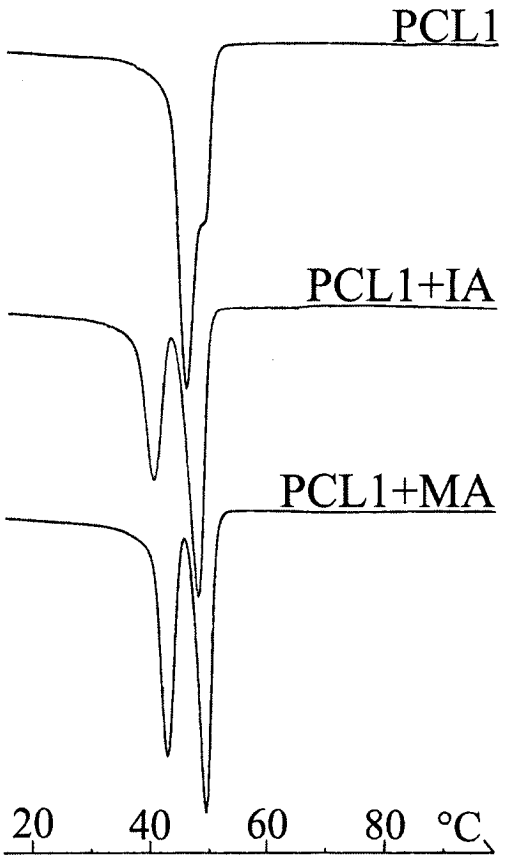


Figure 4. DSC melting endotherms of PCL prepolymer (top), itaconic double bond functionalized prepolymer (middle) and maleic double bond functionalized prepolymer (bottom).

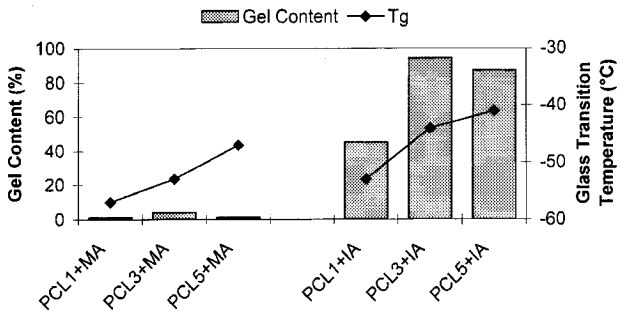


Figure 5. Effect of the functional group on the gel content of thermally crosslinked polymer (with no crosslinking agent). The corresponding glass transition temperatures are marked on the right-hand vertical scale.

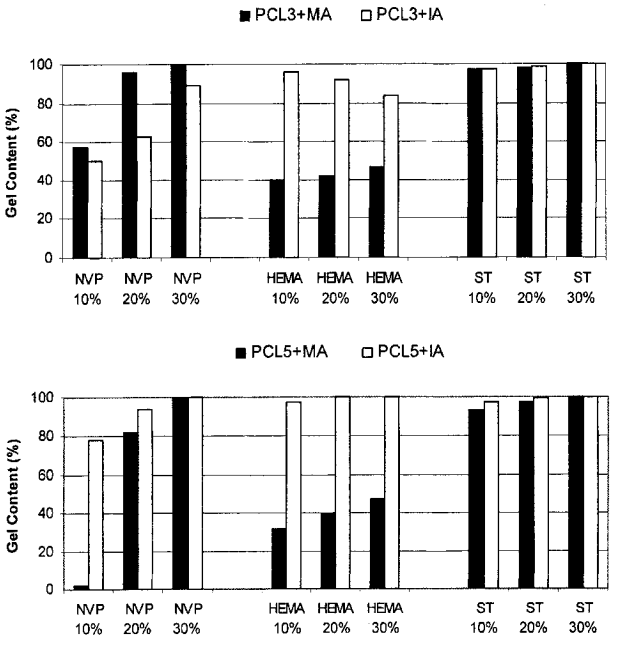


Figure 6. Effect of type and amount of crosslinking agent on the gel content of thermally crosslinked polymers.

for the IA functionalized prepolymers that were crosslinked without crosslinking agent. As a pendant group, the itaconic double bond is sterically less hindered and reacts better in the crosslinking than does the maleic double bond. In fact, the IA-functionalized prepolymers were reactive enough to crosslink spontaneously at room temperature when not inhibited with hydroquinone. Because the proportional amount of the functional groups depends on the size of the macromonomer, it can be expected that the smaller prepolymer leads to higher achievable crosslinking density.[16] This was seen as an increase in the glass transition temperature with decreasing molecular weight of the prepolymer. However, the highest gel content was achieved with the functionalized PCL3 polymer.

Effect of crosslinking agent

The effect of the crosslinking agent on the gel content of the thermally crosslinked polymer samples is shown in Fig 6. The gel content of both PCL3 and PCL5 increased up to nearly 100%, with increase in the NVP concentration. In the presence of ST, the samples were well crosslinked even at low concentrations. The use of HEMA improved the gel content at low concentration (10wt%) (Fig 6). However, owing to the incompatibility of HEMA with the functionalized prepolymers, there was no further improvement in gel content with the 20 and 30wt% HEMA concentrations. The incompatibility was seen as a formation of a separate HEMA phase in samples that crosslinked slowly (PCL1 samples, results not shown here).

It needs to be noted that the gel content does not directly represent the degree of crosslinking, and slight residual reactivity was detected even with the samples of 100% gel content. The excessive gel contents are explained by the interlocking of unreacted fragments in a reasonably dense polymer network which prevents their extraction, or by unreacted chain ends of the polymer network which likewise are not extracted. In addition to residual reactivities, it was noticed that some of the poorly crosslinked samples had a melting endotherm.

The FTIR analyses done on highly crosslinked prepolymer samples confirmed the reaction of double bonds during crosslinking. The disappearance of the double bond absorption (1640 cm^{-1}) was detected after crosslinking, ie the double bonds generated in the functionalized prepolymer (and by the crosslinking agent if used) had reacted.

Table 2. Selected properties of the crosslinked polymers as compared to linear PCL

Material	*Tensile modulus (MPa)*	*Flexural modulus (MPa)*	*Tensile strength (MPa)*	*Tensile strain (%)*	*Compressive strength (MPa)*	*Glass transition (°C)*
Linear PCL[33]	260	n.d.	15.5	>100	n.d.	−60
Crosslinked PCL[a]	30	20	1.4	11.0	30	−41
Crosslinked PCL[b]	420	220	13.9	15.5	120	−28
Crosslinked PCL[c]	100	70	4.8	21.1	n.d.	−28
Crosslinked PCL[d]	300	130	8.5	18.4	n.d.	15

[a] PCL5 functionalized with IA double bonds, crosslinked thermally.
[b] PCL5 functionalized with IA double bonds, crosslinked thermally with 30wt% NVP.
[c] PCL5 functionalized with IA double bonds, crosslinked thermally with 30wt% HEMA.
[d] PCL5 functionalized with MA double bonds, crosslinked thermally with 30wt% NVP.
n.d., not determined.

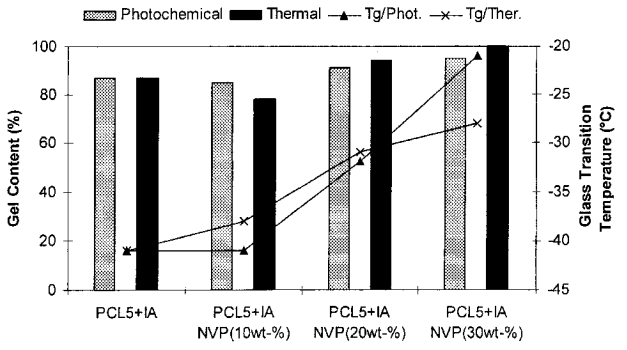


Figure 7. Comparison of the gel content of thermally and photochemically crosslinked samples. The corresponding glass transition temperatures are marked on the right-hand vertical scale.

Mechanical testing was conducted on selected thermally crosslinked samples and the results were compared with those obtained for linear PCL. The samples crosslinked without crosslinking agent appeared rubbery and lacked mechanical strength. The utilization of a crosslinking agent produced harder rubbers with higher mechanical strength. Appropriate mechanical properties were achieved, for example, with PCL5+IA with 30 wt% NVP, as shown in Table 2.

Thermal versus *photochemical crosslinking*

Photochemical crosslinking was carried out with the functionalized PCL5 prepolymers with the purpose of comparing thermally and photochemically crosslinked samples. The results of the comparison are shown in Fig 7. Crosslinking of the IA functionalized PCL5 prepolymer was the same whether the crosslinking was thermally induced or photo induced. In contrast, according to the gel content results, the MA functionalized PCL5 prepolymer did not crosslink at all in photo induced crosslinking (data not shown). Both NVP and HEMA, at all concentrations (10, 20 and 30 wt%), increased the gel content to the same level as in the thermally crosslinked samples. From the chemical point of view, the thermal crosslinking suffered from air inhibition, which was seen as a slight tackiness at the air/mixture interface (but not on the surfaces against the mould). The photochemically crosslinked samples were not tacky, most probably because photochemical crosslinking was much quicker than thermal crosslinking. It has been suggested that fast curing overcomes the oxygen inhibition.[14]

CONCLUSIONS

ε-Caprolactone based crosslinkable polyesters were synthesized. Characterization showed the prepolymers to be of six-armed star-shaped structure. Thus, the polyglycerine used as initiator in the ring-opening polymerization had six initiating hydroxyl groups. The molecular weights were tailored by varying the ratio of polyglycerine and ε-caprolactone. In the functionalization phase, the hydroxyl groups of the prepolymer were reacted with a double-bond-bearing anhydride. According to the NMR and FTIR analyses, the degree of substitution was almost complete with both maleic and itaconic anhydrides.

Finally, the functionalized prepolymers were crosslinked. Crosslinking through double bonds was induced either thermally or by visible light, with use of an organic peroxide or a photosensitive initiator, respectively. A considerable degree of crosslinking, observed as gel content, was achieved without addition of crosslinking agent, and 100% gel content was achieved for many compositions with the use of a crosslinking agent. The results showed the itaconic double bond to be much more reactive than the maleic double bond. An increase in the degree of crosslinking raised the glass transition temperature noticeably. The best overall crosslinkability was achieved with the prepolymer that was prepared with 3 mol% polyglycerine as initiator and then functionalized with itaconic anhydride. No noticeable improvement was achieved with the use of prepolymers of smaller molecular weight.

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