

Structure Modification and Crosslinking of Methacrylated Polylactide Oligomers

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ABSTRACT: The effect of molecular architecture on the properties of crosslinked polylactides was studied. D,L-Lactide-based telechelic oligomers with different numbers of arms were functionalized with methacrylic anhydride. Functionalized oligomers were crosslinked with thermal initiation at 90°C, and the mechanical and thermal properties, as well as the gel content, were evaluated. The crosslinking density increased with the number of arms in the oligomers, and the compressive yield strength was built up at the same time. The best mechanical properties (compressive yield strength = 120 MPa, modulus = 2800 MPa, and strain = 5.0%) were obtained with cured polymers prepared with

a 100 : 8 ratio of lactide to pentaerythritol. When dimethacrylated butanediol was used as a reactive monomer in curing, polymers with high crosslinking density and mechanical strength were obtained at 37, 60, and 90°C. The use of the reactive monomer also enabled high conversions with photoinitiated crosslinking. Finally, hydrolytic degradation and strength retention were demonstrated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3616–3624, 2002

Key words: biopolymers; crosslinking; structure-property relations

INTRODUCTION

Biodegradable crosslinked polymers and composites thereof have been of interest to many research groups.^{1–7} Crosslinking provides polymers with properties differing from those of thermoplastic biopolymers, and new synthetic routes to biodegradable materials are opened. Fumarate-based polyesters, for example, have been used in the synthesis of bioresorbable bone-cement composites, which can be injected and cured *in situ*.^{1–3,8,9} The cured composites are reported to have mechanical properties suitable for trabecular bone replacements.³ As demonstrated by Domb et al.,⁵ the mechanical properties of poly(propylene fumarate) (PPF)-based bone cements can be further enhanced through diepoxide or divinyl functionalization.

PPF has reactive double bonds in every repeating unit. However, crosslinked polymers can be prepared from lactide or ϵ -caprolactone by the introduction of reactive groups into either the polymerization or functionalization of low molecular weight oligomers. In the latter case, the polymers contain only a limited number of reactive groups, but the reactivity of the terminal double bonds obtained by functionalization is higher than that of the double bonds along the polymer chains, and so highly crosslinked structures

can be obtained. Storey and coworkers^{1,10,11} synthesized a variety of fumarate- and methacrylate-functionalized oligomers from D,L-lactide and ϵ -caprolactone and their copolymers with glycolic acid or trimethylene carbonate. These oligomers were free-radically crosslinked: ϵ -caprolactone-based oligomers as such and D,L-lactide-based oligomers with an inert diluent.

All the aforementioned crosslinked polymers were cured by thermal initiation. However, curing can also be initiated with photosensitive compounds, as demonstrated by Anseth and coworkers.^{4,12–14} They produced photocrosslinked polymers with high moduli from methacrylated anhydride monomers. These surface-eroding polyanhydrides retain their mechanical properties during hydrolysis, and their degradation behavior and the cellular response can be altered by changes in the composition of the polymer. With the use of redox initiators in combination with photoinitiation, even complex three-dimensional geometries such as screws have been cured from methacrylated polyanhydrides.

The molecular structure of the crosslinked polymers was shown to have an effect on the dynamic mechanical and swelling properties by Peppas and coworkers.^{15,16} They synthesized networks based on water-soluble poly(ethylene glycol) with different numbers of arms and different chain lengths. Recently, we synthesized crosslinked polylactides through triethoxysilane functionalization, and it was found that the properties of the networks could be improved by the ad-

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justment of the molecular structure of the precursor polylactide oligomers.¹⁷ The mechanical strength of the networks was increased by the crosslinking density being increased. In this study, we applied similar structure tailoring to networks based on methacrylated polylactide oligomers. In other words, the objective of this study was to investigate the effect of the molecular architecture, that is, the number of arms in the oligomers and the crosslinking density, on the properties of crosslinked polylactides based on methacrylation. Telechelic polylactide oligomers with different numbers of arms and chain lengths were prepared. They were then functionalized with methacrylic anhydride (MAAH) and crosslinked by thermal initiation. To study the effects of the reactive monomer and curing temperature on the properties of the crosslinked polymers, we crosslinked the functionalized oligomers with dimethacrylated butanediol (BD-Me₂) at different temperatures. Finally, the possibilities of photoinitiation and hydrolytic degradation were demonstrated.

EXPERIMENTAL

Materials

Polylactide oligomers were polymerized from D,L-lactide (Purac) with 1,4-butanediol (BD; Fluka), pentaerythritol (PERYT; Acros Organics), and polyglycerine-06 or polyglycerine-10 (PGL-06 and PGL-10, respectively; Daicel Chemical Industries) as a coiniciator. Sn(II)octoate (Sigma) was used as an initiator in the ring-opening polymerization.

MAAH (Fluka) was used in the functionalization step. The crosslinking was performed thermally with dibenzoyl peroxide (DBPO; Akzo Chemicals) at 90°C or with 2-butanone peroxide (2-BP; Fluka Chemica) as an initiator and cobalt naphthenate (CoNapht; Merck) as a promoter at 60 and 37°C. In photoinitiation, camphorquinone (CQ; Fluka) was used as an initiator, and ethyl-4-*N,N*-dimethylaminobenzoate (4EDMAB; Fluka) was used as a promoter. BD-Me₂ (ABCR) was used as a reactive monomer.

Preparation of linear and star-shaped polylactide oligomers

The polylactide oligomers were polymerized from D,L-lactide in a batch reactor at 160°C for 3 h. The monomer was fed into the reactor with 0.02 mol % Sn(II)octoate as an initiator and an appropriate amount of a coiniciator (the monomer/coiniciator molar ratio was varied between 100 : 12.5 and 100 : 5). The samples are labeled with the lactide/coiniciator ratio used in the preparation. For example, poly(D,L-lactide) oligomers polymerized with a 100 : 5 ratio of lactide to butanediol are designated P(DLLA/BD 100 : 5). The

synthesis and properties of the oligomers are described in detail in a previous article.¹⁸

Functionalization of telechelic polylactide oligomers

Telechelic D,L-lactide-based oligomers were functionalized in a reaction of hydroxyl groups with MAAH. The stoichiometric amount of MAAH was calculated from the theoretical molecular weight of the synthesized oligomer and the functionality of the coiniciator, and double the stoichiometric amount of MAAH was used. The reaction was carried out in a glass vessel for 3 h at 120°C, and the product was purified by distillation under reduced pressure at 140°C.

Crosslinking of methacrylated polylactide oligomers

For crosslinking, the functionalized oligomers were heated to the reaction temperature (90°C), and 0.5 wt % DBPO was mixed with the functionalized oligomer. The mixture was stirred until homogeneity was achieved and was then applied to a bone-cement mold (ASTM F 451-86), producing cylindrical specimens (12 mm high and 6 mm in diameter). The samples were cured in the mold for 24 h at 90°C.

For crosslinking below 90°C, the functionalized oligomer and reactive monomer (BD-Me₂, 10–30 wt %) were first heated to 90°C and mixed until homogeneity was achieved. Then, the temperature was lowered to an appropriate reaction temperature (37 or 60°C), and 2-BP (1.0 wt %) and CoNapht (0.15 wt %) were added to initiate the crosslinking.

For photoinitiation, 1.0 wt % CQ and 4EDMAB were added as the initiator and promoter, respectively. Additions were made to the mixture of the functionalized oligomer and reactive monomer described previously. Curing was performed at 25°C with an ESPE Elipar Highlight instrument emitting blue light (400–500 nm) at approximately 800 mW/cm².

Characterization

The number-average molecular weights (M_n 's), weight-average molecular weights (M_w 's), and molecular weight distributions (MWDs) were determined relative to polystyrene standards by size exclusion chromatography (SEC). The Waters Associates system was equipped with a Waters 700 Satellite wisp injector, a Waters 510 HPLC solvent pump, four linear PL gel columns (10⁴, 10⁵, 10³, and 100 Å) connected in series, and a Waters 410 differential refractometer. All samples were analyzed at room temperature. Chloroform (stabilized with 1% ethanol; Riedel-de Haen Ag) was used as an eluent and was delivered at a flow rate of 1.0 mL/min. The samples were dissolved in chlo-

reform at a concentration of 1.0% (w/v). The injection volume was 200 μmL .

For $^1\text{H-NMR}$ measurements, the samples were dissolved in chloroform- d_1 (deuteration degree $\geq 99.8\%$; Fluka) in 5-mm NMR tubes at room temperature. The sample concentration was about 1.0% by weight. $^{13}\text{C-NMR}$ was performed with a 10% sample concentration in 10-mm tubes. NMR spectra were recorded on a Varian Gemini 2000 300-MHz spectrometer working at 300.032 MHz for $^1\text{H-NMR}$ and 75.445 MHz for $^{13}\text{C-NMR}$.

IR spectra were measured on a Nicolet Magna 750 spectrometer with a 2-cm^{-1} resolution with thin films for crosslinked samples and with KBr discs for uncrosslinked samples. The sample concentration in the discs was 1 wt %.

Differential scanning calorimetry (DSC) measurements were made on a Mettler Toledo Star^c DSC 821^c. The measurements were run from -40 to 180°C at a heating rate of $10^\circ\text{C}/\text{min}$ and at a cooling rate of $10^\circ\text{C}/\text{min}$. The glass-transition temperatures (T_g 's) of the oligomers and functionalized oligomers were measured during the second heating period. For crosslinked samples, the T_g value and residual reaction enthalpy (ΔH) were determined during the first heating period.

The degree of crosslinking (i.e., the gel content) of the polymers was measured by extraction of the soluble phase in acetone with a Soxhlet apparatus for 20 h (ASTM D 2765). The gel content was determined as the weight of nonextractable material divided by the total weight of the original sample and is expressed as a percentage.

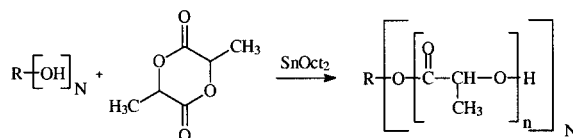
Compressive properties of the samples were measured on an Instron 4204 tensile testing machine with the standard ISO 604-1973(E). The compressive yield strength, strain, and modulus for the polymers were measured for five parallel air-conditioned specimens that had been left for 72 h at 23°C and 50% relative humidity.

A hydrolysis study was performed with five parallel weighed test specimens for each time point. Cylindrical specimens produced with bone-cement molds were immersed in 10 mL of a phosphate buffer solution (pH 7.0) at 37°C in test tubes. The buffer solution was changed once a month. The test specimens were recovered from the test tubes at different intervals and weighed, and their compressive properties were tested. Specimens were then vacuum-dried for 2 weeks and stored for further analysis.

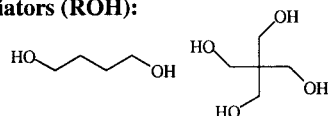
RESULTS AND DISCUSSION

Poly lactide oligomers were polymerized with coinitiators containing different numbers of hydroxyl groups, as shown in Scheme 1(A). The molecular structure of the oligomers was varied by changes in the coinitiator.

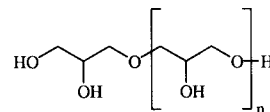
A. Ring-opening polymerization of lactide:



Co-initiators (ROH):

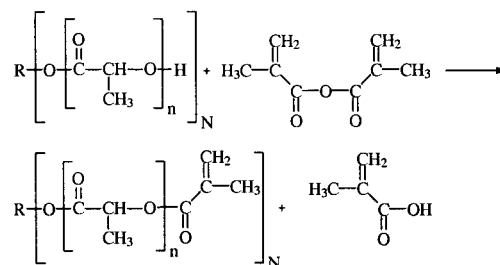


butanediol (BD) pentaerythritol (PERYT)

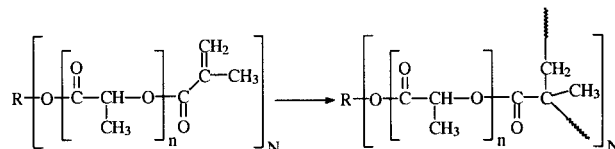


polyglycerine-06 and -10
(PGL-06 (n=5) and PGL-10 (n=9))

B. Functionalization with methacrylic anhydride:



C. Reaction of double bonds leading to crosslinking:



Scheme 1

An increase in the amount of the coinitiator caused the molecular weight to decrease, and this lowered T_g of the oligomers. Linear oligomers were obtained with butanediol, star-shaped four-arm oligomers were obtained with PERYT, and even more branched structures were obtained with polyglycerines (see Table I). All the oligomers were amorphous and hydroxyl-terminated, enabling further synthesis.

Functionalization of polylactide oligomers

Linear and star-shaped oligomers with controlled molecular weights were functionalized to make them crosslinkable. Functionalization was achieved by the reaction of MAAH with telechelic polylactide oligomers to yield methacrylated oligomers [Scheme 1(B)]. MAAH, instead of methacryloyl chloride, was chosen for functionalization as for the preparation of crosslinkable anhydride macromonomers.¹² The use of methacryloyl chloride with polylactide oligomers

TABLE I
Properties of D,L-Lactide-Based Oligomers Before and After Functionalization

| Sample | Theoretical | | | ¹ H-NMR | | | | SEC | | | DSC |
|------------------------|------------------|------------------|-----|--------------------|-------|-----------|-----------------------------|------------------|------------------|------|---------------|
| | M_n (g/mol) | L_{LA} (LA) | N | L_{LA} (LA) | N^a | DS (%) | Monomer ^b (%) | M_n (g/mol) | M_w (g/mol) | MWD | T_g (°C) |
| P(DLLA/BD 100:5) | 2970 | 10.0 | 2 | 10.0 | 2.0 | | | 5100 | 6300 | 1.22 | 30 |
| Functionalized | 3110 | | | | | 89 | 6 | 5100 | 6600 | 1.29 | 31 |
| P(DLLA/BD 100:10) | 1530 | 5.0 | 2 | 5.0 | 2.0 | | | 2500 | 3200 | 1.25 | 19 |
| Functionalized | 1670 | | | | | 87 | 2 | 2700 | 3400 | 1.26 | 21 |
| P(DLLA/PERYT 100:5) | 3020 | 5.0 | 4 | 5.9 | 3.4 | | | 4000 | 5400 | 1.36 | 34 |
| Functionalized | 3300 | | | | | 86 | 1 | 4500 | 5700 | 1.26 | 30 |
| P(DLLA/PERYT 100:8) | 1940 | 3.1 | 4 | 3.2 | 3.9 | | | 2800 | 3300 | 1.19 | 27 |
| Functionalized | 2220 | | | | | 100 | 7 | 3200 | 3900 | 1.20 | 27 |
| P(DLLA/PERYT 100:12.5) | 1290 | 2.0 | 4 | 2.1 | 3.8 | | | 1700 | 2200 | 1.24 | 13 |
| Functionalized | 1570 | | | | | 100 | 8 | 2300 | 2900 | 1.22 | 19 |
| P(DLLA/PGL-06 100:5) | 3340 | 2.5 | 8 | 5.0 | 4.0 | | | 3500 | 4300 | 1.22 | 23 |
| Functionalized | 3890 | | | | | 97 | 2 | 4200 | 5500 | 1.30 | 22 |
| P(DLLA/PGL-10 100:5) | 3640 | 1.7 | 12 | 2.4 | 8.3 | | | 2900 | 3700 | 1.27 | 23 |
| Functionalized | 4470 | | | | | 100 | 2 | 3900 | 5200 | 1.33 | 22 |

^a (L_{LA}) and N were evaluated in ref. 18.

^b The Residual amount of MAAH and MA.

has been reported previously.^{10,11} The properties of the oligomers before and after functionalization are presented in Table I.

As observed with ¹H-NMR, functionalizations proceeded to degrees of substitution (DSs) of 86–100%. The disappearance of the resonances (4.32 and 2.69 ppm; Fig. 1) due to hydroxyl termination of lactide oligomers was used for the calculation of the DS of the methacrylations. The DS approached 100% for most of the star-shaped oligomers, but, unexpectedly, only 87–89% of the hydroxyl groups in linear oligomers reacted with MAAH. Common to all of the functional-

izations that led to high DS values (>95%) was the use of a high absolute amount of MAAH because of the high hydroxyl content in the oligomers. We suggest that a large amount of MAAH served as a diluent. It lowered the viscosity and increased the reaction rate, leading to higher DS values. Moreover, the amount of MAAH used in the functionalization reactions was set at twice the theoretical number of polymer hydroxyl end groups. In general, the initiation activity of the star-shaped coiniciators was slightly lower than the theoretical activity. This led to a lower number of hydroxyl-terminated branches in the branched oli-

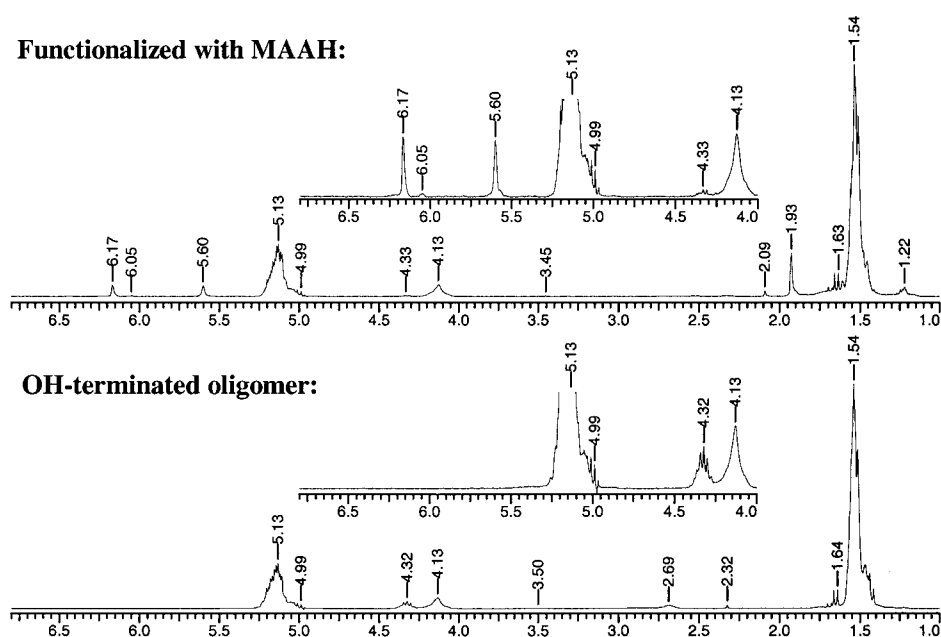


Figure 1 ¹H-NMR spectra of P(DLLA/PERYT 100:5) before and after functionalization. The insets (6.8–4.0 ppm) show the region in which the quantitative analysis was made.

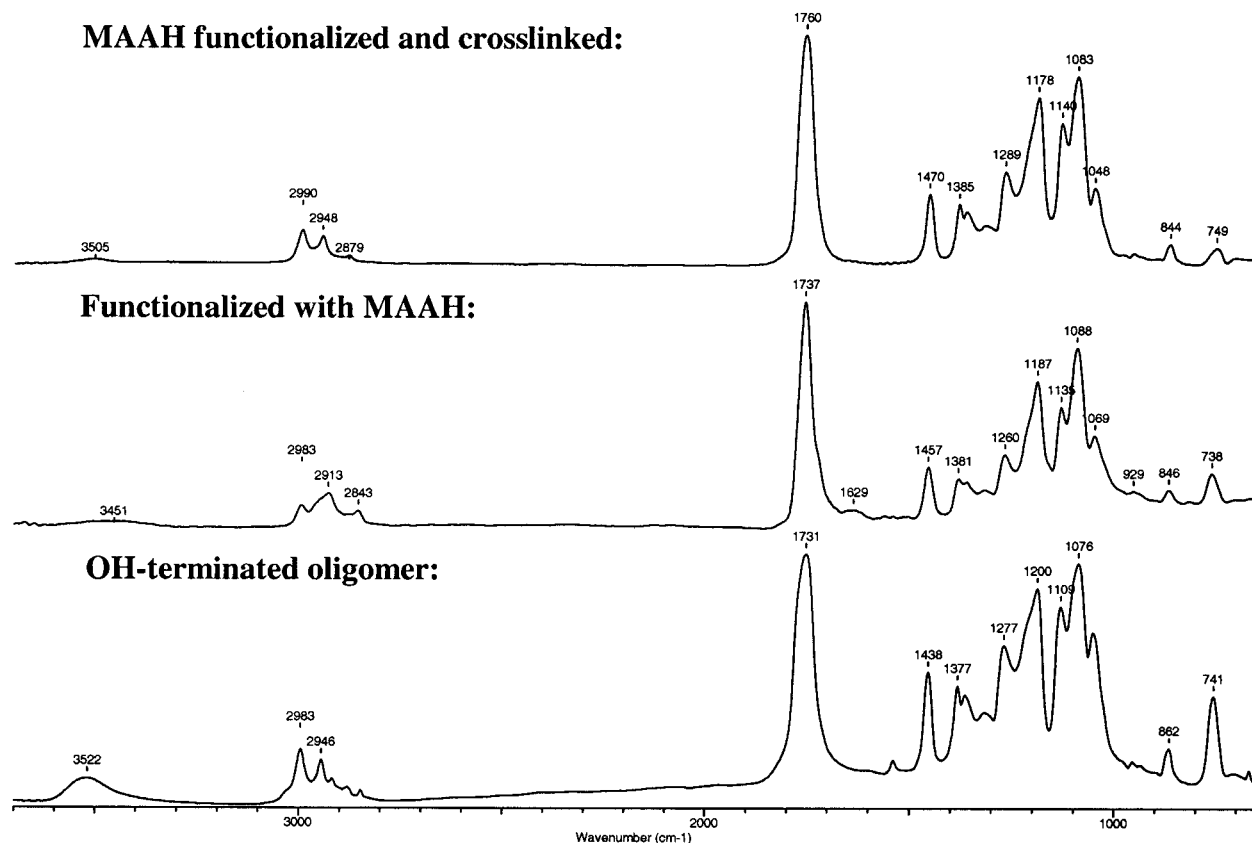


Figure 2 Effect of methacrylic functionalization and crosslinking on P(DLLA/PERYT 100:5) as seen in FTIR spectra.

gomers than the theoretical number; therefore, the true stoichiometric excess of MAAH was higher in these cases.

Peaks characteristic of a methacrylate double bond at the end of a polylactide chain appeared at 6.17 and 5.60 ppm. The excess of MAAH that was used and the methacrylic acid (MA) that formed in the functionalization were removed from the functionalized oligomers by distillation. The purification was performed successfully. In the spectrum of P(DLLA/PERYT 100 : 5) after functionalization (Fig. 1), the peaks for the MAAH monomer at 6.20 and 5.79 ppm and for MA at 6.23 and 5.66 ppm were negligible in size. The amount of monomeric methacrylic groups in the functionalized oligomers ranged from 1 to 8%, as calculated from the ratio of the peak integrals of the free methacrylate groups to the peak integrals of the methacrylate groups connected to polylactide chains (Table I).

The DS was also investigated with ^{13}C -NMR and Fourier transform infrared (FTIR). The resonances of methacrylic end groups were clearly evident in the ^{13}C -NMR spectra of the functionalized oligomers, whereas the peaks due to OH-terminated polylactide chains diminished. In agreement with the ^1H -NMR results, this confirmed the high DS. In the FTIR spectra, functionalization caused a new absorbance to form

at 1629 cm^{-1} (Fig. 2). This was due to the double bond in the methacrylated oligomers. The hydroxyl absorbance at 3522 cm^{-1} disappeared at the same time, when the hydroxyl groups were consumed, giving additional proof of successful functionalization.

As expected, the molecular weights measured by SEC were higher for the functionalized oligomers than those for the original oligomers. Theoretically, each methacrylate group added to M_n by 68 g/mol , and as the number of functionalized hydroxyl groups increased, M_n increased as well. The fact that M_n and M_w changed only slightly during functionalization (see Table I) rules out premature polymerization, in which the oligomers link together and form either linear or crosslinked polymers. Similarly, the functionalized oligomers were thermally stable, as characterized by DSC. No reaction was observed during heating to 180°C . Methacrylation did not have a clear effect on T_g ; only a slight change was observed with some of the samples.

Crosslinking of functionalized polylactide oligomers

The effect of the oligomer structure on the curing and properties of the resulting crosslinked polymers was addressed first. Functionalized oligomers of different

TABLE II
Properties of Crosslinked Polymers

| Sample | Crosslinking | | Composition Me/LA ^a | Compressive | | | Extraction Gel (%) | DSC | |
|------------------------|------------------------------|-----------|-----------------------------------|----------------------------|------------------------|------------------|-----------------------|------------------------|-------------|
| | BD-Me ₂ (wt %) | T (°C) | | Yield strength (MPa) | Yield strain (%) | Modulus (MPa) | | T _g (°C) | ΔH (J/g) |
| Thermal initiation | | | | | | | | | |
| P(DLLA/BD 100:5) | 0 | 90 | 10/100 | 78 ± 2 | 6.5 ± 0.4 | 1800 ± 300 | 85 | 42 | 0 |
| P(DLLA/BD 100:10) | 0 | 90 | 20/100 | 72 ± 3 | 5.2 ± 0.2 | 1800 ± 100 | 85 | 40 | 0 |
| P(DLLA/PERYT 100:5) | 0 | 90 | 20/100 | 91 ± 5 | 6.7 ± 1.0 | 2000 ± 100 | 95 | 46 | 0 |
| P(DLLA/PERYT 100:8) | 0 | 90 | 32/100 | 120 ± 4 | 5.0 ± 0.1 | 2800 ± 100 | 99 | 49 | 0 |
| P(DLLA/PERYT 100:12.5) | 0 | 90 | 50/100 | 107 ± 14 | 5.5 ± 0.4 | 2500 ± 200 | 99 | 51 | 4 |
| P(DLLA/PERYT 100:12.5) | 10 | 90 | 69/100 | 119 ± 6 | 5.4 ± 0.3 | 2800 ± 100 | 100 | 55 | 0 |
| P(DLLA/PERYT 100:12.5) | 10 | 60 | 69/100 | 118 ± 4 | 5.7 ± 0.3 | 2600 ± 200 | 89 | 49 | 0 |
| P(DLLA/PERYT 100:12.5) | 20 | 90 | 93/100 | 118 ± 10 | 5.6 ± 0.5 | 2700 ± 100 | 95 | 57 | 0 |
| P(DLLA/PERYT 100:12.5) | 20 | 60 | 93/100 | 108 ± 7 | 8.2 ± 2.1 | 1900 ± 400 | 100 | 52 | 0 |
| P(DLLA/PERYT 100:12.5) | 20 | 37 | 93/100 | 78 ± 8 | 9.4 ± 0.7 | 1200 ± 200 | 98 | 41 | 53 |
| P(DLLA/PERYT 100:12.5) | 30 | 90 | 124/100 | 124 ± 2 | 6.4 ± 0.4 | 2600 ± 200 | 99 | 52 | 0 |
| P(DLLA/PERYT 100:12.5) | 30 | 60 | 124/100 | 104 ± 10 | 6.0 ± 1.1 | 2200 ± 300 | 100 | 57 | 0 |
| P(DLLA/PERYT 100:12.5) | 30 | 37 | 124/100 | 103 ± 8 | 6.2 ± 0.7 | 2200 ± 300 | 100 | 47 | 22 |
| P(DLLA/PGL-06 100:5) | 0 | 90 | 40/100 | 101 ± 8 | 4.7 ± 0.3 | 2600 ± 100 | 100 | 56 | 0 |
| P(DLLA/PGL-10 100:5) | 0 | 90 | 60/100 | 116 ± 3 | 5.8 ± 0.3 | 2400 ± 200 | 97 | 54 | 0 |
| Photoinitiation | | | | | | | | | |
| P(DLLA/PERYT 100:12.5) | 30 | 25 | 124/100 | 76 ± 10 | 8.4 ± 1.1 | 1100 ± 100 | 95 | 50 | 0 |

^a Theoretical amount of methacrylic units relative to lactide units.

structures were crosslinked with 0.5 wt % DBPO at 90°C [Scheme 1(C)]. The average number of arms (N) in the oligomers characterized by ¹H-NMR ranged from 2.0 in P(DLLA/BD 100 : 5) to 8.3 in P(DLLA/PGL-10 100 : 5). A considerable difference was evident in the crosslinking density and properties of the crosslinked samples. The effect of the number of arms in the oligomer is most clearly seen by a comparison of the samples with a 100 : 5 ratio of lactide to coinitiator (Table II). Among these samples, the best mechanical properties were obtained for the polymers prepared with polyglycerines. The results follow a trend in which the highest strength was obtained for networks with the largest number of arms in the oligomer. The T_g and gel content were also higher as the number of hydroxyl groups in the coinitiator was increased. The results can all be explained by the greater number of arms in the oligomer (see Table II), which led to higher crosslinking density and, eventually, to higher mechanical strength of the cured polymer.

The increase in the number of arms also led to a higher amount of methacrylate groups, which could have had an effect on the properties of the crosslinked samples. However, by comparing the samples prepared with a 100 : 5 ratio of DLLA to PERYT and a 100 : 10 ratio of DLLA to BD, we can exclude this. The samples contained equal amounts of methacrylic units, and their DSs and monomer contents were comparable, but the networks from star-shaped oligomers exhibited a significantly higher strength. This gives additional proof for the strengthening effect of the increasing number of arms.

In a comparison of the polymers prepared from linear and star-shaped oligomers, the amount of soluble components was found to be higher for the linear oligomers. In general, the DSs were lower in functionalizations of two-arm oligomers than in functionalizations of oligomers with several arms. Theoretically, monomethacrylated oligomers could form polymers with methacrylic backbone and polylactide grafts. Moreover, the formation of insoluble networks with branched oligomers does not require that all the double bonds react, but tight networks are obtained with linear oligomers only when the conversion of double bonds is high. According to FTIR, virtually all the double bonds were consumed, as the double-bond absorbance (1629 cm⁻¹) disappeared with the crosslinking of both linear and star-shaped functionalized oligomers. Figure 2 shows the situation for the cured polymer from P(DLLA/PERYT 100 : 5). However, the evaluation of the double-bond conversion was not quantitative, and the incomplete conversion could have had a more deleterious effect on the properties of networks prepared from the linear oligomers than on those prepared from the branched oligomers.

The effect of the average polylactide chain length in the oligomers can be seen from a comparison of polymers cured from star-shaped oligomers coinitiated with PERYT (DLLA/PERYT 100 : 5, 100 : 8, and 100 : 12.5). Corresponding chain lengths for these samples (L_{LA} ; Table I) were 5.9, 3.2, and 2.1 lactide units according to ¹H-NMR. As expected, T_g after curing rose with the amount of the coinitiator. A higher crosslinking density was obtained with a greater amount of the

coinitiator because the lactide chains between crosslinks became shorter. However, the mechanical strength was highest for cured polymers prepared from P(DLLA/PERYT 100 : 8). This indicates that mechanical strength does not depend solely on crosslinking density but also depends on the inherent properties of the constituent lactide and methacrylate blocks.

The effect of lactide blocks on the compressive properties was different with linear oligomers. The strength of the two samples that were tested was around 72–78 MPa when L_{LA} values of the samples were 5.0 and 10.0. The strength was slightly lower for networks with shorter lactide blocks; this could be due to the flexible butanediol units used in the linear oligomers. The influence of the butanediol units is more pronounced when the length of the average lactide blocks decreases, and this may partially explain why higher crosslinking density does not increase the strength of the crosslinked samples as expected. However, Storey et al.¹⁰ obtained higher tensile strengths with longer lactide blocks in networks cured from three-arm oligomers like we did with networks from linear oligomers. It is noteworthy that they used three-arm oligomers with L_{LA} values of 5–20, making the effect of lactide blocks more pronounced than in the networks with higher crosslinking density.

Use of reactive monomers

All the samples previously described were crosslinked at 90°C as the viscosity of the functionalized oligomer at that temperature enabled homogeneous addition of the initiator to the oligomer. For the preparation of crosslinked polymers at lower temperatures, the viscosity of the reactive mixture has to be lowered to an appropriate level. This can be achieved with oligomers with T_g 's as low as possible or through the addition of reactive or unreactive diluents. For this purpose, we added BD-Me₂ as a diluent to P(DLLA/PERYT 100 : 12.5). BD-Me₂ has two methacrylic groups connected with a carbon chain and ester bonds, similar to the oligomers used, and its molecular weight is low in comparison with that of the oligomers. When we added 10 wt % BD-Me₂ to P(DLLA/PERYT 100 : 12.5), we were able to perform the crosslinking at 60°C, and the addition of 20 or 30 wt % of the reactive monomer lowered the viscosity to a low enough level to enable crosslinking at 37°C. Lactide blocks were still dominant with 10 and 20 wt % of the reactive monomer, but with 30 wt % BD-Me₂, there were 1.24 methacrylic groups per lactide unit, as shown in Table II.

The addition of the reactive monomer had a strengthening effect on the mechanical properties of these crosslinked polymers (Table II). At 90°C without the reactive monomer, a compressive yield strength of 107 MPa was obtained. With 10 wt % BD-Me₂, a

strength of 119 MPa was achieved, but a further increase in the amount of BD-Me₂ to 20 or 30 wt % did not improve the strength significantly.

With the lowering of the curing temperature to 60 and then 37°C, the strength of the samples decreased. This can be explained by the less efficient curing at lower temperatures due to the restricted movement of molecules. Moreover, as the conversion increases, reactive double bonds become fewer, and the movement of molecules becomes more restricted, hindering the reaction from proceeding. At higher temperatures, in contrast, the molecules can move more freely, enabling the curing to reach full conversion and high mechanical strength. Another indication of the same thing is that the samples cured at 37°C contained unreacted double bonds, as seen in the exotherm in the DSC thermograph during the first heating. The remaining reaction enthalpy of curing (ΔH) was higher for the sample with 20 wt % of the reactive monomer than that for the sample with 30 wt % of the reactive monomer, probably because of the higher viscosity of the reactive compound and, therefore, limited motion of reactive groups.

The synthesized polymers with high crosslinking density exhibited mechanical properties comparable to those of other biodegradable polymers and composites. We achieved a compressive yield strength of 124 MPa with a modulus of 2.6 GPa, which compare well with the compressive strengths of 120–130 MPa and modulus of 5.1 GPa reported for linear poly(L-lactide)s.¹⁹ For crosslinked biodegradable polymers, however, Storey et al.¹⁰ reported a tensile strength of over 70 MPa for methacrylated polylactide networks. Bone cements based on PPF have compressive strengths of 1–12 MPa with compressive moduli of 20–260 MPa depending on the composition,³ but these strengths have risen as high as 130 MPa with acrylate or epoxide termination and the use of methyl methacrylate or *N*-vinyl pyrrolidone as a reactive monomer.⁵

Photoinitiated crosslinking

To demonstrate the applicability of photoinitiation, we crosslinked P(DLLA/PERYT 100 : 12.5) with 30 wt % BD-Me₂ with CQ as an initiator and with 4EDMAB as a promoter. Blue light was applied to the sample in the bone-cement mold only from the top, and it penetrated through the 12-mm-thick specimen. A 5-min reaction time was sufficient to crosslink the sample to a high conversion with a gel content of 95%, and hard specimens were obtained. CQ has been reported to photobleach when decaying,¹² and our observation supports this because the photoinitiation led to nearly uniform crosslinking throughout the sample. With the light source and reaction time employed, the light penetrated through the sample and the gel content decreased only slightly as the distance from the light

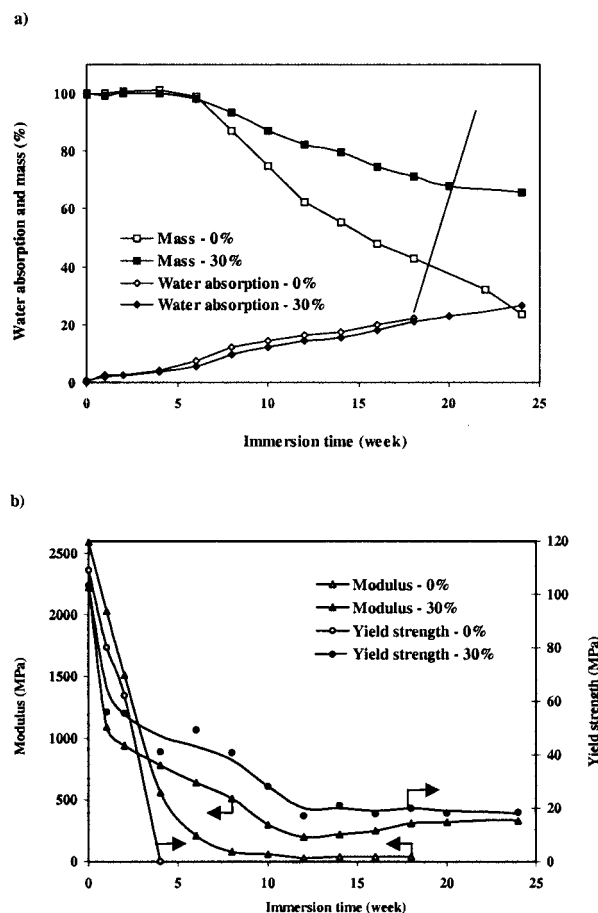


Figure 3 (a) Water absorption and mass and (b) compressive properties of crosslinked polymers from P(DLLA/PERYT 100:12.5) prepared with and without 30 wt % BD-Me₂ as a function of hydrolysis time.

source increased. At the top of the sample, the gel content was 97%; in the middle, it was 94%; and at the bottom, it was 93%. The gel content and T_g of the photopolymerized sample were on the same level as those of the thermally initiated samples. However, the mechanical properties were lower than those of thermally initiated samples of the same composition, as shown in Table II. This difference may be due to the fact that photopolymerization was performed at room temperature and the strength of the samples cured by thermal initiation decreased as the curing temperature decreased.

Hydrolytic degradation

Figure 3(a) shows the hydrolytic degradation of the crosslinked samples. It is known that, in addition to the degradation products of polylactides, the degradation yields small water-soluble oligo(methacrylic acid) chains, which are not accumulated in the circulatory system.^{20–22} Specimens were prepared from P(DLLA/PERYT 100 : 12.5) with and without 30 wt % BD-Me₂ as a reactive monomer with thermal initiation

as previously described. The hydrolytic degradation of the samples proceeded quite steadily for the first 16 weeks. For the first 6 weeks, virtually all of the mass remained, and after 6 weeks, there was a period of constant decrease in mass and increase in water absorption. At the same time, the differences between the samples started to show in the water absorption and remaining mass. The specimens prepared without the reactive monomer lost their shape after 16 weeks, when 40% of the mass remained and the measurement of water absorption became impractical. The observed degradation agrees with the degradation of linear and crosslinked poly(D,L-lactide).^{10,17,23,24} The use of the reactive monomer reduced the water absorption and decelerated the mass loss significantly, and even after 52 weeks, 56% of the mass remained (data not shown). Both the crosslinked samples tested had a high mechanical strength before the hydrolysis, but the strength and modulus decreased early in the hydrolysis, as shown in Figure 3(b). The sample with the reactive monomer retained some of its initial strength even after 52 weeks because of the slower degradation, but the polylactide network cured without the reactive monomer did not exhibit yield strength after 4 weeks.

CONCLUSIONS

Biodegradable polylactide-based polymers were prepared by the functionalization of polylactide oligomers of controlled structures with MAAH and crosslinking. The structures of the oligomers affected the crosslinking density and, therefore, the properties of the crosslinked polymers. Oligomers with more arms and shorter lactide blocks exhibited greater crosslinking density and higher mechanical strength.

With BD-Me₂ as a reactive monomer, the crosslinking temperature could be lowered, even to room temperature. Polymers with high mechanical strength were obtained by both thermal initiation and photoinitiation, and the use of reactive monomers retarded the hydrolytic degradation of the networks. Also, the yield strength and modulus of the network prepared with the reactive monomer were retained for a longer period of time than those in the network cured solely from methacrylated poly(D,L-lactide) oligomers.

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