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Design of Elastomeric Homo- and Copolymer Networks of Functional Aliphatic Polyester for Use in Biomedical Applications

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An unsaturated aliphatic polyester was synthesized by condensation polymerization to yield the pre-polymer, poly(but-2-ene-1,4-diyl malonate) (PBM), which is applicable as an elastomeric network and as a macroinitiator for the polymerization of cyclic ester monomers. The method of preparation was simple and straightforward with no need to purify the monomers or add a potentially harmful catalyst. The number average molecular weight of the pre-polymer could easily be increased from 5000 to 12000 by extending the reaction time. The pre-polymer PBM was successfully cross-linked with UV-radiation to form a clear, transparent, colorless, flexible, and strong film. PBM as a macroinitiator for L-lactide (LLA) and ε-caprolactone (CL) polymerizations highly increased the ductility of the LLA-polymer, while maintaining the strength, compared to PLLA polymerized with common initiators. The tensile properties of PCL were also improved. The linear PCL-PBM and PLLA-PBM polymers were easily cross-linked to give polymers with greater strength and higher modulus as the result.

Introduction

The functionalization of aliphatic polyesters which will extend their properties and increase their utility is an important step in designing materials for biomedical applications. Our group has worked extensively with the synthesis of cyclic ester monomers to tune their architectures[1−5] and functionalizations.[6−8] Functional groups are incorporated by ring-opening polymerization of the cyclic monomer either using initiators with an additional functional group or by relatively complicated modifications of the cyclic monomers.[9−11] The functional groups are then used to promote further modification such as epoxidation, cross-linking, and the attachment of groups that enhance biocompatibility and cell response. Cross-linking of aliphatic polyesters, for example, L-lactide and ε-caprolactone, is frequently performed by the addition of multifunctional cross-linking agents in the polymerization step[1,12,13] or by end-group functionalization.[14,15] Other ways of cross-linking these polyesters are by Michael addition,[16] radical cross-linking at elevated temperature,[17] or radiation modification.[18] However, the polymers are expensive to produce, and the polymerization process is quite complex and requires a very high purity of the chemicals involved. Even though the high molecular weight polymers obtained by ring-opening polymerization (ROP) of the cyclic esters are hard to equal and to prepare, an aliphatic polyester via polycondensation is an easier way to introduce functional groups.

Highly functionalized aliphatic polyesters with a carbon−carbon double bond in the main chain have been synthesized through condensation polymerizations of unsaturated diols and dicarboxylic acids, chlorides, and esters.[19−22]

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A partially saturated polyester based on poly(propylene fumarate) for orthopedic applications has been studied using a metal catalyst.[23,24] In general the resulting polymers have a lower molecular weight and a broader molecular weight distribution than the ring-opened polymers. A metal catalyst or enzyme must be used to reach a number average molecular weight of 1500−10000.[19,22,25,26] The aim was to design functional aliphatic polyesters in an easy and cheap polymerization process, allowing cross-linking or further functionalization either as a homopolymer or as a copolymer with conventional biomedical polyesters. Hydroxyl-terminated aliphatic polyesters containing functionalities in every repeating unit and of a reasonably high molecular weight are well suited for use as macroinitiators in ROP together with Stannous 2-ethylhexanoate ($Sn(Oct)_2$). These create triblock copolymers with a large number of functional groups in the main chain of aliphatic polyesters that are used in biomedical applications. The functionalities facilitate modification, such as epoxidation and cross-linking of polymers such as poly(lactide) and poly(ε-caprolactone), and thus extend the range of material properties and allow the easy creation of covalently bonded elastomers of these polymers by thermal or photoinitiated radical reactions.

Experimental Section

Materials. Malonic acid ReagentPlus 99%, (Sigma-Aldrich, Sweden), 2-butene-1,4-diol (Fluka, Switzerland), ethylene glycol dimethacrylate, EGM (Sigma-Aldrich, Sweden) and benzophenone (Alfa Aesar, Germany) were used as received. L,L-lactide, LLA (Serva Feinbiochemica, Germany), was purified by recrystallization in dry toluene (Merck, Germany). The monomer was then dried for 24 h under reduced pressure at room temperature. ε-Caprolactone, CL, (Sigma-Aldrich, Sweden) was dried over calcium hydride for at least 24 h at room temperature and was then distilled under reduced pressure prior to polymerization. Ethylene glycol (EG) (Sigma-Aldrich, Sweden) was purified by distillation under reduced pressure. $Sn(Oct)_2$, (Sigma-Aldrich, Sweden) was dried before use. Chloroform (LabScan, Ireland), hexane (LabScan, Ireland), and methanol (BDH, United Kingdom) were used as received.

Polymerization Technique. *Synthesis.* The pre-polymer/macroinitiator poly(but-2-ene-1,4-diyl malonate) (PBM) was prepared via a condensation polymerization of malonic acid and 2-butene-1,4-diol. A 1:1.01 molar ratio of malonic acid and 2-butene-1,4-diol was weighed into a round-bottom flask fitted with a magnetic stirrer. The reaciction flask was immersed in an oil-bath at 110 °C, and water was driven off by lowering the pressure gradually. The reaction was allowed to proceed for 3 h. A second step esterification through ester exchange was performed at 210 °C under vacuum for 3 h to increase the molecular weight. The pre-polymer was precipitated in cold ether. The reactions were performed on a 20 g scale.

The macroinitiator PBM was used with $Sn(Oct)_2$ in the bulk polymerizations of ε-Caprolactone (CL) and L,L-lactide (LLA). The $Sn(Oct)_2$-to-monomer and PBM-to-monomer ratios were set to produce polymers with M_n of 80 000 (i.e., a ratio of 1: degree of polymerization). The reactions were performed on a 6 g scale and were allowed to proceed at 110 °C for 15 h under a nitrogen atmosphere. Reference polymers of PCL and PLLA were synthesized with $Sn(Oct)_2$ and ethylene glycol (EG) under the same reaction conditions. The polymers were precipitated in a mixture of cold hexane and methanol (95:5).

Film Preparation. Films were prepared from PBM, PCL-PBM, PLLA-PBM, and the reference polymers by solution-casting. The polymers (1,5 g) were dissolved in chloroform ($CHCl_3$), and films were cast in glass Petri-dishes. The films were dried at room temperature by solvent evaporation. The reference polymers were not cross-linked as well as a few of the PCL-PBM and PLLA-PBM films (for comparison reasons), and the chloroform was allowed to evaporate. For cross-linked films, the photoinitiator benzophenone was used (10 wt %), and for films of PCL-PBM and for pure PBM, ethyleneglycol dimethacrylate (5 wt %) was added to improve the properties of the films. All chemicals were added in the polymer solution and thoroughly mixed. The cross-linking reactions were performed on solidified films by UV-radiation and were allowed to proceed for 6 h.

Characterization. *Nuclear Magnetic Resonance Spectroscopy* (*NMR*). The degree of monomer conversion was determined by ^{1}H NMR spectroscopy, comparing the relative intensities of the polymer peaks originating from the different monomers and the resonance peaks from the monomer and polymer. The monomer sequence was determined by ^{13}C NMR spectra. ^{1}H NMR and ^{13}C NMR analyses were carried out using a Bruker Avance DPX-400 Nuclear Magnetic Resonance Spectrometer operating at 400 and 100 MHz respectively. The samples were prepared by dissolving 10 mg of sample in 1 mL of deuterochloroform ($CDCl_3$) in a 5 mm diameter sample tube. Non-deuterated chloroform was used as an internal standard ($\delta = 7.26$ ppm and $\delta = 77.0$ ppm).

Size Exclusion Chromatography (*SEC*). SEC was used to determine the molecular weights and polydispersity index values after synthesis. The polymers were analyzed with a Viscotek TDA Model 301 with tetrahydrofuran (THF) as mobile phase (1 mL/min, 35 °C). The instrument was equipped with two GMHHR-M columns with TSK-gel from Tosoh Biosep, a VE 5200 GPC autosampler, a VE 1121 GPC solvent pump, and a VE 5710 GPC degasser (all from Viscotek Corp.). A conventional calibration was carried out using narrow linear polystyrene standards. Corrections for flow rate fluctuations were made using toluene as an internal standard. These results are mainly used qualitatively since calibration was performed using polystyrene standards, and this commonly yields a significant increase in the molecular weight for aliphatic polyesters.[27]

Differential Scanning Calorimetry (*DSC*). The thermal properties of the synthesized polymers were investigated using a DSC (Mettler Toledo DSC 820 module) under a nitrogen atmosphere. To erase the thermal history, the specimens were heated above the melting temperature and then cooled at a rate of 10 °C/min. The second scan was used to record the heat of fusion at a

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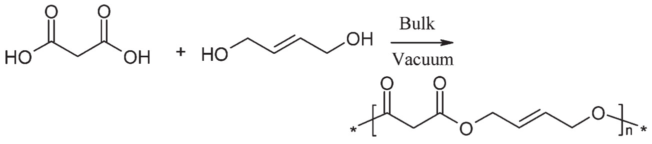
Scheme 1. Synthesis of PBM from Malonic Acid and 2-Butene-1,4-diol



heating rate of 10 °C/min. The melting temperatures, T_m, were noted as the maximum values of the melting peaks, and the midpoint temperature of the glass transition was determined as the glass transition temperature, T_g. The crystallinity, X_c, was calculated according to eq 1,[28]

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \tag{1}$$

where ΔH_f (J/g of the crystalline polymer) is the enthalpy of fusion of the specimen and ΔH_f^0 is the enthalpy of fusion of a 100% crystalline polymer. For PCL and PLLA ΔH_f^0 are 139,5[29] and 93 J/g,[30] respectively. Two or more analyses were performed per sample.

Tensile Testing. The tensile tests were carried out in a computer-controlled Instron 5566 equipped with a pneumatic grip. The computer program used was Bluehill with the settings for film testing. The tensile measurements were performed with a load cell with a maximum of 0.1 kN at a crosshead speed of 300 mm/min and a gauge length of 30 mm. Five different samples of the same material were tested for each polymer. The thickness of each film was measured with a micrometer. The samples were preconditioned before testing in accordance with ASTM D618−96 (40 h at 50 ± 5% relative humidity and 23 ± 1 °C).

Soluble Fraction. The soluble fraction was determined by immersing 3 to 6 samples of each film in chloroform until a constant dry weight was obtained.

Results and Discussion

Synthesis of PBM. The pre-polymer was prepared by condensation polymerization of malonic acid and 2-butene-1,4-diol as described in the Experimental Section (Scheme 1). No catalyst was used. The direct esterification reaction with the diacid and diol (1:1.01) was allowed to proceed until no more water formation could be observed. Thereafter the temperature was increased to increase the molecular weight by esterification through ester exchange while maintaining the hydroxyl end-groups. The product, a slightly yellow and highly viscous liquid, had an number average molecular weight, M_n, of 4750 (Table 1). The ester exchange reaction was stopped after 3 h to obtain a pre-polymer which could also be used as a macroinitiator for further polymerization. When the reaction time was extended to 6 h, the polymer reached a M_n of 12100 and a polydispersity index of 2.6. The polymer was slightly yellow and more rubbery in consistency than the previously synthesized pre-polymer.

Table 1. Number Average Molecular Weight and Thermal Properties of Pre-Polymer PBM

pre-polymer	M_n[a]	PDI[a]	T_g[b] (°C)	T_g[c] (°C)
PBM	4750	4.1	−36.2	−35.0

[a] Determined by SEC using narrow polystyrene standards and THF as eluent. [b] The first heating scan. [c] The second heating scan.

The structure of the pre-polymer was confirmed by ^{1}H- and ^{13}C NMR and is shown in Figure 1. The ^{1}H NMR spectrum, Figure 1 a, of PBM show that the peak corresponding to protons **a** is a singlet while the peaks corresponding to protons **b** and **c** are a doublet and triplet, respectively. The relative intensity of the peak corresponding to protons **b** was twice that of the peaks corresponding to protons **a** and **c**, confirming that the majority of the reactions were due to ester exchange and that only a small part was due to reactions involving the double bond. The presence of hydroxyl end-groups was confirmed by the small doublet peak at 4.25 ppm in the proton NMR (Figure 1a)[19] and by infrared spectroscopy, IR, where a broad OH-stretch was observed at 3400 cm^{-1}. IR also confirmed the presence of carbonyl groups. The ^{13}C NMR, Figure 1b, confirmed that the structure was that of a linear polyester since no (only diminutive) additional peaks that could originate from branches and/or cross-linking were observed. The thermal properties of the PBM were analyzed by DSC. No peaks corresponding to the crystallization or melting of crystals could be observed within the scanned temperature interval, showing that the pre-polymer was amorphous. The glass transition temperature, T_g, was around −35 °C, indicating a relatively flexible chain structure (Table 1).

PBM As Macroinitiator. The synthesized pre-polymer PBM was successfully used as a macroinitiator in the bulk polymerizations of ε-caprolactone (CL) (PCL-PBM) and L-lactide (LLA) (PLLA-PBM). The hydroxyl end-groups were used to initiate ring-opening polymerization together with Sn(Oct)$_2$ and polymers with an M_n of 80000 were obtained. The reactions were performed at 110 °C for 15 h. Homopolymers of poly(ε-caprolactone) (PCL) and poly(L-lactide) (PLLA) with similar molecular weights were also synthesized as reference materials using ethylene glycol (EG) as co-initiator. As shown in Table 2, all the polymerizations reached a high conversion and the desired molecular weight.

According to the SEC results (Figure 2), the PBM completely initiated the monomers since no peak at 4750 was visible in the chromatogram, and only the peak representing a molecular weight around 80 000 was visible. ^{1}H NMR confirmed that the double bond was intact and had not reacted during the polymerization. The glass transition temperature (T_g) and melting temperature (T_m) of the polymers were determined and compared using DSC, see Table 3. Only one T_g was seen in all polymers containing PBM as the macroinitiator because of the relatively short PBM segments that do not form a separate phase but are incorporated into the CL or LLA phase. No significant differences in the T_g were observed

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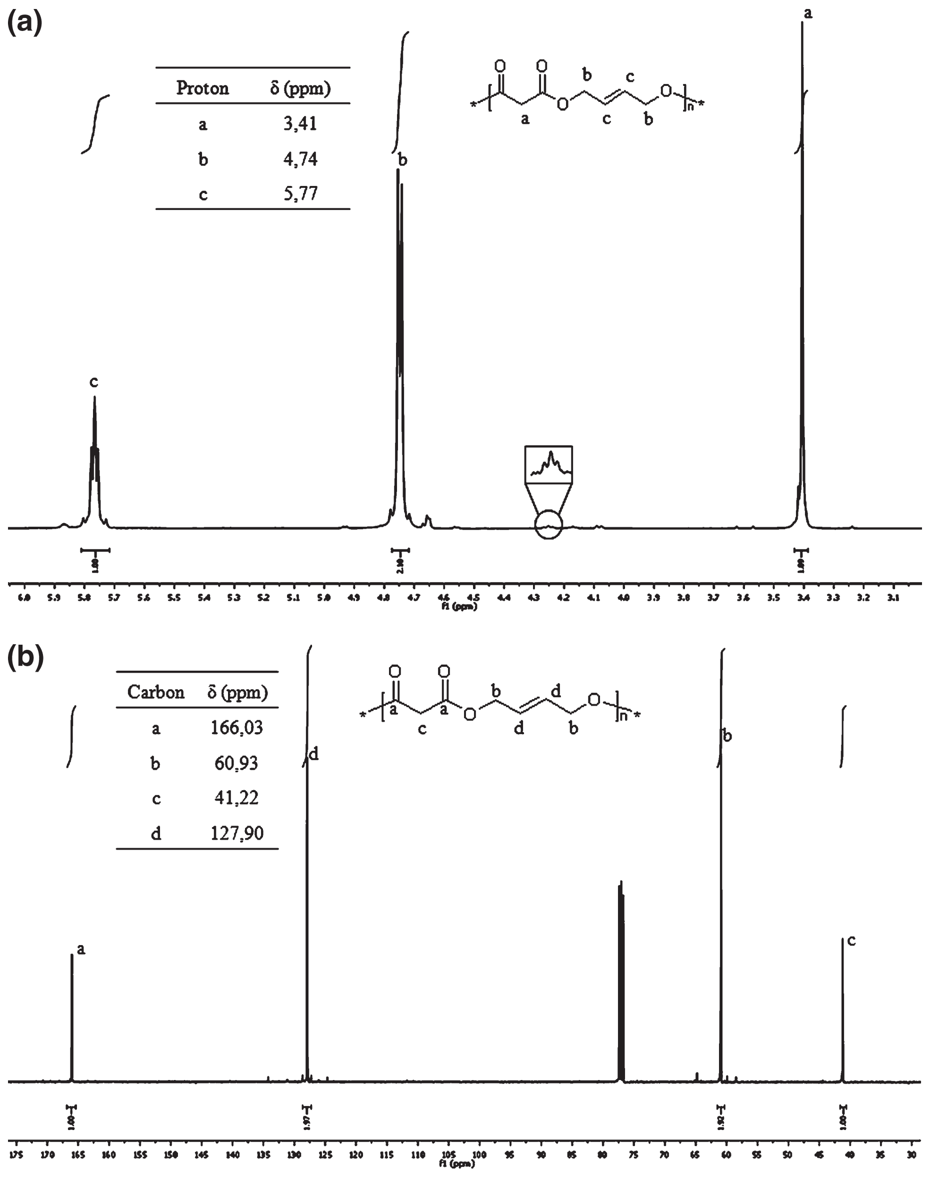

Figure 1. (a) ^{1}H NMR peak assignment of PBM; (b) ^{13}C NMR peak assignment of PBM.

Table 2. Conversion and Number Average Molecular Weight for the Bulk Polymerization of CL and LLA with PBM and EG as Co-Initiators at 110 °C for 15 h

polymer	conversion[a] (%)	M_n[b]	PDI[b]
PCL-PBM	99	75900	3.5
PCL-PBM	97	82000	2.7
PLLA-PBM	95	80100	2.1
PLLA-PBM	97	75600	2.3
PCL-EG	99	70600	1.6
PLLA-EG	99	46000	1.2
PLLA-EG	96	53600	1.4

[a] Determined by ^{1}H NMR in $CDCl_3$. [b] Determined by SEC using narrow polystyrene standards and THF as eluent.

between the PCL and PCL-PBM polymers. This was explained by the low T_g of the PBM segments. In the PLLA-PBM polymers the low T_g of the PBM chain segment lowers the glass transition of the polymer compared to that of the reference polymer of PLLA-EG because of the more flexible PBM segments in the chains. The melting temperatures did not change much for either polymer. However, the crystallinity of the PCL-PBM was slightly lower than that of PCL-EG, whereas the crystallinity of PLLA-PBM was slightly higher than that of PLLA-EG.

Films. The pre-polymer PBM was successfully cross-linked (PBM-X) with benzophenone under UV-radiation to form a clear, transparent, colorless, and flexible film. PCL-PBM and PLLA-PBM were also effectively cross-linked under the same conditions (PCL-PBM-X and PLLA-PBM-X, respectively). In the case of the PBM-X and PCL-PBM-X films, the spacer ethylene glycol dimethacrylate (EGM) was used to improve the film properties. In the case of the PLLA-PBM-X films, a phase separation, causing inhomogeneous crystallization, occurred when the spacer was used. Films from the latter material were therefore cross-linked using only the UV-initiator. Both types of PBM-initiated cross-linked films were opaque. Films of PCL-PBM, PLLA-PBM, and reference films of PCL and PLLA, initiated by EG, were also prepared by solution casting (without subsequent cross-linking).

To compare the extent of cross-linking between the different polymers, the size of the soluble fraction was determined. The samples were immersed in chloroform until a constant dry weight was reached. PBM-X showed a weight loss of 8.8%, and the weight losses for PCL-PBM-X and PLLA-PBM-X were 2.0% and 52%, respectively. PLLA-PBM-X, the only polymer where the use of the spacer was not possible, showed a larger soluble fraction after the same reaction conditions. With a longer reaction time, it should be possible to reach the same degree of cross-linking as in the other polymer networks. Compared to other previously produced unsaturated aliphatic polyesters synthesized by Olson et al.,[21] the size of the soluble fraction of PBM-X was lower. Their cross-linking reactions were performed at higher reaction temperatures and had a longer reaction time, 24 h, compared to the PBM synthesis. The thermal properties of the cross-linked materials are shown in Table 4. The T_g for PBM-X and PCL-PBM-X was approximately 10 °C higher than that of the linear analogues, which was expected considering the decreased chain mobility induced by the cross-links. PLLA-PBM-X did not show any change in T_g because of the lower cross-linking density. The crystallinity decreased by 22% and 6% for PCL-PBM-X and PLLA-PBM-X, respectively. The melting temperature of the polymers in the second heating scan was lower because the reformation of crystals was hindered by the cross-links.

Table 3. Thermal Properties of PCL and PLLA with PBM and EG as Initiators

polymer	T_g[a] (°C)	T_g[b] (°C)	T_m[a] (°C)	T_m[b] (°C)	X_c[b] (%)
PCL-EG	−54.9 ± 0.3		61.8 ± 0.3	57.3 ± 0.5	42.6
PCL-PBM	−58.1 ± 1.1	−58.8	60.2 ± 0.1	55.8 ± 2.6	38.5
PLLA-EG	57.9 ± 3.2	56.5 ± 1.4	172.8 ± 1.5	171.0 ± 0.7	46.0
PLLA-PBM	46.7 ± 3.0	48.1 ± 2.0	172.7 ± 0.1	172.0 ± 0.1	52.4

[a] The first heating scan. [b] The second heating scan.

Tensile Properties. The tensile properties of PBM-X as well as those of the cross-linked and linear PCL-PBM and PLLA-PBM were examined and compared among themselves and with the reference films of PCL and PLLA (Table 5). Cross-linked materials are named with an -X at the end for clarification. Before cross-linking, PBM is a sticky and very viscous liquid whereas PBM-X is a flexible strong film with a stress at max load of 4.5 MPa, a strain of 47%, and a modulus of 12 MPa. Compared to other aliphatic polyester networks,[21] PBM-X have a higher strength and stiffness in general, but the elongation at break is shorter. Linear PCL-PBM is more ductile than the reference PCL while it retains the strength and modulus. The PCL-PBM-X is stronger and stiffer than the reference PCL but shows a highly decreased strain at break. However, the strain at break for PCL-PBM-X was higher than the strain at yield (the area where the tensile properties of linear polymers fail) of the PCL-PBM and the PCL reference. Compared to the PLLA reference the linear PLLA-PBM polymer show a more ductile behavior while the strength (stress at yield) and modulus are in similar ranges. For PLLA-PBM-X, both the strength and ductility are similar to the PLLA-ref; however, the materials stiffness has increased. Compared to linear PLLA-PBM

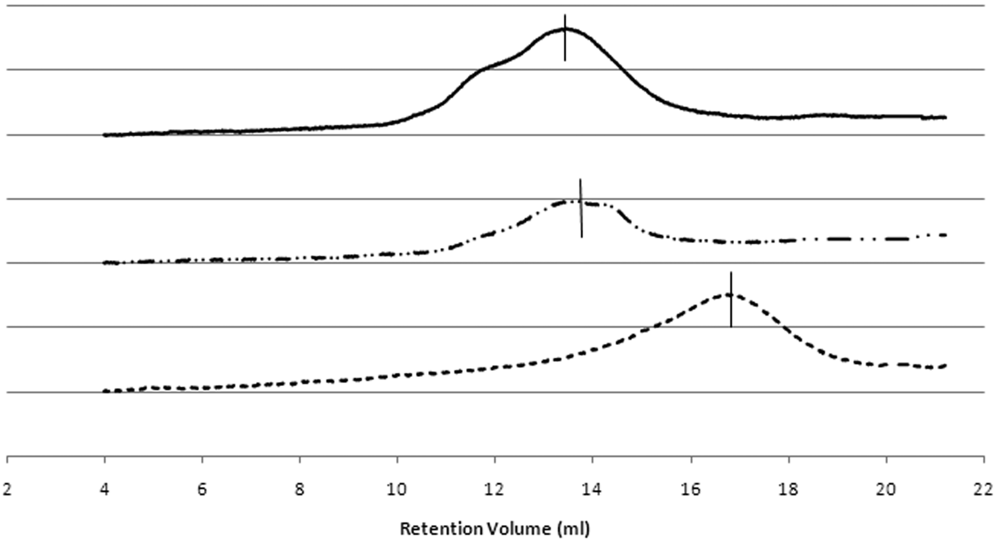

Figure 2. SEC curves for PCL-PBM (solid line), PLLA-PBM (dash-double dotted line), and PBM (dashed line).

Table 4. Thermal Properties of the Cross-Linked Polymers

polymer[a]	T_g[b] (°C)	T_g[c] (°C)	T_m[b] (°C)	T_m[c] (°C)	X_c[c] (%)
PBM-X	−24.5 ± 0.2	−24.5 ± 0.8			
PCL-PBM-X	−47.8 ± 0.1	−49.4 ± 0	63.1 ± 0.1	48.1 ± 0.2	16.4
PLLA-PBM-X		47.1 ± 0.2	167.0 ± 0.3	164.7 ± 0.2	46.9

[a] -X, the polymer is cross-linked. [b] The first heating scan. [c] The second heating scan.

Table 5. Tensile Properties of PCL-PBM, PLLA-PBM, PBM-X, PCL-PBM-X, PLLA-PBM-X, and Reference Polymers

polymer[a]	stress at break (MPa)	strain at break (%)	modulus (MPa)	stress at yield (MPa)	strain at yield (%)
PBM-X	4.5 ± 0.40	47 ± 6.4	12 ± 1.4		
PCL-EG	16 ± 0.50	340 ± 72	250 ± 9.8	17 ± 0.40	16 ± 1.9
PCL-PBM	16 ± 0.80	570 ± 28	260 ± 3.5	17 ± 0.30	12 ± 2.0
PCL-PBM-X	23 ± 0.90	31 ± 3.2	330 ± 18		
PLLA-EG	35 ± 0.04	9.5 ± 0.80	630 ± 46		
PLLA-PBM	25 ± 6.3	100 ± 47	840 ± 14	32 ± 0.80	16 ± 0.30
PLLA-PBM-X	37 ± 0.80	12 ± 0.30	930 ± 56		

[a] -X, the polymer is cross-linked.

the elongation is clearly decreased, but the stiffness of the materials has increased.

Conclusion

An aliphatic polyester which has a double bond in every repeating unit and a very short distance between the ester bonds in the polymer chain has been synthesized. PBM was produced with great ease through condensation polymerization without the use of any (potentially harmful) catalysts. Furthermore, no particular purification of monomers or silanization of reaction vessels are necessary. The versatility in applicability of PBM was shown by the creation of a hydroxyl-terminated pre-polymer suitable for both cross-linking and use as a macroinitiator in insertion-coordination polymerization. By prolonging the reaction time, the number average molecular weight of PBM could easily be increased. PBM with a reasonably low number average molecular weight is amorphous, with a low glass transition temperature. When used as a macroinitiator for L-lactide (LLA) and ε-caprolactone (CL) polymerizations catalyzed by $Sn(Oct)_2$, PBM greatly increased the ductility, while retaining the strength, of the LLA-polymer in contrast to PLLA polymerized with ethylene glycol. The tensile properties of PCL were also slightly improved. The thermal properties of both PBM-initiated polymers were relatively unchanged, except for the glass transition temperature of PLLA-PBM which was lowered by several degrees Celsius. The double bond made it possible to easily cross-link linear PCL-PBM and PLLA-PBM polymers to achieve polymers with a higher strength and modulus. Cross-linking of the pre-polymer PBM creates a strong, flexible, clear, and transparent film for possible use in biomedical applications.

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