

Resilient Bioresorbable Copolymers Based on Trimethylene Carbonate, L-Lactide, and 1,5-Dioxepan-2-one

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The new combinations of monomers presented in this work were evaluated in order to create an elastic material for potential application in soft tissue engineering. Thermoplastic elastomers (TPE) of trimethylene carbonate (TMC) with L-lactide (LLA) and 1,5-dioxepan-2-one (DXO) have been synthesized using a cyclic five-membered tin alkoxide initiator. The block copolymers were designed in such a way that poly(trimethylene carbonate-*co*-1,5-dioxepan-2-one) formed an amorphous middle block and the poly(L-lactide) (PLLA) formed semicrystalline terminal blocks. The amorphous middle block consisted of relatively randomly distributed TMC and DXO monomer units, and the defined block structure of the PLLA terminal segments was confirmed by ^{13}C NMR. The properties of the TMC-DXO-LLA copolymers were compared with those of triblock copolymers based either on LLA-TMC or on LLA-DXO. Differential scanning calorimetry and dynamic mechanical analysis data confirmed the micro-phase separation in the copolymers. The mechanical properties of the copolymers were evaluated using tensile testing and cycling loading. All of the copolymers synthesized showed a highly elastic behavior. The properties of copolymers could be tailored by altering the proportions of the different monomers.

Introduction

The emerging request for new supplies of synthetic materials for soft tissue engineering encourages the search for innovative polymers having interesting properties. The abundance of publications on biodegradable polymers for medical applications still leaves many unexplored niches that can reveal interesting data.

One of the commonly used monomers for the manufacture of biocompatible polymers is L-lactide (LLA), both as homopolymer and in copolymers. Poly(L-lactide) (PLLA) degrades in the body to lactic acid that can be easily metabolized by the living systems.^{1,2} Although PLLA is an ideal polymer for temporary implants, it has some disadvantages such as high crystallinity and rigidity at body temperature. A common path to evade this drawback is to copolymerize LLA with other monomers, e.g., ϵ -caprolactone (CL),^{3–5} to reduce the glass transition temperature (T_g) of the copolymer and make it more flexible. Another monomer which has been used as a softening component in copolymers with LLA is trimethylene carbonate (TMC). Several publications describe the copolymerization of TMC and lactones to yield copolymers with different architectures.^{6–15} Some of these articles considered the synthesis of thermoplastic elastomers (TPE) of TMC and LLA using stannous octoate, SnOct_2 , as catalyst.^{6–8} In those copolymers, poly(trimethylene carbonate) (PTMC) formed the soft amorphous middle block, whereas PLLA formed hard semicrystalline terminal blocks. Kricheldorf et al. first reported the synthesis of such elastic A–B–A type block copolymers based on TMC and LLA using tin alkoxide as initiator,¹⁶ which gave a better control of the block length of the copolymers than was possible

with SnOct_2 . The same tin alkoxide initiator system has been used for the preparation of elastic multiblock copolymers of LLA, TMC, and CL.¹¹

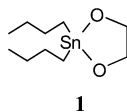
Another interesting comonomer that can be used to modify the properties of highly crystalline polymers such as PLLA is 1,5-dioxan-2-one (DXO). Our group has worked for many years with the homo- and copolymerization of DXO; for example, poly(1,5-dioxepan-2-one) (PDXO) was used to form the amorphous middle block in TPE based on CL and DXO.^{17,18} Highly elastic triblock copolymers with a middle amorphous PDXO block and semicrystalline terminal PLLA blocks of controlled length have been synthesized using a five-membered tin-alkoxide initiator.^{19,20} The introduction of TMC repeating units into the middle PDXO block of TPE based on DXO and LLA is a further step to alter the copolymer properties. Our hypothesis is that creating heterogeneity in the middle soft block will affect the elastic properties of the copolymer and change the degradation pattern in a predictable manner. Depending on the application, the soft tissue implants vary widely in the properties. For example the cartilage implant must be hydrophilic and very smooth and have sufficient strength, whereas the wound dressing should be elastic and flexible, with exceptional permeability requirements.²¹ Both the elastic properties and the controlled degradability of the material are of crucial importance in soft tissue engineering.

The primary goal of this work was to design an elastic, strong, and flexible material with good resilience. To achieve this goal, a block copolymer with semicrystalline LLA terminal blocks and an amorphous heterogeneous middle block formed of DXO and TMC was created using a five-membered tin-alkoxide initiator. The second task was to examine how the proportions of DXO and TMC in the middle soft block influence the properties of the TMC–DXO–LLA copolymers, and to compare their properties with those of the triblock copolymers based either on LLA–TMC or on LLA–DXO.

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Experimental Section

Materials. Dibutyltin oxide (Aldrich, Germany) and ethylene glycol (Merck, Germany) were used as received. Trimethylene carbonate (TMC) was kindly supplied by Radi Medical System AB, Sweden, and used as received. Chlorobenzene (VWR, Sweden) was dried over P_2O_{10} and distilled at reduced pressure in an inert atmosphere. Tetrahydro-4H-pyran-4-one (Maybridge Chemical, U.K.), diethyl ether, and P_4O_{10} (VWR, Sweden) were used as received. L-Lactide (Serva Feinbiochemica, Germany) was purified by recrystallization from dry toluene three times, and dried at room temperature under reduced pressure (10^{-2} Torr) for at least 48 h.



The bifunctional five-membered cyclic tin initiator (**1**) was prepared from dibutyltin oxide and ethylene glycol, as previously described in the literature.^{22,23} Characterization by 1H NMR confirmed the structure. DXO was synthesized from tetrahydro-4H-pyran-4-one through the Bayer-Villiger oxidation in accordance with the literature.²⁴ The DXO obtained was purified by recrystallization from dry diethyl ether and two subsequent distillations. The monomer was dried over CaH_2 for at least 15 h prior to a final distillation.

Polymerization. The copolymerizations were carried out in a previously silanized three-necked 50 mL round-bottomed flask under a nitrogen atmosphere with mechanical stirring. The reactions were performed in a concentrated solution (5 M with respect to each monomer concentration), using chlorobenzene as a solvent. The monomer(s) (TMC, DXO, or both) and the initiator were weighed in an inert atmosphere inside a glovebox (MBraun MB 150B-G-I, Germany). The previously distilled chlorobenzene was then transferred to the reaction flask with a flame-dried syringe through a rubber septum using inert-atmosphere techniques. The polymerization was started by immersing the reaction vessel in an 80 °C thermostated oil bath. The temperature was held constant (± 1 °C FUZZY-optimized) using an Ikatron ETC D3 temperature-regulator (IKA Labortechnik, Germany). The polymerization progressed until almost complete monomer conversion had taken place, which was determined by 1H NMR analysis. 1H NMR and SEC samples were withdrawn from the reaction mixture with a flame-dried syringe under a nitrogen atmosphere before the addition of the comonomer, LLA. The LLA was weighed into a flask and transferred to the reaction vessel containing the polymer-initiator complex under nitrogen purge. The polymer formed was dissolved in chloroform or dichloromethane and precipitated in cold diethyl ether. 1H NMR and SEC samples were collected before the completion of polymerization and after the precipitation of the final copolymer.

Preparation of Solution-Cast Films. Films for mechanical and thermomechanical tests were cast on glass plates from the copolymer solutions in chloroform at an approximate concentration of 0.15 g/mL. The films were allowed to dry under the fume hood overnight, after which they were further dried in a vacuum oven VacuCell 55 (MMM Medcenter GmbH, Germany) under pressure of 10^{-1} Torr at room temperature for at least one week. The films obtained had an average thickness of 0.1 mm. Strips with dimensions 80 × 5 mm were cut from the films with a punch from Elastocon AB, Sweden.

Characterization. Nuclear Magnetic Resonance (NMR). 1H NMR and ^{13}C spectra were recorded with a Bruker Avance DPX-400 nuclear magnetic resonance spectrometer operating at 400 MHz, $T = 25$ °C. Deuterated chloroform ($CDCl_3$) was used as solvent. Nondeuterated chloroform was used as an internal standard ($\delta = 7.26$ ppm for 1H NMR and $\delta = 77.0$ ppm for ^{13}C NMR).

Size Exclusion Chromatography (SEC). A Waters 717plus auto sampler and a Waters model 510 apparatus equipped with three PL gel 10 μm mixed-B columns, 300 × 7.5 mm (Polymer Labs., U.K.) connected to an IBM-compatible PC were used. Chloroform was used

as eluent at a flow rate of 1.0 mL/min. Narrow polystyrene standards in the 580–500 000 g/mol range were used for calibration. Millenium³² version 3.20 software was used to process the data.

Differential Scanning Calorimetry (DSC). The thermal properties of the synthesized copolymers were investigated using a Mettler-Toledo DSC 820 module. The samples were studied in a nitrogen atmosphere, and a heating/cooling rate of 10 °C/min was used. The range of scans was from –60 to +190 °C. In evaluating the crystallinity of the copolymers, it was assumed that the only contribution to the heat of fusion was from the PLLA segments.

Thermogravimetric Analysis (TGA). Thermal stability was estimated by thermogravimetric analysis (TGA) under a nitrogen atmosphere (nitrogen flow rate 50 mL/min) with a sample mass of 10 ± 1 mg and a heating rate of 10 °C/min. The scan range was from +25 to +450 °C.

Dynamic Mechanical Analysis (DMA). Thermomechanical properties were evaluated by means of a dynamic mechanical analysis (DMA) on a TA Instruments Q800 DMA. The measurements were made in the tensile mode with a distance of 12.86 mm between the grips. The temperature program worked from –70 to +80 °C at a rate of 3 °C/min. The measurements were performed at 1 Hz, and a static force of 1 N was applied. The width of the samples was 5 mm, and the average sample thickness was 0.1 mm.

Tensile Testing. The tensile testing of the copolymers was performed using an Instron 5566 equipped with pneumatic grips and controlled by a Dell 466/ME computer. The tensile measurements were performed with a crosshead speed of 50 mm/min and an initial grip separation of 32 mm. The elongation-at-break (ϵ_b) was calculated from the grip separation, because of the large elongation of the samples. The films had a thickness of approximately 0.1 mm and were preconditioned before testing (48 h at $50 \pm 5\%$ RH and 23 ± 1 °C). Five different samples from the same film were tested for each copolymer. The average thickness of each sample was calculated from five different measurements with a Mitutoyo micrometer. All tests were carried out in accordance with ASTM D638M-89.

Tensile Cycling Test. Cycling tests have been performed using a servo-hydraulic test machine MTS-30kN, upgraded with an Instron 8500+ digital controller equipped with a 10 N load cell. Cycling loading was performed with a crosshead speed of 50 mm/min and an initial grip separation of 32 mm. The film samples were strained to 50%. The test was performed in two steps: in the first step, 20 cycles were made followed by 16 h of recovery. After this recovery time, 5 more cycles were performed.

Results and Discussion

The one-pot copolymerization was performed in two steps: in the first step, the middle amorphous block composed of DXO and TMC was formed through the ring-expansion polymerization^{10,16,19} initiated by the five-membered tin alkoxide initiator (**1**). In the second step, the semicrystalline LLA blocks were subsequently copolymerized onto each side, creating an A-(B/C)-A block copolymer. To perform a comparative study, the A–B–A triblock copolymers of LLA with a middle block of DXO or TMC have been synthesized under the same conditions. The copolymer compositions were chosen based upon the results of our earlier work.^{20,25,26} The polymerization was designed to create a middle amorphous blocks with 400 repeating units; in the case of the two-monomer middle block, the relations between DXO and TMC repeating units were 300:100, 200:200, and 100:300. The terminal LLA blocks consisted of 100 repeating units each. The compositions of the copolymers and the SEC results are presented in Table 1.

The reactions were followed by 1H NMR to calculate the monomer conversion and to confirm the polymer formation. When the polymerization was performed with a mixture of DXO

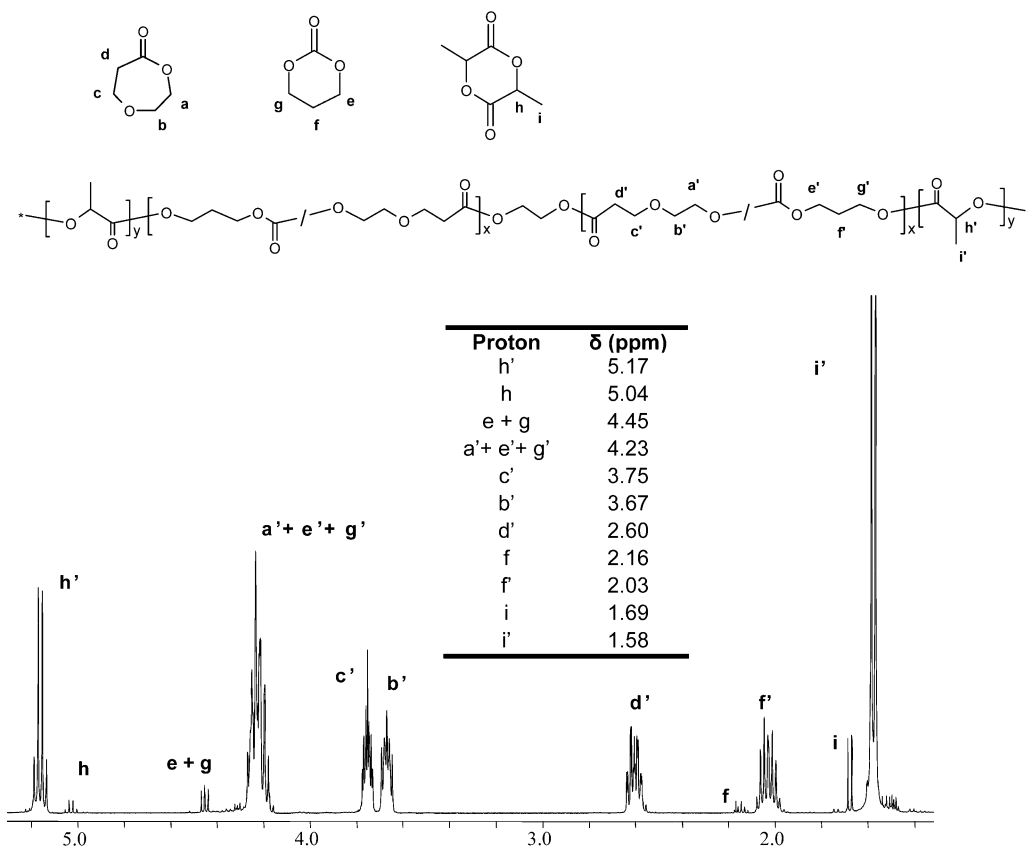


Figure 1. 400 MHz ^1H NMR spectrum of the poly((DXO-co-TMC)-block-LLA) before precipitation and the peak assignments.

Table 1. Characteristics of Copolymers Synthesized in Chlorobenzene at 80 $^\circ\text{C}$

polymer	feed ratio $[\text{M}]_0/[\text{I}]^a$			M_n^b	M_n^c	M_w/M_n^d	yield, %
	DXO	TMC	LLA				
P1	0	400	200	68000	62800	1.32	81.1
P2	100	300	200	66500	57300	1.30	76.1
P3	200	200	200	67800	73400	1.30	86.6
P4	300	100	200	73100	60000	1.25	90.6
P5	400	0	200	68600	51000	1.20	79.0

^a $[\text{M}]_0$, initial monomer concentration; $[\text{I}]$, initiator concentration. ^b Theoretical average molecular weight of the triblock copolymer calculated from the actual monomer feed. ^c Average molecular weight obtained with size exclusion chromatography using narrow polystyrene standards. Because of the calibration with the polystyrene standards, the SEC results were used mainly to control the distribution and change in molecular weight during the reaction. ^d Obtained with size exclusion chromatography using narrow polystyrene as standards.

and TMC, it was observed that the DXO reacted faster than the TMC. The DXO monomer was consumed first followed by slower conversion of TMC. After the complete conversion of both DXO and TMC, the LLA was added to the reaction mixture. A representative ^1H NMR spectrum of the DXO-TMC-LLA copolymer synthesized in this way before precipitation is shown in Figure 1.

The ^1H NMR indicated the presence of residual TMC monomer after the first precipitation in the cold diethyl ether, but this disappeared after the second precipitation. The DSC results that will be discussed later did not however exclude the possibility that the polymer might be contaminated with monomer, even though it could not be detected by the NMR analysis.

The ^{13}C NMR analysis of the final copolymers confirmed the formation of perfect block copolymers. The carbonyl region of the spectrum showed a sharp single peak at 169.5 ppm

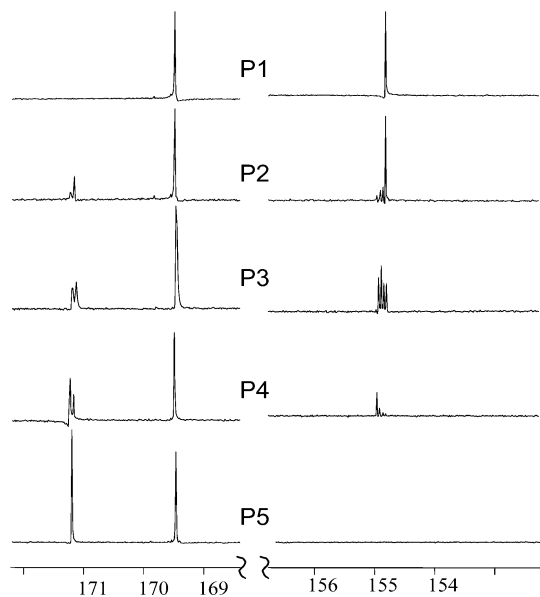


Figure 2. Expanded ^{13}C NMR spectra of the carbonyl region of the copolymers based on DXO, TMC and LLA.

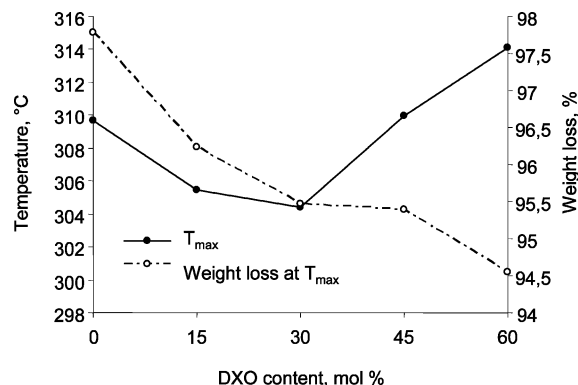
corresponding to the LLA side blocks. The middle block gave a single peak when it was composed either of DXO ($\delta = 171.2$ ppm) or TMC ($\delta = 154.8$ ppm). The ^{13}C NMR spectra of the copolymers with the mixed DXO-TMC middle block showed a relatively random distribution of the repeating units which can be attributed to the transesterification reactions during the polymerization of the middle block. The expanded carbonyl region of the ^{13}C NMR spectra of the copolymers is depicted in Figure 2.

The molar composition of the copolymers was calculated from the signal intensities of the ^1H NMR spectra. The calculated

Table 2. Thermal Properties of the Copolymers Based on DXO, TMC, and LLA

polymer ^a	T_{g1} , °C ^b		T_{g2} , °C ^b	T_m , °C ^b		w_c , %	
	1st heating	2nd heating	1st heating	1st heating	2nd heating	1st heating	2nd heating
P1 (0:400:200)	−15.4	−10.6	50.0	159.4	157.9	31.3	29.3
P2 (100:300:200)	−23.3	−21.4	53.8	160.8	156.3	22.1	21.9
P3 (200:200:200)	−29.5	−26.8	43.6	163.5	160.8	27.7	22.9
P4 (300:100:200)	−34.1	−30.4	44.0	159.3	158.2	33.1	26.9
P5 (400:0:200)	−36.7	−31.7	44.8	152.5	146.7	37.0	36.1

^a The estimated composition of copolymer within parentheses (DXO:TMC:LLA). ^b The standard deviations of values were smaller than 0.3 °C.

**Figure 3.** Thermal degradation behavior of the copolymers based on DXO, TMC and LLA plotted against DXO content.

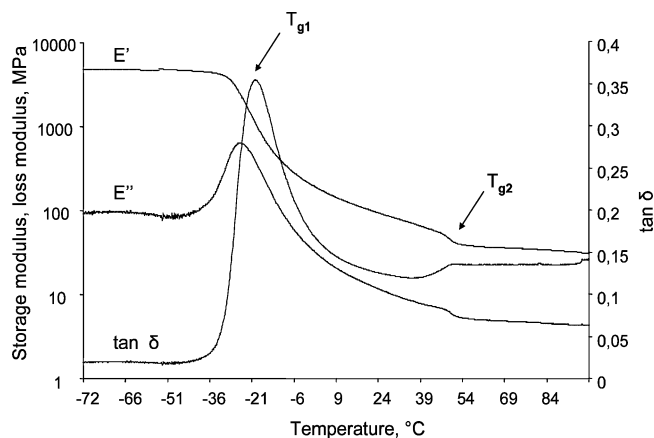
molar composition was in accordance with the monomer feed ratio.

Thermal Properties (DSC and TGA). The DSC results showed two glass transition temperatures (T_g) as expected for this type of copolymers. The first clear transition between the T_g of the respective homopolymers, PDXO (−39 °C) and PTMC (−17 °C), indicated the formation of a relatively random middle block. The second glass transition corresponding to the T_g of the PLLA side blocks (55 °C) was relatively weak and somewhat difficult to determine. This T_g was also slightly lower than expected. Since no scrambling during formation of the PLLA blocks was detected by ¹³C NMR analysis, the lower T_g values of PLLA segments could be attributed to the relatively short PLLA block length. Another possibility could be a partial mutual “contamination” of the hard phase by the soft phase or vice versa.¹¹ The single melt temperature (T_m) due to PLLA segments was registered for all the copolymers. The T_m values were somewhat lower than the T_m values reported for pure PLLA, for reasons similar to those described above for the T_g of PLLA. The approximate crystallinity of the copolymers, w_c , was calculated according to

$$w_c = \frac{\Delta H_f}{\Delta H_f^0} \quad (1)$$

where ΔH_f is the heat of fusion of the sample, and ΔH_f^0 is the heat of fusion of 100% crystalline PLLA. The value of ΔH_f^0 used for the calculations was 93 J/g.²⁷ Thermal properties of the copolymers are summarized in Table 2.

To foresee the behavior of the copolymers during a possible thermal processing, a thermogravimetric analysis of the copolymers was performed. The thermal stability of all of the copolymers was fairly similar, with decomposition starting just above 200 °C. The temperature of the maximum rate of weight loss, T_{max} , varied between 304 and 314 °C. The percentage weight loss at T_{max} decreased slightly with increasing DXO content. The thermal behavior is illustrated in Figure 3.

**Figure 4.** Storage modulus (E'), loss modulus (E''), and $\tan \delta$ as function of temperature of copolymer P3 (the estimated composition of copolymer is 200:200:200 (DXO:TMC:LLA)). T_{g1} and T_{g2} are the glass transitions of the TMC-DXO block and LLA block, respectively.

DMA. The microphase separation was confirmed by the DMA analysis. The DMA traces demonstrated a pronounced transition in the region corresponding to the T_g of the amorphous middle block and a second weaker transition around the T_g of the PLLA block. A representative DMA curve is shown in Figure 4.

The results of DMA measurements are summarized in Table 3. The T_g values determined by DMA were in agreement with the results obtained by DSC analysis (Figure 5). The storage modulus of the copolymers, E' , was higher with a higher content of DXO in the middle block (Figure 6). The loss modulus E'' peak shifted toward lower temperatures with increasing content of DXO.

Mechanical Properties. Soft-tissue engineering applications put specific demands on the properties of the copolymers. Besides biocompatibility, the mechanical characteristics such as modulus and elasticity of the material are of a crucial importance for the suitability of the material as a temporary implant. To provide insight into the mechanical properties of the copolymers synthesized, tensile measurements and cycling loading have been performed. The copolymers showed a similar tensile behavior up to 10–20% strain (Figure 7); thereafter, they performed differently. The copolymers composed of two monomers (TMC and LLA or DXO and LLA) showed a behavior similar to that of crystal-bearing elastomers,²⁸ with increasing strength until break and pronounced strain hardening (strain-induced crystallization). The TMC–LLA copolymer, P1, showed significantly higher stress at break, around 35 MPa, than the other copolymers tested. The introduction of DXO repeating units into the TMC block resulted in more flexible chains. The copolymer with the mixed DXO–TMC middle block (copolymers P2–P4) showed a relatively consistent stress until failure and a significantly higher strain at break than copolymers P1 and P5. The copolymer P3 with the middle block containing equal molar parts of TMC and DXO showed the

Table 3. DMA Data for the Copolymers Based on DXO, TMC, and LLA

polymer ^a	storage modulus at 23 °C,	loss modulus peak value,	loss modulus peak,	loss tangent peak value		loss tangent peak, °C ²	
	MPa	MPa (T_{g1})	°C (T_{g1}) ^b	T_{g1}	T_{g2}	T_{g1}	T_{g2}
P1 (0:400:200)	58.5	574.1	-11.7	0.50	0.08	-7.8	55.0
P2 (100:300:200)	86.5	445.0	-18.0	0.35	0.13	-12.9	53.3
P3 (200:200:200)	94.3	585.7	-24.4	0.36	0.13	-19.3	50.1
P4 (300:100:200)	53.9	583.9	-28.9	0.33	0.13	-23.3	51.5
P5 (400:0:200)	60.6	728.5	-32.8	0.38	0.14	-27.3	52.0

^a The estimated composition of copolymer within parentheses (DXO:TMC:LLA). ^b The standard deviations of the values were smaller than 0.2 °C.

Table 4. Tensile Properties of the Copolymers Based on DXO, TMC, and LLA

polymer ^b	stress at upper yield,	strain at upper yield,	stress at break,	Young's modulus,	
	MPa	%	MPa	strain at break, %	MPa
P1 (0:400:200)			35.6 (5.0)	593 (85)	62.2 (4.6)
P2 (100:300:200)	6.0 (0.1)	320 (26)	4.5 (0.9)	918 (114)	67.6 (1.9)
P3 (200:200:200)	6.3 (0.3)	705 (78)	5.9 (0.4)	1089 (140)	65.6 (4.1)
P4 (300:100:200)	5.3 (0.4)	551 (42)	4.9 (0.2)	690 (74)	53.0 (6.1)
P5 (400:0:200)			9.8 (1.7)	557 (24)	48.7 (2.3)

^a The values within parentheses are the standard deviations. ^b The estimated composition of copolymer within parentheses (DXO:TMC:LLA)

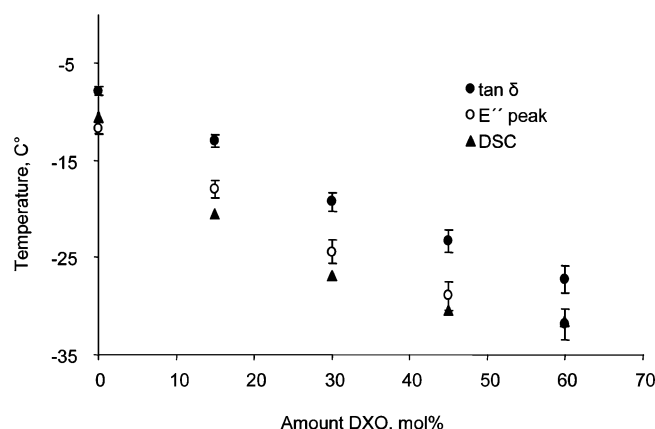


Figure 5. Effect of DXO content on the glass transition temperature of the copolymers based on DXO, TMC and LLA; temperatures at the loss modulus peak (●) and at the $\tan \delta$ peak (○), and the values obtained with DSC measurements (▲) are shown. The error bars indicate the confidence interval of 95%. The standard deviation of the single DSC data points was smaller than 0.3 °C.

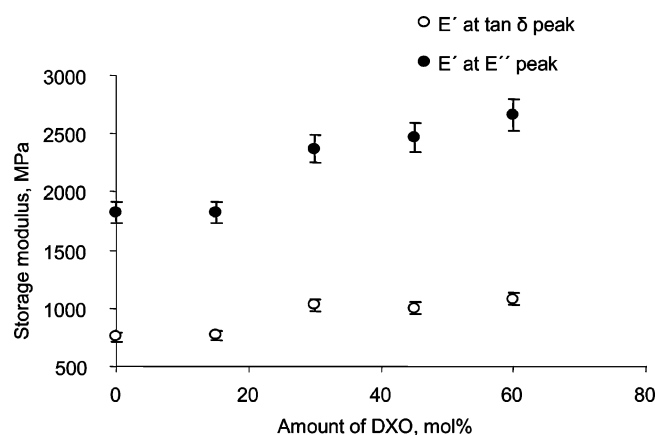


Figure 6. Effect of DXO content on the storage modulus E' of the copolymers based on DXO, TMC and LLA (E' values at loss modulus peak (●) and at $\tan \delta$ peak (○) are shown). The error bars indicate a 95% confidence interval.

highest strain at break, over 1000%. The initial modulus was generally higher in the copolymers which had a larger amount of TMC. The dependence was not linear: the Young's modulus

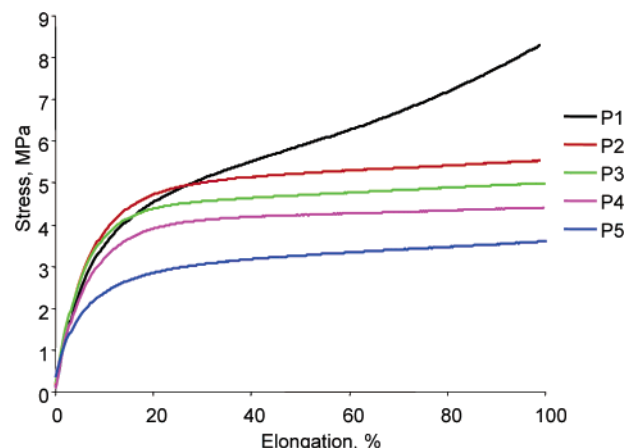


Figure 7. Stress-strain behavior of poly(TMC-*block*-LLA), poly((DXO-*co*-TMC)-*block*-LLA), and poly(DXO-*block*-LLA) during tensile testing up to an elongation of 100%.

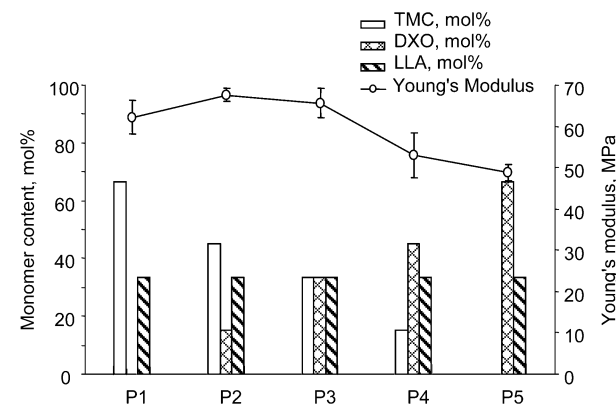


Figure 8. Effect of the copolymer composition on the Young's modulus. The error bars indicate the confidence interval of 95%.

increased slightly with the introduction of DXO into the TMC block and decreased somewhat with increasing DXO content, presumably because of the complex three-component structure of the macromolecules (Figure 8).

Thus, the copolymer P2 in which the middle block consisted of 0.25 mol fraction of DXO and 0.75 mol fraction of TMC

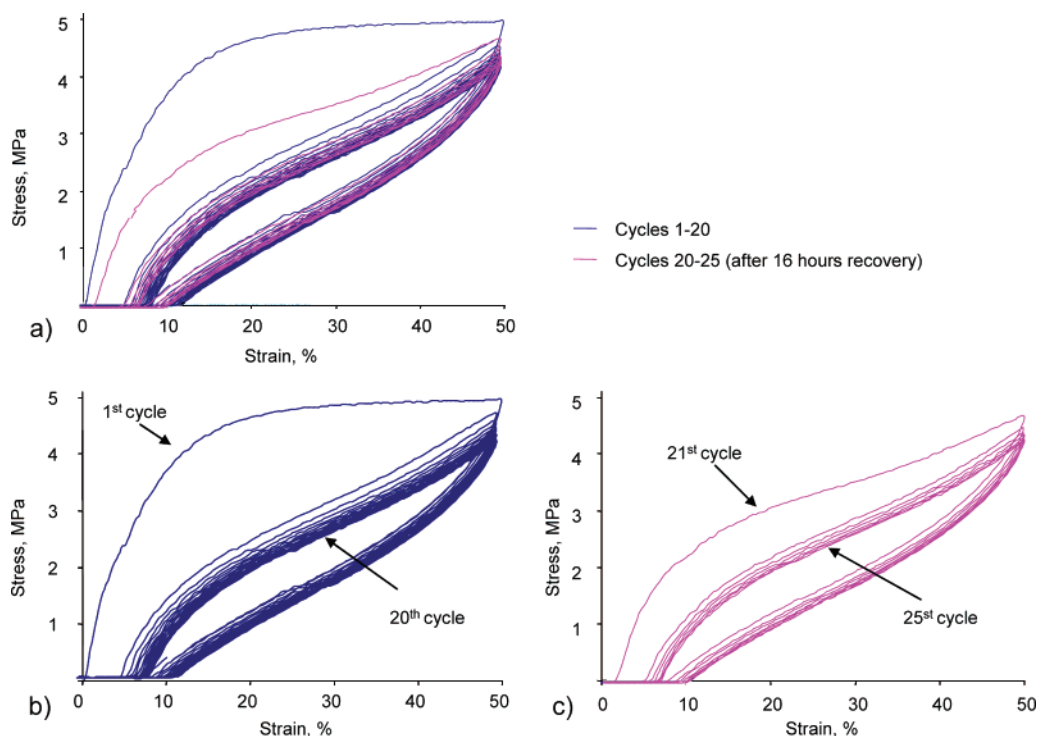


Figure 9. Stress–strain properties of the copolymer P3 (the estimated composition of copolymer is 200:200:200 (DXO:TMC:LLA)) upon cycle loading (a) overlay of all cycles, (b) cycles 1–20, and (c) cycles 21–25 (after 16 h relaxation).

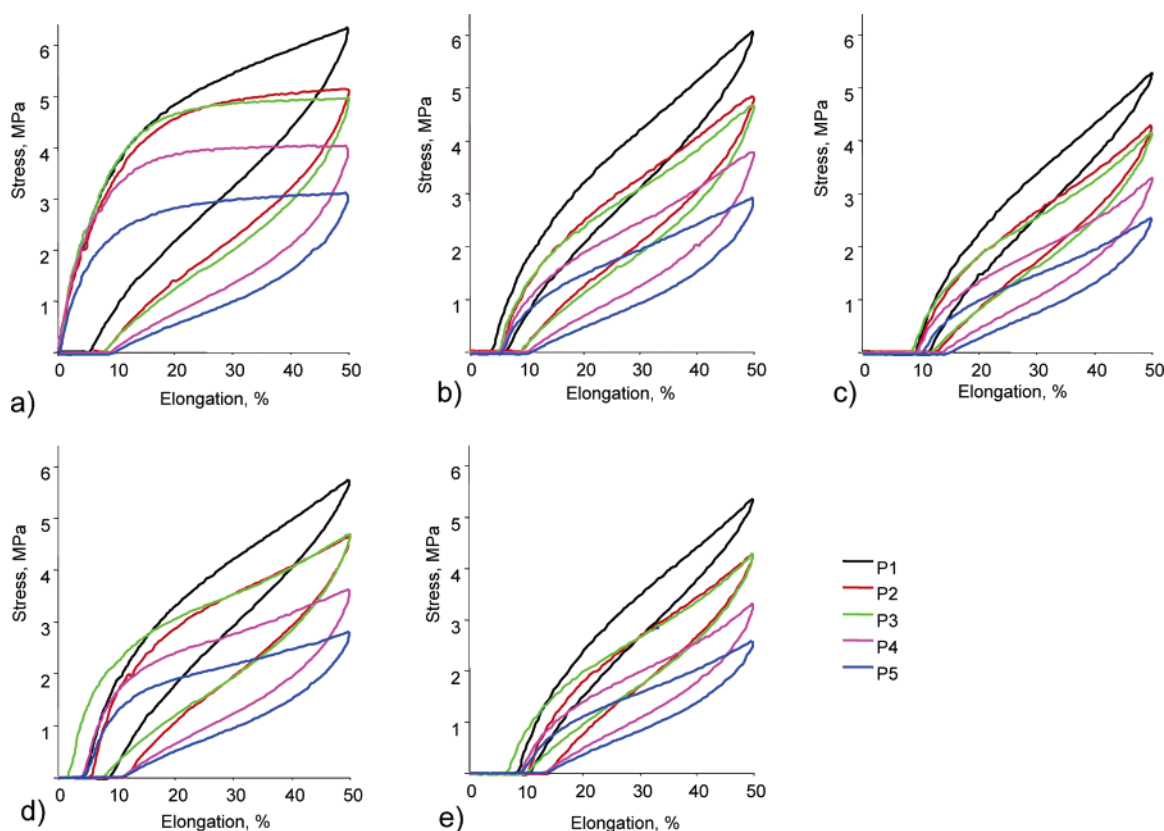


Figure 10. Stress–strain behavior of poly(TMC-*block*-LLA), poly((DXO-*co*-TMC)-*block*-LLA), and poly(DXO-*block*-LLA) upon cycling loading: (a) 1st cycle, (b) 2nd cycle, (c) 20th cycle, (d) 21st cycle (after 16 h relaxation), and (e) 25th cycle (after 16 h relaxation).

had the highest Young's modulus, around 67 MPa. The results of tensile testing are summarized in Table 4.

All of the copolymers were highly elastic, showing ca. 80% recovery even after 25 cycles. The cycle loading tests demonstrated that the mechanical properties of the copolymers were strongly affected by repeated loading, especially after the first

and second cycles. The following phenomena were observed in all of the copolymers studied: a larger mechanical hysteresis was characteristic of the first cycle resulting in a relatively large initial set. The stress softening in the ascending curve in the 1st cycle can be caused by a rearrangement in the crystalline microphase, formed during the film casting.²⁸ The hysteresis

area decreased in the 2nd cycle, and a much smaller additional set was observed. The difference between the ascending curve of the first cycle and the ascending curve of the 2nd cycle can probably be explained by a reorientation of macromolecules combined with the crystallization during straining. During the cycles 3–20, the narrowed hysteresis shape of the second cycle was repeated and produced smaller additional set after each cycle (Figure 9b). After 16 h relaxation (Figure 9c), the permanent set produced during the first cycling decreased markedly, but after the 21st cycle, the stress–strain curves followed the same traces as in the cycles 3–20. The tensile behavior of the copolymers upon cyclic loading is shown in Figure 10. The set after the 20th cycle was lowest for the copolymer P3 (16%) and highest for P5 (20%) (Figure 10c). A similar trend was observed after the 16 h recovery: P3 showed the lowest set (ca 3%), whereas the highest set was observed in P2 (ca 10%).

Conclusions

Resilient copolymers based on DXO, TMC, and LLA were synthesized using a tin alkoxide as initiator. These copolymers were compared to copolymers consisting of either LLA and DXO or LLA and TMC synthesized under the same conditions.

The formation of perfect block copolymers was confirmed by the ^{13}C NMR spectra analysis. The carbonyl region of the spectra showed a sharp single peak corresponding to the LLA terminal blocks in all of the copolymers. In the copolymers in which the middle amorphous block was composed of both TMC and DXO, the appearance of the corresponding peaks indicated the randomized structure of the middle block. The ^1H NMR analyses confirmed that the copolymer compositions were in agreement with the monomer feed ratio.

The microphase separation in the copolymers was confirmed by the DSC and DMA results. The DSC measurements revealed two transitions corresponding to glass transition temperatures of the amorphous and semicrystalline blocks in the copolymer. The T_g values of the amorphous block were correlated with the composition of the middle block of the copolymers.

Tensile testing and cycle loading measurements proved that it is possible to tailor the elastic properties. All of the copolymers synthesized exhibited a highly elastic behavior. The copolymer with a mixed DXO–TMC middle block showed a relatively consistent strain to failure and significantly higher strain at break.

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