

Bicomponent Transparent Polyester Networks with Shape Memory Effect

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ABSTRACT: Elastic bicomponent networks with shape memory effect were obtained via cross-linking reactions of unsaturated polyester with methacrylates. Unlike conventional shape memory polymers, the new material is transparent, rubbery, and can be tailored to various transition temperatures by macromolecular engineering. Various unsaturated copolymers of α -methylene- γ -butyrolactone and ε -caprolactone were synthesized by ring-opening mechanism. Depending on the composition of the unsaturated polyester materials, their mechanical properties and glass transition temperature were varied.

Introduction

Unsaturated polyesters are of high scientific interest and commercial importance for decades.^{1–3} They are preferently obtained via polycondensation reactions of various diols with maleic anhydride. As a result, these unsaturated technically used polyesters contain electron poor double bonds, which allows them to copolymerize with comonomers containing electron-rich double bonds, e.g., styrene or vinyl ethers. Similarly, the polycondensation of itaconic acids with diols leads to polyesters with double bonds in the α -C atom position.^{4,5} While a polycondensation reaction of this type usually requires exact stoichiometry to achieve high molecular mass, polyesters can alternatively be easily prepared via ring-opening polymerization (ROP) of lactones.⁶ This reaction can be lipase-catalyzed, ^{7–11} metal-catalyzed, ^{12–14} and anionically^{15,16} or cationically¹⁷ initiated.

To incorporate double bonds into the polyester chain, α -methylene- γ -butyrolactone (α -MBL)^{18,19} is of potential interest. It is the simplest member of a class of naturally occurring sesquiterpene lactones. Various methods were described for its synthesis and that of related compounds containing the α -methylene- γ lactone structural moiety which are of the interest to medical chemists.²⁰ However, only free-radical polymerizations of the compounds are known. The first free-radical polymerization was accomplished in a patent from McGraw (1953).²¹ Akkappeddi²² reported both the free-radical and anionic polymerization. α -MBL was copolymerized with several monomers, including styrene and methyl methacrylate (MMA).²³ Studies of the freeradical polymerization of exocyclic methylene monomers such as α -methylene- γ -butyrolactone or α -methylene- δ -valerolactone were studied by Ueda and Pittman in the 1980s.²⁴⁻²⁶ In recent years, there has been a renaissance of interest in the chemistry of this lactone.^{27–29} The ring-opening homo- and copolymerization of α -methylene- ε -caprolactone have been investigated.³⁰ Chemospecific ring-opening polymerizations of α -methylenemacrolides have been studied in recent years.³¹ However, up to date, a ring-opening mechanism of α -MBL has not been described. In the present work, the formation of unsaturated polyesters of α -MBL via ring-opening copolymerization with ε -caprolactone is described.

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Shape memory polymers (SMPs) behave like elastomers above their shape transition temperature T_{trans} and can be reversibly deformed. While cooling below T_{trans} , they remain in a temporary shape that can be released to the original shape by reheating above T_{trans} . SMPs have attracted extensive attention and are considered to be promising for many applications, e.g., as implant materials in biomedical applications. Polymers that show a shape memory effect are generally polymer networks. Their performance can be explained by the existence of permanent cross-links. SMPs can be either chemically cross-linked or physically cross-linked polymer networks. Network chains with a thermal transition at T_{trans} serve as molecular switch triggering the shape memory effect. Because of the flexibility of the network chains the polymer can show extensive deformation at temperature above T_{trans} . In contrast, by freezing the SMP below T_{trans} the network chains lose their mobility, and the polymer can be frozen in a temporary shape. The cross-links stabilize the permanent shape of the networks in the course of shape memorizing. SMP networks from oligo(*ε*caprolactone)dimethacrylates have been investigated.^{32,33} The shape memory effect of the poly(caprolactone) (PCL) network was attributed to the crystallization of the PCL segments. Because of the crystalline phase, the SMPs were opaque at their performance temperature. In this work, transparent bicomponent networks with shape memory effect were obtained by chemical cross-linking of unsaturated polyesters and methacrylates.

Experimental Section

Materials. γ -Butyrolactone (Fluka), sodium hydride (60 wt % dispersion, Aldrich), formic acid ethyl ester (Fluka), paraformaldehyde (Aldrich), bismuth(III) trifluoromethanesulfonate (Aldrich), methacrylic acid 2-ethoxyethyl ester, and methacrylic acid tetrahydrofurfuryl ester (Aldrich) were used without further purification. Potassium carbonate (Riedel-de Haën), tetrahydrofuran (THF) (AnalaR NORMAPUR), diethyl ether (technical) (Et₂O) (Riedel-de Haën), and ethanol (absolute) (AnalaR NORMAPUR) were used as received. Paraformaldehyde (Aldrich) was dried over phorsphorus pentoxide in an exicator overnight. ε -Caprolactone was purchased from Aldrich dried over 0.4 nm molecular sieves under an argon atmosphere.

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Characterization. The ¹H NMR spectra were recorded from solutions in deuterated chloroform and dimethyl sulfoxide as solvents on a Bruker DRX 500 operating at 500 MHz. The δ -scale was calibrated to TMS.

Thermal properties were determined using a Mettler Toledo DSC822 controller apparatus in the temperature range of -50 and 250 °C at a heating rate of 10 °C min⁻¹. Three heating cycles were conducted. The melting point values are reported as the average of the peak maxima of the second and the third heating cycle.

Molecular mass and molecular mass distributions were measured by gel permeation chromatography (GPC) using a hydroxyethyl methacrylate (HEMA)-5 μ m column set consisting of a precolumn of 4 nm and main colums of 10³, 10², and 10 nm. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL min⁻¹. For online detection, a Waters 486 tunable absorbance detector ($\lambda = 256$ nm) and a Waters 410 differential refractometer were used. The system was calibrated with polystyrene standards in a molar mass range from 580 to 1 186 000 Da.

Tensile tests were conducted on a Zwick/Roell apparat BTC-FR2.5TN.D09. The samples had a slat shape (5 cm \times 1 cm \times 0.3 cm). The measurements were carried out at 37 °C with an elongation rate of 10 mm min⁻¹.

Synthesis of α -Methylene- γ -butyrolactone (α -MBL) 3. This lactone was prepared from γ -butyrolactone according to the procedure described in the literature.^{18,19} To a stirred suspension of sodium hydride (40 g of 60% oil dispersion, 1 mol) in 800 mL of diethyl ether, absolute ethanol (6 mL, 0.11 mol) was added under N2 atmosphere. It was immediately followed by a mixture of formic acid ethyl ester (80.8 mL, 1 mol) and γ -butyrolactone (77.0 mL, 1 mol). The suspension was stirred over 2 h, and the rate of addition was controlled to give a steady reflux and evolution of H₂. After completing the addition, the mixture was stirred for a further 0.5 h and the solid filtered, washed with Et₂O, and dried in vacuum to give α -formyl- γ butyrolactone sodium salt (2) (yield: 96%). To a stirred suspension of paraformaldehyde (4.5 mol) in THF (1.5 L) α -formyl- γ -butyrolactone sodium salt (1 mol) was added under a N2 atmosphere. The reaction mixture was heated to reflux immediately for 1 h. After cooling down to 10 °C the mixture was treated with 1 M aqueous K₂CO₃ solution (300 mL) and Et₂O (1 L), and the organic layer was separated, dried, and evaporated to dryness to afford a pale yellow oil. Purification by vacuum distillation yielded 3 (64%). ¹H NMR (500 MHz, CDCl₃): $\delta = 2.69$ (2H, m), 4.05 (2H, t, J = 7 Hz), 5.37 (1H, t, J = 3 Hz), 5.83 ppm (1H, t, J = 3 Hz)3 Hz).

Synthesis of Poly(α -methylene- γ -butyrolactone-*co*- ε -caprolactone) 5a-f. A typical experimental procedure can be described as follows: 0.29 g (2.92 mmol) of α -MBL and 1.00 g (8.76 mmol) of ε -CL was mixed with 0.05 mol % of the catalyst bismuth(III) trifluoromethanesulfonate in a 10 mL vial sealed with a septum. The stirred reaction mixture was kept at 130 °C for 1 h. After cooling down to room temperature, the reaction mixture was diluted with 10 mL of chloroform and poured into 300 mL of cold methanol. The precipitated polymer was isolated by filtration and dried under vacuum. ¹H NMR (500 MHz, CDCl₃): δ = 1.31–1.40 (m, $-O(CH_2)_2CH_2(CH_2)_2C=O-$), 1.59–1.69 (m, $-OCHH_2CH_2CH_2CH_2CH_2C=O-$), 2.23–2.31 (t, ³J = 7.5 Hz $-O(CH_2)_4CH_2C=O-$), 2.60–2.62 (t, ³J = 6.6 Hz $-OCHH_2CH_2C+$ (=CH₂)C=O-), 4.01–4.09 (t, ³J = 6.7 Hz $-OCHH_2(CH_2)_4-$ C=O-), 5.59 and 6.20 (each s, $-C(=CH_2)-$).

Cross-Linking of Poly(α -methylene- γ -butyrolactone-*co*- ϵ caprolactone) with Methacrylates 8a–d. A typical experimental procedure can be described as follows: 2.48 g of unsaturated polyester 5a and 12.4 g of methacrylic acid 2-ethoxyethyl ester 6 were added to a 25 mL two-neck round-bottom flask equipped with a septum. The reaction mixture was purged with nitrogen for 30 min. After dissolving the polyester completely, 0.07 wt % Scheme 1. (a) Synthesis of α -MBL^{18,19} and (b) Reaction Scheme of the Ring-Opening Copolymerization of α -MBL and ϵ -CL



Table 1. Ch	aracteristics	of a-MBL	Copolymers
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entry	[ε-CL]/ [α-MBL]	ln (χ _{CL})	$\frac{M_{ m n}{}^{a}}{10^{3}~{ m g~mol}^{-1}}$	PD^{a}	$T_{\rm m}{}^b/{}^{\rm o}{\rm C}$	yield/%
5a	1	0.94	4.1	2.3	43.5	40
5b	1.5	0.31	6.77	2.6	49.9	58
5c	3	0.22	7.25	1.8	51.8	56
5d	5	0.05	12.5	1.5	52.3	48
5e	20	0.01	16.6	1.5	53.5	68
5f	50	0.006	13.7	1.5	53.7	52

^{*a*}GPC with poly(styrene) calibration. ^{*b*}DSC, average of the second and third heating cycle.

radical initiator 2,2'-azobis(2,4-dimethyl)valeronitrile was added to the reaction mixture. The liquid was injected into a mold and heated to 60 °C for 24 h. The cross-linked polymer was removed from the mold. In a vacuum drying cabinet the rest monomer was extracted from the polymer (125 °C and 1.2 mbar, 2 days). DSC: $T_g = -20$ °C.

Results and Discussion

The copolymerization of α -methylene- γ -butyrolactone, accessible by a literature procedure,^{18,19} and ϵ -CL was carried out via ring-opening polymerization by using of bismuth(III) trifluoromethanesulfonate as catalyst (Scheme 1). In initial experiments we carried out the ROP of α -MBL with various catalysts. But the lactone was not able to be ring-opening polymerized by using common catalysts like tin(II) 2-ethylhexanoate, titanium(IV) n-butoxide, or Novozym 425. Among the metal organic catalysts only bismuth(III) trifluoromethanesulfonate is able to catalyze a ring-opening polymerization of this lactone. As the ring-opening polymerization is metalcatalyzed, we suggest a coordination-insertion mechanism. The results obtained from the polymerization experiments are summarized in Table 1. The conversion of α -MBL is significantly slower compared to the more reactive ε -CL under the applied condition. The molar content of α -MBL in the obtained copolymers was estimated by ¹H NMR spectroscopy by comparing the integrated signal of the hydrogen atoms of the double bond in α -MBL (singlets at 5.55 and 6.17 ppm) with the integrated signal of the hydrogen atoms of the $-CH_2C=O-$ group of ε -CL (triplet at 2.29 ppm) in the copolymer. The integrated signals of the exovinylidene hydrogen atomes (f in Figure 1) are equal to those of $-O-CH_2$ (h in Figure 1) or $-CH_2C(CCH_2)$ (g in Figure 1). Thus, the exovinylidene group remains unmodified. Because of that, a consequent radical polymerization reaction can be employed. The achieved M_n values of the obtained copolymers are in the molecular range of 10^4 g mol⁻¹.

Poly(ϵ -caprolactone) homopolymer crystallizes at about 55 °C. In the investigated copolymers the α -MBL sequences in copolyester disturb the crystallization process, and consequently an increasing amount of α -MBL in copolymer causes a decrease of the melting point of the copolyester. Equation 1 describes the



Figure 1. ¹H NMR of poly(α -methylene- γ -butyrolactone-*co*- ε -caprolactone) **5d** in CDCl₃.



Figure 2. Dependence of the reciprocal melting point $1/T_{\rm m}$ on the negative natural logarithmic mol fraction $-\ln \chi_{\rm CL}$ of ε -CL in copolyester **5**.

Scheme 2. Reaction Scheme of the Cross-Linking of Poly(α-MBL-coε-CL) 5a with Methacrylate



influence of noncrystallizable components on the melting point of a crystalline material. $T_{\rm m}$ is the melting point of the copolymer, and $T_{\rm m}^0$ is the melting point of the ε -CL homopolymer under the same crystallization conditions. $\Delta H_{\rm m}$ represents molar heat of fusion of the repeat unit.³⁴ The activity *a* can be substituted by the mole fraction $\ln(\chi_{\rm CL})$ which leads to approximation (2).

$$\frac{1}{T_{\rm m}} - \frac{1}{T_{\rm m}^0} = -\frac{R}{\Delta H_{\rm m}} \ln(a) \tag{1}$$

$$\frac{1}{T_{\rm m}} - \frac{1}{T_{\rm m}^0} = -\frac{R}{\Delta H_{\rm m}} \ln(\chi_{\rm CL}) \tag{2}$$

The reciprocal melting points of the copolymers **5a**–**f** show a linear dependence to the negative natural logarithmic mole fraction of ε -CL (Figure 2). From the *y*-axis intercept of the linear equation of the straight line the value for $T_{\rm m}^0 = 53.6$ °C (lit.:³⁵ $T_{\rm m}^0 = 55$ °C) was calculated. $\Delta H_{\rm m} = 69.3$ kJ/mol was calculated from the slope of the linear equation.

Table 2. Variation of T_g in Dependence of the Amount of Poly(α -MBL-*co-\varepsilon*-caprolactone) 5a and Methacrylates 6 and 7



Figure 3. Elongation measurements of 8b and 8c at 37 $^{\circ}$ C with an elongation rate of 10 mm min⁻¹.



Figure 4. Photoseries demonstrating the shape memory effect of the polymer network 8b (from left to right) showing the transition from a tempory shape to a permanent shape at room temperature after twisting and freezing at -20 °C depending on time.

The exo-vinylidene group of incorporated α -MBL in copolyester can be used for further radical reactions. In this work they were used for cross-linking reactions with methacrylates 6 and 7 to yield bicomponent networks (Scheme 2). These networks do not crystallize. Thus, they are transparent. In a control experiment a radical copolymerization of the monomer 6 in unmodified $poly(\varepsilon$ -caprolactone) was carried out. It does not lead to a polymer network. Thus, the double bond containing polyester is necessary for the radical cross-linking reaction with methacrylates. The $T_{\rm g}$ values of the homopolymers of monomers 6 and 7 are 2 and 240 °C, respectively. The T_g decreases with increasing amounts of unsaturated polyester 5a (Table 2). Because of that, it can be assumed that the polyester acts as a plasticizer. In addition to it, the mechanical performance of the bicomponent networks was investigated. Depending on the amount of unsaturated polyester in the network the elasticity of the cross-linked material can be varied (Figure 3). Increasing amounts of polyester increase the degree of cross-linking, which should result in a decrease of elasticity. Surprisingly, since the polyester obviously acts as a plasticizer the elastic modulus decreases from 1.75 (8b) to 1.12 N mm^{-2} (8c) (Figure 3).

The cross-linked material **8a**–**d** also show an interesting shape memory effect which depends on the transition temperature T_{trans} of the transparent material. Figure 4 shows a photoserie demonstrating the shape memory effect of the polymer network **8b** as one example. T_{trans} is related to the glass transition temperature T_g of a material. Raising the T_g of a SMP increases its T_{trans} . Above T_g the SMP can be deformed. It can be fixed in a tempory shape by cooling below the T_g (Figure 4, t = 0 min). After reheating above T_g it automatically recovers to its original shape (Figure 4, t = 5-17 min). In this work variations in T_g of the cross-linked material were achieved by using different amounts of unsaturated polyester and a mixture of two methacrylates. For example by using a mixture of methacrylic acid 2-ethoxyethyl ester and methacrylic acid tetrahydrofurfuryl ester, the T_g was increased to 29 °C (8a).

Conclusion

Unsaturated polyesters can be synthesized by ring-opening polymerization of lactones. For the first time α -methylene- γ -butyrolactone was copolymerized via ring-opening. These unsaturated polyesters can be cross-linked with methacrylates by radical reactions. The obtained material is transparent and elastic and shows shape memory effect. The elasticity and the glass transition temperature of the material can be controlled in a range of -26 up to 29 °C.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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