Shape-Memory Polymer Networks from Oligo[(ϵ-hydroxycaproate)-*co*-glycolate]dimethacrylates and Butyl Acrylate with Adjustable Hydrolytic Degradation Rate

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Degradable shape-memory polymer networks intended for biomedical applications were synthesized from oligo[(ϵ-hydroxycaproate)-*co*-glycolate]dimethacrylates with glycolate contents between 0 and 30 mol % using a photopolymerization process. In addition AB copolymer networks were prepared by adding 60 wt % *n*-butyl acrylate as comonomer. All synthesized polymer networks are semicrystalline at room temperature. A melting transition T_m between 18 and 53 °C which can be used as switching transition for the shape-memory effect can be attributed to the crystalline poly(ϵ-hydroxycaproate) phase. At temperatures below T_m the elastic properties are dominated by these physical cross-links. At temperatures higher than T_m the E modulus of the amorphous polymer networks is lowered by up to 2 orders of magnitude, depending on the chemical cross-link density. Copolymer networks based on macrodimethacrylates with a M_n of up to 13 500 g·mol^{-1} and a maximum glycolate content of 21 mol % show quantitative strain recovery rates in stress-controlled cyclic thermomechanical experiments. Hydrolytic degradation experiments of polymer networks performed in phosphate buffer solution at 37 °C show that the degradation rate can be accelerated by increasing the glycolate content and decelerated by the incorporation of *n*-butyl acrylate.

Introduction

Materials which obtain their functionality after application of a functionalization process such as that described for shape-memory polymers can be referred to as *functionalized materials*.[1] An actual trend in polymer science is the design of materials which show multifunctionality, meaning an unexpected combination of material functionalizations such as the combination of hydrolytic degradability and shape-memory functionality.[2−4] The shape-memory effect results from the combination of the polymer architecture with a certain processing and programming technology. The permanent shape of shape-memory polymers is defined by physical or chemical cross-links, while switching segments formed by domains, which are associated with a thermal transition $T_{trans.}$, enable the fixation of the temporary shape.[1,5] To obtain a defined shape change upon transition of a switching temperature T_{switch}, the temporary shape has to be programmed by application of a thermomechanical treatment. Examples for polymers which combine shape-memory functionality and biodegradability are amorphous polyesterurethane networks based on poly(*rac*-lactide-*co*-glycolate) segments having a glass transition temperature T_g around 55 °C.[5] Poly[(3-hydroxybutyrate)-*co*-(3-hydroxyvalerate) (35 mol % 3-hydroxyvalerate) obtained by a biotechnological process showed a shape-memory effect when samples which were programmed by a cold drawing were submitted to temperatures above 75 °C. The melting transition used to trigger the shape-memory effect and to define the permanent shape simultaneously ranged from 37 to 115 °C.[6]

Examples for polymers showing a thermally induced shape-memory effect which contain poly(ϵ-hydroxycaproate), being conterminous with poly(ϵ-caprolactone), switching segments are thermoplastic polyurethanes[7] and multiblock copolymers containing a biodegradable hard segment forming blocks coupled via diurethane units.[8] Segmented copolymers can also be obtained from oligo(ϵ-hydroxycaproate)diols coupled via hard segment forming aramid units.[9] The parameters to influence mechanical properties and shape-memory behavior of these polymers are the molecular weight of oligo(ϵ-hydroxycaproate)diols and the ratio of hard segment to switching segment forming blocks. An alternative method to obtain shape-memory polymers is the incorporation of poly(ϵ-hydroxycaproate) blocks into covalently cross-linked polymer networks.[10−13] Either covalent cross-linking is reached by photocuring of multiblock copolymers with incorporated cinnamic acid units[10,11] or photoset networks can be obtained by cross-linking of oligo(ϵ-hydroxycaproate)dimethacrylates using UV light.[12,13] In the latter case $T_{trans.}$ associated with the switching phase formed by oligo(ϵ-hydroxycaproate) segments is a melting temperature T_m. The crystallization behavior of the polymer networks has been evaluated as the basic principle for the functionalization process.[12] By increasing the number average molecular weight M_n of macrodimethacrylates from 2000 to 10 000 g·mol^{-1}, T_m can be increased from 32 to 52 °C and it is possible to alter the mechanical properties of the polymer networks in a wide range, such as the elongation at break ϵ_R at room temperature from 20 to 290%. Shape-memory properties such as strain fixity and strain recovery rate have been quantified in cyclic thermomechanical tensile experiments for different maximum elongations.[12] The photoset materials show excellent shape-memory properties with values for the strain recovery rate $R_{r,tot.}$ between

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92 and 97% and average strain fixity rates R_f between 86 and 97% after five cycles.

By incorporation of a second soft segment forming phase in addition to the poly(ϵ-hydroxycaproate) phase, AB copolymer networks with shape-memory properties could be prepared by copolymerization of oligo(ϵ-hydroxycaproate)dimethacrylates with *n*-butyl acrylate as comonomer. The poly(*n*-butyl acrylate) segments are forming an additional amorphous phase with a low T_g and allow the adjustment of mechanical properties of the temporary shape at temperatures below T_m.[13] At room temperature ϵ_R can be varied between 20 and 550%, depending on M_n of the oligo(ϵ-hydroxycaproate)dimethacrylates which directly influences the crystallinity. The influence of the poly(*n*-butyl acrylate) soft segments on the mechanical properties is demonstrated by performing tensile tests. The elastic modulus decreases with increasing *n*-butyl acrylate comonomer ratio for temperatures above or below T_m.

All samples reach similar total shape recovery rates with values for $R_{r,tot.}$ above 99% after three cycles. Whereas the strain recovery ratio increases with increasing *n*-butyl acrylate content, strain fixity rates decrease, reflecting the decreasing ratio of crystalline domains of the material. AB copolymer networks have proven to be hydrolytically degradable in vitro and cell compatible.[14,15]

A strategy to control the degradation rate of poly(α-hydroxyalkanoates) is the incorporation of easily hydrolizable ester bonds into the polyester segments as weak links.[16−21] For this purpose macrodiols from ϵ-hydroxycaproate and diglycolate are prepared by ring-opening copolymerization in the presence of the catalyst dibutyltin oxide. As a transesterification catalyst dibutyltin oxide not only works as catalyst for the ring-opening polymerization but also promotes transesterification in the formed copolyester chain. Depending on reaction time and temperature, co-oligomers with a random sequence distribution are obtained according to ^{1}H NMR analysis.[16] A random distribution of the comonomers is achieved after a certain reaction time. Oligo[(ϵ-hydroxycaproate)-*co*-glycolate] blocks are incorporated as biodegradable switching segments into multiblock copolymers showing shape-memory properties.[22]

In this paper oligo[(ϵ-hydroxycaproate)-*co*-glycolate] blocks are incorporated as chain segments into two different polymer network architectures: copolymer networks from oligo[(ϵ-hydroxycaproate)-*co*-glycolate]dimethacrylates and AB copolymer networks that are synthesized by copolymerization of these macrodimethacrylates and *n*-butyl acrylate as comonomer. Macrodimethacrylates are cross-linked via a photoinitiated free radical polymerization in the melt at 70 °C without the addition of a photoinitiator, resulting in the copolyester networks. The glycolate content of the chain segments is limited to 30 mol % to avoid a pronounced influence of oligo(glycolate) segments on the crystallization behavior of these segments. Changes in crystallinity are reflected by changes in thermal properties as T_m and melting enthalpy ΔH_m and as a consequence influence mechanical properties at a temperature lower than T_m. In this way the incorporation of easily hydrolizable glycolate ester bonds is supposed to produce polymer networks with accelerated hydrolytic degradability but still advantageous thermal and mechanical properties comparable to polymer networks and AB-polymer networks based on oligo(ϵ-hydroxycaproate) chain segments.[12,13]

Experimental Section

Materials. ϵ-Hydroxycaproate (ϵ-caprolactone) (99%, Sigma-Aldrich) was distilled prior to use. Diglycolate (Boehringer Ingelheim) was recrystallized from dry ethyl acetate. Ethylene glycol 99.8% (H_2O < 0.05%), dibutyltin(IV) oxide (98%), and poly(ϵ-hydroxycaproate)diols, with number average molecular weights M_n of 10 000 g·mol^{-1} (all Sigma Aldrich), were used without purification. Triethylamine p.a. (Fluka) was distilled and stored over molecular sieves (pore size, 0.4 nm). Methacryloyl chloride (98+%) and *n*-butyl acrylate (99+%) (both Sigma-Aldrich) were used as received. All solvents (dichloromethane, chloroform, methanol, diethyl ether, ethyl acetate, 2-propanol, and 1,4-dioxane) from Sigma-Aldrich were of pro analysis (p.a.) or HPLC quality. Dichloromethane p.a. was dried over molecular sieves (pore size, 0.4 nm). Hexane fraction (Exxon Mobile) was used without further purification.

Syntheses. Oligo[(ϵ-hydroxycaproate)-*co*-glycolate]diols with different contents of glycolate were synthesized according to a ring-opening polymerization described in the literature.[16] Oligo[(ϵ-hydroxycaproate)-*co*-glycolate]dimethacrylates were synthesized according to a procedure reported in the literature.[23] The respective macrodiol is dissolved in dry CH_2Cl_2 in a nitrogen atmosphere. Upon cooling in an ice bath, triethylamine (3.8 equiv) and methacryloyl chloride (3.8 equiv) are added dropwise. At this temperature the mixture is stirred for 3 days under room temperature. The precipitated salt is separated by filtration. The concentrated filtrate is solved in a 10-fold excess of ethyl acetate (referred to the amount of macrodiol), and the sediment is removed. The oligomers are precipitated in a 10-fold excess of a hexane/diethyl ether/methanol (18/1/1 by volume) mixture and washed with hexane. The product is dried under vacuum at room temperature. The polymer networks were synthesized according to the procedure reported in the literature.[12,13] For the film preparation by subsequent photocuring the macrodimethacrylate or the mixture thereof with butyl acrylate was heated to 70 ± 2 °C and filled into a mold formed by two glass plates (10 cm × 10 cm) and a Teflon spacer of 0.50 mm thickness. For copolymer network photocuring without addition of butyl acrylate the macrodimethacrylates were molten directly onto a glass plate before the mold was sealed. To achieve a good homogeneity, the mold was stored at T_m for another hour. The assembly was irradiated with a Heraeus Noble Light Excimer Laborsystem (λ_{max} = 308 nm) for 30 min for the networks N-CG and 60 min for the AB-CG networks. The distance between the UV source and the sample was 7.5 cm. The sample was swollen and extracted with a 100-fold excess of chloroform for 24 h at room temperature.

Determination of Water Content by Karl Fischer Method. The water content of the solvents was determined by potentiometric titration according to the Karl Fischer method using a KF-Coulometer 684 from Metrohm. Solvents were used for synthesis having a water content of ≤5 ppm.

Gel Content and Degree of Swelling. The sample was swollen in a 100-fold volume excess of chloroform for 24 h at room temperature. The swollen film was weighed to determine m_s after washing in chloroform. The films were dried at 35 °C first under atmospheric pressure and subsequently under vacuum (1 mbar), and the weight of the dried film m_d was determined. The degree of swelling Q was calculated by the following expression:

$$Q = 1 + \frac{\rho_1}{\rho_2}\left(\frac{m_s}{m_d} - 1\right) \tag{1}$$

ρ_1 and ρ_2 are the specific densities of the swelling medium and the polymer.[13,24] The gel content G of a network was calculated according to eq 2:

$$G = \frac{m_d}{m_{iso}} \tag{2}$$

m_d is the weight of the dried sample after extraction, and m_{iso} is the isolated weight of the sample before extraction. The densities of amorphous poly(ϵ-hydroxycaproate) (ρ_2 = 1.09 g·cm^{-3}) and poly(butyl acrylate) (ρ_2 = 1.08 g·cm^{-3}) are assumed, since swollen networks are amorphous.

Table 1. Composition and Molecular Weight of Macrodiols DOH-CG and Macrodimethacrylates DMAC-CG [Composition and Degree of Methacrylation D_M Determined by ^{1}H NMR Spectroscopy; Number Average and Weight Average Molecular Weight M_n and M_w Determined by ^{1}H NMR Spectroscopy and GPC)

macrodiol ID[a]	M_n(^{1}H NMR), g·mol^{-1}	M_n(GPC), g·mol^{-1}	M_w(GPC), g·mol^{-1}	macrodimethacrylate ID[a]	M_n(^{1}H NMR), g·mol^{-1}	D_M(^{1}H NMR), %
DOH-CG(14)-3	3 700	3 300	5 900	DMAC-CG(14)-3	3 500	99
DOH-CG(14)-5	6 200	6 100	9 400	DMAC-CG(14)-5	4 900	100
DOH-CG(14)-7	8 400	7 800	11 600	DMAC-CG(14)-7	6 900	100
DOH-CG(14)-10	11 700	10 700	16 500	DMAC-CG(14)-10	12 800	99
DOH-CG(0)-10	9 700	10 500	16 500	DMAC-CG(0)-10	10 800	76
DOH-CG(12)-10	9 300	10 500	16 300	DMAC-CG(12)-10	12 400	95
DOH-CG(21)-10	13 400	10 400	15 900	DMAC-CG(21)-10	13 500	98
DOH-CG(30)-10	14 300	10 000	16 000	DMAC-CG(30)-10	8 700	98

[a] Nomenclature of oligomers: for X-CG(χ_G)-M_n, X = end group functionality, DOH = α,ω-dihydroxy, DMAC = α,ω-dimethacrylate, C = ϵ-hydroxycaproate, G = glycolate, χ_G = molar ratio of the glycolate units of the whole amount of hydroxycarboxylate repeat units (mol %) determined by ^{1}H NMR spectroscopy, and M_n = number average molecular weight of the oligomers in 10^3 g·mol^{-1} calculated from monomer to initiator ratio

Degree of Methacrylation. The degree of methacrylation D_M was determined by ^{1}H NMR spectroscopy recorded on a Varian 400 MHz Inova NMR spectrometer in deuterochloroform ($CDCl_3$). Tetramethylsilane was used as an internal standard.

Multidetector Gel Permeation Chromatography. The setup for multidetector gel permeation chromatography (GPC) consisted of an 1120 HPLC pump (Polymer Laboratories Ltd., Amherst, MA), a 600 mm × 7.5 mm PL-gel mixed-D column (Polymer Laboratories), a combination of a differential viscosimetry/light-scattering detector (T60A, Viscotek; 670 nm; scattering angle, 90°; Houston, TX), and an Optilab differential diffractometer (8721 ERC, Wyatt Technology, Santa Barbara, CA). Chloroform was used as eluent (HPLC grade, Promochem) at a flow rate of 1.0 mL min^{-1} at room temperature and a pressure of 58 bar. The weight average molecular weight M_w was calculated from the viscosity average of the molecular weight M_η determined by the differential viscosimetry detector. For universal calibration polystyrene standards (Polymer Laboratories) with low polydispersity ($M_w/M_n = 1.05$) and molecular weights between 580 and 995 600 g·mol^{-1} were used.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC7. The sample was heated to 80 °C and kept at this high temperature for 2 min. Subsequently, it was cooled to −80 °C and reheated after 2 min. Heating and cooling was performed using a rate of 10 K·min^{-1}. The transitions were evaluated from the second heating run.

Mechanical and Cyclic Thermomechanical Experiments. Tensile tests were performed on dumbbell-shaped specimen with a gauge length of 3.0 mm and a total length of 10.0 mm. The gauge width and the thickness of the specimen were determined with a slide gauge (precision, 0.05 mm) and a micrometer screw (precision, 0.005 mm), respectively. As tensile testing machine, a Zwick 2.5N1S, (Zwick GmbH & Co.) equipped with a 50 N load cell was used for the measurements at 22 °C. For tensile tests at 37 °C in water, samples were immersed in a 2 L water bath which was connected to a thermostat Ecoline (RE 106, Lauda). As tensile tester for the measurements at 37 and 70 °C, a Zwick 1425 (Zwick GmbH) with a Climatix thermochamber and an Eurotherm temperature controller was used. The deformation rate for all tests was 10 mm·min^{-1}. Cyclic thermomechanical tests were performed on specimen with dimensions as described above for tensile tests. As testing machine a Zwick 1425 (Zwick GmbH) with a Climatix thermochamber (BW 91250, Zwick GmbH) controlled by a controller unit (Eurotherm 902P) was used. The tests in water were performed on a Zwick 2.5N1S, equipped with a 2 L water bath which was connected to a thermostat. The program for strain-controlled cyclic thermomechanical tests consisted of stretching the sample to maximum extension $\epsilon_m = 75\%$ with 10 mm·min^{-1} at a temperature $T_{high} = 70$ °C, holding for 5 min, cooling to a temperature $T_{low} = 0$ °C with 10 K·min^{-1} while keeping under constant strain at ϵ_m, holding for 5 min, heating up to $T_{high} = 70$ °C with 10 K·min^{-1}, and holding T_{high} for 5 min. This cycle was repeated 5 times ($N = 5$). To precondition the specimen for the stress-controlled cyclic thermomechanical experiments, the sample was heated to $T_{high} = 70$ °C for 5 min and strained to $\epsilon_m = 100\%$ for three times. Stress-controlled test cycles consisted of heating the samples to $T_{high} = 70$ °C, with 2 K·min^{-1} stretching to $\epsilon_m = 100\%$ (75% for N-CG-(14)-3) with 10 mm·min^{-1}, cooling to $T_{low} = 15$ °C (5 °C for N-CG-(14)-3), holding T_{low} for 6.5 min, unloading to zero stress, holding for 8.5 min, heating to T_{high}, and holding for 2 min. This cycle is performed once ($N = 1$). For investigating shape recovery in an aqueous medium the temporary shape is programmed in air as described before but is recovered in water using a heating rate of 3 K·min^{-1}. This cycle is performed once ($N = 1$).

Hydrolytic Degradation Experiments. The hydrolysis experiments were performed with planar samples (10 mm × 15 mm × 0.5 mm) at 37 °C in a phosphate buffer solution from Na_2HPO_4 (0.1 mol·L^{-1}) and KH_2PO_4 (0.063 mol·L^{-1}) at pH 7.0. The capacity of the buffer solution of a volume of 15 mL was sufficient to buffer 85 mmol acid. A 0.25 g·L^{-1} amount of sodium azide was added to avoid the growth of microorganisms. At the beginning of the experiment m_{init}, the mass of the dry sample before starting the degradation, was determined. The samples were removed from the hydrolysis medium at defined time periods. The partially degraded sample is dried under vacuum (1 mbar) at 30 °C until constant weight m_t was reached. The relative mass loss μ_{rel} is calculated according to following equation:

$$\mu_{rel} = \frac{m_t}{m_{init}} \tag{3}$$

Results and Discussion

Synthesis of Macromonomers and Copolymer Networks. Two series of oligo[(ϵ-hydroxycaproate)-*co*-glycolate]dimethacrylates are synthesized. In the first series the number average molecular weight is kept constant at 10 000 g·mol^{-1} under variation of the glycolate content from 0 to 30 mol %. For the second series of macrodimethacrylates M_n of the macrodimethacrylates is varied between 3000 and 10 000 g·mol^{-1}, while the glycolate content is kept constant at 14 mol %. Thus, cross-link density and crystallinity of the resulting copolymer networks can be adjusted.

The macrodiols are prepared by ring-opening polymerization of ϵ-hydroxycaproate and diglycolate initiated by ethylene glycol using dibutyltin oxide as catalyst. The molecular composition of the macrodiols is shown in Table 1. The ratio of the repeating units in the cooligomers is determined by ^{1}H NMR spectroscopy. A detailed sequence structure analysis of the hydroxytelechelic oligomers has been described in the literature.[16,19,21] Here, the reaction time as well as the catalyst were selected comparably to these references, where a random distribution of the repeating units was reached. The molecular weights are determined using ^{1}H NMR spectroscopy and multidetector gel permeation chromatography (GPC) analysis. M_n determined by GPC show minor deviation from the values expected from the molar ratio of cyclic monomers to initiator compared to the values for M_n obtained by ^{1}H NMR analysis.

Table 2. Results of Swelling Experiments in Chloroform and Thermal Properties Determined by DSC of Polymer Networks N-CG-10 and AB-CG-10 under Variation of the Molar Content of Glycolate in the Prepolymers and N-CG(14) with Varying M_n of Chain Segments[a]

polymer network ID[b]	Q, %	G, %	T_g, °C	Δc_p, J·(g·K)$^{-1}$	T_{g2}, °C	Δc_{p2}, J·(g·K)$^{-1}$	T_m, °C	ΔH_m, J·g^{-1}
N-CG(14)-3	440 ± 20	90 ± 7	−56	0.37			26	32
N-CG(14)-5	550 ± 80	93 ± 1	−53	0.28			30	36
N-CG(14)-7	620 ± 50	91 ± 8	−53	0.27			36	41
N-CG(14)-10	960 ± 40	81 ± 2	−53	0.21			38	42
N-CG(0)-10	890 ± 40	76 ± 2	−59	0.20			53	59
N-CG(12)-10	990 ± 10	74 ± 4	−55	0.23			44	48
N-CG(14)-10	960 ± 10	81 ± 2	−53	0.21			38	42
N-CG(21)-10	890 ± 80	82 ± 6	−53	0.30			28	36
N-CG(30)-10	880 ± 50	79 ± 8	−50	0.59			18	17
AB-CG(0)-10	1150 ± 10	86 ± 1	−62	0.21	−46	0.18	50	27
AB-CG(12)-10	1180 ± 20	84 ± 2	−61	0.21	−50	0.26	39	25
AB-CG(14)-10	1110 ± 10	83 ± 0	−58	0.18	−49	0.26	34	18
AB-CG(21)-10	1130 ± 20	80 ± 1	−54	0.26	−47	0.21	25	5

[a] Q is the degree of swelling, G is the gel content, T_g and T_{g2} are the glass transition temperatures, T_m Is the melting temperature, Δc_p and Δc_{p2} are the changes of the heat capacities, and ΔH_m is the melting enthalpy. [b] Polymer network ID: for nomenclature of copolymer networks N-CG(χ_G)-M_n and AB-copolymer networks AB-CG(χ_G)-M_n, C = ϵ-hydroxycaproate, G = glycolate, χ_G = molar ratio of the glycolate units of the whole amount of hydroxycarboxylate units (mol %), and M_n = number average molecular weight of the oligomers in 10^3 g·mol^{-1} calculated from monomer to initiator ratio.

The end group functionalization of the oligo[(ϵ-hydroxycaproate)-*co*-glycolate]diols is based on a conversion of the terminal hydroxyl group with methacryloyl chloride in the presence of triethylamine as base. The results of the ^{1}H NMR analysis of the macrodimethacrylates DMAC-CG for the determination of the degree of methacrylation are shown in Table 1. The degree of methacrylation of the oligomers D_m determined by ^{1}H NMR spectroscopy is between 95 and 100%. The value for D_m of DMAC-CG(0)-10 is lower than the values for the other macrodimethacrylates.

Copolymer networks N-CG from oligo[(ϵ-hydroxycaproate)-*co*-glycolate]dimethyacrylates and AB copolymer networks AB-CG based on oligo[(ϵ-hydroxycaproate)-*co*-glycolate]dimethacrylates and 60 wt % of *n*-butyl acrylate are prepared by photocross-linking in the melt at 70 °C without addition of a photoinitiator. The copolymer network films obtained are swollen in $CHCl_3$ to extract unreacted components. The swelling experiments in $CHCl_3$ were used simultaneously to evaluate the reached cross-link density via determination of the reached gel content G and the degree of swelling Q.

Swelling Behavior of the Copolymer Networks. The values determined for Q and G of the copolymer networks N-CG(14) in chloroform with varying M_n of chain segments are shown in Table 2. Q of the copolymer networks N-CG(14) increases with increasing M_n of chain segments of the oligomers from 440 to 960%. G is in the range of 90−93% up to a M_n of the oligomers of 6900 g·mol^{-1}. G for the copolymer network N-CG(14)-10 is only 81%. A possible explanation is the lower concentration of methacrylate end groups that can react with each other unless they are in sufficient proximity. The swelling behavior of the copolymer networks N-CG-10 and AB copolymer networks AB-CG-10 under variation of the glycolate content in the macrodimethacrylates at constant M_n of segment chains is also shown in Table 2. The variation of the glycolate content shows no influence on Q and G of the copolymer networks N-CG-10 within the limits of accuracy. The determination of Q of the AB-copolymer networks shows that the relatively low content of glycolate moieties has a negligible influence on the solvent uptake. Q of the AB-copolymer networks of around 1140% is slightly higher in comparison to the average value of 920% of the copolymer networks. A difference in polarity of the AB copolymer system as a result of the presence of 60 wt % oligo(butyl acrylate) segments as well as a lower cross-linking density as a consequence of the introduction of oligo(butyl acrylate) segments could be responsible for this finding. Q of the investigated AB-CG-10 copolymer networks decreases slightly with increasing glycolate content.

Thermal Characterization. Two types of thermal transition are expected: a T_g originating from the noncrystallizable chain segments and a T_m associated with the crystalline domains formed by oligo(ϵ-hydroxycaproate) chain segments. In the case of the AB-copolymer networks an additional T_g of the amorphous phase which is formed on the poly(butyl acrylate) segments is expected. In the case of an incomplete phase segregation in the AB-copolymer networks an amorphous mixed phase would also be expected.

The thermal transitions of the polymer networks and macromonomers based on oligo[(ϵ-hydroxycaproate)-co-glycolate] were determined in DSC experiments in a temperature range between −80 and +80 °C. The results from the second heating run under variation of the molecular weight and the glycolate content are shown in Table 2 for polymer networks and in Table 3 for the respective macrodiols and macrodimethacrylates. Co-oligoester diols show a glass transition resulting from an amorphous mixed phase of the repeating units and a melting transition of the crystalline fraction of the oligo(ϵ-hydroxycaporate) segments ranging over a temperature interval of less than 10 K. The T_g found for oligo(ϵ-hydroxycaproate)diol is −62 °C (Table 3). The value for the T_g of poly(glycolate) is at 36 °C.[25] The T_g of the macrodiols having a glycolate content of 14 mol % is around −55 °C. The T_g of the macrodiols having molecular weight around 10 000 g·mol^{-1} increases with increasing glycolate content (up to 30 mol %) from −62 to −48 °C, indicating the increasing influence of the glycolate units. With increasing M_n the value for T_m of macrodiols with 14 mol % glycolate rises slightly from 42 to 44 °C, while an increase in glycolate content from 0 to 30 mol % causes a significant decrease of T_m of the oligo(ϵ-hydroxycaproate) domains from 54 to 24 °C. An increasing ratio of glycolate units inhibits the crystallization of ϵ-hydroxycaproate-rich sequences. Thus, pure oligo(ϵ-hydroxycaproate)diols are expected to show the highest melting enthalpy ΔH_m. However, the determined value for ΔH_m of DOH-CG(0)-10 which was obtained from a commercial source is lower than the value of macrodiols with 12 mol % glycolate and comparable molecular weight. This could possibly be traced back to the fact that diethylene glycol is used as an initiator in the synthesis of DOH-CG(0)-10 instead of ethylene glycol. The DSC thermograms of the macrodiols with glycolate

Table 3. Thermal Properties of the Macrodiols DOH-CG and the Macrodimethacrylates DMAC-CG Determined by DSC[a]

macrodiol ID[b]	T_g, °C	Δc_p, J·(g·K)$^{-1}$	T_m, °C	ΔH_m, J·g^{-1}	macrodimethacrylate ID[c]	T_g, °C	Δc_p, J·(g·K)$^{-1}$	T_m, °C	ΔH_m, J·g^{-1}
DOH-CG(14)-3	−56	0.24	42, (45)[c]	68	DMAC-CG(14)-3	−48	0.15	42,[e] 46	60
DOH-CG(14)-5	−56	0.21	43, (46)[c]	67	DMAC-CG(14)-5	−48	0.21	44,[e] 49	62
DOH-CG(14)-7	−56	0.26	44, (46)[c]	67	DMAC-CG(14)-7	−49	0.21	45,[e] 48	62
DOH-CG(14)-10	−55	0.20	44, (46)[c]	67	DMAC-CG(14)-10	−48	0.24	42,[e] 46	64
DOH-CG(0)-10	−62	0.12	54,[e] 57	58	DMAC-CG(0)-10	−60	0.25	55	79
DOH-CG(12)-10	−56	0.20	49, (51)[c]	68	DMAC-CG(12)-10	−57	0.28	47,[e] 50	66
DOH-CG(21)-10	−53	0.25	34,[e] 41	58	DMAC-CG(21)-10	−51	0.27	29, 38[e]	56
DOH-CG(30)-10	−48	0.33	24,[e] 54	47	DMAC-CG(30)-10[d]	−49	0.30	19,[e] 21	35

[a] T_g is the glass transition temperature, T_m is the melting temperature, Δc_p is the change in heat capacity at glass transition, and ΔH_m is the melting enthalpy. [b] Nomenclature of oligomers: for X-CG(χ_G)-M_n, X = end groups functionality, DOH = α,ω-dihydroxy, DMAC = α,ω-dimethacrylate, C = ϵ-hydroxycaproate, G = glycolate, χ_G = molar ratio of the glycolate units of the whole amount of hydroxycarboxylate units (mol %), determined by ^{1}H NMR spectroscopy, and M_n = number average molecular weight of the oligomers in 10^3 g·mol^{-1} according to theoretical molecular weight. [c] Values shown in parentheses represent a shoulder in the melting peak. [d] Melting peak showed a second local maximum at 53 °C. [e] Absolute maximum of melting peak.

contents of 0, 21, and 30 mol % show two maxima of the melting peak. This melting behavior of the macrodiols could be caused by the formation of different oligo(ϵ-hydroxycaproate) crystallite modifications or crystallite sizes.

Table 3 also shows the thermal properties of macrodimethacrylates depending on M_n and the glycolate content. T_g of the macrodimethacrylate DMAC-CG(14) shows no systematic dependency on the molecular weight. The values for T_g of the functionalized oligomers are about 7 to 8 K higher in comparison to T_g of the macrodiols. T_g of the macrodimethacrylates with comparable M_n rises with increasing glycolate content from −60 to −49 °C. T_m of the macrodimethacrylates increases with increasing molecular weight, since a higher chain segment length promotes the formation of larger oligo(ϵ-hydroxycaproate) crystallites. For constant M_n with increasing glycolate content, ΔH_m decreases slightly. This effect can be led back to the decreasing crystallinity. ΔH_m of the oligomers increases with increasing chain segment length in analogy to T_m. Values for ΔH_m of the macrodiols decrease upon the functionalization with methacrylate end groups.

In analogy to the thermal transitions of the macrodiols and macrodimethacrylates, the copolymer networks and AB-copolymer networks show glass transitions at low temperature between −62 and −53 °C and melting transitions with T_m between 18 and 53 °C (Table 2). The transition temperature for the triggering of the shape-memory transition is provided by the melting transition. In the case of AB-copolymer networks an additional T_g is observed, which can be correlated to the additional amorphous domains provided by oligo(butyl acrylate) segments. The results of the thermal analysis of copolymer networks N-CG(14) by DSC are shown in Table 2. While T_g of copolymer network N-CG(14)-3 is −56 °C, the values for T_g of the copolymer networks with higher chain segment M_n are at −53 °C. With increasing molecular weight of the macrodimethacrylates T_m of the copolymer networks increases continuously from 26 to 38 °C. The values found for ΔH_m increase analogously. This is interpreted in terms of a hindrance of chain segments' crystallization upon incorporation into polymer networks. This effect is more pronounced for lower molecular weight chain segments (Figure 1, Table 2).

The investigation of T_g depending on M_n of prepolymers shows that T_g of the macrodiols rises slightly with increasing molecular weight, whereas M_n does not influence T_g of the macrodimethacrylates (Table 3). T_g of the copolymer networks N-CG(14) is constant when a value for M_n of the prepolymers of 4800 g·mol^{-1} is exceeded (Table 2). The values for T_g of the copolymer networks are higher than that of the macrodiols. T_g of the prepolymeric dimethacrylates are about 5 K higher than those of the resulting copolymer networks (Table 2).

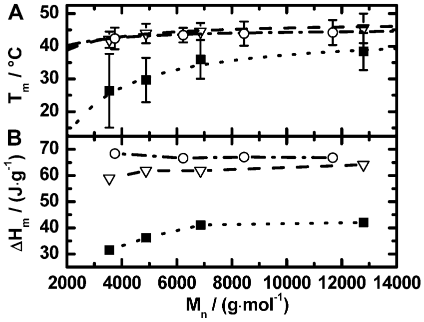

Figure 1. Melting temperature T_m (A) and melting enthalpy ΔH_m (B) of macrodiols DOH-CG(14) (○ and − · −), of macrodimethacrylates DMAC-CG(14) (▽ and −), and polymer networks N-CG(14) (■ and ···) determined by DSC as a function of the number average molecular weight M_n (^{1}H NMR). The glycolate content is 14 mol %. The error bars give the temperature range of the melting peak.

T_m of the macrodiols and macrodimethacrylates with the same glycolate comonomer ratio show a tendency to increase for 2−3 K at maximum with increasing M_n in the investigated range of molecular weights (Table 3). In contrast the T_m of the copolymer networks N-CG(14) shows a much more pronounced influence on M_n of chain segments. T_m of the copolymer networks can thus easily be adjusted in the temperature range between 25 and 40 °C by choosing macrodimethacrylates with M_n between 3000 and 13 000 g·mol^{-1} (Table 2). The increase of T_m is caused by the formation of more pronounced crystallites as a result of the increase of the average chain segment molecular weight.

A variation of the glycolate content between 0 and 30 mol % causes an increase of copolymer networks' T_g starting from −59 °C by 9 K at maximum. T_m of the copolymer networks can be varied in a temperature range between 53 and 18 °C by an increase of the glycolate content up to 30 mol % (Table 2). In analogy to macrodimethacrylates the change of the heat capacity Δc_p of the copolymer networks increases with a decrease in crystallinity (Tables 2 and 3).

AB-copolymer networks containing 60 wt % oligo(butyl acrylate) segments show an additional T_g compared to the copolymer networks. The glass transition temperatures T_{g1} and T_{g2} are thereby slightly higher than T_g of poly(ϵ-hydroxycaproate) of −64 °C and poly(butyl acrylate) of −55 °C. T_{g1} increases with increasing content of glycolate, whereas T_{g2} remains approximately constant within the limits of accuracy of the DSC analysis. Therefore it is assumed that T_{g1} is representing primarily the oligo[(ϵ-hydroxycaproate)-*co*-glycolate] phase and T_{g2} the oligo(butyl acrylate) phase. The molecular composition of the macrodimethacrylates does not

Table 4. Mechanical Properties of Polymer Networks N-CG and AB-CG-10 at 22 and 70 °C[a]

	22 °C					70 °C		
polymer network ID[b]	*E*, MPa	ϵ_s, %	σ_s, MPa	ϵ_R, %	σ_{max}, MPa	*E*, MPa	ϵ_R, %	σ_{max}, MPa
N-CG(14)-3	4.0 ± 0.3			120 ± 25	3.5 ± 0.9	4.5 ± 0.4	90 ± 20	3.0 ± 0.6
N-CG(14)-5	33 ± 6			210 ± 20	13 ± 3	2.3 ± 0.1	85 ± 10	1.4 ± 0.3
N-CG(14)-7	36 ± 6			210 ± 40	11 ± 2	1.4 ± 0.1	120 ± 10	1.0 ± 0.1
N-CG(14)-10	46 ± 4			360 ± 30	14 ± 1	1.0 ± 0.2	185 ± 15	1.1 ± 0.2
N-CG(0)-10	90 ± 14	33 ± 6	13 ± 1	345 ± 21	19 ± 2	0.8 ± 0	230 ± 25	1.6 ± 0.2
N-CG(12)-10	70 ± 2	34 ± 2	9.0 ± 0.4	305 ± 25	15 ± 1	0.4 ± 0	280 ± 25	0.8 ± 0.1
N-CG(14)-10	46 ± 4	44 ± 0	8.6 ± 0.1	360 ± 30	14 ± 1	1.0 ± 0.2	185 ± 15	1.1 ± 0.2
N-CG(21)-10	31 ± 1			290 ± 25	8.9 ± 0.7	1.1 ± 0.1	170 ± 45	1.1 ± 0.2
N-CG(30)-10	1.8 ± 0.2			210 ± 30	2.0 ± 0.4	0.6 ± 0.1	230 ± 60	0.9 ± 0.2
AB-CG(0)-10	12 ± 1			285 ± 55	6.2 ± 0.9	0.7 ± 0.1	150 ± 45	0.5 ± 0.1
AB-CG(12)-10	8.0 ± 0.2			285 ± 20	3.1 ± 0.3	0.6 ± 0.1	125 ± 20	0.4 ± 0.1
AB-CG(14)-10	3.6 ± 0.6			365 ± 45	3.1 ± 0.5	0.7 ± 0.1	145 ± 20	0.5 ± 0.1
AB-CG(21)-10	0.8 ± 0.1			365 ± 45	1.1 ± 0.2	0.6 ± 0.1	140 ± 20	0.4 ± 0.1

[a] *E* is the elastic modulus, ϵ_s and σ_s are elongation and stress at the yield point, ϵ_R is the elongation at breakage, and σ_{max} is the tensile strength. [b] Polymer network ID: for nomenclature of copolymer networks N-CG(χ_G)-M_n and AB-copolymer networks AB-CG(χ_G)-M_n, C = ϵ-hydroxycaproate, G = glycolate, χ_G = molar ratio of the glycolate units of the whole amount of hydroxycarboxylate units (mol %), and M_n = number average molecular weight of the oligomers in 10^3 g·mol^{-1} calculated from monomer to initiator ratio.

affect the thermal transition of the oligo(butyl acrylate) phase. In contrast, T_m and ΔH_m show a dependency on the glycolate content and decrease with increasing glycolate content. The AB-copolymer networks have a lower T_m for an average of 4 K than the copolymer networks. Presumably less pronounced crystallites are formed due to the lower content of ϵ-hydroxycaproate moieties. Correspondingly, ΔH_m decreases which shows the difference between the non-cross-linked and the cross-linked materials more notedly. ΔH_m of the copolymer networks from macrodimethacrylates is about 20−30 J·g^{-1} lower than that of the prepolymers, while ΔH_m of the AB-copolymer networks is even lower (Table 2).

Mechanical Characterization of Polymer Networks. The fraction of crystalline domains and the chain segment length dominate the mechanical behavior of the copolymer and AB-copolymer networks in the temperature range between T_g and T_m. The mechanical properties of the networks determined at 22 °C (a temperature below T_m) and at 70 °C (above T_m) are shown in Table 4.

In tensile tests of polymer networks at 22 °C an increase in tensile strength σ_{max} as well as elongation at breakage ϵ_R can be observed with increasing M_n of the used macrodimethacrylates. For the stress−strain curves of the copolymer networks from higher molecular weight macrodimethacrylates a stress-induced crystallization and by that hardening can be observed. In contrast to this, the polymer network N-CG(14)-3 shows elastic behavior in mechanical testing. Typical stress−strain curves at 22 °C for a copolymer network N-CG(14) with varying M_n of the used macrodimethacrylates are shown in Figure 2A. The Young's modulus *E* increases continuously with increasing chain segment length. *E* is exceptionally low in the case of the copolymer network N-CG(14)-3 with T_m = 26 °C due to the low degree of crystallinity observed around 22 °C. The broad temperature range of melting indicates a broad size distribution of crystallites. Therefore cristallinity is already reduced at 22 °C. A maximum value for *E* of 46 MPa is reached for network N-CG(14)-10 with the highest M_n of the cross-linked macrodimethacrylates. Moreover, only this material shows a pronounced yield point. This tough material shows an elongation at break ϵ_R of 360%. The value for the tensile strength σ_{max} of network N-CG(14) remains almost constant with values around 11−14 MPa when M_n of the used prepolymers is about 4900 g·mol^{-1} and higher. Also ϵ_R shows a correlation to the chain segment length.

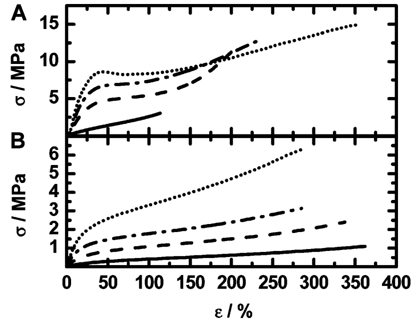

Figure 2. Result of tensile test at 22 °C. (A) copolymer network N-CG(14) M_n of macrodimethacrylate was varied (—, N-CG(14)-3; --, N-CG(14)-5; — • —, N-CG(14)-7; •••, N-CG(14)-10), and (B) AB-copolymer network AB-CG-10 glycolate content of macrodimethacrylates was varied (•••, AB-CG(0)-10; — • —, AB-CG(12)-10; -- AB-CG-(14)-10; — AB-CG(21)-10); the *n*-butyl acrylate content is 60 wt %.

The polymerization of the macrodimethacrylates in the presence of *n*-butyl acrylate leads via the formation of an additional amorphous phase based on oligo(butyl acrylate) to a decrease in crystallinity. By variation of the glycolate content between 0 and 21 mol % the crystallinity and by this the Young's modulus of the AB-copolymer networks can be adjusted between 0.8 and 12 MPa (Table 4, Figure 2B).

The influence of the glycolate content on the stress−strain behavior of the copolymer networks with M_n = 10 000 g·mol^{-1} is investigated at 22 °C. With increasing glycolate content from 0 to 21 mol % *E* decreases from 90 to 31 MPa. For a glycolate content of 30 mol % the value for *E* decreases to 1.8 MPa. The stress−strain curves of materials with the same chain segment length show a yield point for glycolate contents up to 14 mol % glycolate. In analogy to *E* the values reached for σ_R are correlated with the materials' crystallinity. Crystallites act as physical and multifunctional net points which contribute to the mechanical toughness of the copolymer network. Copolymer networks with a glycolate content up to 21 mol % are semicrystalline at a temperature of 22 °C reaching values for ϵ_R between 290 and 360%. In contrast copolymer network N-CG(30)-10 with a T_m = 18 °C is amorphous at 22 °C. A relatively low value for ϵ_R of 210% and a low value for σ_{max} is observed for this material. Here the mechanical properties are dominated by the existing cross-link density (Table 4).

Figure 2B shows examples for stress−strain curves of AB-copolymer networks with varying glycolate content measured

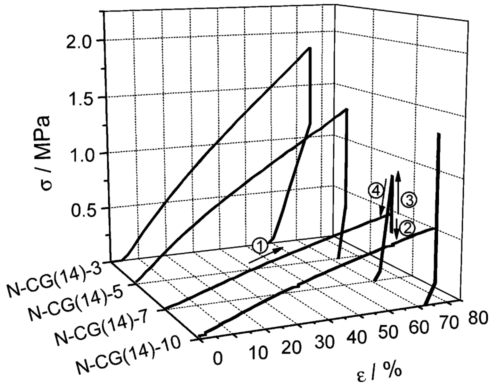

Figure 3. Fifth cycle of a strain-controlled cyclic, thermomechanical tensile experiment of copolymer networks N-CG(14) with $T_{high} = 70$ °C, $T_{low} = 0$ °C, $\epsilon_m = 75\%$, and various M_n values of macrodimethacrylates.

at 22 °C. With increasing glycolate content the stress at break σ_R decreases. High values for ϵ_R in the range between 285 and 365% are reached without showing a yield point. Table 4 displays the results of the performed mechanical tests. The cross-linked copolymers with T_m above 25 °C are semicrystalline at 22 °C. The introduction of oligo(butyl acrylate) segments with a simultaneous increase of the glycolate content results in decreasing crystallinity with a more pronounced elastomeric character of the AB copolymer network.

All the copolymer networks described are fully amorphous at 70 °C. Therefore the influence of the molecular parameters on the mechanical properties can be observed independently from the influence of crystalline domains. At 70 °C the copolymer networks show rubber-elastic behavior: E and σ_{max} are proportional to the cross-link density, while ϵ_R increases with increasing chain segment M_n (Table 4). As expected values for E and σ_{max} are reduced compared to the results of mechanical tests performed at temperatures below 70 °C. Also values for ϵ_R recorded at 70 °C are lower than the values found for lower temperatures (Table 4).

In tensile tests at 70 °C no systematic influence of the glycolate content on the mechanical properties of copolymer networks N-CG-10 and AB-copolymer networks is found. AB-copolymer networks display unexpectedly low values for ϵ_R compared to copolymer networks, indicating a low free elastic chain segment length. This could give a hint of additional cross-linking in the oligo(butyl acrylate) segments. AB-copolymer networks' values for ϵ_R decrease with increasing temperature, reaching values of around 140% at 70 °C.

Shape-Memory Properties of Polymer Networks. Shape-memory properties are quantified by cyclic, thermomechanical tensile tests.[26,27] In strain-controlled, cyclic thermomechanical tests the strain applied to the sample with respect to the relative distance of the clamps of the tensile tester is controlled while the developing stress is recorded.[26] Alternatively, in stress-controlled experiments the straining of the test specimen with respect to the distance of the clamps is recorded while a defined stress is kept.[27] Stress-controlled, cyclic thermomechanical tests are performed using two different routines. First, programming and strain recovery are performed in air. Second, to simulate conditions relevant for medical application in the body, the strain recovery of samples, which are programmed in air, is performed in water.

Figure 3 shows the programming of the temporary shape in the fifth cycle of a strain-controlled, cyclic, thermomechanical tensile test of copolymer networks N-CG(14). Divergent from the standard program due to the limit in ϵ_R, the tests are performed using a maximum elongation of 75%. By applying a deformation stress at a T_{high} above $T_{trans.}$, the specimen from copolymer networks are stretched to ϵ_m (step 1 in Figure 3). The stress to be applied is dependent on the cross-link density. For the stretched networks under load a decrease in stress is observed during the cooling to T_{low} caused by the samples expansion due to entropy elasticity (step 2 in Figure 3). The ϵ-hydroxycaproate dominated segments crystallize below $T_{trans.}$. As a consequence of the crystallization process the observed stress increases (step 3 in Figure 3). After release of the stress the temporary shape is fixed by the physical cross-links formed by the crystallites (step 4 in Figure 3). Copolymer networks N-CG(14)-7 and N-CG(14)-10 with higher molecular weight segment chains and higher crystallinity show slightly different stress−strain curves with a renewed increase in stress after crystallization. The pronounced crystallinity of the stretched copolymer networks is accompanied by a loss in free volume and an increase in density. Results of cyclic, thermomechanical investigations for polymer networks with varying chain segment M_n and varying glycolate content are shown in Table 5.

In the case of strain-controlled cyclic thermomechanical tests, strain fixity rates are determined according to eq 6 in ref 26 and strain recovery rates are determined according to eqs 4 and 5 in ref 26. For the stress-controlled tests, values for R_f are determined according to eq 1 in ref 27 and values for R_r are determined according to eq 2 in ref 27. In strain-controlled cyclic thermomechanical tests, copolymer networks with a M_n for the prepolymers of at least 4900 g·mol^{-1} show R_f above 94% and

Table 5. Shape-Memory Properties of Copolymer Networks N-CG Determined by Strain- and Stress-Controlled, Cyclic Thermomechanical Tensile Tests[a]

	strain-controlled cyclic thermomechanical tensile tests			stress-controlled, cyclic thermomechanical tensile tests							
	determined in air								determined in water		
polymer network ID[b]	$R_f(1-5)$, %	$R_r(1)$, %	$R_{r,tot.}$, %	ϵ_l, %	$R_{f,stress\ contr.}$, %	$R_{r,stress\ contr.}$, %	T_{switch}, °C	v_r, min^{-1}	R_{r,H_2O}, %	T_{switch,H_2O}, °C	v_{r,H_2O}, min^{-1}
N-CG(14)-3	82.0 ± 1.9	93.6	93.2	123	80.6	100.0	23	0.22	99.3	29	1.3
N-CG(14)-5	97.3 ± 1.0	100.0	100.0	147	86.3	96.9	31	0.34	nd[c]	nd[c]	nd[c]
N-CG(14)-7	94.1 ± 0.2	99.7	100.0	145	98.4	97.5	36	0.49	100.0	35	1.6
N-CG(14)-10	96.8 ± 0.2	99.7	100.0	142	97.7	100.0	37	0.76	100.0	36	2.5
N-CG(0)-10				151	91.9	100.0	52	1.6	100.0	49	1.9
N-CG(14)-10				142	97.7	100.0	37	0.76	100.0	35	2.5
N-CG(21)-10				176	74.0	100.0	27	0.31	100.0	29	0.83

[a] The chosen maximum elongation ϵ_m in the strain-controlled tensile tests is 75%. $R_f(1-5)$ is the average strain fixity rate over five cycles, $R_r(1)$ is the strain recovery rate of the first cycle, and $R_{r,tot.}$ is the total strain recovery rate. The standard maximum elongation ϵ_m in stress-controlled tests is 100%, except for N-CG(14)-3 with $\epsilon_m = 75\%$. ϵ_l is the elongation after cooling, R_f is the strain fixity rate, R_r is the strain recovery rate, T_{switch} is the switching temperature, and v_r is the strain recovery speed. R_{r,H_2O}, T_{switch,H_2O}, and v_{r,H_2O} are the corresponding properties determined in water. The fixation of the samples, whose strain recovery is induced in water, is performed in air under strain control. [b] Polymer ID: for nomenclature of copolymer networks N-CG(χ_G)-M_n and AB-CG(χ_G)-M_n, C = ϵ-hydroxycaproate, G = glycolate, χ_G = molar ratio of the glycolate units of the whole amount of hydroxycarboxylate units (mol %), and M_n = number average molecular weight of the oligomers in 10^3 g·mol^{-1} calculated from monomer to initiator ratio. [c] Not determined.

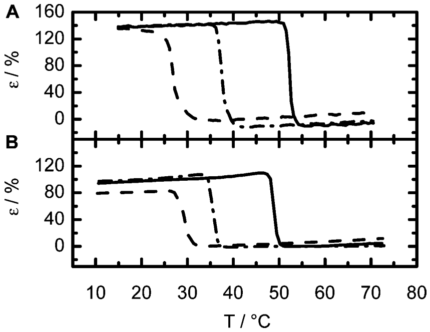

Figure 4. Characteristic strain ϵ as a function of the temperature T of copolymer networks N-CG-10 in the strain recovery process of a stress-controlled thermomechanical tensile test in air (A) and in water (B) (--, N-CG(21)-10; − • −, N-CG(14)-10; −, N-CG(0)-10). The programming of all samples was performed strain-controlled in air. The variation in strain at the beginning of the strain recovery results from different programming processes. $T_{high} = 70$ °C, $\epsilon_m = 100\%$, $T_{low} = 15$ °C, and $N = 1$.

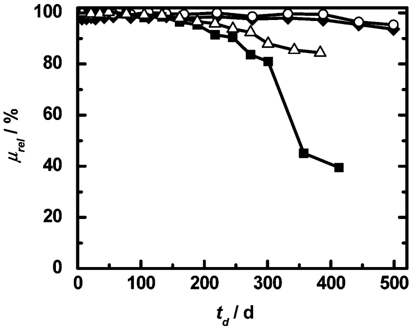

Figure 5. Hydrolytic degradation of polymer networks. Influence of the degradation time t_d on the relative mass loss μ_{rel} of the degraded samples (37 °C, pH 7.0): −◆−, N-CG(0)-10; −○−, AB-CG(0)-10; −△−, N-CG(09); −■−, N-CG(13).

$R_{r,tot.}$ above 99%. For copolymer network N-CG(14)-3 with low M_n chain segments, a decreased value for R_f due to the reduced crystallinity is found. In addition $R_{r,tot.}$ is reduced during the first cycle. Defects may be induced in the copolymer network by chain break due to the short free elastic chain length.

Copolymer networks N-CG(14) are additionally submitted to stress-controlled cyclic, thermomechanical experiment using standard test parameters (Table 5). With increasing M_n of chain segments, the values obtained for R_f increase, reflecting the degree of crystallinity. Moreover, values determined for R_f depend on the effective maximum strain ϵ_l, which is influenced by two factors: the creeping of the test specimen under constant load and temperature and an expansion of the deformed specimen during the cooling process. With increasing M_n of the cross-linked prepolymers, ϵ_l tends to increase. The observed creep is in the range of 3−5%, related to ϵ_m. The described temperature-dependent strain increases with increasing cross-link density. The strain recovery is almost complete for all copolymer networks. By a variation of chain segments' M_n between 3500 and 12 800 g·mol^{-1}, T_{switch} determined in air is between 23 and 37 °C with a deviation from T_m determined via DSC of 3 K at maximum. In comparison T_{switch} detected in water shows even less deviation. With increasing M_n of chain segments' the shape-memory transition takes place in a more narrow temperature interval. In addition, a higher strain recovery speed v_r is observed.[28] The values for v_r are higher in water than in air due to the more efficient heat transfer in water.

Stress-controlled, cyclic thermomechanical tests of copolymer networks with varying glycolate content of the prepolymers show complete strain recovery (Figure 4). Due to a positive thermal expansion coefficient at the beginning of the heating process, the programmed polymer network samples show a slight elongation before the onset of the strain recovery step. With increasing glycolate content T_{switch}, which is correlated with the temperature at the inflection point of the strain-recovery curve, increases independently from the surrounding medium, water or air. A higher glycolate content results in lower values for v_r. Table 5 shows the results for stress-controlled cyclic, thermomechanical tests in air and in water for copolymer networks N-CG-10 under variation of the glycolate content. For copolymer networks synthesized from oligomers of the same M_n of around 10 000 g·mol^{-1}, T_{switch} is determined by the glycolate content, varying between 27 and 52 °C. There is a significant difference for T_{switch} when determind in air or in water. For the comparison of T_{switch} and T_m, it has to be considered that T_m is derived from a thermal transition, while T_{switch} represents a thermomechanical transformation. While T_m is measured by means of a nonstretched test specimen, T_{switch} is determined for stretched samples. Although different heating rates are used for the determination of T_{switch} in air of 2 K·min^{-1}, in water of 3 K·min^{-1}, and T_m by means of DSC of 10 K·min^{-1}, the values are in good agreement.

Hydrolytic Degradation of the Copolymer Networks. The hydrolytic degradation of poly(hydroxyalkanoates) results from a hydrolysis of the ester bonds in the main chain.[29] Thereby lower molecular weight fragments are formed that are converted to water soluble degradation products by progressive hydrolyzation of ester bonds.[30,31] The stability of hydrolyzable bonds has a direct influence on the rate and mechanism of degradation. The rate of degradation can be influenced by the crystallinity and the stability of the chemical bonds against hydrolysis.[32] In general two mechanisms are found: surface degradation and bulk degradation.[33] In semicrystalline polymers the degradation starts in the amorphous domains.[34] As a consequence the crystallinity of the polymer system increases with proceeding degradation. In the literature a multistage mechanism for the bulk degradation of poly(hydroxyalkanoates) is proposed.[35,36] This degradation includes the swelling of the polymers in water, the decrease of the molecular weight combined with a loss of mechanical stability, and the loss of the integrity of the polymer matrix.

The copolymer and AB-copolymer networks based on poly(hydroxyalkanoate) chain segments are hydrolytically degradable. The segments contain ester bonds in their main chain that can be cleaved by water molecules. The copolymer networks from oligoester methacrylates contain oligomethacrylate segments where the main chain is not hydrolytically cleavable. However, they possess ester bonds in the cross-linking chains. With proceeding hydrolyzation of these linking segments, oligomers of methacrylic acid emerge. Those are soluble in water and nontoxic in lower dose rates.[23] In contrast, a significantly higher molecular weight of the oligoacrylate segments can be expected for the AB-copolymer networks that have high contents of oligo(butyl acrylate). Here, a molecular weight of 200 000 g·mol^{-1} is a critical upper limit for water soluble biostabile macromolecules in biomedical applications, since above this molecular weight an accumulation in the blood circuit takes place, independently from the nature of the polymer.[37]

The degradation behavior of four selected polymer networks in phosphate buffer solution at pH 7.0 and 37 °C has been investigated. The relative mass loss of the sample weight of the four investigated copolymer networks during the degradation experiments is shown in Figure 5. The selection of the materials comprises cross-linked oligo(ϵ-hydroxycaproate)dimethacrylate N-CG(0)-10 as well as two copolymer networks from oligo[(ϵ-hydroxycaproate)-*co*-glycolate]dimethacrylates with different contents of glycolate (N-CG(09)-10 and N-CG(13)-10) and an example of AB-copolymer network (AB-CG(0)-10). The relative mass loss μ_{rel} is evaluated for the four different polymer networks, which is the quotient of the starting weight m_{init} and the weight of the degraded sample m_t after a defined degradation time period (eq 3). The material AB-CG(0)-10 retains 95% and (N-CG(0)-10) retains 94% of the original weight at the end of the test series after 499 days. In contrast, the weight of glycolate-containing copolymer networks starts to decrease significantly after 105 days (N-CG(13)-10) or rather 161 days (N-CG(09)-10). The copolymer network with a glycolate content of 13 wt % shows the fastest weight loss, losing 60% of its original weight within 413 days. The copolymer network with 9 wt % glycolate reaches a mass loss of 16% after 383 days.

The water uptake of the materials is below 2 vol % at the start of degradation. This value does not change in the case of the network N-CG(0)-10 in the observed degradation period. The water uptake increases with starting mass loss in the copolymer networks that contain glycolate units. N-CG(09)-10 shows a water uptake of 16 vol % after 383 days. In copolymer network N-CG(13)-10 the water uptake increases to 48 vol % after 301 days. After this time period, a determination of the water uptake is not possible, since the degradation proceeded such that the materials disintegrated. After drying under vacuum, a semicrystalline waxy mass is obtained. The complete recovery of the degraded sample is difficult. Thus, a relative error of 10−15% is admeasured to the values of the relative mass loss of copolymer network N-CG(13)-10 at time points above 301 days.

The change of the cross-link density of the degraded samples is studied by the determination of the gel content G and the degree of swelling Q in chloroform. Over the degradation time G of all investigated materials exhibits an approximately linear decrease. The glycolate-containing copolymer networks reach values for G representing the insoluble components of the polymer network in the investigation time range below 1 wt % after 245 days (N-CG(13)-10) or after 383 days for N-CG(09)-10. Polymer network N-CG(0)-10 shows a gel fraction of 48 wt % after 499 days degradation; i.e., about half of the original network segments remain bound covalently in the three-dimensional network. Q as the parameter representing the swelling behavior of the remaining gel fraction of the samples in chloroform increases constantly during the time range of the degradation experiment. This allows one to assume a decrease in cross-link density. The increase of Q of the materials increasing in the order N-CG(0)-10 > N-CG(09)-10 > N-CG-(13)-10 showed the inverse trend as the determined values for G. The material with the highest content of glycolate, N-CG-(13)-10, nearly quintuples the value for Q of its gel fraction in chloroform, before the material reaches complete solubility in chloroform (G < 1 wt %) after 245 days (Supporting Information, Figure 1). The clear and continuous change of the cross-linking density of all materials beginning at the starting point of degradation is, beside the swelling in water, additional evidence for bulk degradation of the material. A surface degradation would lead to a loss of weight without an influence on the cross-link density.[33]

Mechanical Properties of Degraded Copolymer Networks. The mechanical properties of the partially degraded samples are determined in tensile tests at 37 °C (Supporting Information, Figure 2). The different materials show different tendencies in their mechanical properties as a function of the degradation time. N-CG(0)-10 shows a strong increase of the value for E at the starting point of degradation. ΔH_m increases from 65 to 98 J·g^{-1} in the same period, so that the observed increase of the elastic modulus is attributed to an increasing crystallinity. A further increase is detected in the progressive course of the experiment. Values for ϵ_R of the material stay constant at about 300% until a degradation period of 140 days and decrease strongly after this time. Samples that are degraded for longer than 276 days become so brittle that it is not possible to prepare the necessary dumbbell-shaped specimen for tensile tests.

Copolymer networks N-CG(09)-10 show a similar development of properties over degradation time. The value for E increases in the initial phase, which can be related to the simultaneous increase of ΔH_m from 49 to 66 J·g^{-1} in the first heating run of the DSC experiment. ϵ_R is nearly constant up to a degradation time period of 49 days and decreases significantly after 77 days. After 161 days, tensile tests cannot be performed any further, since the samples become too brittle.

In contrast to the described materials, the copolymer networks with the highest content of glycolate, N-CG(13)-10, become softer with proceeding of the degradation, which is shown by a decrease of E from 0.7 to 0.15 MPa. ϵ_R decreases continuously from 250 to below 100% in the investigated time period. The end of the mechanical investigations after 133 days for this material was due to the fact that both crystallinity and cross-link density are not sufficient to further maintain the 3-D shape of the sample.

All materials show a nearly constant ϵ_R at the beginning of the degradation. Therefore ϵ_R is independent from the cross-link density in this area. ϵ_R decreases rapidly as soon as the cross-link density reaches a critical value. An exception is copolymer networks AB-CG(0)-10 where the values for ϵ_R and other mechanical properties are almost maintained over the whole degradation time.

Conclusion

This work describes synthesis and properties of a biodegradable shape-memory photoset polymer network system. The combination of only five different monomer units and the realization of two network architectures allows the design of polymeric materials with a broad spectrum of properties and functionalities. By variation of the molecular network parameters, it is possible to adjust the shape-memory transition temperature T_{switch} and the mechanical properties of the photosets below and above the thermal transition temperature $T_{\mathrm{trans.}}$. By variation of the copolymer networks' glycolate content, the hydrolytic degradability can be tailored.

The networks have been synthesized by cross-linking polymerization of oligo[(ϵ-hydroxycaproate)-*co*-glycolate]dimethacrylates. By variation of the molecular weight and the glycolate content of the switching segment, T_m, which correlates with T_{switch} for the shape-memory transition, can be adjusted between 18 and 52 °C.

By polymerization of the macromonomers in the presence of *n*-butyl acrylate as comonomer, AB-cross-linked materials are obtained that contain amorphous and not crystallizable soft segments of oligo(butyl acrylate). The low T_g of this additional soft segment forming phase contributes additional elasticity to the material at a temperature relevant for potential applications. By introduction of the amorphous soft segment phase, the ratio of crystalline domains below the transition temperature of the switching segments and thus the mechanical properties are influenced. The Young's modulus E of the AB-networks in tensile tests at 22 °C decreases with increasing content of glycolate and can be adjusted between 12 and 0.8 MPa.

Mechanical properties below T_m are dominated by materials' crystallinity. Values of E increase as a function of ΔH_m. Due to the influence of the temperature on the crystallinity, the test parameters of the stress−strain experiment have a strong influence on the determined mechanical properties. One has to consider that at a temperature of 37 °C for the tensile test performed in water some of the polymer networks are still semicrystalline while others are amorphous. The mechanical strength of the polymer networks has to correspond to the needs given in a specific application.

The copolymer networks show good to excellent shape-memory properties in cyclic thermomechanical tensile tests between 0 and 70 °C, combining a good strain fixity rate of the temporary shape, fast attainment of a stable cyclic behavior, and only little loss of the permanent shape in the first cycles. Copolymer networks from oligo[(ϵ-hydroxycaproate)-*co*-glycolate]dimethacrylates with M_n of the cross-linked macromonomers of at least 6900 g·mol^{-1} and a glycolate content of 14 mol % show almost complete strain fixity with values for R_f above 94%. Upon thermal stimulation for all copolymer networks more or less quantitative strain recovery with R_r above 97% is observed. Shape recovery is not effected by the medium, either air or water, used for heating the material in the thermocyclic tensile tests.

Hydrolytic degradation experiments of the polymer networks at pH 7.0 and 37 °C show that the materials are biodegradable. The presence of glycolate units accelerates the course of hydrolytic chain scission and the mass loss. In contrast to this, the presence of oligo(butyl acrylate) segments decreases the hydrolytic degradation rate.

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Supporting Information Available. Influence of the degradation time t_d on the gel content G, the degree of swelling Q of the degraded sample, the melting temperature T_m, the E modulus, the tensile strength σ_{max}, and the elongation at breakage ϵ_R. This material is available free of charge via the Internet at http://pubs.acs.org.

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