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Shape-Memory Polymers

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Multiphase Polymer Networks With Shape-Memory

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ABSTRACT

Tailoring of properties and functions of shape-memory polymer networks to the requirements of specific applications demands a knowledge-based approach. A comprehensive database enabling the analysis of structure-property relationship is obtained by the systematic variation of molecular parameters. Here, we investigated the influence of the nature of thermal transition on the shape-memory behavior of polymer networks. Furthermore, additional amorphous phases were introduced enabling tailoring of elastic properties especially in the temporary shape. The structure property relationships were derived for different designs of such multiphase polymer network architectures.

INTRODUCTION






A recent development in shape-memory polymer technology is the design of shape-memory polymers as multifunctional materials. While the intrinsic properties of a material are determined by its molecular structure, the functionality of material arises from the combination of a suitable polymer architecture and a specific process [1]. Multifunctionality is the unexpected combination of two or more functions of a material. While usually functionalities are combined on purpose, the term unexpected results from the fact that such combinations are not apparent. An interesting example of such multifunctional materials are hydrolytically degradable shape-memory polymers, which combine the functionalities degradability and the shape-memory capability. While degradability could be obtained by the introduction of easily cleavable bonds, the shape-memory capability requires a suitable polymer network architecture in combination with an appropriate programming procedure. Several previous articles described the programming process and the characterization of the shape-memory effect and gave definitions for shape fixity (R_f) and shape recovery rates (R_r) [2-6]. In this article, we focused on the design of suitable polymer networks architectures enabling the shape-memory capability and the parameters to control the shape-memory properties. For a better comparability of the results presented, we will limit our considerations to polymer networks based on macrodimethacrylates.

DISCUSSION

Polymer network architectures

Suitable polymer networks structures having shape-memory capability are displayed in Scheme 1. General parameters for controlling the shape-memory behaviour of covalently crosslinked polymer networks are the functionality of the crosslinks, the network chain segment length, the nature of the switching segment and the number of phases. The functionality of crosslinks and the chain segment length control the crosslink density and influence in this way the mechanical properties while the nature of the switching segment influences the hydrolytic degradation as well as the characteristics of the shape-memory effect. The switching domains can be either related to a melting transition (T_m) or a glass

transition (T_g) resulting in either a sharp melting transition (T_m) or a glass transition (T_g) extending over a broader temperature interval.

polymer network class	crystallizable switching segment	amorphous switching segment
1	(co)polymer network poly(ϵ -caprolactone) PCL poly(ϵ -caprolactone-co-glycolide) PCG 	(co)polymer network poly[(L-lactide)- <i>ran</i> -glycolide] PLLG 
2	AB copolymer network PCL/acrylate PCG/acrylate 	AB copolymer network PLLG/acrylate 
3		ABA block copolymer network poly[(<i>rac</i> -lactide)- <i>block</i> -PPO- <i>block</i> -(<i>rac</i> -lactide)] 

Scheme 1: (Multiphase) polymer network architectures and suitable starting materials

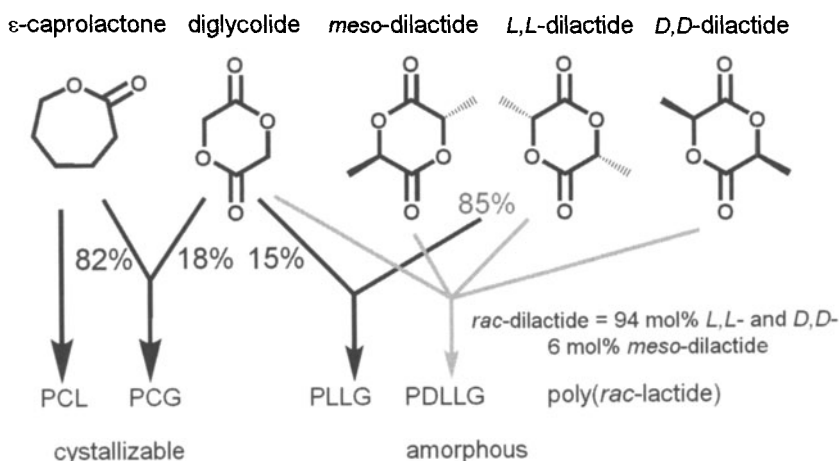
In the following we will focus on telechelics having two reactive groups as starting materials. In polymer networks with a crystallizable switching segment the molecular length can be used for controlling the switching temperature as well. Appropriate macromonomers for polymer networks of class 1 are listed in Scheme 1.

Another strategy for influencing the mechanical properties of the shape-memory polymer networks was the incorporation of a second comonomer which led to the formation of an additional amorphous phase, which contributed to the overall elasticity of the polymer network (class 2). Such polymer networks were prepared from crystallizable as well as amorphous switching segments. In such polymer networks the phases determining the shape-memory capability as well as the phases providing the additional elasticity were on the molecular level distributed among different monomers. In amorphous polymer networks from poly[(*rac*-lactide)-*block*-polypropyleneglycol-*block*-(*rac*-lactide)]dimethacrylate it was demonstrated, that the phase providing additional elasticity could both be provided by the same linear macromonomer (class 3).

Synthesis

Polymer network synthesis could be realized by covalently crosslinking of macrodimethacrylates. The polymerization could be initiated by a thermal radical initiator or by UV light. Photopolymerization is favorable with respect to a biomedical application of the shape-memory materials as harmful effects of the initiator as well as from its degradation products are avoided [7]. Both kinds of polymerizations required the formation of macrodimethacrylates from macrodiols. Such macrodiols were prepared in a ring-opening polymerization (ROP) using hydroxytelechelic initiators. Copolymerization enabled control over the nature of the switching segment. While copolymerization of ϵ -caprolactone with diglycolide resulted in semicrystalline macrodiols, amorphous macrodiols were obtained from the copolymerization of L,L-dilactide and diglycolide especially when a transesterification

catalyst was added. The different sets of comonomers used in the synthesis of macrodiols are shown in Scheme 2.



Scheme 2: Synthesis macrodiols from lactones and cyclic diesters and influence of starting materials on nature of thermal transition associated to switching domains.

The nature of the thermal transition related to the phase formed by the macrodiols can be additionally controlled by using a catalyst during ROP. The copolymerization of ϵ -caprolactone and diglycolide without addition of a transesterification catalyst resulted in crystallizable macrodiols having a blocky sequence structure. An amorphous macrodiol with a random copolymer structure was obtained, when the same copolymerization is performed in the presence of a catalyst capable of transesterification.

Macrodimethacrylates were obtained by esterification of the synthesized macrodiols with methacryloyl chloride. Depending on the macrodiols these macrodimethacrylates can be used for polymer network formation with amorphous or crystalline switching domains. The polymer networks according to type 1 with $T_{\text{trans}} = T_m$ were formed from acrylate or methacrylate functionalized poly(ϵ -caprolactone)diols (PCL) or poly[(ϵ -caprolactone)-*co*-glycolide]diols (PCG) while polymer networks with $T_{\text{trans}} = T_g$ were formed from poly[(*L*-lactide)-*ran*-glycolide]diols (PLGA). In both cases polymerization was initiated by irradiation with UV-light.

AB copolymer networks having a second amorphous phase providing additional elasticity according to type 2 were prepared in case of $T_{\text{trans}} = T_m$ from oligo[(ϵ -caprolactone)-*co*-glycolide]dimethacrylate and *n*-butyl acrylate. *n*-Butyl acrylate was chosen as comonomer as it provides an additional amorphous and non-crystallizable phase of poly(*n*-butyl acrylate) associated to a low glass transition temperature [T_g of poly(*n*-butyl acrylate) = -55 °C]. Copolymerization of poly[(*L*-lactide)-*ran*-glycolide]dimethacrylate with *n*-ethyl acrylate, *n*-butyl acrylate or *n*-hexyl acrylate yielded AB copolymer networks $T_{\text{trans}} = T_g$. Both polymer network systems having $T_{\text{trans}} = T_m$ or $T_{\text{trans}} = T_g$ were obtained by photopolymerization.

ABA networks with $T_{\text{trans}} = T_g$, in which the elasticity providing phase is incorporated in the polymer main chain of the macromonomer could be formed by suitable oligomers of different molar mass. ROP of *rac*-dilactide with poly(propylene oxide) as macroinitiator in presence of

diethyltin oxide as catalyst was applied for macrodiol formation. The macrodimethacrylates were obtained by endgroup functionalization of these ABA triblock copolymer diols having a middle block of poly(propylene oxide) with methacrylate groups. The final polymer networks based on such macrodimethacrylates were generated by photocrosslinking using UV-light.

Thermal Properties

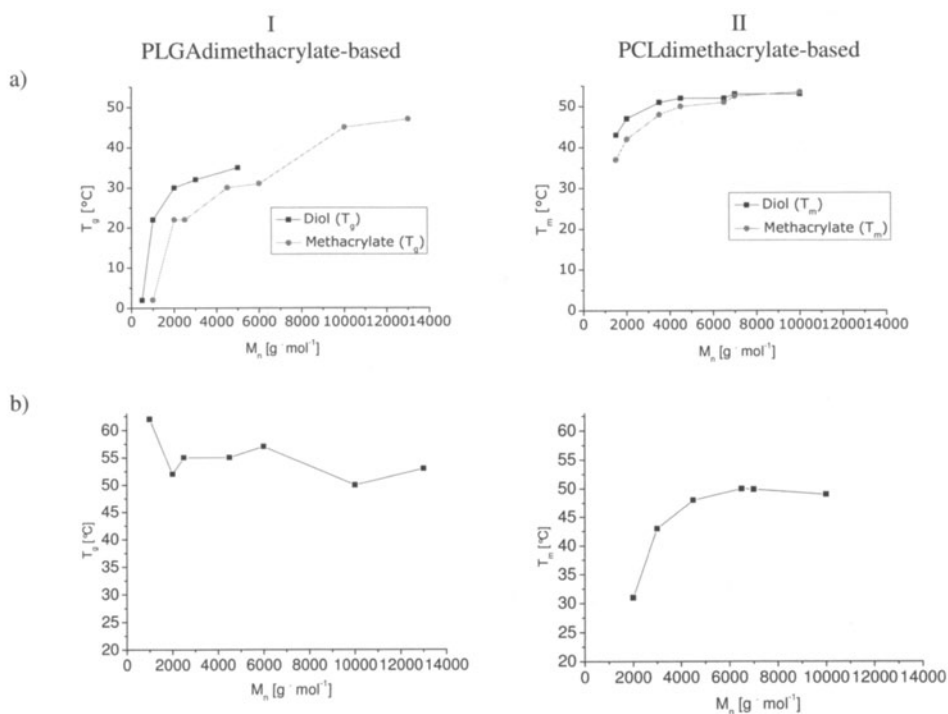


Figure 1: Thermal transition temperatures of macrodiols, macrodimethacrylates (a) and polymer networks (b) having amorphous (I) and crystallizable switching phases (II)

Macrodiols and macrodimethacrylates of PLGA and PCL exhibited a similar correlation of transition temperature with molecular weight of the oligomers. The telechelics reached individual maximum T_{trans} with increasing molecular weight (M_n) (Figure 1). A similar behavior was determined for T_m of PCL networks which increased with increasing molecular weight of the oligomers used as starting material. In case of PCG the dependence of T_m for macrodimethacrylates and polymer networks displayed a similar correlation between T_m and M_n . In contrast, the glass transition temperatures of PLGA networks were independent from the M_n of the precursor if the molecular weights of the macrodimethacrylate precursors are above 2 kD.

In AB-type shape-memory polymer networks having a crystallizable switching domains T_m is decreasing with increasing *n*-butyl acrylate content. Increasing *n*-butyl acrylate content caused a decrease in crystallinity and in melting enthalpy ΔH_m of the polymer networks. The content of

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acrylate also influences the mechanical properties of the polymer networks. These polymer networks became more elastic with increasing amount of *n*-butyl acrylate. Such a behavior was shown for AB networks from *n*-butyl acrylate and poly(ϵ -caprolactone)dimethacrylate or poly[(ϵ -caprolactone)-*co*-glycolide]dimethacrylate [7, 8]. In polymer networks from oligomeric macromonomers with a smaller molar mass this influence is more pronounced than for polymer networks obtained from oligomers having a larger molar mass.

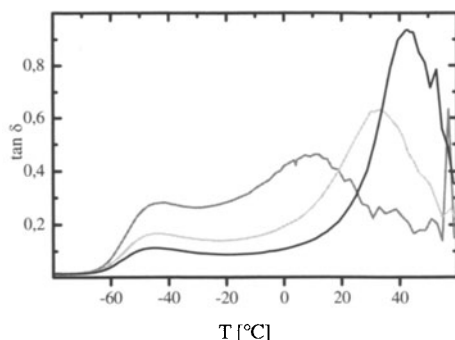


Figure 2. Thermomechanical properties of networks from ABA triblockdimethacrylates determined by DMTA (M_n (NMR) of macrodiols: dark grey 6 kD, light grey 8 kD, black 10 kD) [9].

In the shape-memory polymer network presented above the switching domains were formed by a one segment type. In ABA polymer networks synthesized from poly[(*rac*-lactide)-*block*-polypropyleneglycol-*block*-(*rac*-lactide)]dimethacrylate precursors (PRxtytN) a T_g of the phase provided by the poly(propylene oxide) of -50 °C and a T_g of 50 °C of the phase resulting from the poly(*rac*-lactide) was expected. The thermomechanical properties of three polymer networks from ABA triblockdimethacrylates were determined in dynamic mechanical experiments at varied temperature (DMTA). In these polymer networks a distinct phase separation of the resulting polymer networks could be observed for macrodimethacrylate precursors with $M_n > 10$ kD only. When M_n of the macrodimethacrylate precursors was below 10 kD an additional mixed phase transition between the phase transition resulting from the poly(propylene oxide) and the poly(*rac*-lactide) as well as the phase transition from the poly(propylene oxide) could be detected. The influence of the mixed phase could be observed and is shown in Figure 2.

Shape-memory properties

The shape-memory properties of the different polymer network architectures were investigated in cyclic, thermomechanical tests. In Figure 3 the result of such a test, which was performed in strain-controlled mode, is shown for a network from PCL-dimethacrylate by plotting stress as a function of strain. In the first step the sample was loaded and elongated to ϵ_m (I). When the strain is kept constant a decrease in stress during lowering of T could be observed, resulting from the entropy elasticity of the amorphous chain segments (II). During cooling to T_{low} crystallization of the switching segments is occurring. During the ongoing cooling process (III) the crystallization results in a dramatic increase of stress to a maximum stress at T_{low} (after thermal contraction; σ_l).

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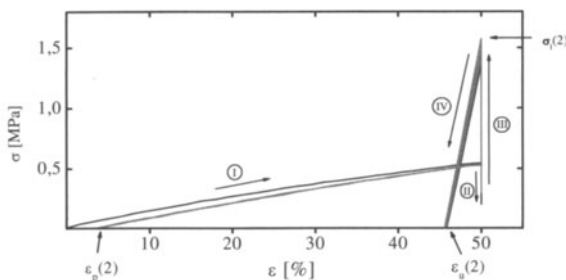
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Figure 3. Cyclic thermomechanical, strain-controlled test of a polymer network from PCL-dimethacrylate with $T_h = 70\text{ }^\circ\text{C}$, $T_l = 0\text{ }^\circ\text{C}$, and $\epsilon_m = 50\%$ ($\sigma = \text{stress}$) in air. The data of the graph are obtained from five subsequent cycles, black: first cycle, grey: cycles 2-5 [10].

This increase in stress is related on the one hand to the oriented crystallization of the strained crystalline segments as well as on the other hand on the entropy elastic expansion. Nevertheless, the newly formed crystallites are acting as physical crosslinks which are fixing the tensile-loaded shape of the sample. Upon unloading, the stress-strain curve intersected the σ axis at a temporary strain (ϵ_0), representing the temporary shape of the specimen (IV). A residual strain (ϵ_p) remained after reheating and recovery of the permanent shape, so that the second cycle ($N = 2$) was slightly differing from the previous cycle. Generally the permanent shape was recovered by more than 90%, but this value might be increased in subsequent cycles because the preorientation of the sample resulting from processing of the shaped body was deleted. A typical protocol consisted of five cycles.

The mechanical as well as the shape-memory properties of the polymer network having crystalline switching domains could be significantly influenced by the introduction of a second amorphous phase [7, 8]. Here *n*-butyl acrylate was chosen as a second comonomer, which influenced the ratio of crystalline domains below T_{trans} of the switching domains. In these AB polymer networks from PCG-dimethacrylate and *n*-butylacrylate, the glycolide content of the crystalline segments was kept constant as well as the ratio of the *n*-butyl acrylate while the length of the crystallizable segments was varied. Results from strain-controlled thermomechanical experiments cycles of these polymer networks are shown in Figure 4. The curves of the polymer networks N-CG(14)-7 and N-CG(14)-10 were similar to the curve described for the polymer networks purely consisting of crystalline switching segments shown in Figure 3. The curves of the polymer networks N-CG(14)-3 and N-CG(14)-5 differed from the curves described in Figure 3 because the ϵ -hydroxycaproate-sequences dominated segments were relatively short forming less stable crystallites, stabilizing the temporary shape.

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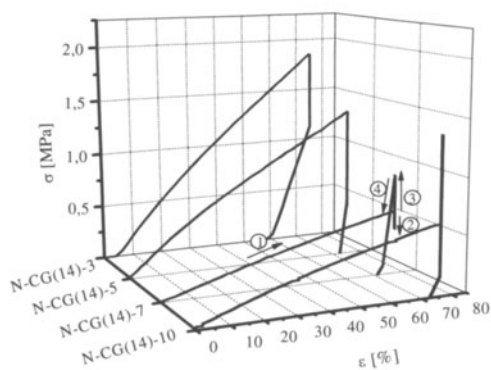
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Figure 4. Fifth cycle of a strain-controlled cyclic, thermomechanical tensile test of copolymer networks N-CG(14)-X from macrodimethacrylates with X = 3, 5, 7 or 10 kD of the oligomer in air. $T_h = 70\text{ }^\circ\text{C}$, $T_l = 0\text{ }^\circ\text{C}$, $\epsilon_m = 75\%$ [8].

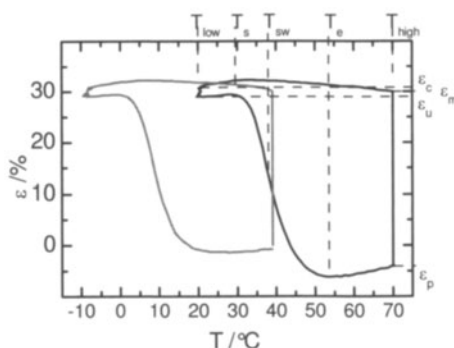


Figure 5. Stress-controlled cyclic, thermomechanical tests of AB copolymer networks from poly[(*L*-lactide)-*ran*-glycolide]dimethacrylate and *n*-ethyl acrylate, (black line: 34 wt% *n*-ethyl acrylate, grey line: 85 wt% *n*-ethyl acrylate) [11].

In AB shape-memory polymer networks having an amorphous phase associated to a T_g , the second phase, which contributes additional elasticity to the material might also influence the shape-memory properties, when the phase separation between both amorphous phases is not sufficient [11]. In Figure 5 the curves of two cyclic, thermomechanical tests under stress-controlled conditions are presented from polymer networks obtained from copolymerization of poly[(*L*-lactide)-*ran*-glycolide]dimethacrylate with *n*-ethyl acrylate. In such cycles the switching temperature T_{sw} of the thermally-induced shape-memory effect could be determined. T_{sw} was defined as inflection point of the recovery sector of cyclic, thermomechanical tests displayed in Figure 5. The *n*-ethyl acrylate content of the polymer networks was varied between 34 and 85wt%. From the curves obtained, it could be concluded that T_{sw} was significantly lowered with increasing weight content of *n*-ethyl acrylate.

A disadvantage of AB polymer networks with an *n*-butyl acrylate content of more than 50 wt-% was a decrease in shape fixity ratio R_f . Shape-memory polymer networks, which were elastic at $T < T_{sw}$ and avoided the decreased R_f of AB polymer networks were realized by ABA polymer networks from poly[(*rac*-lactide)-*block*-poly(propylene oxide)-*block*-poly(*rac*-lactide)]dimethacrylate.

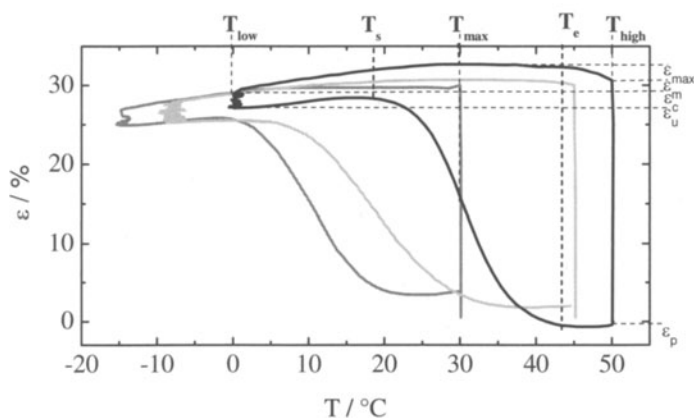


Figure 6. Cyclic thermomechanical tensile experiment at constant stress σ_m during cooling and $\sigma = 0$ during reheating for polymer networks from poly[(*rac*-lactide)-*block*-poly(propylene oxide)-*block*-poly(*rac*-lactide)]dimethacrylates. (dark grey: PR4t6tN; light grey PR4t8tN; black: PR4t10tN) [9]

As expected from the DMTA measurements, T_{sw} was closely associated to T_g and was increasing with increasing T_g determined for the ABA polymer networks. The temperature interval of the strain recovery increased between 29 K and 37 K with increasing molecular weight of the chain segments. Additionally, R_f was increasing with increasing molecular weight of the poly(*rac*-lactide) blocks. The chain segments reshaped into the random coil conformation at T_{sw} in the order PR4t6tN < PR4t8tN < PR4t10tN. This behavior could be explained by the increase of the molecular weight of the chain segment per unit volume. In these polymer systems the highest measured entropy gain, which drove the strain recovery, was determined for the block copolymer network PR4t10tN. Consequently, the highest R_f value of 99.5% was measured in case of PR4t10tN. It could be concluded that ABA polymer networks have a suitable polymer network architecture, which provided appropriate elasticity as well as sufficient shape-memory properties. Nevertheless, the phase separation between both phases needed to be sufficient otherwise T_{sw} was closely related to the T_g of the mixed phase. In such a case an independent control of the thermal as well as the shape-memory properties was not given. With increasing M_n of the building blocks sufficient phase separation could be achieved.