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(54) Title: AMORPHOUS POLYESTER URETHANE NETWORKS HAVING SHAPE MEMORY PROPERTIES

(57) Abrégé/Abstract:
The invention relates to a novel system of amorphous polymer networks comprising one or several segments with shape memory properties in order to avoid structural heterogeneities in the networks. Said networks are preferably composed of biodegradable and biocompatible components and can be used in the medical domain. The systemic character of the materials allows the thermal and mechanical properties as well as the decomposition behavior to be adjusted in a specific manner. The invention particularly makes it possible to produce polyphase amorphous networks.

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(54) Title: AMORPHOUS POLYESTER URETHANE NETWORKS HAVING SHAPE MEMORY PROPERTIES

(54) Bezeichnung: AMORPHE POLYESTERURETHAN-NETZWERKE MIT FORM-GEDÄCHTNIS-EIGENSCHAFEN

(57) Abstract: The invention relates to a novel system of amorphous polymer networks comprising one or several segments with shape memory properties in order to avoid structural heterogeneities in the networks. Said networks are preferably composed of biodegradable and biocompatible components and can be used in the medical domain. The systemic character of the materials allows the thermal and mechanical properties as well as the decomposition behavior to be adjusted in a specific manner. The invention particularly makes it possible to produce polyphase amorphous networks.

(57) Zusammenfassung: Um strukturelle Inhomogenitäten in den Netzwerken zu umgehen, wird in Übereinstimmung mit der vorliegenden Erfindung ein neues System amorpher Polymernetzwerke aus ein oder mehreren Segmenten mit Formgedächtniseigenschaften zur Verfügung gestellt. Die Netzwerke setzen sich bevorzugt aus bioabbaubaren und biokompatiblen Komponenten zusammen und eröffnen die Möglichkeit für den Einsatz im medizinischen Bereich. Der Systemcharakter der Materialien erlaubt eine gezielte Einstellung der thermischen und mechanischen Eigenschaften sowie des Abbauverhaltens. Die vorliegende Erfindung erlaubt insbesondere die Herstellung mehrphasiger amorpher Netzwerke.

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Amorphous Polyester Urethane Networks Having Shape Memory Properties

The invention under consideration relates to cross-linked, preferably biodegradable polyester urethanes with shape memory properties.

State of the Art

Biodegradable, covalent polymer networks with shape memory properties are usually obtained by means of free radical polymerization of, e.g., macrodimethacrylates. This method of production comprises a total of three steps: synthesis of macrodiols, methacrylation of the terminal groups and radical cross-linking.

The radical reaction mechanism is subject to a random process in which the microscopic structure of the cross-link points can be regulated only to a limited degree, so that structural heterogeneities can arise in the networks. Furthermore, with a chain reaction of that type, regulation and checking of the reaction is difficult, so that even if the starting materials in the network itself are very uniform, widely varying areas may be present, e.g., areas having a high cross-link density and areas having a lower cross-link density. This affects the use of materials of this type in some application areas, however. At the same time, such heterogeneities can also lead to variability in the physical properties.

Object of the Invention

The object of the invention under consideration is, therefore, to provide a new material and accompanying method for production with which the disadvantages of the state of the art can be overcome.

Short Description of the Invention

The object described above is solved by means of polymeric networks, obtained by the reaction of hydroxytelechelic prepolymers with diisocyanate, wherein said hydroxytelechelic prepolymers have a number-average molecular weight of at least 4,400 g/mol and comprise polyester and/or polyether segments having a number-average molecular weight of at least 1,000 g/mol.

The invention is also directed to a method for the production of such polymeric

networks, which comprises the reaction of the hydroxytelechelic prepolymers wherein the prepolymers comprise polyester and / or polyether segments, with diisocyanate.

Detailed Description of the Invention

In order to avoid structural heterogeneities in the networks, the invention under consideration provides a novel system of amorphous polymer networks comprising one or several segments with shape memory properties. The networks are preferably composed of biodegradable and biocompatible components and they open up the possibility for use in the medical domain. The systemic character of the materials allows the thermal and mechanical properties, as well as the decomposition behaviour, to be adjusted in a specific manner. In particular, the invention under consideration makes it possible to produce polyphase amorphous networks.

In contrast to the already developed biodegradable, covalent polymer networks with shape memory properties, which are obtained by means of free radical polymerization of, for example, macro-dimethacrylates, the invention under consideration calls for the use of a different method of production, namely polyaddition. In this process, a total of only two synthesis steps are necessary: synthesis of macrotriols or macrotetrols and polyaddition.

The networks according to the invention are based on star-shaped prepolymers with hydroxyl terminal groups, which are produced using known methods. This procedure makes it possible to produce structurally uniform networks (particularly even on a larger scale). By means of starting the production with multifunctional prepolymers, it is possible to ensure a very high degree of homogeneity of the networks, because the essential parameters of the networks can be specified just by the comparably low-molecular parent compounds as a result of the number of possible coupling points and the chain lengths of the prepolymers, which simplifies the control. At the same time, the cross-link points themselves are also already pre-shaped, which further facilitates the control.

The networks according to the invention comprise multifunctional constitutional units (derived from the abovementioned prepolymers), preferably trifunctional and / or tetrafunctional constitutional units, each of which preferably has a hydroxyfunctionality at the reactive ends or an equivalent grouping before the production of the network. The production

of the network then takes place by reaction with a suitable diisocyanate or another suitable compound, preferably with a slight excess of diisocyanate.

The multifunctional constitutional units (prepolymers) comprise a central unit, which corresponds to the later cross-link points in the network. This central unit is preferably derived from suitable low-molecular multifunctional compounds, preferably with three or more hydroxyl groups, in particular, three to five and, more preferably, three or four hydroxyl groups. Suitable examples are pentaerythritol and 1,1,1-tris(hydroxymethyl)ethane. An appropriate number of prepolymer chains (corresponding, for example, to the number of hydroxyl groups) is bound to this central unit, wherein these chains preferably comprise monomer units bound by ester bonds and / or monomer units bound by ether bonds. Preferred examples are chains on the basis of lactic acid, caprolactone, dioxanone, glycolic acid and / or ethylene glycol or propylene glycol.

Preferred in this case are, in particular, chains of lactic acid (D or L or DL), optionally in combination with one of the other abovementioned acid constitutional units (as block copolymers or as statistical copolymers, wherein statistical copolymers are preferred). Alternatively, the chains comprise segments from the acid constitutional units (in the possible combinations mentioned above), together with segments from the ether constitutional units, wherein a combination with a polypropylene glycol segment is particularly preferred here. Preferably, such constitutional units possess two segments in each chain: a polyester segment and a polyether segment (particularly polypropylene glycol), wherein it is preferred for the polyether segment to be provided at the central unit, with the polyester segment affixed thereto, so that the chain ends are formed by the polyester segment.

The prepolymers normally have a number-average molecular weight (determined by GPS) of from 1,000 to 20,000 g/mol, preferably from 2,500 to 15,000 g/mol, particularly from 5,000 to 12,000 g/mol and furthermore preferably from 8,000 to 11,000 g/mol. In accordance with the invention as claimed, the number-average molecular weight is however of at least 4,400 g/mol. In the case of prepolymers with segments of polyether units, the segments of polyether units preferably have a number-average molecular weight of from 1,000 to 6,000, and the polyester segments

coupled thereto have a number-average molecular weight of from 1,000 to 12,000 g/mol, so that these prepolymers altogether again have a number-average molecular weight as described above.

Because prepolymers of this type can be produced by means of easily controlled methods, the prepolymers used in accordance with the invention preferably have a relatively large degree of homogeneity (PD), preferably in the range of from 1 to 2, particularly from 1 to 1.5. A good degree of homogeneity of this type also gives the networks according to the invention a good degree of homogeneity.

It is particularly preferred if the prepolymers have lactic acid units (lactate units). If further acid constitutional units are present, the lactate units preferably account for the greater portion of the acid units in the polyester segment. For the other abovementioned acid constitutional units, preferred proportions, in addition to lactate units, are as follows:
Glycolate: 0 to 55% by mass, preferably 10 to 30% by mass.
Caprolactone or dioxanone: 0 to 45% by mass, preferably 10 to 25% by mass, particularly roughly 15% by mass.
The respective proportions can easily be adjusted by checking the quantity of monomers in the production of the prepolymers.

The prepolymers constructed as described above are reacted into the networks according to the invention by a polyaddition reaction. In this process, the reaction with the diisocyanates results in a chain linkage to the hydroxyl groups at the ends of the multifunctional prepolymers, so that the chains are then connected via diurethane units. Because of the hydrolysis sensitivity of the individual segments, this results in the development of a network that can be biodegradable, particularly in the physiological area. The selection of the components for the prepolymers furthermore particularly also allows the production of amorphous networks. In particular, the use of lactic acid (preferably DL form) and the use of atactic polypropylene glycol allow the production of completely amorphous networks.

In this process, the decomposition behaviour can be controlled by means of the proportion of individual monomers. Glycolate units, caprolactone units and dioxanone units generally delay the decomposition reaction.

Furthermore, the mechanical property profile of the network can also be controlled by means of the chain length and the respective proportion of monomers. Low molar masses of the prepolymers normally lead to networks with a high cross-link density, which can possibly have low mechanical stabilities, however. In return, the swelling capacity of such networks is limited.

The introduction of glycolate units, caprolactone units and / or dioxanone units furthermore allows control of the transition temperature and therefore the switch temperature for the shape memory effect (the shape memory effect is already extensively described in the state of the art; in this context, therefore, reference is merely made to the already existing literature, e.g., further patent applications made by the Mnemoscience company). In this way, desired switch temperatures can be selectively adjusted for an application.

The prepolymers according to the invention additionally also allow the production of phase-segregated networks, which is advantageous for some application areas. The following strategies lend themselves to the production of such phase-segregated networks.

1. Prepolymers according to the invention having only polyester segments are reacted with diisocyanate in the presence of polyether macromonomers with unsaturated terminal groups. These polyether macromonomers are then photochemically cross-linked, resulting in an IPN.
2. Prepolymers according to the invention having both polyester segments and polyether segments are reacted with diisocyanate. The result is a network with segregated phases.
3. Prepolymers according to the invention having only polyester segments are reacted with diisocyanate with prepolymers with only polyether segments. The result is a network with segregated phases, wherein, unlike in 2., polyester segments and polyether segments

are not present in one prepolymer, but instead in separate prepolymers, coupled via diurethane units.

4. Prepolymers according to the invention having only polyester segments are reacted with diisocyanate. The resulting network is swollen in the presence of acrylate monomers and the acrylate monomers intercalated in this way are then photochemically cross-linked into a network, resulting in an IPN.

Preferred molecular weights for the macromonomers (1.) correspond to the values specified above for the polyether segment in the prepolymer. Also preferred here is a polypropylene glycol segment.

Preferred acrylate monomers for option 4. are ethyl acrylate, butyl acrylate, hexyl acrylate and hydroxyethyl acrylate, as well as the corresponding methacrylates. The total mass proportion in the resulting IPN for these monomers preferably amounts to from 1 to 35 % by mass, more strongly preferred from 8 to 25 % by mass. Hydroxyethyl acrylate particularly allows an adjustment of the hydrophilicity of the IPN.

Preferred networks according to the invention are as follows:

Type I: Polymer networks of triols or tetrols and diisocyanate,

Type II: Polymer networks of triols and tetrols and diisocyanate,

Type III: Polymer networks of triols or tetrols with diisocyanate and an interpenetrating network of a macrodimethacrylate,

Type IV: Sequential interpenetrating polymer networks of a network of triols or tetrols with diisocyanate and subsequently polymerized low-molecular acrylates.

The networks according to the invention can be used in all areas in which biocompatible or degradable materials are used, e.g., in the medical area.

The networks according to the invention can possess additional constituents, such as filling substances, biologically active substances, colouring substances, diagnostics, etc. The use of such additional constituents depends on the particular purpose.

Short Description of the Figures

Figure **1** shows the glass temperature of the polyurethane networks (Type 1) with oligo[(*rac*-lactate)-*co*-glycolate] segments having various segment lengths.

Figure **2** illustrates the restoration behaviour (shape memory effect) of a previously elongated network (Type 1) with oligo[(*rac*-lactate)-*co*-glycolate] segments in the heating process.

Figure **3** shows the glass temperature of the polyurethane networks (Type 1) with oligo(lactate-co-hydroxycaproate) and oligo(lactate-hydroxyethoxy acetate) segments with variable lactate content.

Figure **4** illustrates the restoration behaviour (shape memory effect) of several polyurethane networks (Type 1) from Figure **3** in the heating process.

Figure **5** represents the thermal properties of the multiphase polymer networks (Type 1) with oligo(propylene glycol) and oligo(lactate-co-glycolate) segments.

Figure **6** is a schematic depiction of the fixation of a pre-IPN by the subsequent cross-linking of the additional component (Type III).

Figure **7** shows the swelling capability of an IPN (Type IV) in water with a variable proportion of 2(hydroxyethyl) acrylate.

Production of the Networks

The networks according to the invention can be simply obtained by means of the reaction of the prepolymers with diisocyanate in solution, e.g., in dichloromethane, and subsequent drying (Types 1 and II). In the production of the IPN with a second network of acrylate monomers, the network according to the invention is swollen in monomers after the production, whereupon the cross-linking of the monomers (Type IV) follows. In the case of the IPN with a second network of polypropylene glycol macromonomers, the network according to the invention is produced in the presence of the macromonomers (in solution, as described above), which are subsequently cross-linked (Type III). In principle, mass polymerization is also possible, i.e., crosslinking reactions without the use of a solvent. This option is particularly useful in view of a processing of the materials according to the invention in injection moulding, because the thermoplastic starting materials are shaped in this process, whereupon the crosslinking into the desired shape follows.

Examples

The following examples illustrate the invention under consideration.

Abbreviated designations of the oligomers and the polymer networks

Cooligomers of the rac-dilactide

X-LY(μ_Y)-Z

X Initiator of the ring-opening polymerization
- E Ethylene glycol
- P Pentaerythrite
- T 1,1,1-Tris(hydroxymethyl)ethane

L *rac*-lactate

Y Comonomer units
- C ε-hydroxycaproate
- D β-hydroxyethoxy acetate
- G Glycolate

μ_Y Proportion by mass of the comonomer Y according to ^{1}H-NMR relative to the total mass of the repeating units without initiator segment in % by mass

Z According to the initial weight of the reactands, expected number-average molar mass of the oligomers in g·mol^{-1} rounded to 1,000 g·mol^{-1}

Oligo(propylene glycol)

F-PPG-Z

F Terminal groups
- D Diol
- M Dimethacrylate
- T Triol

PPG Oligo(propylene glycol)

Z Number-average molar mass of the hydroxyfunctional oligomers according to manufacturer's information, in g·mol^{-1}; exception: M-PPG-560: in this case, Z is the number-average molar mass of the macrodimethacrylate according to manufacturer's information, in g mol^{-1}

Star-{oligo(propylene glycol)-block-oligo[(rac-lactate)-co-glycolate]} triols

T-PPG-Z-*b*-LG-Z

T-PPG Commercially obtainable oligo(propylene glycol) triol prepared by initiation with glycerin
Z Number-average molar mass of the oligo(propylene glycol) triol used according to manufacturer's information, in $g \cdot mol^{-1}$
b Block sequence structure
LG Oligo[(*rac*-lactate)-*co*-glycolate] segment with 15% by mass glycolate according to initial weight
Z According to the initial weight of the reactands, expected number-average molar mass of the star-{oligo(propylene glycol)-*block*-oligo[(*rac*-lactate)-*co*-glycolate]}triol, in $g \cdot mol^{-1}$

Networks (except for interpenetrating polymer networks)

The designations for the prepolymers used with the prefix N apply.
An exception is given by the networks that are produced by polyaddition of mixtures of oligo(propylene glycol) triols, oligo[(*rac*-lactate)-*co*-glycolate] tetrols and TMDI. In this case, the following abbreviated designations apply:

N-T-PPG(μ_{PPG})-Z-LG

N Network
T-PPG Commercially obtainable oligo(propylene glycol) triol prepared by initiation with glycerin
μ_{PPG} Proportion by mass of the oligo(propylene glycol) triol used, relative to the total mass of the prepolymers, in % by mass
Z Number-average molar mass of the oligo(propylene glycol) triol according to manufacturer's information, in $g \cdot mol^{-1}$
LG Oligo[(*rac*-lactate)-*co*-glycolate] tetrol P-LG(17)-10000

The networks N-EA, N-BA and N-HEA form additional exceptions. These are networks that are obtained by means of photochemically initiated polymerization of ethyl acrylate, butyl acrylate or (2-hydroxyethyl)acrylate. A volume of 0.5 % by volume of the oligo(propylene glycol)dimethacrylate M-PPG-560 and the photoinitiator 2,2'-dimethoxy-2-phenylacetophenone (10 mg/mL) is added to the acrylates.

Interpenetrating polymer networks

N-LG-*ip*X-N-Y(μ_Y)-Z

N-LG Network of N-P-LG(17)-10000 and TMDI
ip Interpenetrating polymer network
X Number of steps in which swelling and radiation take place (optional); if X = 1, not explicitly mentioned
N-Y Network of oligo(propylene glycol)dimethacrylate and the component Y:

EA	Ethyl acrylate
BA	Butyl acrylate
HEA	(2-hydroxyethyl)acrylate
M-PPG	Oligo(propylene glycol)dimethacrylate

μ_Y Proportion of the component Y in % by mass; in the case of *in situ* sequential IPNs, according to the initial weight of oligo(propylene glycol)dimethacrylate
Z Molar mass of the oligo(propylene glycol)diol used in the synthesis of the macrodimethacrylate; if M-PPG-560 is used, not explicitly mentioned

In the case of interpenetrating systems whose components Y are prepared in a non-cross-linked form, (pre-IPNs), the auxiliary N is dropped in front of this component.

Prepolymers (macrotriols and macrotetrols)

The preparation of star-shaped prepolymers such as oligo[(*rac*-lactate)-*co*-glycolate] triol or -tetrol is done by means of ring-opening copolymerization of *rac*-dilactide and diglycolide in the melting of the monomers with hydroxyfunctional initiators, with the addition of the catalyst dibutyltin (IV)oxide (DBTO). This synthesis path had proven to be suitable in the literature on the production of linear and branched oligomers with defined molar mass and terminal group functionality (D. K. Han, J. A. Hubbell, *Macromolecules* **29,** 5233 (1996); D. K. Han, J. A. Hubbell, *Macromolecules* **30,** 6077 (1997); R. F. Storey, J. S. Wiggins, A. D. Puckett, J. *Polym. Sci.: Part A: Polym. Chem.* **32,** 2345 (1994); S. H. Kim. Y.-K. Han, Y. H. Kim, S. I. Hong, *Makromol. Chem.* **193,** 1623 (1992)). Ethylene glycol, 1,1,1-tris(hydroxy-methyl)ethane or pentaerythrite are used as initiators of the ring-opening polymerization.

Oligo(lactate-co-hydroxycaproate) tetrols and oligo(lactate-hydroxyethoxy acetate) tetrols, as well as [oligo(propylene glycol)-block-oligo(rac-lactate)-co-glycolate)] triols are produced in a similar fashion.

Tab. 1: Composition and molecular weight of the prepolymers oligo[(*rac*-lactate)-*co*-glycolate]s.

χ_G molar proportion of glycolate units, μ_G mass proportion of glycolate units, number-average relative molar mass M_n and polydispersity PD, according to ^{1}H-NMR spectroscopy (^{1}H-NMR), vapour pressure osmometry (VPO) and gel permeation chromatography (GPC). The proportion by mass of glycolate used in the reaction batch is μ_{G_R} and M_{calc} is the number-average molar mass expected on the basis of the initial weight of the reactands.

Oligomer[a)]	μ_{G_R}	χ_G[b)]	μ_G[b)]	M_{calc}	M_n[b)] (^{1}H-NMR)	M_n (VPO)	M_n (GPC)	PD (GPC)
	% by mass	mol %	% by mass	g mol^{-1}	g mol^{-1}	g mol^{-1}	g mol^{-1}	
E-LG(15)-1000	15	18	15	1100	1100	n. d.	1200	1.56
E-LG(17)-2000	15	20	17	2100	2000	1800	2300	1.63
E-LG(15)-5000	15	18	15	5100	5000	n. d.[c)]	5600	1.44
E-LG(17)-7000	15	20	17	7100	6200	4200	5400	1.67
E-LG(16)-9000	15	19	16	9100	9500	5600	7900	1.60
E-LG(15)-12000	15	18	15	12000	12500	4400	6200	1.75
T-LG(17)-1000	15	20	17	1100	980	n. d.[c)]	970	1.49
T-LG(15)-2000	15	18	15	2100	2300	1900	2800	1.40
T-LG(17)-5000	15	20	17	5100	4500	3100	4400	1.43
T-LG(17)-7000	15	20	17	7100	6000	4200	7200	1.41
T-LG(16)-9000	15	19	16	9200	7900	7700	9600	1.42
T-LG(16)-10000	15	19	16	10100	9200	4700	6400	1.60
T-LG(18)-12000	15	21	18	12200	11700	6,000	7600	1.64
P-LG(17)-1000	15	20	17	1100	820	1300	760	1.92
P-LG(18)-2000	15	21	18	2100	2500	n. d.[c)]	5400	1.11
P-LG(15)-5000	15	18	15	5100	4900	4000	7600	1.23
P-LG(15)-7000	15	18	15	7100	7300	4700	8000	1.30
P-LG(16)-9000	15	19	16	9100	8200	4200	6300	1.91
P-LG(17)-10000	15	18	17	10100	10500	5100	10800	1.60
P-LG(12)-12000	15	15	12	12100	10100	8700	14400	1.24
P-LG(0)-10000	0	0	0	10100	9200	6700	11100	1.21
P-LG(8)-10000	8	10	8	10100	11600	9200	13400	1.13
P-LG(13)-10000	10	16	13	10100	10500	9700	14000	1.27
P-LG(30)-10000	30	35	30	10100	10700	7400	9200	1.41
P-LG(48)-10000	50	53	48	10100	9700	6100	10800	1.36
P-LG(52)-10000	50	57	52	10100	9900	7800	12600	1.21

a) Explanation of the abbreviations: see above.

b) The molar proportion of glycolate units χ_G is calculated using the ^{1}H-NMR spectra and converted into proportions by mass μ_G. The determination of the composition of the oligomers and the calculation of M_n according to ^{1}H-NMR are described in Chap. 12.2.1.

c) n.d.: not determined
E = Ethylene glycol
P = Pentaerythrite
T = 1, 1,1-tris(hydroxymethyl)ethane

Tab. 1a: Molar χ_D or mass proportion μ_D of ß-hydroxyethoxy acetate, number-average molar mass M_n, and polydispersity PD of the oligo[(*rac*-lactate)-*co*(β-hydroxyethoxy acetate)]s according to ^{1}H-NMR spectroscopy (^{1}H-NMR), vapour pressure osmometry (VPO) and gel permeation chromatography (GPC). The proportion by mass of β-hydroxyethoxy acetate used is μ_{D_R} and M_{calc} is the number-average molar mass expected on the basis of the initial weight of the reactands according to Eq. 4.2. The prepolymers are prepared by initiation with pentaerythrite.

Oligomer[a)]	μ_{D_R}	χ_D[b)]	μ_D[b)]	M_{calc}	M_n[b)] (^{1}H-NMR)	M_n (VPO)	M_n (GPC)	PD (GPC)
	% by mass	mol %	% by mass	g·mol^{-1}	g·mol^{-1}	g·mol^{-1}	g·mol^{-1}	
P-LD(12)-1000	15	9	12	1100	980	1200	1300	1.58
P-LD(15)-2000	15	11	15	2100	2600	1800	2900	1.39
P-LD(13)-5000	15	10	13	5200	5900	3300	7100	1.32
P-LD(13)-7000	15	10	13	7200	7300	3500	8700	1.32
P-LD(12)-10000	15	9	12	10100	9500	4100	12300	1.37
P-LD(8)-10000	10	6	8	10100	6500	3900	11200	1.26
P-LD(17)-10000	20	12	17	10100	6300	4100	12300	1.37
P-LD(20)-10000	20	15	20	10100	7200	n.d.[c)]	n.d.[c)]	n.d.[c)]
P-LD(25)-10000	30	19	25	10100	6900	4400	10900	1.29
P-LD(45)-10000	50	37	45	10100	10100	3200	11100	1.25
P-LD(65)-10000	70	56	65	10100	10000	2500	9400	1.21

a) See above.
b) The molar proportion of β-hydroxyethoxy acetate units χ_D is calculated by evaluating the ^{1}H-NMR spectra and converted into proportions by mass μ_D. The determination of the composition of the oligomers and the calculation of M_n according to ^{1}H-NMR.
c) n. d.: not determined.

Tab. 2b: Proportion by mass μ_{PPG} of oligo(propylene glycol), number-average molar mass M_n according to ^{1}H-NMR spectroscopy (^{1}H-NMR) or gas permeation chromatography (GPC) and polydispersity PD of the star-{oligo(propylene glycol)-*block*-oligo[(*rac*-lactate)-*co*-glycolate]} triols and the macroinitiators. M_{calc} is the number-average molar mass that is expected due to the initial weight of the reactands. The number-average molar mass of the oligo[(*rac*-lactate)-*co*-glycolate] segments is $M_{b\text{-}LG}$ and the proportion of converted terminal groups of the oligo(propylene glycol) triols D_P. The mass proportion of oligo(propylene glycol) used in the reaction batch is $\mu_{PPG\text{-}R}$.

Oligomer[a)]	$\mu_{PPG\text{-}R}$	μ_{PPG}[b)]	M_{calc}[c)]	M_n[b)]	M_n	PD	$M_{b\text{-}LG}$[b)]	D_P[b)]
				(^{1}H-NMR)	(GPC)	(GPC)		
	% by mass	% by mass	g·mol^{-1}	g·mol^{-1}	g·mol^{-1}		g·mol^{-1}	%
T-PPG-1000	100	100	1000	930	1200	1.03	-	0
T-PPG-1000-*b*-LG-2000	50	41	2000	2300	2700	1.09	440	95
T-PPG-1000-*b*-LG-4000	25	22	4000	4200	6000	2.35	1100	> 99
T-PPG-1000-*b*-LG-6000	17	14	6000	6500	6600	1.33	1900	> 99
T-PPG-1000-*b*-LG-9000	11	10	9000	9000	8500	1.34	2700	> 99
T-PPG-3000	100	100	3000	3400	3600	1.07	-	0
T-PPG-3000-*b*-LG-4000	75	82	4000	4200	6100	1.01	250	95
T-PPG-3000-*b*-LG-6000	50	54	6000	6500	11400	2.80	1000	98
T-PPG-3000-*b*-LG-9000	33	38	9000	9100	8700	1.41	1900	92
T-PPG-6000	100	100	6000	5600	7000	1.44	-	0
T-PPG-6000-*b*-LG-9000	67	60	9000	9300	13400	1.65	1300	86
T-PPG-6000-*b*-LG-12000	50	48	12000	11700	7600	2.56	2000	76

a) See above.
b) The determination of μ_{PPG}, D_P and M_n (^{1}H-NMR) is done using ^{1}H-NMR spectroscopy.
c) M_n of the macroinitiators according to the manufacturer's information is the basis for the values n_I and M_I.

Networks

The network synthesis takes place by means of polyaddition of the star-shaped macrotriols and tetrols with an aliphatic diisocyanate as a bifunctional coupling reagent (Type 1). Work is done here in solutions in dichloromethane. In standard experiments, an isomer mixture of 2,2,4 and 2,4,4 trimethylhexane-1,6-diisocyanate (TMDI), for example, is used as the diisocyanate. The intended purpose of the use of the isomer mixture is to prevent possible crystallization of diurethane segments. Also suitable are other diisocyanates.

Alternatively, mixtures of different prepolymers can be reacted with a diisocyanate, e.g., oligo(rac-lactate)-co(glycolate) tetrol with oligo(propylene glycol) triol and TMDI (Type II).

A different synthesis strategy is applied in the case of networks of Type III. In this case, a mixture of a tetrol, an oligo(propylene glycol)dimethacrylate and TMDI is produced. First the tetrol and the TMDI react together into a first network (pre-IPN). Subsequently, the radical cross-linking of the dimethacrylate is initiated by means of UV radiation, by means of which a second network is created (sequential IPN). As a result of the use of pre-IPNs, the permanent shape of the shape memory materials can be relatively easily and quickly adjusted to special requirements and geometries by means of UV radiation (Figure 6).

Another synthesis strategy consists of swelling a polyurethane network of Type I in an acrylate, and subsequently triggering a radical polymerization using UV light. Suitable are ethyl, butyl, hexyl or (2-hydroxyethyl) acrylate. In this way, one obtains an IPN of Type IV. Regardless of the acrylate used, two glass transitions are usually observed. When 2-(hydroxyethyl) acrylate is used, it is possible to adjust the hydrophilicity of the material (Figure 7). The bandwidth of medical applications of the prepared materials is expanded because of this possibility.

Tab. 2: Gel content G and degree of swelling Q in chloroform as well as glass transition temperature T_g according to DSC (2^{nd} heating process) of networks of P-LG(17)-1000 or P-LG(17)-10000 with various diisocyanates or isomer mixtures of diisocyanates (Type 1).

Diisocyanate	Isomers	M_n (prepolymer) according to ^{1}H-NMR	G	Q	T_g
		g·mol^{-1}	% by mass	% by vol.	°C
-		820	100	n.d. [d]	59
		10500	96 ± 1	490 ± 0	54
		820	n. d.[d]	160 ± 40	66
		10500	98 ± 2	690 ± 70	53
		820	100	n. d.[d]	72
		10500	98	470 ± 10	57
		820	99	n. d. [d]	75
		10500	98	460 ± 10	57
		820	97 ± 1	n. d. [d]	80
		10500	100	480	57

a) Isomer mixture of 2,2,4 and 2,4,4-trimethylhexane-1,6-diisocyanate; b) *cis/trans* mixture of the isophorone diisocyanate, c) *cis/trans* mixture of the 4,4'-methylene-bis(cyclohexyl isocyanate), d) n. d.: not determined. Networks of P-LG(17)-1000 are destroyed during the swelling in chloroform, so that determination of G and Q are only possible with restrictions.

Tab. 2a: Gel content G and theoretical number-average molar mass $M_{c\text{-}ideal}$ of the segments of networks of oligo[(*rac*-lactate-*co*-(ß-hydroxyethoxy acetate)] tetrols and TMDI (Type 1). The values for $M_{C\text{-}ideal}$ are calculated with the number-average molar mass of the oligomers according to ^{1}H-NMR spectroscopy. The number-average molar mass of the free elastic chains $M_{c\text{-}affin}$ and $M_{C\text{-}Phantom}$ is determined by using the degree of swelling Q in chloroform, on the basis of the affine or phantom network model.

Network [A)]	G	Q	$M_{c\text{-}ideal}$	$M_{c\text{-}affin}$ [b)]	$M_{C\text{-}Phantom}$ [b)]
	% by mass	% by vol.	g mol^{-1}	g mol^{-1}	g mol^{-1}
N-P-LD(12)-1000	100 [c)]	n. d. [d)]	700	n. d.[d)]	n. d. [d)]
N-P-LD(15)-3000	100	310	1500	1700	1100
N-P-LD(13)-5000	100	590	3200	7200	4200
N-P-LD(13)-7000	100	500 ± 10	3900	5000 ± 200	3000 ± 100
N-P-LD(12)-10000	92 ± 1	860 ± 50	5000	15400 ± 1600	8700 ± 1000
N-P-LD(8)-10000	98 ± 0	610	3400	7600	4500
N-P-LD(17)-10000	93 ± 1	820 ± 10	3400	14000 ± 300	8000 ± 200
N-P-LD(20)-10000	97 ± 1	560	3700	6400	3800
N-P-LD(25)-10000	91 ± 2	690 ± 30	3800	9900 ± 900	5700 ± 500
N-P-LD(45)-10000	93 ± 1	760 ± 30	5300	12000 ± 1000	6900 ± 500
N-P-LD(65)-10000	90	870 ± 80	5200	15800 ± 2900	8900 ±1600

a) See above.
b) The solubility parameter δ_P is only insubstantially influenced by the ß-hydroxyethoxy acetate content. For PPDO, a value of 19.0 MPa$^{0.5}$, which corresponds to the value for PDLLA, is determined according to the group contribution method with molar attraction constants according to *Small.* All calculations therefore take place with a value for the interaction parameter x of 0.34. The density of the amorphous networks ρ_p is always set equal to 1.215 g cm^{-3}.
c) The determination of G is done by means of extraction with a mixture of diethyl ether and chloroform in a proportion by volume of roughly 1: 1.
d) n. d.: not determined. Networks are destroyed during the swelling process in chloroform.

Tab. 3b: Gel content G and mass-related degree of swelling S in chloroform of networks of star-{oligo(propylene glycol)-*block*-oligo[(*rac*-lactate)-*co*-glycolate]} triols and TMDI (Type I).

Network [a)]	G % by mass	S % by mass
N-T-PPG-1000	97 ± 2	n. d. [b)]
N-T-PPG-1000-*b*-LG-2000	97 ± 2	350 ± 10
N-T-PPG-1000-*b*-LG-4000	93 ± 4	870 ± 60
N-T-PPG- 1000-*b*-LG-6000	94 ± 0	960 ± 10
N-T-PPG-1000-*b*-LG-9000	90 ± 1	1390 ± 130
N-T-PPG-3000	98 ± 1	700 ± 10
N-T-PPG-3000-*b*-LG-4000	94 ± 1	1330 ± 400
N-T-PPG-3000-*b*-LG-6000	73	3670
N-T-PPG-3000-*b*-LG-9000	58	3650 ± 780

a) See above.
b) n. d.: not determined, is destroyed during swelling in chloroform.

Tab. 2c: Gel content G and mass-related degree of swelling S in chloroform, proportion by mass μ_{PPG-R} of oligo(propylene glycol) in reaction batch and proportion by mass μ_{PPG} determined by means of ^{1}H-NMR-spectroscopy in networks of P-LG(17)-10000, oligo(propylene glycol) triols of varying molar weight and TMDI (Type II).

Network [a)]	μ_{PPG-R} % by mass	μ_{PPG} [b)] % by mass	G % by mass	S % by mass
N-P-LG(17)-10000	-	-	98 ± 2	830 ± 80
N-T-PPG(10)-1000-LG	10	n. d. [c)]	98 ± 8	680 ± 70
N-T-PPG(20)-1000-LG	20	10	91 ± 1	740 ± 20
N-T-PPG(30)-1000-LG	30	28	94 ± 1	720+30
N-T-PPG(50)-1000-LG	50	39	94 ± 7	830 ± 130
N-T-PPG(70)-1000-LG	70	68	79 ± 3	1750 ± 70
N-T-PPG-1000	100	n. d. [c)]	97 ± 2	n. d. [c)]
N-T-PPG (10)-3000-LG	10	n. d. [c)]	96 ± 8	810 ± 40
N-T-PPG (20)-3000-LG	20	16	92 ± 1	770 ± 40
N-T-PPG(30)-3000-LG	30	28	92 ± 10	970 ± 20
N-T-PPG(50)-3000-LG	50	57	902 ± 12	1340 ± 90
N-T-PPG(70)-3000-LG	70	n. d. [c)]	67	2640
N-T-PPG-3000	100	n. d. [c)]	98 ± 1	700 ± 10

a) See above.
b) Determined by means of ^{1}H-NMR spectroscopic examinations after reaction of the contained networks with deuterated trifluoroacetic acid.
c) n. d.: not determined.

Tab. 2d: Mass-related degree of swelling S in chloroform and proportion by mass μ_{PPG-R} of oligo(propylene glycol) in reaction batch of interpenetrating polymer networks of P-LG(17)-10000, TMDI and M-PPG-560. For comparison, the mass-related degree of swelling of the network N-P-LG(17)-10000 (Type III) is also shown.

IPN [a)]	μ_{PPG-R}	S [b)]
	% by mass	% by mass
N-P-LG(17)-10000	0	830 ± 80
N-LG-*ip*-N-M-PPG(10)	10	690 ± 190
N-LG-*ip*-N-M-PPG(20)	20	630 ± 30
N-LG-*ip*-N-M-PPG(30)	30	640 ± 40
N-LG-*ip*-N-M-PPG(50)	50	540 ± 20

a) See above.

b) IPNs break during the swelling.

Tab. 2e: Mechanical properties of network systems at 25° C that are obtained by means of coupling oligo[(*rac*-lactate)-*co*-glycolate] tetrols with TMDI and oligo(propylene glycol) dimethacrylates before and after UV radiation has taken place. E is the E module, σ_S the yield stress, ε_s the apparent yield point, σ_b the breakage stress and ε_b the elongation at break.

Network [a)]	E	σ_S	ε_s	σ_b	ε_b
	MPa	MPa	%	MPa	%
N-P-LG(17)-10000	340 ± 60	40.0 ± 5.0	8 ± 3	36.2 ± 5.9	250 ± 210
N-LG-*ip*-M-PPG(10)	115 ± 40	17.1 ± 3.2	24 ± 8	15.1 ± 3.2	370 ± 115
N-LG-*ip*-M-PPG(20)	20 ± 3	-	-	11.5 ± 3.4	660 ± 200
N-LG-*ip*-M-PPG(30)	15 ± 10	-	-	8.4 ± 1.3	635 ± 115
N-LG-*ip*-M-PPG(50)	1.5 ± 0.3	-	-	2.2 ± 0.2	500 ± 125
N-LG-*ip*-N-M-PPG(10)	350 ± 10	35.4 ± 1.7	13 ± 3	27.5 ± 3.2	260 ± 110
N-LG-*ip*-N-M-PPG(20)	415 ± 90	39.3 ± 1.3	10 ± 2	36.2 ± 2.9	230 ± 20
N-LG-*ip*-N-M-PPG(30)	270 ± 80	32.4 ± 3.5	17 ± 2	33.3 ± 6.8	225 ± 45
N-LG-*ip*-N-M-PPG(50)	150 ± 30	23.2 ± 4.6	24 ± 3	28.1 ± 3.5	105 ± 20
N-M-PPG-560	22 ± 7	-	-	3.1 ± 1.0	15 ± 5

a) See above.

Tab. 3: Glass transition temperatures T_{g1} and T_{g2} (DSC, 2nd heating process at a heating rate of 30 $K \cdot min^{-1}$) and changes to the isobaric heat capacity ΔC_{p1} and ΔC_{p2} at the glass transitions of IPNs that are produced by swelling the network N-P-LG(17)-10000 in acrylate solutions and subsequent radiation (Type IV). For comparison, the thermal properties of the networks N-EA, N-BA and N-HEA are listed.

Network [a]	T_{g1}	ΔC_{p1}	T_{g2}	ΔC_{p2}
	°C	$J \cdot K^{-1} \cdot g^{-1}$	°C	$J \cdot K^{-1} \cdot g^{-1}$
N-P-LG(17)-10000	-[b]	-[b]	61	0.50
N-LG-*ip*-N-EA(15)	-[b]	-[b]	56	0.34
N-LG-*ip*-N-EA(19)	-[b]	-[b]	56	0.39
N-LG-*ip*-N-EA(38)	0	0.02	56	0.16
N-LG-*ip*-N-EA(55)	1	0.12	45	0.04
N-EA	-7	0.40	-[b]	-[b]
N-LG-*ip*-N-BA(8)	-[b]	-[b]	62	0.39
N-LG-*ip*-N-BA(14)	-[b]	-[b]	58	0.35
N-LG-*ip*-N-BA(19)	-[b]	-[b]	57	0.37
N-LG-*ip*-N-BA(36)	-43	0.08	57	0.21
N-LG-*ip3*-N-BA(81)	-36	0.49	57	0.07
N-BA	-38	0.61	-[b]	-[b]
N-LG-*ip*-N-HEA(30)	-4	0.10	51	0.31
N-LG-*ip*-N-HEA(50)	-2	0.06	51	0.15
N-LG-*ip*-N-HEA(59)	2	0.11	51	0.13
N-LG-*ip*-N-HEA(61)	9	0.04	53	0.09
N-HEA	-1	0.31	-[b]	-[b]

a) See above.
No thermal transition is detected in the case of the network system N-LG-*ip2*-N-BA(56).
b) A second glass transition is not detected.

Shape memory properties

Tab. 4: Elongation fixation ratio $R_f(N)$, elongation restoration ratio $R_r(N)$ and E module E(N) (70 °C) in cycle N of networks of oligo[(*rac*-lactate)-*co*-glycolate] triols or tetrols with constant glycol content and TMDI at the reached stretching ε_m in controlled-position, cyclic thermomechanical experiment under standard condition.

Network [a)]	ε_m	$R_f(1)$	$R_r(1)$	$R_f(2\text{-}5)$	$R_r(2\text{-}5)$	E(1)	E(2-5)
	%	%	%	%	%	MPa	MPa
N-T-LG(17)-5000	50[b)]	91.3	98.5	94.6 ± 2.7	98.6 ± 0.9	2.04	1.68 ± 0.25
N-T-LG(17)-7000	100	94.3	> 99	94.3 ± 0.1	99.3 ± 0.4	1.00	0.71 ± 0.13
N-T-LG(16)-9000	100	95.5	> 99	91.2 ± 0.3	98.8 ± 0.5	0.89	0.69 ± 0.02
N-T-LG(I8)-12000	100	91.8	97.3	91.7 ± 0.1	96.9 ± 0.4	0.70	0.35 ± 0.10
N-P-LG(15)-5000	50[b)]	90.3	> 99	91.1 ± 2.4	96.4 ± 1.3	1.68	1.75 ± 0.12
N-P-LG(15)-7000	100	92.0	> 99	92.3 + 0.1	> 99	1.63	1.60 ± 0.03
N-P-LG(16)-9000	100	95.8	> 99	96.8 ± 2.1	98.6 ± 1.6	0.53	0.52 ± 0.01
N-P-LG(17)-10000	100	96.5	92.6	95.0 ± 0.0	90.1 ± 0.9	2.03	1.70 ± 0.12
N-P-LG(12)-12000	100	92.8	94.8	94.6 ± 2.7	90.9 ± 3.5	1.18	0.78 ± 0.11

a) See above.
b) The samples break when the value of ε_m is 100%.

The examples according to the invention demonstrate that the networks of the invention are shape memory materials that can be selectively produced, wherein good control of the network properties is possible. Preferred networks are amorphous and biodegradable and / or phase-segregated.

WHAT IS CLAIMED IS:

1. A polymeric network obtained by the reaction of a hydroxytelechelic prepolymer with diisocyanate, wherein said hydroxytelechelic prepolymer has a number-average molecular weight of at least 4,400 g/mol and comprise polyester and/or polyether segments having a number-average molecular weight of at least 1,000 g/mol.

2. The polymeric network according to claim 1, wherein the prepolymer has units derived from lactic acid, caprolactone, dioxanone, glycolic acid, ethylene glycol or polypropylene glycol.

3. The polymeric network according to claim 1 or 2, wherein the prepolymer has a number-average molecular weight of from 5,000 to 15,000 g/mol.

4. The polymeric network according to any one of claims 1 to 3, comprising a second network that is not covalently connected to the polymeric network but that rather only penetrates this polymeric network (IPN), wherein the second network is a network derived from acrylate monomers or polypropylene glycol macromonomers.

5. The polymeric network according to any one of claims 1 to 4, wherein the prepolymer comprises units derived from lactic acid and glycolic acid, lactic acid and caprolactone, lactic acid and dioxanone or lactic acid and propylene glycol.

6. The polymeric network according to claim 5, wherein the prepolymer comprises units derived from lactic acid and propylene glycol and wherein these units are present in a block-like distribution.

7. The polymeric network according to any one of claims 1 to 6, wherein the prepolymer has a central unit derived from a trifunctional or tetrafunctional compound.

8. The polymeric network according to claim 7, wherein the trifunctional or tetrafunctional compound is 1,1,1-tris(hydroxymethyl)ethane or pentaerythritol.

9. The polymeric network according to any one of claims 1 to 8, obtained by means of the reaction of two or three different prepolymers.

10. A method for the production of a polymeric network according to claim 1, comprising the reaction of the hydroxytelechelic prepolymer comprising polyester and/or polyether segments as defined in claim 1, with diisocyanate.

11. The method according to claim 10, wherein the prepolymer has units derived from lactic acid, caprolactone, dioxanone, glycolic acid, ethylene glycol or polypropylene glycol.

12. The method according to claim 10 or 11, wherein the prepolymer has a number-average molecular weight of from 5,000 to 15,000 g/mol.

13. The method according to any one of claims 10 to 12, comprising a further stage of the production of a second network that is not covalently connected to the polymeric network, but that rather only penetrates this polymeric network (IPN), wherein the second network is a network obtained by means of the polymerization of acrylate monomers or polypropylene glycol macromonomers.

14. The method according to any one of claims 10 to 13, wherein the prepolymer comprises units derived from lactic acid and glycolic acid, lactic acid and caprolactone, lactic acid and dioxanone or lactic acid and propylene glycol.

15. The method according to claim 14, wherein the prepolymer comprises units derived from lactic acid and propylene glycol and wherein these units are present in a block-like distribution.

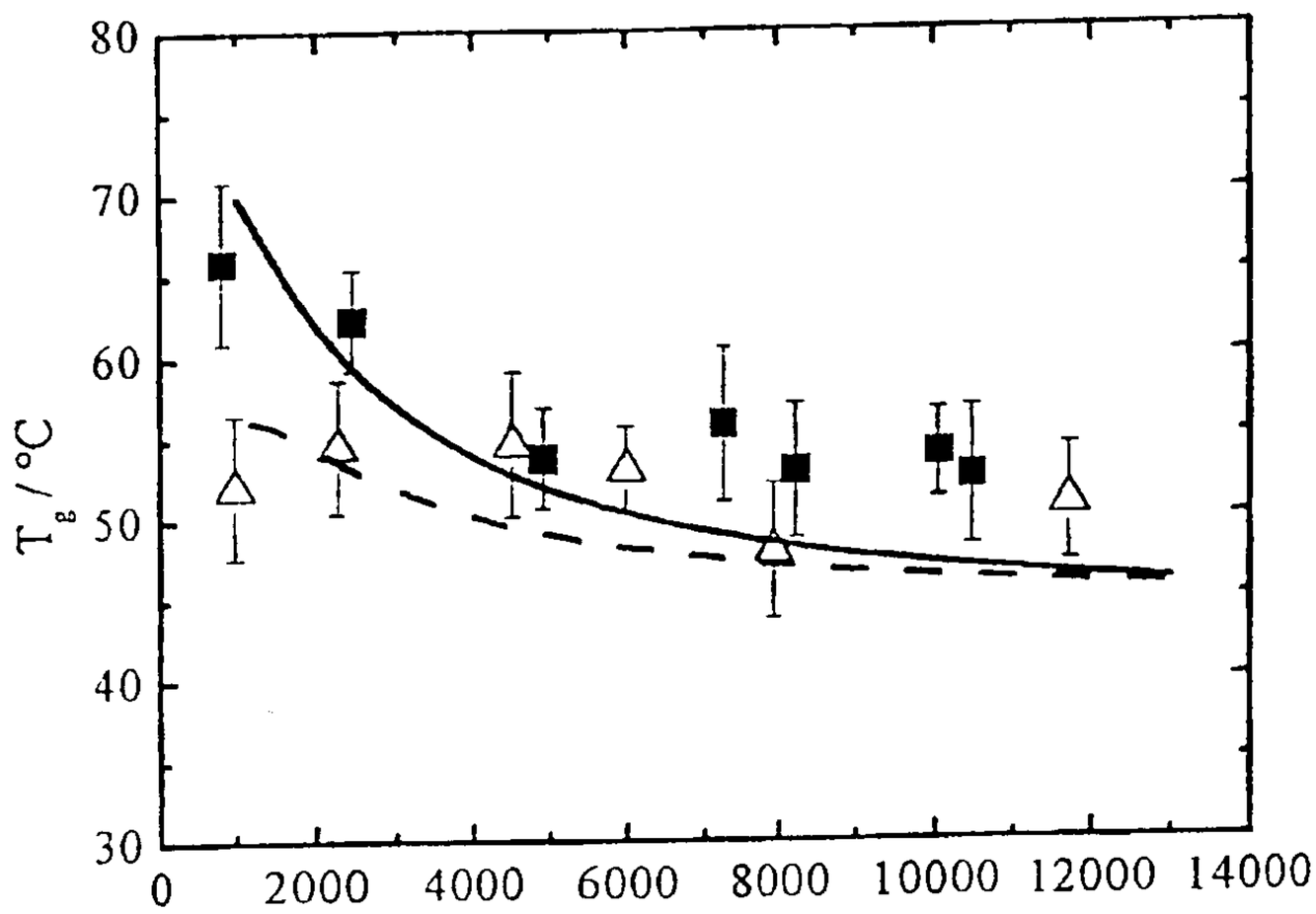

FIG. 1

Glass transition temperature T_g (DSC, 2nd heating process) of the networks of oligo[(*rac*-lactate)-*co*-glycolate] triols (▲) or tetrols (■) coupled with TMDI (Type 1) dependent on M_n of the oligomers with a constant proportion of glycolate. Additionally shown are the values for T_g calculated according to Eq. 4.14 dependent on M_n of the macrotriols (---) and macrotetrols (-). The basis is given for the values for T_g^{∞} and K_o (Tab. 4.4) and for p_x according to Eq. 4.15 with M_n of the prepolymers according to ^{1}H-NMR. The determination of K_x is done by means of a regression analysis of the experimental values. The bars indicate the width of the temperature interval at the glass transition.

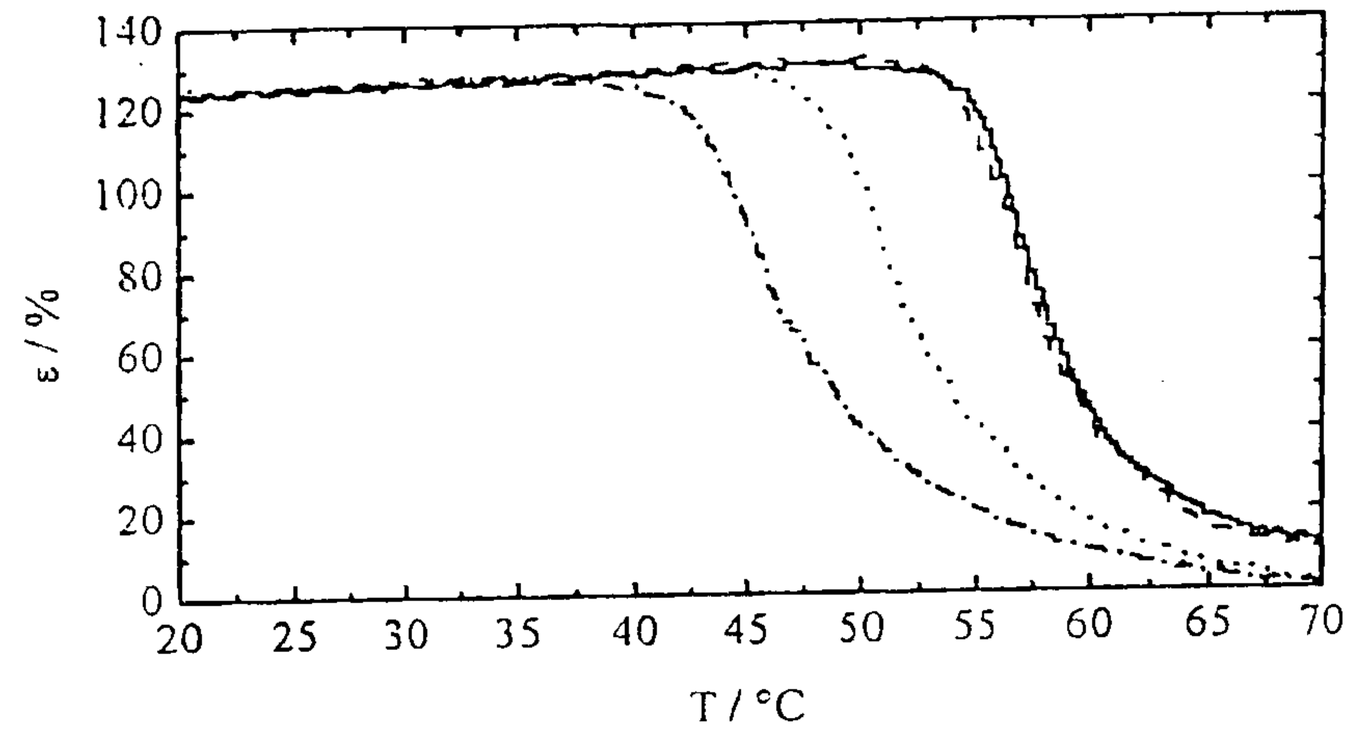

FIG. 2

a) Curve of the elongation ε of networks of macrotetrols with varying glycolate content (Type 1) in the heating process of the position-controlled, cyclic thermomechanical tension-elongation measurements dependent on the temperature T. (-) N-P-LG(0)-10000,
(---) N-P-LG(17)-10000, (...) N-P-LG(30)-10000,
(-.-) N-P-LG(52)-10000.

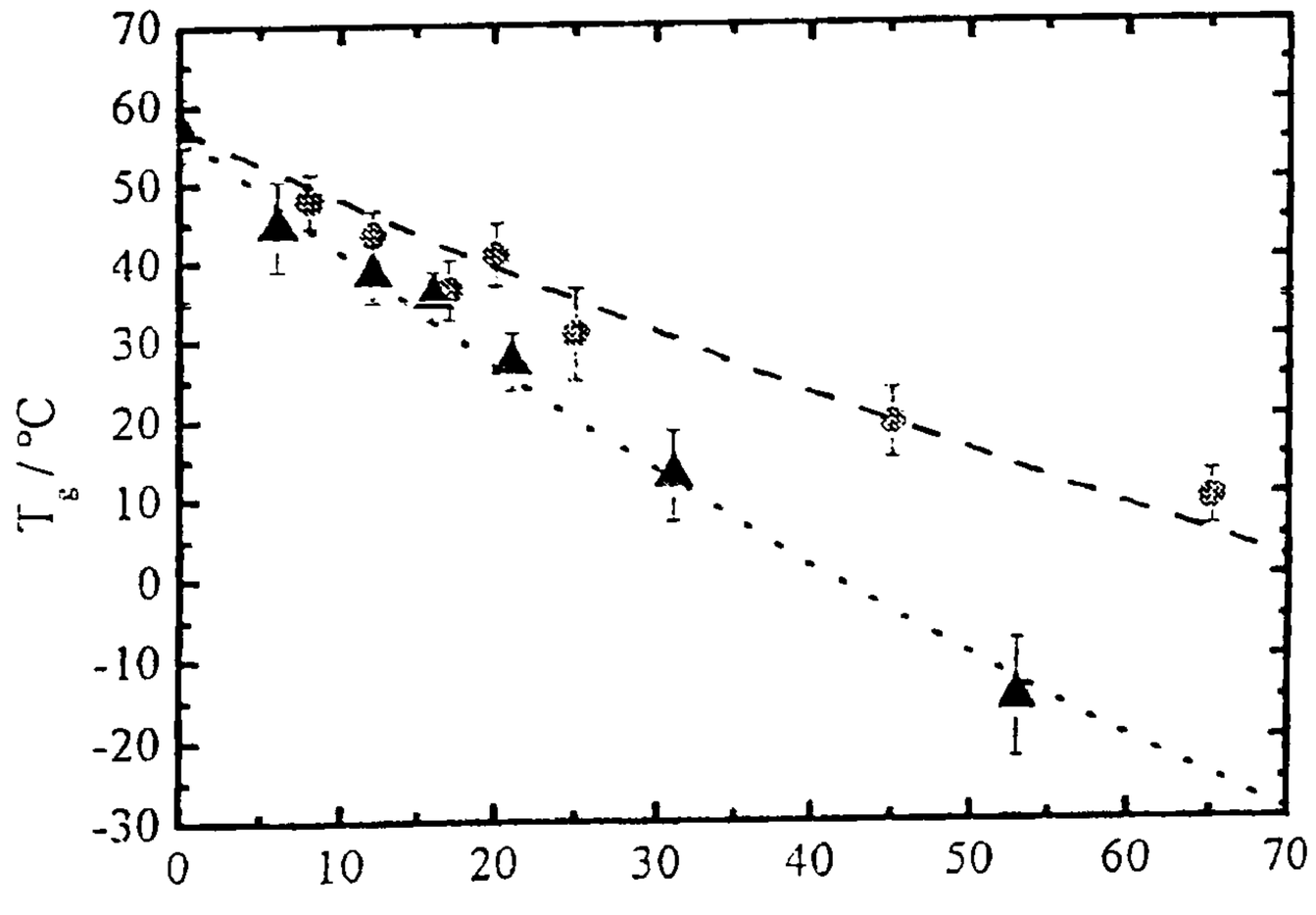

FIG. 3

Glass transition temperature T_g of the networks of macrotetrols and TMDI (Type I) according to DSC (2^{nd} heating process) depending on the proportion by mass of β-hydroxyethoxy acetate (○) or ε-hydroxycaproate (▲) of the prepolymers (M_{calc} = 10100 g·mol^{-1}) and calculated values for T_g depending on the comonomer ratio (... or ---) according to a non-linear regression analysis according to Eq. 4.9. The bars indicate the width of the temperature interval at the glass transition.

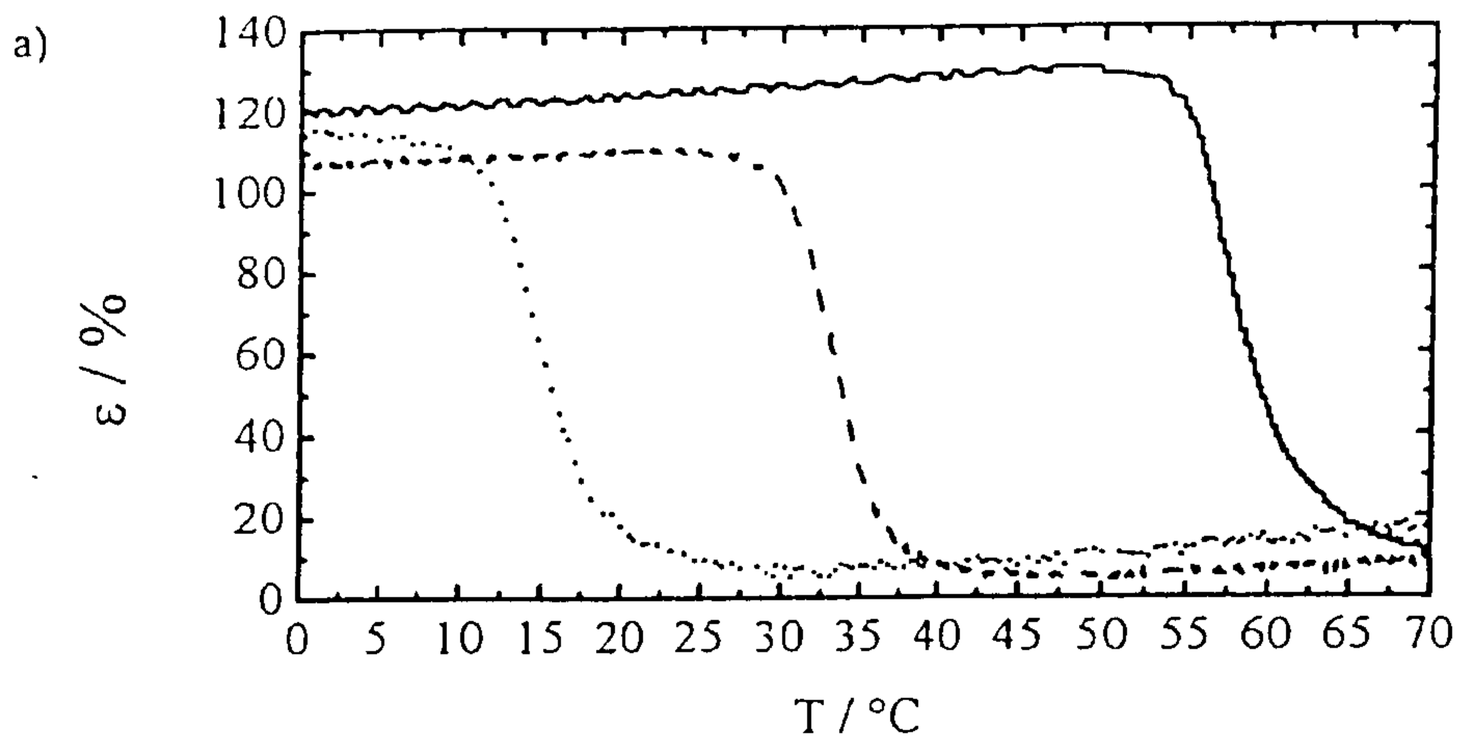

FIG. 4

a) Elongation ε depending on the temperature T of the networks of macrotetrols with varying ε-hydroxycaproate content (M_{calc} = 10100 g·mol^{-1}) and TMDI (Type 1) in the restoration process of the stress-controlled, cyclic thermomechanical tension-elongation experiments.
(-) N-P-LG(0)-10000, (---) N-P-LC(16)-10000,
(...) N-P-LC(31)-10000.

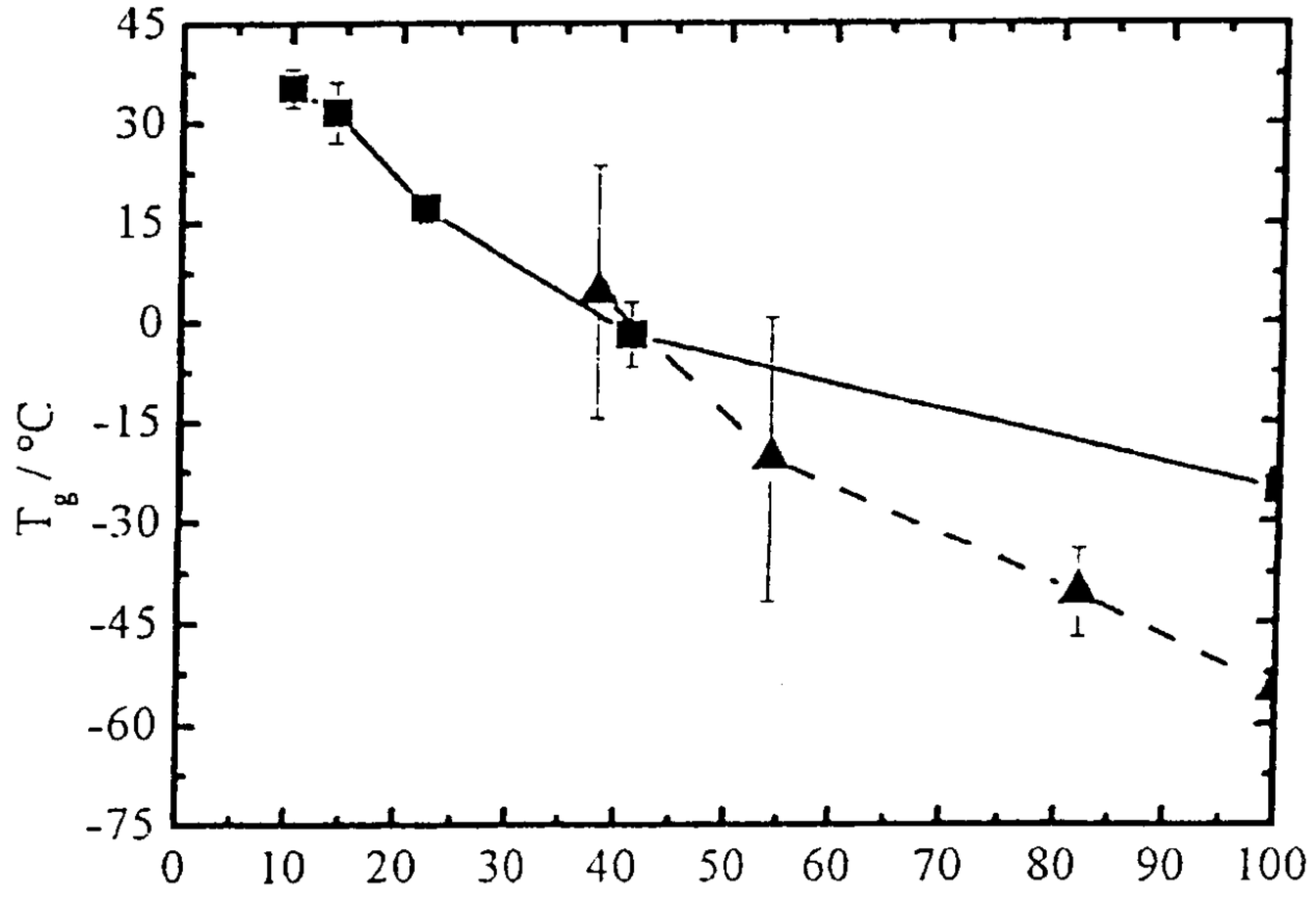

FIG. 5

Glass transition temperature T_g (DSC, 2nd heating process) of networks of star-{oligo(propylene glycol)-*block*-oligo[(*rac*-lactate)-*co*-glycolate]}triols and TMDI (Type 1) depending on the proportion by mass of oligo(propylene glycol) μ_{PPG} of the prepolymers according to ^{1}H-NMR-spectroscopy. The bars indicate the width of the temperature interval at the glass transition.
Macroinitiator: -■- T-PPG-1000 or - ▲- T-PPG-3000.

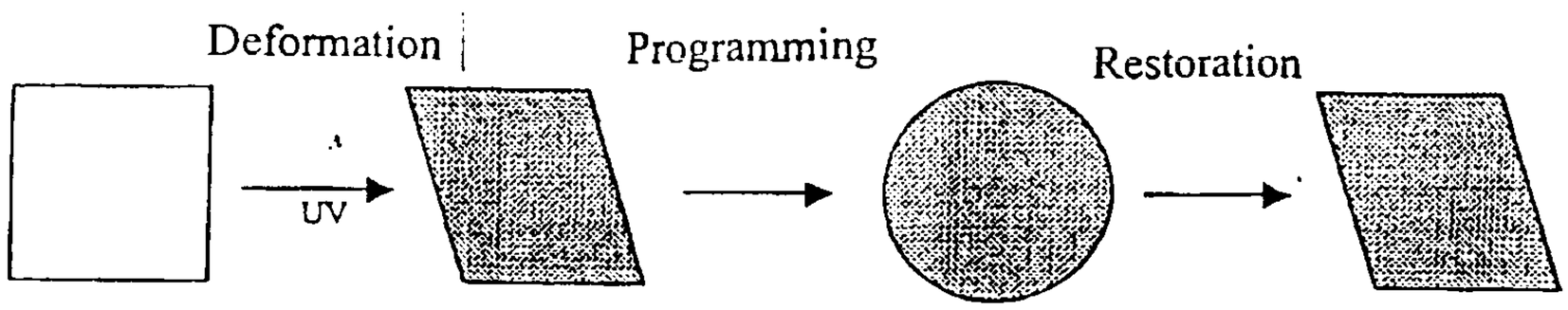

FIG. 6 Schematic representation of the fixation of a pre-IPN in the permanent shape for the resulting IPN (Type III) and of the shape memory effect of the IPN.

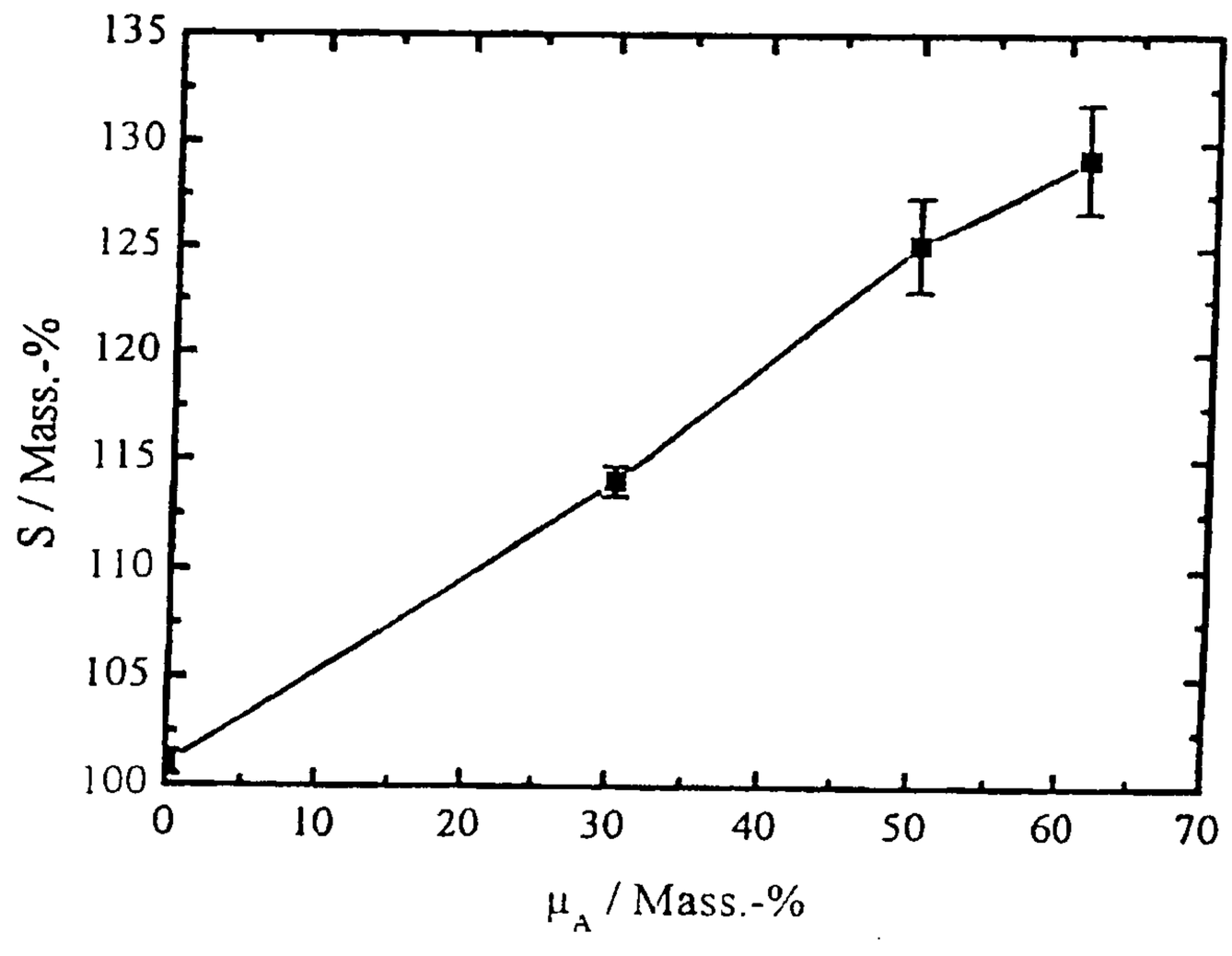

FIG. 7 Mass-related degree of swelling S in water of IPNs that are obtained from swelling the network N-P-LG(17)-10000 in hydroxyethyl acrylate solution and subsequent UV radiation (Type IV), depending on the proportion by mass μ_A of the poly(acrylate) component in the IPN.