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(54) Title: POLYMER MATERIAL USEFUL FOR MEDICAL DEVICES

(57) Abstract: The present invention concerns polymer materials useful for medical devices as well as medical devices prepared therefrom, including in particular surgical sutures, artificial ligaments, nets for tissue regeneration or vascular plugs. The present invention also concerns a method for preparing such articles, in particular filaments suitable for the preparation of sutures and nets.

Polymer Material Useful for Medical Devices

The present invention concerns polymer materials useful for medical devices as well as medical devices prepared therefrom, including in particular surgical sutures, artificial ligaments, nets for tissue regeneration or vascular plugs. The present invention also concerns a method for preparing such articles, in particular filaments suitable for the preparation of sutures and nets.

Bioabsorbable fibers useful for the manufacture of medical devices are known in the art. US 5,425,984 and EP 024125282 disclose fibers made from a polymer containing from about 15 to about 30 mol% glycolide and absorbable ligament and tendon prostheses made from a polymer of lactide containing up to 10% glycolide as comonomer. One drawback of this conventional material is the fact that the high susceptibility towards hydrolysis of the glycolide polymers renders articles made therefrom unsuitable for applications requiring a long-term stability of the material properties, such as strength, resistance against cycles of changing mechanical loads/forces etc.

One approach addressing the drawbacks associated with the glycolide polymers is the introduction of further comonomers, in particular monomers derived from caprolactone. US 4,605,730 and US 4,700,704 disclose copolymers of caprolactone and glycolide useful for preparing surgical articles, in particular surgical sutures. These sutures have a Young's modulus of less than 250000 psi. However, the introduction of caprolactone comonomers into glycolide polymers leads also to a reduction in strength. Similar results were also observed with polymer materials comprising lactide monomers as well as trimethylene carbonate monomers, optionally in combination with caprolactone monomers.

US 6,486,295 B1 describes a method to regulate copolymer structure using lipase catalyzed transesterification reactions. This document discloses copolymers comprising caprolactone units and pentadecalactone units. The molecular weight of the polymer disclosed is on average (all values Mn, g/mol) from 10000 to 29000. This document, however, does not disclose any particular suitability of the polyester produced but focuses on the use of lipases for preparing polymer structures. EP1362872 A1 discloses polyester urethanes comprising polypentadecalactone segments wherein the

polypentadecalactone segments preferably have a molecular weight (Mn) of from 2000 to 3000.

However, also these materials are not able to maintain a sufficient portion of their initial strength over a prolonged duration of time, a requirement which often is important for medicinal articles, in particular, surgical articles such as those exemplified above.

Accordingly, it is an object of the present invention to provide polymers which enable the preparation of medical articles, in particular, surgical articles such as sutures, nets for tissue regeneration, ligament and tendon prostheses and surgical meshes for hernia repair. The materials aimed for by the present invention shall fulfil at least one of the following requirements:

(1) high strength
(2) optimum hydrolytic stability, i.e. maintaining sufficient strength over a prolonged duration of time even after having been used in a surgical procedure
(3) particle-free degradation properties
(4) minimal elongation under load
(5) resistance towards cycles of changing mechanical forces/loads
(6) stability even under high strain

Brief description of the present invention

The present invention achieves these objects with the polymer as defined in claim 1. Preferred embodiments are outlined in the dependent sub-claims. Furthermore, the present invention provides the surgical articles as defined in the claims and also a method for preparing fibers suitable for the preparation of surgical articles.

Detailed description of the present invention

The polymer in accordance with the present invention is a semi-crystalline copolymer comprising repeating units derived from pentadecalactone and/or para-dioxanone (designated also first repeating units) in combination with repeating units derived from at least one further monomer yielding ester repeating units (designated also second

repeating units). Preferably the at least one further monomer is selected among caprolactone and para-dioxanone or a mixture thereof. However, in principle any type of ester repeating unit generating monomer may be used as the at least one further monomer. In particular when the copolymer comprises repeating units from dioxanone as the first repeating units the copolymer does not comprise repeating units derived from glycolic acid or derivatives therefrom. A particular preferred embodiment of this kind is a copolymer of para-dioxanone with caprolactone, wherein the repeating units are distributed in the copolymer in block form (dioxanone blocks and caprolactone blocks), preferably linked together by means of a urethane linkage, for example obtained by the below discussed isocyanate linking method. For this embodiment the following description applies, in particular regarding the preferred embodiments concerning molecular weight of the final copolymer as well as of the building blocks, and also concerning the method of synthesis and the mechanical properties.

In another embodiment of the present invention the copolymer is as defined as the other alternative in the main claim, i.e. the copolymer comprises repeating units derived from pentadecalactone in combination with repeating units derived from at least one further monomer yielding ester repeating units.

The copolymer in accordance with one aspect of the present invention has a crystallinity of at least 25% (determined using DSC equipment) and a melting temperature of at least 70°C. Preferably the crystallinity amounts to more than 25%, more preferably more than 30% and in embodiments more than 40% or ever more than 50%. Preferably the upper limit for the crystallinity is 90%, and in embodiments also 80%, 75%, 70% or 60%.

Preferred are copolymers having a number average of the molecular weight of at least 30000, more preferably at least 45000, even more preferably at least 50000 (all values refer to g/mol, determined by GPC analysis versus a polystyrol standard). Copolymers having a number average molecular weight of as high as 75000, and in embodiments more than 100000, preferably more than 150000 (all values refer to g/mol, determined by GPC analysis versus a polystyrol standard) are also envisaged by the present invention.

Preferred are copolymers wherein the different comonomers are distributed within the copolymer in the form of distinct blocks, although also random copolymers are suitable.

Preferred are, however, semi-crystalline phase segregated copolymers, comprising blocks derived from pentadecalactone or dioxanone and blocks derived from the at least one further monomer, preferably selected from caprolactone, para-dioxanone and mixtures thereof. Preferably, the copolymer in accordance with the present invention does not comprise any further repeating units derived from other monomers, except for pentadecalactone, caprolactone and/or para-dioxanone.

The preferred copolymer in accordance with the present invention is a copolymer showing a block-like distribution of the different repeating units within the copolymer. The different blocks of the repeating units may be introduced into the copolymer by means of preformed macromonomers, prepared by conventional polyester chemistry from the above-outlined monomers. These macromonomers preferably are present in the form of diols, i.e. possessing two terminal hydroxyl functionalities. The different blocks, i.e. the macromonomers may then be combined to form the copolymer in accordance with the present invention using diisocyanates in order to prepare urethane linkaging groups for binding the macrodiols to each other. The resulting copolymers can be designated as polyester urethanes, i.e. polymeric structures, comprising blocks corresponding to the initial macromonomers which are polyester segments, bound to each other by means of urethane segments. Preferred diisocyanates for the preparation of the polyester urethanes in accordance with the present invention are compounds of the formula

O=C=N-R-N=C=O,

wherein R represents a divalent aromatic or aliphatic group. Preferably R is aliphatic, having a carbon chain of from 1 to 10, preferably 2 to 8, more preferably 4 to 7 carbon atoms, preferably a straight chain. This carbon chain can either be saturated with hydrogen (aliphatic unsaturated group) or this chain may show further substituents, preferably short chain alkyl groups having from 1 to 6, more preferably from 1 to 4 carbon atoms, in particular methyl groups. A particular preferred diisocyanate is trimethylhexane-1,6-diisocyanate, another example being hexamethylene diisocyanate.

The macromonomers employed for the preparation of polyester urethanes in accordance with the present invention preferably have a number average molecular weight of from 1000 to 50000 g/mol (as determined by GPC compared to a polystyrene standard), more preferably 1000 to 20000 g/mole and in embodiments more preferably 1500 to 15000

and, in particular, preferably 2000 to 10000. In particular, suitable macromonomers are macrodiols of pentadecalactone having a number average of the molecular weight of from 1000 to 10000, preferably 1500 to 5000, more preferably 2000 to 3000, macrodiols of caprolactone having a number average of the molecular weight of 3000 to 11000, preferably 4000 to 10000 and para-dioxanone macrodiols having a number average of the molecular weight corresponding to the number averages disclosed above for the two other segments. In one embodiment the polymer comprises para-dioxanone macrodiols with an average molecule weight of 2000 to 6000 g/mol, preferably 3000 to 5500 g/mol, in combination with caprolactone derived macrodiols having an average molecular weight of 1500 to 2500, preferably about 2000 g/mol.

As outlined above, the copolymer in accordance with the present invention, i.e. also the polyester urethane in accordance with the present invention preferably has a molecular weight (number average) of at least 50000, in particular 50000 to 200000, more preferably 60000 to 190000 (g/mol, determined by GPC in comparison to a polystyrene standard). Particularly preferred are high molecular weight triblock copolymers, comprising for example one block derived from pentadecalactone and two blocks derived from other ester repeating units or vice versa. Such triblock copolymers can be prepared using suitable macromonomers in suitable ratios, using in particular the above outlined isocyanate linking technology.

The copolymers in accordance with the present invention comprise preferably blocks derived from pentadecalactone wherein the macrodiol corresponding to the pentadecalactone block in the final copolymer has a melting point of at least 20°C, preferably more than 25°C and in embodiments more than 30°C or even 35°C.

The copolymers in accordance with the present invention preferably comprise pentadecalactone in an amount of from 10 to 90% by weight, more preferably 25 to 60% and more preferably 30 to 50%. Particularly preferred copolymers in accordance with the present invention are copolymers showing a ratio of pentadecalactone to the further comonomers of from 40/60 to 30/70.

With respect to the above-described preferred embodiment wherein the polymer comprises para-dioxanone macrodiols in combination with caprolactone derived macrodiols, it is further preferred when para-dioxanone derived segments and a

caprolactone derived segments are present in the final polymer in a weight ratio of about 1:1, so that approximately equal weights of dioxanone units and caprolactone units are present. In this connection, it is furthermore preferred when the macrodiols are linked by means of the above-described reaction using diisocyanates and, in this connection; it is particularly preferred when diisocyanate employed is hexamethylene diisocyanate. These polymers preferably show an average molecular weight (Mn) of from 45000 to 60000, preferably about 50000 g/mol. Such a polymer preferably shows a melting temperature, being defined at the peak maximum of a DSC measurement (defined as the maximum of the heat flow dQ/dT, see also the below cited reference R.F. Schwarzl) carried out under nitrogen and between -70°C and 150°C with a heating and cooling rate of 10 K/min, wherein a peak is recorded in the second cycle, of preferably above 90°C, such as from 90 to 98°C, for example 95 or 96°C.

Preferably such a polymer displays a crystalline content with respect to the segments derived from para-dioxanone of above 20%, such as from 20 to 60%, preferably 25 to 50%, again determined by DSC (second cycle, heating and cooling conditions and temperature range as indicated above, also designated calorie metric crystallinity, obtained by comparing the measured enthalpy increase with the value extrapolated for a 100% crystalline substance, see also F.R.,Schwarzl, Polymer-Mechanik, Springer Verlag Berlin Heidelberg 1990, p. 278).

As outlined above, in other embodiments the copolymers in accordance with the present invention possess a melting point of at least 70°C and preferably a crystallinity of at least 25%.

The above-discussed copolymers in accordance with the present invention and in particular the preferred embodiments as derivable from the above are suitable for the preparation of medical articles, in particular surgical articles, including preferably sutures, surgical nets and meshes, in particular surgical measures for hernia repair, as well as prosthetic tendons and ligaments and vascular plugs. Fibers and filaments prepared from the copolymers in accordance with the present invention enable the preparation of improved surgical articles, such as those exemplified above. Due to the structure of the copolymer in accordance with the present invention it is possible to prepare medicinal articles showing a good balance of mechanical properties in association with a desired degradation profile. As identified above the copolymers in accordance with the present

invention enable in particular the preparation of fibres having high strength and sufficient hydrolytic stability so that the mechanical properties can be maintained for a desired time period.

Surgical articles prepared from the copolymers in accordance with the present invention are fully resorbed by the body after surgery in less than 3 years, while retaining at least 50% of the original strength for at least 3 weeks after surgery, preferably at least 6 weeks after surgery.

Monofilaments prepared from the copolymers in accordance with the present invention show an elastic modulus of more than 1000 MPa, preferably more than 1200 MPa and in embodiments more than 1500 MPa. Further they display a tensile strength of more than 100 MPa, at an elongation of less than 1200%, preferably of more than 120 MPa and in embodiments more than 150 MPa. Typical monofilaments in accordance with the present invention can be prepared from the copolymers in accordance with the present invention having diameters of between 750 and 25 µm, preferably 600 to 30 µm, more preferably 500 to 40 µm. The copolymers in accordance with the present invention can also be processed to multifilaments wherein again the single filaments within the multifilament material show a filament diameter in accordance with the ranges outlined above for the monofilament. Monofilaments and multifilaments in accordance with the present invention enable the preparation of surgical articles, such as sutures, surgical measures and nets, in particular for tissue regeneration and hernia repair, as well as prosthetic tendons and ligaments satisfying the highest requirements with respect to maintenance of strength after surgery. At the same time, these surgical articles are biocompatible and may be resorbed by the body, so that the use of these materials in the medicinal field is plausible.

The present invention furthermore provides a method for preparing filaments from the copolymers in accordance with the present invention. This method preferably comprises the melt spinning of a copolymer in accordance with the present invention using standard melt spinning equipment. Preferably, melt spinning is conducted using a pre-dried polymer granulate (for example, pre-dried at a pressure of 0.1 mbar at 40°C for more than 24 hours). This pre-dried product can then be stored, preferably under moisture reducing or moisture excluding conditions, for example, at slightly increased temperature using a gas phase in contact with the copolymer having a very low thaw

point, such as a thaw point of below -10°C, preferably below -15°C. This pre-dried material can then be introduced into an extruder, preferably a single screw extruder having distinct zones for adjusting a temperature profile. A suitable extruder has, in particular, at least three different temperature zones, which can be regulated for the processing of the copolymers in accordance with the present invention to temperature in the ranges of 130 to 170°C, 150 to 200°C and 150 to 210°C, respectively. It is possible to have one or more zones of lower temperature at the inlet, such as having 20 to 100°C and to increase the temperature at the outlet of the extruder to slightly higher values, such as from 115 to 215°C. After leaving the extruder, the molten extrudate is fed using a suitably heated (150 to 215°C) line to an optional filter unit (having a pore size of from 50 to 250 µm, preferably 50 to 10 µm, followed by feeding the melt to a spinning nozzle being provided in a suitable heated (160 to 220°C) spinner head. The nozzle has at least one opening of a usual size and design enabling the preparation of desired monofilament or multifilaments. After leaving the spinning nozzle, the produced filaments are preferably cooled by means of blowing air having a temperature of between 0 and 50°C, preferably 4 to 40°C. The span filaments can then be wound onto suitable devices. As alternative, it is possible to cool the fibers using a water bath having a temperature similar to the temperature discussed above in connection with the blowing air. Such a water bath usually has a length of from 10 to 200 cm. The span filaments can then be again wound onto suitable devices. During cooling, after cooling prior to storage or after storage, the filaments in accordance with the present invention may be subjected to further standard processing steps, such as stretching etc., in order to further modify the filament properties.

The filaments prepared in accordance with the above process, or prepared by any other standard procedure, may be advantageously used for the preparation of the surgical articles discussed above. It is in this connection also possible to use other molding processes, such as extrusion processes, injection-molding processes etc., depending on the type of the surgical article desired.

The filaments of the invention preferably comply with the requirements for "Sterile, resorbierbare, synthetische Fäden; Fila resorbilia synthetica monofilamenta sterilia", Europäisches Arzneibuch, 3. Ausgabe, 1997, S. 1321 f.f., so that e.g. their length and

diameter is constant as specified therein, they withstand the given forces until break with and without needle, and are packed and labelled accordingly.

The filaments of the invention have a high reproducibility concerning the force that is excerted when triggering the change from temporary to permanent shape. As knots can be tied from shape memory filaments by triggering the shape memory effect, the force that is exerted when using the material of the invention is much more reproducible than when tieing by hand and even when using known shape memory polymers. Therefor such shape memory filaments have lower requirements concerning the tearing resistance than known suture materials, what allows to optimize other properties.

In another preferred embodiment the filaments of the invention therefore only withstand a lower force until break than the force specified in the Europäisches Arzneibuch cited above, but are advantageous over known filaments in other parameters (e.g. elasticity, biodegradability, biocompatibility, etc.)

The copolymers which are processed to yield the articles as outlined above may either be the pure copolymers or they may be compounded previously or during processing with conventional additives, such as active principles, contrast agents, diagnostic agents, filler, etc. These additives may be used in conventional amounts as long as they do not interfere with the desired end property of the surgical article.

Example

Suture Formed of Biodegradable Shape Memory Polymer

1. Synthesis of Biodegradable Shape Memory Polymer

In the first step of the synthesis, macrodiols were synthesized via ring opening polymerization with a low molecular weight diol as initiator and purified according to reported methods (A. Lendlein, P. Neuenschwander, U. W. Suter, *Macromol. Chem. Phys.*, 201, 1067, (2000)). Oligo(ε-caprolactone)diol (M_n 2000 g/mol) was chosen as precursor for the switching segments (soft segments) having a melting transition temperature (T_{trans}). Crystallizable oligo(p-dioxanone)diol (M_n 4000 g/mol) with a melting transition temperature (T_m=T_{perm}) was chosen as hard segment to provide the physical crosslinks.

In the second step, the two macrodiols were coupled with hexamethylene diisocyanate as follows: equal weights of both macrodiols were dissolved in 1,2-dichloroethane and heated to 80° C. An equimolar amount of hexamethylene diisocyanate was added. The synthesis was carried out under exclusion of water; solvents and monomers were dried by standard techniques. The crude product was precipitated in hexane. The resulting polymer has a molecular weight (M_n) of about 50 000 g/mol, the melting temperature Tm was greater than 90 °C and the crystallinity due to the oligo(p-dioxanone)diol segments was about 35 %.

2. Shape memory property of the biodegradable memory polymer

To quantify shape memory properties, programming and recovery were investigated by cyclic thermomechanical tests as follows: the material was pressed to films having a thickness of 300-500 µm. Dog-bone shaped samples (length between clamps: 6 mm, width: 3 mm) were punched out of the films and mounted in a tensile tester equipped with a thermo-chamber (see K. Sakurai, Y. Shirakawa, T. Kahiwagi, T. Takahashi, *Polymer* 35, 4238 (1994)). The tests were carried out at 200% strain at a strain rate of 10 $mm \cdot min^{-1}$ with T_{low}=-20° C. and T_{high}=50° C. The samples were held at T_{low} for 10 min before removing load (see H. Tobushi, H. Hara, E. Yamada, S. Hayashi, *S.P.I.E.* 2716, 46 (1996)).

This simple test describes shape memory in one dimension, however, the effect takes place in all three dimensions. The effect is commonly described using two important parameters. The strain fixity rate R_f describes the ability of the switching segment to fix the mechanical deformation which has been applied during the programming process. For the polymer described herein, R_f is about 99%. The strain recovery rate R_r quantifies the ability of the material to recover its permanent shape. R_r depends on the cycle number and gradually approaches 100% because of reorientation of the polymer chains in the unoriented, pressed films during the early cycles, due to inelastic behavior. In the first cycle, R_r is about 80% for the disclosed multiblockcopolymer and is about 100 % in the third cycle.

3. In vitro test of biocompatibility

The tissue-compatibility of the polymers described herein was investigated using chorioallantoic membrane tests (CAM-tests) which are a sensitive method to evaluate toxicity (K. Spanel-Borowski, *Res. Exp. Med.* (*Berl*) 189, 69 (1989)). Nine separate

experiments were carried out. All tests showed good tissue-compatibility when graded according to Folkman (R. Crum, S. Szabo, J. Folkman, *Science* 230, 1375 (1985)). The test results showed that there was no detectable change in the number or shape of blood vessels or damage under or in the vicinity of the polymer film (sample length: left Ã0.3 cm, right Ã0.5 cm). For a positive control sample, see A. Lendlein, *Chem. in unserer Zeit* 33, 279 (1999).

4. In vitro test of the tying of a suture knot

The highly elastic shape memory thermoplastics was extruded into monofilaments by extrusion at 90° C. through a rod die on a Haake Polylab single-screw extruder. Sutures sterilized with ethylene oxide at 45° C were programmed under sterile conditions by exerting a controlled stress on the extruded fiber and subsequent thermal quenching. Sutures that are 0.29 mm in diameter were thereby obtained. A loose knot was tied and the filament held fixed on both sides. On warming of the filament above 40 °C, the knot contracted exerting a maximum force, that was highly reproducible when repeating the experiment for 10 times and was almost independent from the temperature, as long as it was high enough to trigger the change in shape and not near T_m. This reproducibility allows to use filaments for suture, that have a lower resistance in break tests than known materials.

Claims

1. Copolymer, comprising repeating units derived from pentadecalactone and/or dioxanone in combination with further repeating units derived from at least one additional ester repeating units yielding monomer, having a melting temperate of at least 70 °C and an overall crystalline content of at least 25 %, or a crystalline content of the repeating units derived from pentadecalactone and/or dioxanone of at least 20%.

2. Copolymer in accordance with claim 1, wherein the individual comonomers are distributed within the copolymer in the form of repeating units being distributed in distinct blocks.

3. Copolymer in accordance with claim 1 or 2, wherein the copolymer shows a number average of the molecular weight of at least 50000 g/mol.

4. Copolymer in accordance with claim 1, 2 or 3, wherein the copolymer has a melting temperature of at least 80°C.

5. Copolymer in accordance with claim 1, 2, 3 or 5, wherein the copolymer has a crystallinity of at least 35%.

6. Copolymer in accordance with any of claims 1 to 5, wherein the copolymer is a polyester urethane, comprising blocks of identical repeating units connected via a divalent urethane segment.

7. Copolymer in accordance with claim 6, wherein the blocks derived from pentadecalactone possess a number average of the molecular weight of 1000 to 20000 g/mol.

8. Copolymer in accordance with any of the previous claims, comprising 10 to 90 wt% pentadecalactone.

9. Copolymer in accordance with any of the preceding claims, wherein the at least one additional ester repeating units yielding monomer is selected from caprolactone, para-dioxanone or mixtures thereof.

10. Surgical article, comprising a copolymer in accordance with any one of claims 1 to 9.

11. Surgical article in accordance with claim 10, selected from sutures, surgical nets and measures, in particular for hernia repair and prosthetic tendons and ligaments.

12. Filament, prepared from a copolymer in accordance with any one of claims 1 to 9, wherein the filament has an average diameter of from 500 to 40 µm.

13. Filament in accordance with claim 12, having an elastic modulus of more than 1000 MPa, and/or a tensile strength of more than 100 MPa at an elongation of less than 1200%.

14. Method for preparing a filament according to any of claims 12 and 13, employing a copolymer in accordance with any one of claims 1 to 9, comprising melting the copolymer in accordance with any one of claims 1 to 9, optionally admixing the copolymer in the melt phase or prior to melting with further conventional additives, followed by extruding the molten copolymer through a spinning nozzle, followed by cooling of the spun filament, followed by winding the filament onto a suitable device.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/42 C08G63/08 C08G63/664 A61L27/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 486 295 B1 (GROSS ET AL) 26 November 2002 (2002-11-26) cited in the application column 2, line 43 - line 54 column 6, line 45 - column 8, line 34 column 10, line 57 - line 67; claims 1,14,15,35-39; examples C1,C2,D	1-5,8,9
X	EP 1 362 872 A (MNEMOSCIENCE) 19 November 2003 (2003-11-19) cited in the application page 2, line 26 - page 4, line 7 page 5, line 36 - page 9, line 22; claims 1-8	1-10

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Bourgonje, Andreas

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ANNETTE M. SCHMIDT: "Bioabbaubare polymernetzwerk-Systeme mit kristallisierbarem Schaltsegment" 6 June 2002 (2002-06-06), MENSCH&BUCH VERLAG , BERLIN , XP002260848 page 138 - page 146; figure 5.2	1-9
A	WO 2004/090042 A (MNEMOSCIENCE) 21 October 2004 (2004-10-21) page 5, line 33 - page 8, line 14; claims 1-6,9,10; tables 0.1,0.2	1,2,9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/001194

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6486295 B1	26-11-2002	NONE	
EP 1362872 A	19-11-2003	AT 329950 T	15-07-2006
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