

Vinylcyclohexane-based polymers

The present invention relates to vinylcyclohexane (VCH)-based polymers and copolymers which have a predominantly isotactic configuration, to a process for the
5 production thereof, and to the use thereof as an optical material. The materials can be processed by extrusion or injection moulding and are particularly suitable as a substrate for optical materials, prisms, lenses and compact discs.

Transparent plastics such as aromatic polycarbonates, polymethyl methacrylate or
10 polystyrene can be used as a substrate for optical materials. Addition copolymers formed from ethylene and a norbornene derivative or a tetracyclododecene derivative, as well as hydrogenated products of ring-opened metathesis polymers of norbornene or tetracyclododecene, are also suitable for this purpose.

15 Optical materials comprising a hydrogenation product of a polymer of an aromatic alkenyl hydrocarbon compound or a copolymer thereof are described in GB 933,596 (= DE-AS 1 131 885), EP-A 317 263, US 4,911,966 and US 5,178,926. There is no mention of their configuration.

20 The hydrogenation of polystyrene was first described by Hermann Staudinger in 1929. More recent patent literature is concerned with the underlying microstructure of polyvinylcyclohexane or hydrogenated polystyrene. The current state of knowledge is that amorphous vinylcyclohexane polymers possess an atactic configuration and crystalline VCH (vinylcyclohexane) polymers possess either an isotactic or a
25 syndiotactic configuration (EP-A 0 322 731, EP-A 0 423 100, US-A 5,654,253; US-A 5,612,422, WO 96/34896). Isotactic PVCH (polyvinylcyclohexane) is produced in the presence of Ziegler catalysts, and has a high melting point (J. Polym. Sci., A2, 5029 (1964)). EP-A 0 322 731 states that vinylcyclohexane polymers with a syndiotactic configuration and which are produced by the hydrogenation of
30 syndiotactic polystyrene are crystalline, wherein the amount of dyads is at least 75 % and the amount of pentads is at least 30 %. WO 94/21694 describes a process for the production of hydrogenated aromatic polyalkykenyl polymers and aromatic

polyalkenylpolydiene block polymers. Syndiotactic polystyrene is mentioned in a general sense.

Processes which result in isotactic, syndiotactic and atactic hydrogenated polystyrene which exhibits the material properties which were known previously are described in WO 94/21694 and in US-A 5,352,744, wherein special catalysts are used. Processes for the hydrogenation of atactic polystyrene to form atactic hydrogenated polystyrene using special catalysts are described in US-A 5,654,253, US-A 5,612,422 and WO 96/34896.

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Atactic polymers are regular polymers. According to their definition, they possess the possible configurative basic components in equal amounts, with an ideal random distribution from molecule to molecule (IUPAC). They are distinguished by the same number of iso- and syndiotactic dyads. They are described as an amorphous material with only one glass phase and without a crystalline constituent.

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The present invention relates to a vinylcyclohexane-based polymer or copolymer which has an isotactic configuration, wherein olefines, alkyl esters of acrylic acid derivatives, maleic acid derivatives, vinyl ethers or vinyl esters can be used for the production thereof, characterised in that the amount of dyads is greater than 50.1 % and less than 74 %, and is most preferably 51-70 %. These vinylcyclohexane-based polymers are amorphous polymers.

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The polymers according to the invention are distinguished by their high transparency, low extent of birefringence and high dimensional stability when hot, and can therefore be used as a substrate material for optical data storage media. The known isotactic PVCH, which is produced using Ziegler Natta catalysts and which comprises a proportion of isotactic dyads >75%, is unsuitable for optical applications due to its crystallinity (J. Polymer Sci, A2, 5029 (1964)).

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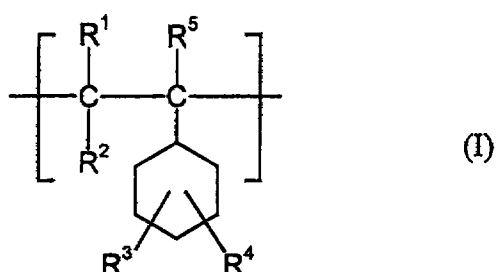
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The present invention relates to hydrogenated products of polystyrene, which result in an amorphous hydrogenated polystyrene comprising an excess of isotactic dyads.

The vinylcyclohexane polymer of this invention is a new amorphous polymer with a defined stereostructure, which is distinguished by the predominant occurrence of an isotactic dyad configuration and which can be produced by the process described.

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The preferred vinylcyclohexane-based polymer comprises a recurring structural unit of formula (I)



wherein

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R^1 and R^2 , independently of each other, represent hydrogen or a C_1 - C_6 alkyl, preferably a C_1 - C_4 alkyl, and

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R^3 and R^4 , independently of each other, represent hydrogen or a C_1 - C_6 alkyl, preferably a C_1 - C_4 alkyl, particularly methyl and/or ethyl, or R^3 and R^4 jointly represent an alkylene, preferably a C_3 or C_4 alkylene (a condensed-on 5- or 6-membered cycloaliphatic ring),

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R^5 represents hydrogen or a C_1 - C_6 alkyl, preferably a C_1 - C_4 alkyl, and

R^1 , R^2 and R^5 , independently of each other, represent hydrogen or methyl in particular.

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Apart from the stereoregular head-to-tail linkage, the linkage may comprise a small proportion of head-to-head linkages. The vinylcyclohexane-based, amorphous, predominantly isotactic polymer may be branched via branching centres and may have a star-shaped structure, for example.

The following can be used as comonomers during the polymerisation of the initial polymer (polystyrene which is optionally substituted) and can be incorporated in conjunction into the polymer: olefines which generally comprise 2 to 10 C atoms, such as ethylene, propylene, isoprene, isobutylene or butadiene, C₁-C₈, preferably C₁-C₄ alkyl esters of acrylic or methacrylic acid, unsaturated cycloaliphatic hydrocarbons, e.g. cyclopentadiene, cyclohexene, cyclohexadiene, norbornene which is optionally substituted, dicyclopentadiene, dihydrocyclopentadiene, tetracyclodecenes which are optionally substituted, styrenes comprising alkylated nuclei, α -methylstyrene, divinylbenzene, vinyl esters, vinylic acids, vinyl ethers, vinyl acetate, vinyl cyanides such as acrylonitrile, methacrylonitrile and maleic anhydride for example, and mixtures of these monomers.

The amorphous vinylcyclohexane polymer according to the invention has a content of isotactic dyads, as determined by two-dimensional NMR spectrometry, of 50.1 to 74 %, preferably of 51 - 70 %. Methods of elucidating the microstructure by means of ¹³C-¹H correlation spectroscopy of the methylene carbon atoms of a polymer backbone are generally known and are described by A.M.P. Ros and O. Sudmeijer (A.M.P. Ros, O. Sudmeijer, *Int. J. Polym. Anal. Charakt.* (1997), 4, 39).

The signals of crystalline isotactic and syndiotactic polyvinylcyclohexane are determined by means of two-dimensional NMR spectrometry. The methylene carbon atom (in the polymer backbone) of isotactic polyvinylcyclohexane splits into 2 separate proton signals in the 2 D-CH correlation spectrum, and indicates a pure isotactic dyad configuration. In contrast, isotactic polyvinylcyclohexane only exhibits one signal for the C 1 carbon atom in the 2 D-CH correlation spectrum. Amorphous, isotactic-enriched polyvinylcyclohexane exhibits an excess of integral signal intensity for isotactic dyads compared with a syndiotactic dyad configuration.

The last-mentioned substance exhibits a high degree of dimensional stability when hot and a low water absorption, whilst possessing satisfactory mechanical properties, and is therefore an ideal material for optical applications.

The vinylcyclohexane (co)polymers generally have absolute weight average molecular weights $M_w > 1000$, preferably from 1500 - 400,000, most preferably from 1500 - 380,000, as determined by light scattering.

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In general, the vinylcyclohexane-based homopolymers according to the invention have a glass transition temperature $> 90^\circ\text{C}$, preferably $> 95^\circ\text{C}$, as determined by DSC.

The copolymers can exist either as random copolymers or as block copolymers.

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The polymers can have a linear chain structure or can have branching locations due to co-units (e.g. graft copolymers). The branching centres may comprise star-shaped or branched polymers, for example. The polymers according to the invention may comprise other geometric forms of the primary, secondary, tertiary or optionally of the quaternary polymer structure. Examples thereof include a helix, a double helix, a folded lamella, etc., or mixtures of these structures.

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Block copolymers comprise di-blocks, tri-blocks, multi-blocks and star-shaped block copolymers.

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The VCH (co)polymers are produced by the polymerisation of derivatives of styrene with the corresponding monomers, by a radical, anionic or cationic mechanism or by metal complex initiators or by catalysts, and by subsequent complete or partial hydrogenation of the unsaturated aromatic bonds (see WO 94/02720 and EP-A 322 731 for example). They are distinguished by the predominant occurrence of the isotactic configuration of the vinylcyclohexane units of the present invention.

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In general, this process results in what is practically the complete hydrogenation of the aromatic units. As a rule, the degree of hydrogenation is $> 80\%$, preferably $> 90\%$, most preferably $> 99\%$ to 100% . The degree of hydrogenation can be determined by NMR spectrometry or UV spectroscopy, for example.

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The initial polymers which are used are generally known (e.g. WO 94/21 694).

The amount of catalyst to be used is described in WO 96/34896, for example.

- 5 The amount of catalyst used depends on the process which is carried out. This process can be conducted continuously, semi-continuously or batch-wise.

In a continuous system, the time of reaction is considerably shorter: it is influenced by the dimensions of the reaction vessel. In a continuous procedure, it is possible to use a
10 trickling system or a liquid pool system, which both employ fixed catalysts, and it is also possible to use a system comprising a suspended catalyst, which can be recycled for example. Fixed catalysts can exist in the form of tablets or as an extruded product, for example.

- 15 The polymer concentrations with respect to the total weight of solvent and polymer generally range from 80 to 1, preferably from 50 to 10, particularly from 40 to 15 % by weight.

Hydrogenation of the initial polymers is effected by methods which are generally
20 known (e.g. WO 94/21 694, WO 96/34895, EP-A-322 731). There is a multiplicity of known hydrogenation catalysts which can be used as catalysts. The preferred metal catalysts are cited in WO 94/21 694 or in WO 96/34 896, for example. Any catalyst which is known for hydrogenation reactions can be used as a catalyst. Catalysts having a large specific surface (e.g. 100 - 600 m²/g) and a small average pore diameter (e.g.
25 20 - 500 Å) are suitable. Other suitable catalysts include catalysts which have a small specific surface (e.g. ≥ 10 m²/g) and a large average pore diameter, and which are characterised in 98 % of the pore volume comprises pores with a pore diameter larger than 600 Å (e.g. about 1000 - 4000 Å) (see US-A 5,654,253, US-A 5,612,422, JP-A 03076706 for example). Raney nickel, nickel on silica or on silica/alumina, or nickel
30 on carbon as a support, and/or noble metal catalysts on silica, silica/alumina and alumina, especially Pt, Ru, Rh or Pd, are used in particular.

The reaction is generally conducted at temperatures between 0 and 500°C, preferably between 20 and 250°C, particularly between 60 and 200°C.

The solvents which are customary for hydrogenation reactions are described in DE-AS
5 1 131 885 for example (see above).

The reaction is generally conducted at pressures from 1 bar to 1000 bar, preferably from 20 to 300 bar, particularly from 40 to 200 bar.

10 The polymers or copolymers which are based on vinylcyclohexane according to the invention are outstandingly suitable for the production of optical materials, e.g. lenses, prisms and optical discs.

Examples of optical data storage media include:

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- the magneto-optical disc (MO disc)
- the mini-disc (MD)
- the ASMO (MO-7) ("advanced storage magnetooptic")
- the DVR (12 Gbyte disc)
- 20 - the MAMMOS ("magnetic amplifying magneto optical system")
- the SIL and MSR ("solid immersion lens" and "magnetic superresolution")
- the CD-ROM (read only memory)
- the CD, the CD-R (recordable), the CD-RW (rewritable), the CD-I (interactive), and the photo-CD
- 25 - the super audio CD
- the DVD, the DVD-R (recordable), the DVD-RAM (random access memory)
- the DVD=digital versatile disc
- the DVD-RW (rewritable)
- the PC RW (phase change and rewritable)
- 30 - the MMVF (multimedia video file system)

- Moreover, due to their outstanding optical properties, the polymers according to the invention are particularly suitable for the production of optical materials, e.g. for lenses, prisms, mirrors, colour filters, etc., and are also suitable as media for holographic imaging (e.g. cheques, credit cards, passes, three-dimensional
5 holographic images). The materials can be used as transparent media for inscribing three-dimensional structures, e.g. from focused coherent radiation (LASERS), and can be used in particular as three-dimensional data storage media for the three-dimensional imaging of objects.
- 10 The material can usually be employed instead of or in combination with glass up to temperatures of use of 145°C. External applications for the transparent materials include roof claddings, window panes, sheeting, and for the glazing of greenhouses, e.g. in the form of double-ribbed panels. Other applications include coverings, which at the same time exhibit a high level of transparency, for the protection of mechanically
15 sensitive systems, e.g. in the photovoltaic sphere, particularly solar cells or solar collectors. The plastics according to the invention can be coated with other materials, and in particular can be coated with nanoparticles in order to increase their scratch-resistance, or with metals or other polymers.
- 20 Examples of domestic applications include transparent packaging materials which exhibit a low permeability to moisture, domestic articles which are produced by extrusion or injection moulding, e.g. tumblers and containers, and also domestic appliances and transparent lamp covers.
- 25 The plastics can be used as temperature-resistant rigid foams for insulation in the building and engineering sectors (house and appliance insulation, e.g. for refrigerators), and can replace polystyrene or polyurethane foam for example. One advantage is the high temperature of continued use of these materials.
- 30 Due to their low density ($d < 1$) and the saving in weight which results therefrom, the materials are particularly suitable for applications in the automobile, aviation and space

travel industries, e.g. for instrument panels and transparent coverings for instrument systems, and also for light sources, for vehicle glazing and as an insulation material.

5 The materials are insulators for electric current and are therefore suitable for the production of capacitors (e.g. dielectrics), electronic switching circuits and appliance housings. There are other applications in the electronics industry, particularly on account of the combination of a high level of optical transparency with a high level of dimensional stability when hot, and low water absorption in association with light from suitable emitting sources. The materials are therefore suitable for the production of light-
10 emitting diodes, laser diodes, matrices for organic, inorganic and polymeric electroluminescent materials, opto-electric signal recording devices, the replacement of glass fibres in data transmission systems (e.g. polymeric wave guides), and transparent materials for electronic display media (screens, displays, projection apparatuses) e.g. those comprising liquid crystalline substrates.

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The materials are suitable for applications in medical technology, e.g. for transparent extruded or injection moulded articles for sterile and non-sterile analysis vessels, Petri dishes, microfilter plates, object supports, flexible tubing, breathing tubes, contact lenses, spectacles and containers, e.g. for infusion solutions or solutions of
20 medicaments, extruded and injection moulded articles for applications in contact with blood, particularly for the production of syringes, cannulas, catheters, short- and long-term implants (e.g. artificial lenses), blood tubing, membranes for the washing of blood, dialysers, oxygenators, transparent wound dressings, blood bottles and stitching materials.

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Examples

Example 1

- 5 An autoclave was flushed with inert gas (argon). The polymer solution and the catalyst were added (Table 1). After closing the autoclave, it was repeatedly pressurised with a protective gas and then with hydrogen. After releasing the pressure, the respective hydrogen pressure was set and the batch was heated with stirring to the corresponding reaction temperature. After the consumption of hydrogen had
10 commenced, the reaction pressure was held constant.

After the reaction was complete, the polymer solution was filtered. The product was precipitated in methanol and dried at 120°C. The isolated product had the physical properties listed in Table 2.

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Comparative example A

Syndiotactic polyvinylcyclohexane

- 20 A baked-out 250 ml three-necked flask, which was fitted with a reflux condenser and which was maintained under argon, was charged with 50 ml abs. toluene, 20 ml methylaluminumoxane (10% solution in toluene), 16.5 mg (0.075 mmol) titanium cyclopentadienyltrichloride and 10.4 g (0.1 mol) styrene, in this sequence.. The reaction mixture was heated to 50°C and was maintained for 2 hours at this
25 temperature. The reaction was stopped by adding acidic methanol. The polymer was repeatedly washed with 200 ml methanol and was dried at 80°C.

- 12.5 g palladium on barium sulphate were reduced with hydrogen and were rendered inert by a protective gas. A 1 litre pressurised reactor was flushed with inert gas. 2.5 g
30 syndiotactic polystyrene dissolved in cyclohexane were introduced into the autoclave together with the catalyst (Table 1). The hydrogen pressure was adjusted to 50 bar and the batch was heated to 200°C. After 24 hours the reaction was stopped, the autoclave

was depressurised and the polymer solution was filtered. The filtrate was precipitated in methanol and the product was dried under vacuum at 120°C. The isolated product had the physical properties listed in Table 2.

5 **Comparative example B**

Isotactic polyvinylcyclohexane

100 ml abs. toluene, 12.5 g (0.11 mol) vinylcyclohexane and 5 mmol
10 triethylaluminium were introduced at room temperature into a baked-out 1 litre three-necked flask fitted with a reflux condenser.

1 ml triethylaluminium (1 M) and 2 ml titanium(IV) chloride (1 M) in 12.5 ml toluene were stirred for 30 minutes at 80°C and were added to the monomer solution.

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The reaction mixture was heated to 60°C, was stirred for 50 minutes at this temperature and was subsequently held at 85°C for 90 minutes. Polymerisation was stopped by adding methanol. The product was boiled in methanol under reflux, filtered off, and was subsequently washed with methanol and acetone. The polymer
20 was dried under vacuum at 60°C. The product had the physical properties listed in Table 2.

Comparative example C

25 Polycarbonate from 2,2-bis(4-hydroxyphenyl)propane

A film of polycarbonate, 150 µm thick, based on 2,2-bis-(4-hydroxyphenyl)propane (Makrolon CD 2005, Bayer AG) was produced by a melt pressing process. A glass transition temperature of 142°C and a rheo-optical constant of +5.4 GPa⁻¹ were
30 measured for this film (see Table 2).

Table 1

Hydrogenation of polystyrenes with different tacticity

Example No.	Weight of polymer g	Solvent ml	Weight of catalyst g	Reaction temp. °C	Hydrogen pressure bar	Time of reaction hours	Degree of hydrogenation %
I	2.5 ²⁾	300 ml cyclohexane	12.5 ³⁾	200	50	6	100
A	2.5	300 ml cyclohexane	12.5 ⁴⁾	200	85	24	100

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- 1) Determined by ¹H NMR spectrometry
- 2) Polystyrene standard, Mw = 2500, Aldrich
- 3) Ni /SiO₂/Al₂O₃, 64-67 % nickel, Aldrich
- 4) 5 % palladium on barium sulphate, Aldrich

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Table 2

Thermal and optical properties of different vinylcyclohexane homopolymers

Example No.	Isotactic dyads ² %	Syndiotactic dyads ² %	Glass transition temp. Tg °C	Melting pt. Tm °C	Transparency of solution films +/-
1	55	45	98	-	+
A	< 2	> 98	126	295	-
B	> 98	< 2	11)	369	-
C	-	-	142	-	+

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1) not detected by DSC measurements

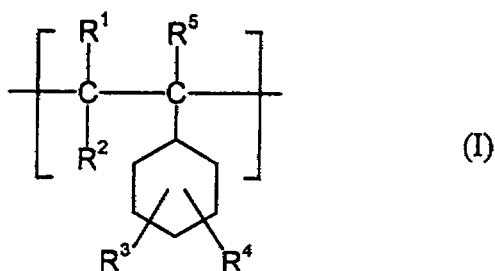
2) determined by two-dimensional nuclear magnetic resonance spectrometry (2D NMR).

The amorphous polyvinylcyclohexane according to the invention (Example 1) is distinguished by the predominant occurrence of isotactic dyads. Compared with polycarbonate, the material also exhibits a high level of transparency and a high level of dimensional stability when hot (glass transition temperature). On account of their crystallinity and low transparency, the syndiotactic and isotactic materials which have been described hitherto are unsuitable for optical applications.

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Claims

1. A vinylcyclohexane-based polymer or copolymer which has an isotactic configuration, wherein the comonomers which can be used for the production thereof are selected from at least one monomer of the group comprising olefines, alkyl esters of acrylic acid or methacrylic acid, cyclopentadiene, cyclohexene, cyclohexadiene, norbornene which is optionally substituted, dicyclopentadiene, dihydrocyclopentadiene, tetracyclododecene which is optionally substituted, styrenes comprising alkylated nuclei, α -methylstyrene, divinylbenzene, vinyl esters, vinylic acids, vinyl ethers, vinyl acetate, acrylonitrile, methacrylonitrile and maleic anhydride, characterised in that the amount of dyads is greater than 50 % and less than 74 %.
2. A polymer according to claim 1, wherein the amount of dyads is 51 to 70%.
3. A polymer according to claim 1, wherein the vinylcyclohexane-based polymer comprises a recurring structural unit of formula



wherein

R^3 and R^4 , independently of each other, represent hydrogen or a C_1 - C_6 alkyl, or R^3 and R^4 jointly represent an alkylene, and



R^1 , R^2 and R^5 , independently of each other, represent hydrogen or a C_1 - C_6 alkyl.

- 5 4. The use of polymers or copolymers according to claims 1 to 3 for the
production of optical data storage media, mouldings and sheeting.
5. Optical data storage media obtainable from vinylcyclohexane-based polymers
or copolymers according to claim 1.
- 10 6. Mouldings and sheeting obtainable from vinylcyclohexane-based polymers or
copolymers according to claim 1.

