Substrates for optical storage media

Plastics, such as aromatic polycarbonate, poly(methyl methacrylate) or polystyrene can be used as a substrate for optical data memories. Addition copolymers formed from ethylene and a norbornene derivative or a tetracyclododecene derivative, and also hydrogenated products of decyclized metathesis polymers formed from norbornene- or tetracyclododecene are also suitable.

For very high densities of data storage (> 5, in particular > 10 Gbytes, based on a wafer of 120 mm diameter), however, none of the common substrate materials can be used without limitation. For that purpose, very low birefringence, a very low moment of inertia, very low water absorption and high heat distortion temperature are necessary, accompanied at the same time by adequate mechanical properties and low melt viscosity.

Although aromatic polycarbonates have very good mechanical properties and heat distortion temperature, they have too high a birefringence and water absorption.

Polystyrene has too high a birefringence and too low a heat distortion temperature.

Poly(methyl methacrylate) has too high a water absorption and too low dimensional stability.

Addition copolymers formed from ethylene and a nonpolar norbornene- or tetracyclododecene have low birefringence and almost no water absorption.

Said materials are, however, very expensive to produce. The materials can be produced in optically pure quality only with difficulty. The presence of gel components likewise reduces their application as optical materials. The removal of the catalysts and cocatalysts is associated with appreciable technical expenditure.

In the case of asymmetrically structured optical data media (for example, CD, MO, MD, ASMO, DVR), in particular, the water absorption of the substrate material and the swelling associated therewith results in an additional deformation (for example increase in the angle tilting). This results in an impairment of the read-out signal (greater jitter, higher crosstalk) and consequently does not permit the maximum permissible data density or requires expensive electronic/optical correction modules (tiltservo) (F. Bruder, R. Plaetschke, H. Schmid, Jpn. J. Appl. Phys. Vol. 37 (1998) 2120).

Swelling of the substrate layers, in particular at interfaces with information layers and protective layers, may result in mechanical stresses that effect an accelerated separation of the information layers from the substrate layers.

The invention relates to substrates based on homopolymers and/or copolymers of vinyl- cyclohexane, comonomers being selected from at least one of the group of the olefins, acrylic acid derivatives, maleic acid derivatives, vinyl ethers and vinyl esters or mixtures thereof comprising at least 2 comonomers, the moment of inertia of the substrate being in general from 280 to 50 $g \cdot cm^2$, particularly preferably from 260 to 100 $g \cdot cm^2$, very particularly preferably from 250 to 150 $g \cdot cm^2$, determined from torsional vibration, and the density being from 1 to 0.8 $g \cdot cm^3$, preferably 0.98 to 0.90 $g \cdot cm^3$.

The invention furthermore relates to an optical substrate that exhibits very low interference due to birefringence, in particular in the case of highly focusing optics (high numerical aperture > 45), characterized in that the path difference of the light that is incident on the substrate has a path difference differential in general of 0 to 60 nm, preferably 0 to 50 nm, very particularly preferably from 0 to 40 nm, as a function of the angle of incidence for perpendicular angles and angles deviating therefrom by up to 27°.

The substrates according to the invention are remarkable for high dimensional stability, high transparency, low birefringence and high heat distortion temperature and are therefore eminently suitable as substrate material for optical data memories. The substrates are particularly suitable for producing optical storage media having high storage density.

Vibrations of the data medium are reduced in comparison to the data media used at present, for example polycarbonate.

The saturation water absorption of a preform according to the invention of the optical storage medium is in general less than 0.5%, preferably less than 0.2%, very particularly preferably less than 0.1%, in particular less than 0.06%, measured according to DIN 53 495.

The material has a high modulus of elasticity. Associated therewith is a high flexural strength, which in turn permits the construction of dimensionally stable substrate discs. Thinner substrate thicknesses permit higher data densities since optics having high numerical aperture NA and low laser wavelength λ become less critical (spot diameter ~ λ / NA, G. Bouwkuis, J. Braat, A. Huijser, J. Pasman, G. van Rosmaten, K. Schonhauer, Immiuk, Principles of Optical Disc Systems (Adam Hilger Ltd, 1995)).

At high rotational speeds of the optical disc, a slight dilation of the information layer occurs in the radial direction. This is important, in particular, for high data densities for high read-out and write-in reliability of the information.

For wavelengths greater than 400 nm, the optical transmission is greater than 89%. The material is therefore a preferred optical material for short-wave and long-wave light, in particular for wavelengths from 300 to 800 nm.

Substrates having low path difference differentials as a function of the angle of incidence of the light are particularly suitable for improving the optoelectronic write-in and read-out signals and are ideal substrates for readable only, writable and rewritable data media.

The materials have a high heat distortion temperature Tg and permit high operating and working temperatures.

Other materials can be deposited on the optical discs, with or without pretreatment of the surface. Particularly suitable for modifying the surface, if necessary, are plasma processes and wet-chemical processes.

Preferred materials for the deposition are metals, metal compounds and dyes.

Particularly suitable as metals are aluminium, gold, silver, copper, tin, zinc, germanium, antimony, tellurium, terbium, selenium, iron, cobalt, gadolinium and their alloys.

Particularly suitable as metal compounds are tin oxide, silicon oxide, silicon nitrogen compounds and zinc sulfide.

Suitable as dyes are cyanine, phthalocyanine and azo dyes.

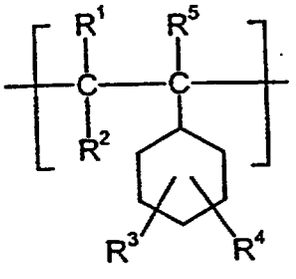
Said materials can be applied by spin-coating and sputtering procedures.

As optical data memories, the following are mentioned by way of example:

- magneto-optical disc (MO disc)
- mini-disc (MD)
- ASMO (MO-7) ("advanced storage magneto-optic")

- DVR (12 Gbyte disc)
- MAMMOS ("magnetic amplifying magneto-optical system")
- SIL and MSR ("solid immersion lens" and "magnetic superresolution")
- CD-ROM (read only memory)
- CD, CD-R (recordable), CD-RW (rewritable), CD-I (interactive), photo-CD
- super audio CD
- DVD, DVD-R (recordable), DVD-RAM (random access memory); DVD = digital versatile disc
- DVD-RW (rewritable)
- PC + RW (phase change and rewritable)
- MMVF (multimedia video file system)

Preferred are substrates formed from a polymer based on vinylcyclohexane containing the repetitive structural unit of the Formula (I)



(I)

in which

R^1 and R^2 stand, independently of one another, for hydrogen or C_1-C_6-alkyl, preferably C_1-C_4-alkyl and

R^3 and R^4 stand, independently of one another, for hydrogen or for C_1-C_6-alkyl, preferably C_1-C_4-alkyl, in particular methyl and/or ethyl, or R^3 and R^4 stand jointly for alkylene, preferably C_3- or C_4-alkylene (fused 5-member or 6-member cycloaliphatic ring),

R^5 stands for hydrogen or C_1-C_6-alkyl, preferably C_1-C_4-alkyl,

R^1, R^2 and R^5 stand, independently of one another, in particular for hydrogen or methyl.

In addition to the stereoregular head-to-tail linkage, the linkage may exhibit a small proportion of head-to-head linkage. The amorphous, predominantly syndiotactic polymer based on vinylcyclohexane may be branched via centres and have, for example, a star-shaped structure.

In the polymerization of the starting polymer (optionally substituted polystyrene) the following may preferably be used as comonomers and incorporated in the polymer: olefins containing in general 2 to 10 carbon atoms, such as, for example, ethylene, propylene, isoprene, isobutylene, butadiene, C_1-C_8-alkyl esters, preferably C_1-C_4-alkyl esters of acrylic or methacrylic acid, unsaturated cycloaliphatic hydrocarbons, for example cyclopentadiene, cyclohexene, cyclohexadiene, optionally substituted norbornene, dicyclopentadiene, dihydrocyclopentadiene, optionally substituted tetracyclododecenes, ring-alkylated styrenes, α-methylstyrene, divinylbenzene, vinyl esters, vinyl acids, vinyl ether, vinyl acetate, vinyl cyanides, such as, for example, acrylonitrile, methacrylonitrile, maleic anhydride and mixtures of said monomers.

As amorphous vinylcyclohexane polymers, those having a syndiotactic diad component, determined by two-dimensional NMR spectroscopy, ranging from 50.1 to 74%, preferably from 52 to 70%, may be used. Methods for microstructure elucidation on the basis of ^{13}C-^1H correlation spectroscopy of the methylene carbon atoms of a polymer backbone are generally known and are described, for example, by A.M.P. Ros and O. Sudmeijer (A.M.P. Ros, O. Sudmeijer, Int. J. Polym. Anal. Charakt. (1997), 4, 39).

The birefringence determined on these substrates measured on the basis of the rheooptical constant C_R is less than or equal to -0.3 GPa^{-1}, this amount being less

than that for polycarbonate (C_R = + 5.4 GPa^{-1}) by more than a power of ten. The method of measuring the rheooptical constant is described in EP-A 0 621 297. The plane-parallel 150 to 1000 µm test pieces needed for this purpose can be produced by melt pressing or film casting. Compared with polycarbonate, the material can be regarded as free of birefringence.

The vinylcyclohexane (co)polymers have in general absolute weight-average molecular weights M_w of 1000 to 10,000,000, preferably 60,000 to 1,000,000, very particularly preferably 70,000 to 600,000, determined by light scattering.

Particularly preferably, the vinylcyclohexane (co)polymers have absolute molecular weights M_w of 70,000 to 450,000 g/mol, in particular 100,000 to 450,000 g/mol. The molecular weight distribution is preferably characterized by a polydispersity index (PDI = M_w/M_n) of 1 to 3, any oligomer component up to a molecular weight of 2000 not being taken into account in calculating the polydispersity index. Any oligomer component up to an M_w of 3000 is less than 5%, based on the weight of the polymer.

The copolymers may be either random copolymers or block copolymers.

The polymers may have a linear chain structure and also have branching points due to co-units (e.g. graft copolymers). The branching centres comprise, for example, star-shaped or branched polymers. The polymers according to the invention may have other geometrical forms of the primary, secondary, tertiary, optionally quaternary polymer structure, in which connection mention may be made of a helix, a double helix, a folded leaf etc., or mixtures of these structures.

Particularly preferred are styrene-isoprene copolymers, in particular poly(styrene-block-co-isoprene) and star-shaped poly(styrene-block-co-isoprene).

Block copolymers include diblocks, triblocks, multiblocks and star-shaped block copolymers.

The VCH (co)polymers are produced by free-radical, anionic, cationic polymerization or polymerization with metal complex initiators or catalysts of derivatives of styrene with the corresponding monomers and then completely or partially hydrogenating the unsaturated aromatic bonds (cf., for example, WO 94/21694, EP-A 322 731).

The VCH (co)polymers can furthermore be produced, for example, by hydrogenation of aromatic polystyrenes or their derivatives in the presence of a catalyst, in which connection the solvent used is an ether which does not have an α-hydrogen atom on a carbon atom adjacent to the ether function or a mixture of such ethers or a mixture of at least one of the ethers mentioned with solvents suitable for hydrogenation reactions.

The starting polymers are hydrogenated by generally known methods (for example, WO 94/21 694, WO 96/34 895, EP-A-322 731). A multiplicity of known hydrogenation catalysts can be used as catalysts. Preferred metal catalysts are mentioned, for example, in WO 94/21 694 or WO 96/34 896. Any known catalyst for the hydrogenation reaction can be used as catalyst. Catalysts having a large surface area (for example, 100-600 m^2/g) and a low mean pore diameter (for example, 20-500 Å) are suitable. Furthermore, those catalysts having a small surface area (for example, $\geq$ 10 m^2/g) and large mean pore diameters are suitable that are characterized in that 98% of the pore volume comprises pores with pore diameters greater than 600 Å (for example, approximately 1000-4000 Å) (cf., for example, US-A 5,654,253, US-A 5,612,422, JP-A 03076706). In particular, Raney nickel, nickel on silicon dioxide or silicon dioxide/aluminium oxide, nickel on carbon as a support and/or noble-metal catalysts, for example Pt, Ru, Rh, Pd are used.

The reaction is carried out in general at temperatures between 0 and 500°C, preferably between 20 and 250°C, in particular between 60 and 200°C.

The solvents which can be used as standard solvents for hydrogenation reactions are described, for example, in German Auslegeschrift 1 131 885 (see above).

The reaction is in general carried out at pressures from 1 bar to 1000 bar, preferably 20 to 300 bar, in particular 40 to 200 bar.

The substrates are produced from the thermoplastic moulding compositions containing homopolymers and/or copolymers based on vinylcyclohexane and, optionally, further conventional additives, such as processing aids and stabilizers by processing the moulding compositions at temperatures above 280°C.

Examples

Example 1

The 40 l autoclave is flushed with inert gas (nitrogen). The polymer solution and the catalyst are added (Table 1). After sealing, the mixture is exposed several times to protective gas and then to hydrogen. After letting down, the respective hydrogen pressure is established and heating is carried out to the appropriate reaction temperature while stirring. After the hydrogen absorption has started, the reaction pressure is kept constant. The reaction time is defined from heating up the mixture to the time at which the hydrogen absorption tends to its saturation value.

After the reaction is complete, the polymer solution is filtered. The polymer solution is stabilized with 4000 ppm of Irganox XP 420 FF (Ciba Speciality Chemicals, Basel, Switzerland), freed of solvent at 240°C and the product is processed further to form granules.

From the granules, shoulder rods, optical discs and further test pieces, for example, are produced by injection moulding for determining the physical properties (Table 2).

Table 1

Hydrogenation of polystyrene

Example No.	Polymer[2] mass, kg	Solvent, l	Catalyst mass, g	Reaction temp., °C	Hydrogen pressure, bar	Reaction time, h	Degree of hydrogen[1], %
1	4.8	15.1 cyclo-hexane 10.1 methyl tert-butyl ether	625 [3]	160	100	19	100

1) Determined by ^{1}H-NMR spectroscopy

2) Polystyrene, type 158 k, glass-clear, Mw = 280,000 g/mol, BASF AG, Ludwigshafen, Germany

3) Ni-SiO_2/Al_2O_3, Ni-5136 P, Engelhard, De Meern, The Netherlands

Example 2

Preparation of poly(styrene-block-co-isoprene)

The syntheses are carried out by standard inert gas procedures. 138 kg of absolute cyclohexane are introduced into a 250 l reactor. 6.3 kg of absolute styrene are added to the reactor at room temperature. The temperature is increased to 55°C, and 102 ml (0.255 mol) of n-butyllithium (23% in n-hexane) are introduced into the reactor. The reaction mixture is heated to 70°C and stirred for 30 minutes.

1.4 kg of absolute isoprene and 6.3 kg of absolute styrene are simultaneously introduced into the reactor. The mixture is kept at 70°C for 2 hours. The reaction solution is cooled to room temperature and a solution of 10 g of 2-propanol in 500 g

of cyclohexane is added. The polymer solution is concentrated to 16.6 wt.% at 40 to 45°C under vacuum.

Example 3

Preparation of hydrogenated poly(styrene-block-co-isoprene)

22 kg of the polymer solution (Example 2) are transferred under nitrogen to a 40 l autoclave. After adding 421.5 g of Ni-5136 P (Engelhard), the autoclave is exposed several times to nitrogen and hydrogen. The reaction solution is heated to 170°C at 100 bar. After the heating phase, the reaction is continued by means of an automatic pressure system at 150 bar until the pressure is constant and stirring is continued for two hours.

The catalyst is filtered from the polymer solution. The polymer solution is stabilized with 4000 ppm of Irganox XP 420 FF (Ciba Geigy, Basel, Switzerland), freed of solvent at 240°C and processed further as granules.

Table 2

Physical properties of a common substrate material for optical discs based on the example of polycarbonate compared with polymers 1 and 3 (example B and C) based on vinylcyclohexane

Examples	Density[1], g/cm³	Saturation water absorption[2], %	Modulus of elasticity[3], GPa	Moment of inertia, g·cm²	a) path difference[4], vertical light incidence, nm	b) path difference[4], 27° from the normal, nm	Differential a) - b), nm	Optical transmission[5] greater than 400 nm, %	Rheooptic constant C_R, GPa^{-1}	Glass transition temperature[6] Tg, °C
A comparison	1.18	0.35	2.3	294	+30	+95	+65	87	+5.4	142
B acc. to the invention	0.94	0.03	3.2	229	-12	-19	-7	>89	-0.3	149
C acc. to the invention	0.94	0.03	2.3	228	+3	+2	-1	>89	+0.1	139

A bisphenol A polycarbonate, Makrolon CD 2005, Bayer AG
CD preforms were produced on an injection moulding machine supplied by the Netstal company, type Diskjet 600
CD preforms: internal diameter 15 mm, external diameter 120 mm, substrate thickness 1.2 mm
1) Determined according to DIN 53 479 method A
2) Determined according to DIN 53 495
3) Determined according to DIN 53 455
4) Path difference measured by means of polarization optics
5) Optical transmission measured with Perkin Elmer Lambda 900 spectrophotometer with photometer sphere
6) Determined by differential scanning calorimetry (DSC)

A CD preform (CD substrate) produced from a bisphenol A polycarbonate (Makrolon CD 2005, Bayer AG, Leverkusen, Germany) is used as comparison Example A and CD preforms produced from polymers based on polyvinylcyclohexane in accordance with Examples 1 and 3 are used as Examples B and C. The CD preforms are produced on an injection moulding machine supplied by the Netstal company, type Diskjet 600. Compared with common substrate material in accordance with Comparison Example A (Table 2), the CD performs in accordance with Examples B and C exhibit for use as high-density optical storage media the important combination of low moment of inertia, low water absorption, high dimensional stability (high modulus of elasticity), low density, low path difference differential as a function of the angle of incidence of the light, high optical transparency at short and long wavelengths, as well as low birefringence accompanied at the same time by high heat distortion temperature. Example C exhibits a rheooptical constant C_R which is optimized further, accompanied by very low path difference differential as a function of the angle of incidence of the light and has a glass transition temperature at the level of polycarbonate.

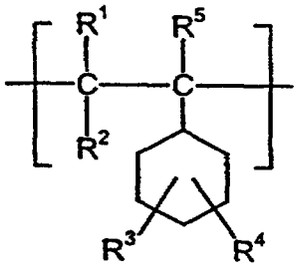
Patent Claims

1. Substrates based on homopolymers, copolymers and/or block polymers of vinylcyclohexane, comonomers being selected from the group of the olefins, acrylic acid derivatives, maleic acid derivatives, vinyl ethers and vinyl esters or mixtures thereof comprising at least two comonomers, characterized in that the moment of inertia of the substrate is 280 to 50 g·cm^{2}and the density is 1 to 0.8 g/cm^3.

2. Substrates according to Claim 1, characterized in that the moment of inertia is 260 to 100 g·cm^2.

3. Substrates according to Claim 1 or 2, characterized in that the density is 0.98 to 0.90 g/cm^3.

4. Substrates according to any of Claims 1 to 3, based on a vinylcyclohexane (co)polymer or a mixture of vinylcyclohexane (co)polymers containing the repetitive structural unit of Formula (I).



(I)

in which

R^1 and R^2 stand, independently of one another, for hydrogen or C_1-C_6-alkyl,

R^3 and R^4 stand, independently of one another for hydrogen or for C_1-C_6-alkyl, or R^3 and R^4 stand jointly for alkylene, and

R^5 stands for hydrogen or C_1-C_6-alkyl.

5. Substrates based on styrene-isoprene block and/or copolymers.

6. Substrates according to one or more of the preceding claims, characterized in that the path difference of the light which is incident on the substrate has a path difference differential in general from 0 to 60 nm, as a function of the angle of incidence for vertical angles and angles deviating therefrom by up to 27°.