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(54) Film forming material and preparation of surface relief and optically anisotropic structures by irradiating a film of the said material

(57) The present invention relates to a film forming, photoactive material comprising a complex prepared from (a) at least one ionic photosensitive compound which may undergo a photoreaction, selected from photoisomerizations, photocycloadditions and photoinduced rearrangements, wherein the photosensitive compound is of formula I or formula II

$$[R\text{-}P\text{-}R']^{n+}\ n/x\ A^{x-} \qquad (I)$$

or

$$n/x\ A^{x+}\ [R\text{-}P\text{-}R']^{n-} \qquad (II)$$

wherein P is a group capable of photoisomerization, and R and R' are independently selected from optionally substituted or functionalised aryl-containing groups at least one of which is positively or negatively charged, A is an oppositely charged cation or anion, n is an integer, and x is 1, 2 or 3, and/or the photosensitive compound is of formula III or IV:

$$[R^1\text{-}Q\text{-}R^{1'}]^{n+}\ n/x\ A^{x-} \qquad (III)$$

or

$$n/x\ A^{x+}\ [R^1\text{-}Q\text{-}R^{1'}]^{n-} \qquad (IV)$$

wherein Q is a group capable of participating in a photocycloaddition or photoinduced rearrangement reaction, and R^1 and $R^{1'}$ are independently selected from optionally substituted or functionalized groups having electron-accepting properties and optionally substituted or functionalized aryl-containing groups and from such groups which together with Q form an aryl ring or heteroaryl ring, wherein either at least one of R^1 and $R^{1'}$ is positively or negatively charged or the ring structure and/or a substituent thereon will carry at least one positive or negative charge, wherein A, n and x are defined as for formulae I and II, with the proviso that in all compounds of formulae (I) to (IV) contained in one complex, the charge of [R-P-R'] and/or $[R^1\text{-}Q\text{-}R^{1'}]$ has the same sign, and (b) at least one polyelectrolyte carrying charges which are opposite to those of the active groups [R-P-R'] and/or $[R^1\text{-}Q\text{-}R^{1'}]$ of the photosensitive material.

If films prepared from this material are homogeneously or heterogeneously irradiated with polarized light, optical anisotropy and/or a surface relief structure may be reversibly or irreversibly induced in/on the films, depending on specific parameters detailed in the specification.

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Description

[0001] The present invention relates generally to a new type of film forming material having unique photochemical properties. Non-scattering, optically clear films formed from the new materials can be easily prepared. They allow light-induced generation of optical anisotropy (photo-induced dichroism and birefringence) therein and of topological surface structures, e.g. such as surface relief gratings (SRG). The material comprises a complex prepared from at least two components: 1) an anionic or cationic polyelectrolyte and 2) an oppositely charged cationic or anionic photosensitive low molecular weight compound having the ability to undergo E/Z isomerisation or to participate in a light induced cycloaddition or in a photoinduced rearrangement reaction or another reaction capable of generating optical anisotropy in the material upon irradiation. The material based on this complex readily forms films, preferably on solid substrates or between two such substrates from water/alcoholic or organic solvents.

[0002] It is known that amorphous and liquid crystalline polymers containing azobenzene or other photoactive moieties such as stilbenes, cinnamates, coumarins in side chains or main chains can be used for the induction of anisotropy by photoorientation (K.Ichimura, Chem. Rev. 2000, 100, 1847; A. Natansohn et al., Chem. Rev. 2002, 102, 4139; V. Shibaev et al., Prog. Polym. Sci. 28 (2003) 729—836; X. Jiang, et al., WO 98/36298). Azobenzene derivatives are also known for their ability to form SRG when being exposed to gradient light field (A. Natansohn et al., Chem. Rev. 2002, 102, 4139).

[0003] Different types of azobenzene containing materials were used for optical anisotropy and/or SRG generation. In one approach ("guest-host" systems), this was attained by mixing of photochromic azobenzene derivatives, e.g. 4-[4-N-n-hexyl-N-methylamino-phenylazo]-benzoic acid or modified Direct Red 1 azodye with readily available polymer PMMA as a matrix (J. Si et al., APPL. PHYS. LETT. 80, 2000, 359; C. Fiorini et al., Synthetic Metals 115 (2000), 121-125). However, the effects to be observed are rather weak, due to low dye loading caused by dye-polymer segregation. Relatively high loading of the photochromic material in the polymer matrix could be observed with specially synthesized dyes, which allow avoiding a dye-polymer segregation (C. Fiorini et al., see above). But in such systems the photo-induced dichroism was not stable, and the SRG formation was not effective (up to 50 nm deep). Relatively stable birefringence has been induced only when commercially available Direct Red 1 was introduced into very high-T_g poly(ether ketone). It is unknown whether SRGs can be generated in the latter system. Such materials were used for the recording of orientational holograms.

[0004] Better results have been obtained by chemically binding azodye compounds to a polymeric material. The material is characterized by covalent bonds between the photoactive units and the polymeric backbone. In addition to the fact that the results observed are much better than in the "guest-host" approach, such polymer materials normally have good film forming properties. However, environmentally non-friendly organic solvents have to be used. Often the solubility of the polymers is a problem which is hardly to overcome. Special synthesis is required to manufacture such functional polymers from commercially available chemicals, and consequently, they are expensive. Moreover, the purification of the polymers is a difficult problem as well.

[0005] Recently, a specially synthesized monomeric azobenzene derivative has been found which is able to form glassy films (V. Chigrinov et al., 1106 • SID 02 DIGEST; V.A. Konovalov, et al., EURODISPLAY 2002, 529; W.C.Yip et al., Displays, 22, 2001, 27). In films of these low molecular weight glass forming compounds optical anisotropy was induced by irradiation with linearly polarised light.

[0006] Moreover, a layer-by-layer (LBL) dipping procedure has been employed to obtain films for photo-induced orientation and SRG formation (see e.g. A. M.-K. Park et al, Langmuir 2002, 18, 4532; Ziegler et al., Colloids and Surfaces, A 198-200 (2002), 777-784; V. Zucolotto et al., Polymer 44 (2003), 6129-6133). In such systems, readily available polyelectrolytes and low molecular weight azodyes possessing at least two ionic groups, azobenzene containing bolaamphiphiles, ionenes or polyelectrolytes covalently substituted with azobenzene moieties are used. In the typical procedure, a substrate is alternately immersed for about 10-20 min in an aqueous solution of a cationic polyelectrolyte, such as poly-DADMAC, and an anionic azobenzene containing compound, respectively. Each immersion results in the formation of a monolayer on the substrate surface with typical thickness of about 1 nm. Numerous repetition of this procedure results in a multilayer film. About 150 layers are required to obtain a reasonable thickness of the resulting layer. Films up to 700 layers can be produced. SRGs with an amplitude of up to 120-140 nm can be generated, wherein a photoinduced orientation of the azobenzene moieties can be observed. The procedure is tedious and time consuming. Moreover, rather thick films are necessary for the inscription of deep SRG, and such films are difficult to obtain.

[0007] Another approach using H-bonds between the polymeric backbone and the photochromic compounds has been employed (E.B. Barmatov et al., Polymer Science, Ser. A, Vol 43 (3), 2001, 285). In this way, films with the ability for photoorientation were obtained.

[0008] In these concepts, the components are bound to each other by Coulomb attraction or H-bonds. Similar attraction is possible between oppositely charged ionic moieties in solution. The interaction of polyelectrolytes with dyes in dilute solutions has been studied (W. Dawydoff et al., Acta Polym. 1991, 42, 592). Recently, complexes of polyelectrolytes with another, oppositely charged polyelectrolyte containing azobenzene moiety in the side chain were fabricated as a solid material (A.F. Thunemann et al., Macromolecules 1999, 32, 7414; 2000, 33, 5665). The molecular photochemistry and light-induced subsequent physical processes of these materials such as photoorientation and photo-induced diffusion, were not investigated.

[0009] In summary, a multiplicity of chemical systems making use of the photochemical properties of photochromic azobenzene dyes has been developed during the past few years. Such compositions may form films, which allow introduction of optical anisotropy and/or the generation of surface relief structures therein. However, despite the intense search for effective and readily available compositions, they are all connected with certain disadvantages as outlined above.

[0010] The inventors found a novel, photoactive, film forming material combining high efficiency of the induction of optical anisotropy as well as of surface relief structures with the simplicity of material preparation.

[0011] The material consists of a complex prepared from at least two components: 1. an anionic or cationic polyelectrolyte and 2. a opposite charged cationic or anionic photosensitive compound, in general a low molecular weight molecule. Further components such as plasticizers, conventional organic oligomers or polymers, other photosensitive compounds, dyes, or liquid crystalline compounds can be added to modify formulation properties, and the properties of the films (flexibility of the film, hydrophilic/hydrophobic properties and the like). The invented materials readily form films on solid substrates from water/alcoholic or organic solvents. Optical anisotropy and/or surface relief structures can be induced in these films upon irradiation with light.

[0012] The photosensitive compound suitable for the present invention is an ionic compound which is capable to undergo a photoreaction, and mainly selected from photoisomerization, photocycloaddition reactions and photoinduced rearrangements. If it is capable to undergo a photoisomerization, it is of formula I or II

$$[R\text{-}P\text{-}R']^{n+}\ n/x\ A^{x-} \qquad (I)$$

or

$$n/x\ A^{x+}\ [R\text{-}P\text{-}R']^{n-} \qquad (II)$$

wherein P is a group which is capable of photo-induced E/Z isomerization , and R and R' are independently selected from optionally substituted and/or functionalized aryl-containing groups at least one of which is positively or negatively charged, A is a cation or anion which is oppositely charged, n is preferably 1 or 2, more preferably 1, but may in specific cases be higher (3 or 4), and x is 1 or 2. Preferably, P is an azo group -N=N-, or comprises more than one such group. However, the invention is not restricted to compounds of formulae I or II containing one or more azo groups. For example, P may be —C=N- or, -C=C-. It is preferred in any of the mentioned cases that at least one of the aryl moiety is directly bound to the group P.

[0013] If the ionic compound is capable to undergo a photocycloaddition or photoinduced rearrangement, it is of formula III or IV:

$$[R^1\text{-}Q\text{-}R^{1'}]^{n+}\ n/x\ A^{x-} \qquad (III)$$

$$[R^1\text{-}Q\text{-}R^{1'}]^{n+}\ n/x\ A^{x-} \qquad (IV)$$

wherein Q is a group capable of participating in a photocycloaddition, preferably a (2+2) addition or a (4+4) addition, or capable of participating in a photoinduced rearrangement, preferably the rearrangement of spiropyranes to merocyanines, or the so called Photo-Fries reaction, and R^1 and $R^{1'}$ are independently selected from optionally substituted or functionalized groups which have electron-accepting properties or comprise at least one aryl moiety or such (a) group(s) which together with Q form an aryl ring or heteroaryl ring. At least one of R^1 and $R^{1'}$ is positively or negatively charged, or the ring structure and/or a substituent thereon will carry at least one positive or negative charge. A, n, and x are defined as for formulae I and II.

[0014] In case the photocycloaddition is a (2+2) addition, Q will preferably contain a —C=C- or a —C=N- bond and will more preferably consist of the group —CR^2=$CR^{2'}$- or —CR^2=N- wherein R^2 and $R^{2'}$ are independently selected under H or a C_1-C_4 group. Preferably, Q is part of a conjugated $p\pi$-electron system. Examples for respective compounds are cinnamates, imines, stilbenes, chalcones, or p-phenylene diacrylic esters or amides, wherein at least one of R^1 and $R^{1'}$ is an optionally substituted or functionalized phenyl or other aryl or heteroaryl ring and the other is also an optionally substituted or functionalized phenyl or other aryl or heteroaryl ring or a carboxylic ester or carbonamide group or a phenyl carbonyl residue. All the said groups or residues may be substituted or functionalized, and at least one of R^1 and $R^{1'}$ must carry at least one positive or negative charge. Alternatively, Q may be a —C=C- group which is part of a carbocyclic or heterocyclic, preferably aromatic ring, e.g. in coumarins, in thymine or cytosine derivatives or in maleinic acid anhydride derivatives. According to the above definition, R^1 and $R^{1'}$ are in such cases fused to form a ring structure, together with Q.

[0015] One or more atoms of this ring structure or, alternatively, a substituent attached thereto may carry the respective at least one positive or negative charge. Again, such compounds, if carrying at least one positive or negative charge, will fall under the scope of the present invention.

[0016] In specific cases, when the photocycloaddition is not a (2+2) cycloaddition, Q may comprise more atoms in its backbone and may e.g. be an aromatic C_6 ring which can be fused within an aromatic system or may carry suitable residues at least one of which carries the respective charge(s). One example is an anthracene derivative. Anthracenes are known to undergo a (4+4) cycloaddition whereby carbon atoms 9 and 10 will form bridges to a neighbour atom, resulting in formation of a sandwich-like dimer structure.

[0017] Of course, compounds (I) to (IV) may carry more than one group P or Q, respectively. For example, the said compounds are intended to include bisazobenzenes or trisazobenzenes as well as diacrylic ester compounds, e.g. p-phenylene-diacrylic esters.

[0018] If R, R', R^1 and/or $R^{1'}$ is an aryl group, it may be or may comprise a homocyclic or heterocyclic ring. Optionally, this ring may be fused to an aromatic system, e.g. a naphthalene or anthracene system. Further, the ring can be substituted or functionalized by one or more substituents.

[0019] In the definitions given above, the term "functionalized" shall mean substituted by a substituent which implies an additional functionality to the molecule, e.g. a substituent carrying a charge, like a SO_3H group, or a substituent which can provide the capability of polymerization or polyaddition, e.g. a S-H group, or a polymerizable —C=C-group. The term "substituted" shall mean any other substituent.

[0020] The compounds as defined above may be used in any kind of salts as available, e.g. ammonium or sodium salts, chlorides, sulfates and the like, or they may be acidic or basic compounds e.g. carboxylic acids, sulfonic acids, amines, or a hydroxy group carrying compounds, and the like, which are capable of reacting with an oppositely charged polyelectrolyte to yield a respective ionic complex. As outlined above, they can be positively or negatively charged, with one or more charges.

[0021] The polyelectrolyte to be used carries charges which are opposite to those of the photosensitive compound, i.e. is a polycation or polyanion. The ionic strength of its cations or anions may be strong or weak. The polyelectrolyte may be of natural origin, or may be synthetically prepared. Examples are polyethyleneimine, poly(allylamine hydrochloride), poly(dimethyldiallylammonium chloride), carageenans, polyacrylic acid, sulfonated cellulose, polystyrenesulfonate, Nafion, sol-gel products of alkoxysilanes functionalised with a proton acceptor (e.g. amino-group) to yield ammonium groups or to yield carboxylate groups. The polyelectrolyte can be described as having formula $mx/n\ Z^{n+}\ [B^{x-}]_m$ or $mx/n\ Z^{n-}\ [B^{x+}]_m$ wherein m is the number of monomer-units in the polyelectrolyte and x is the number of the charge each of the monomer-unit carries. Z is a cation or anion carrying n charges which are opposite to those of the polymer-moiety. Z can be the same as A as defined for formulae I to IV and m may be in the order of from 2 to 1000 or even more, while n and x are as defined for formulae I to IV.

[0022] In order to obtain the material of the present invention, at least one polyelectrolyte as defined above and at least one photosensitive compound as defined above are each dissolved in a suitable solvent. Since both components are ionic, they are usually soluble in protic and polar solvents, in most cases in water or a lower alcohol or a mixture of both. The mixtures are preferably considerably concentrated, often until saturation. The ratio of photosensitive compound to polyelectrolyte should preferably be not less than 0.5:1, in relation to the number of charges. This means that per each charge of the polyelectrolyte, at least 0.5 charges of a photosensitive compound should be present. The remaining charges of the polyelectrolyte can be compensated by additives, e.g. ionic oligomers or additional ionic dyes or the like, as required and/or desired. An excess of photosensitive compound is not critical, i.e. the ratio can be 1:1 or even higher in order to achieve higher dye loading (and to improve consequently the effectivity of the material).

[0023] The solutions are then mixed in order to obtain the complex of ionic photosensitive compound and polyelectrolyte. This complex may be described to consist of one or more of the following:

$$k[R\text{-}P\text{-}R']^{n+}\ [B^{x-}]_m\ ,\ k[R\text{-}P\text{-}R']^{n-}\ [B^{x+}]_m,\ k[R^1\text{-}Q\text{-}R^{1'}]^{n+}\ [B^{x-}]_m\ ,\text{ or } k[R^1\text{-}Q\text{-}R^{1'}]^{n-}\ [B^{x+}]_m,$$

wherein k is 0.5->1 (mx/n) and the other indices and residues are as given above, or the complex .

[0024] To obtain the said complex, it is alternatively possible to mix the said photosensitive compound with a non-ionic polymer, the polymer having groups within each monomeric unit which only upon addition of protons (acid) or a Lewis base become ionic and charged so that the polymer is converted into a polyelectrolyte. Examples for such non-ionic polymers are polymers comprising a Lewis base in each of their monomer units which may accept a proton or acid groups from which a proton can be taken. In such cases,a respective Lewis base or proton donor compound is added after mixing, in order to obtain the desired, inventive complex.

[0025] Depending on the nature of other parts of the complex, it will either remain soluble in the mixture, or it might be less soluble, due to a lower polarity. If the complex precipitates at least partly, it can be taken up and redissolved in a less polar solvent, e.g. in water/alcohol mixtures containing more alcohol, in a longer chain alcohol, in a mixture of alcohol with another solvent, e.g. an aprotic solvent, or in an acetone or an ether like tetrahydrofuran, if desired. Further, it is possible to exchange any of the solvents of the initial solutions against another, more desired solvent, e.g. by evaporating the first solvent and taking up the complex with another solvent or solvent mixture.

[0026] Additives may be incorporated at any stage prior to forming the films, as appropriate. They may either be added to any of the solutions prior to the preparation of the complex, or may be added to the complex in any stage. Additives may be, for example, organic polymers, compounds having film forming abilities, plasticizers, liquid crystals and/or photosensitive compounds differing from the photosensitive compounds having formulae (I) to (IV).

[0027] The complex according to the present invention is rather stable, due to its ionic character. Specifically, it will be resistant against the influence of heat in a much larger extent than comparable materials which are not of ionic nature. Such materials will in general soften at lower temperatures.

[0028] In a specific embodiment of the invention, the materials of the present invention comprise the inventive complex, together with one or more additional components which may undergo or provide cross-linking of the film, preferably after structurization. Such components may be selected from additional organic monomers which are capable to bind to specific groups of the polyelectrolyte, forming bridges and/or an organic network. In one embodiment, this component is selected from monomeric photosensitive molecules which are capable to undergo photopolymerisation or photo-cross-linking. Preferably, the conditions of photopolymerisation or cross-linking should be such that a wavelength is used which is different from that used for "recording" (SRG formation) as mentioned above. In another embodiment, this component is susceptible to thermal curing or polymerizes/provides bridges or a cross-linking network upon thermal treatment.

[0029] Depending on the solvent, any of the conventional film forming techniques like spin-coating or casting, doctor's blading and the like can be used to prepare homogeneous films on a substrate in merely one step. In addition, ink-jet printing to produce patterned films, is also readily available using e.g. water/alcoholic media. After the film has been deposited on the substrate or the respective basic layer, it is allowed to dry, preferably at room temperature, for example in air.

[0030] The thickness of the films may vary in a broad range, depending on the desired application. For example, it may vary between 10 nm and 50 μm, typically between 200 nm and 5 μm. If desired, additional layers may be deposited, either between the substrate and the film of the inventive photosensitive material and/or as one or more covering layers on the upper surface of the film.

[0031] The photoactive material according to the invention is light-sensitive, due to the presence of groups in the complex which may either undergo light-induced E/Z isomerization and/or photocycloaddition reactions, or light induced rearrangement reactions. Under homogeneous irradiation with polarized actinic light, optical anisotropy is induced within films made from this material. The optical anisotropy may be stable, unstable or erasable in dependence on the material composition, treatment and irradiation conditions, as outlined below. Under inhomogeneous irradiation, both a modulation of optical anisotropy and a deformation of film surface may be achieved. Most surprisingly, the latter process is as effective or even more effective as reported for azobenzene containing functionalized polymers that have been known as the most effective for the surface relief gratings formation. In this regard the material of the present invention is a viable alternative to the covalently bonded polymer systems used until now.

[0032] As mentioned above, the properties of the proposed material may be optically modified in different ways. If irradiated homogeneously with polarized light, the film becomes anisotropic, that means, birefringence and/or dichroism are induced. This is due to aphotoorientation process in the steady state of the photoisomerisation in the material upon polarized irradiation. For example, if the material contains groups which undergo E/Z isomerization, light irradiation will result in an orientation of such groups. In case of photocycloadditions or other photoreactions, an angular-selective photo-decomposition or angular-selective formation of photoproducts will be observed.

[0033] The optical anisotropy induced in such a way may relax back, be erased thermally or by irradiation with light, or may be stable. For example since Z isomers relax back to the thermodynamic stable E isomers, the induced orientation based on the E/Z isomerization may be stable, may undergo relaxation, or may be erased thermally or photochemically. Thus, the optical anisotropy of azobenzene systems is only temporary induced (while surface relief gratings formed therewith are long-term stable, see below). However, optical anisotropy and surface gratings due to photocycloaddition will remain stable since the reaction is not reversible. Stability of optical anisotropy may also be achieved by using a material which allows further curing or crosslinking, e.g. by building up an organic network within the film. In such cases, light induced optical anisotropy may be "frozen" in the material when the material is cured after inducing said anisotropy.

[0034] The velocity of the induction and relaxation processes, if any, may be controlled through adjusting the temperature and/or the parameters of irradiating/erasing light. In this way a variety of thin film polarization elements like polarizer or retarder may be created that may be permanent or optically switchable. The light-induced change of birefringence or dichroism in this material may be also effectively used for optical data storage and, if reversible, for optical processing.

[0035] If a film is irradiated with an inhomogeneous light field, i.e. a light field wherein the intensity or/and polarization of irradiating light is spatially modulated, the induced anisotropy is correspondingly modulated through the film. One example of this is irradiation through a mask. In this way, pixel thin film polarization elements may be fabricated. Another example is irradiation with an interference pattern, i.e. holographic irradiation. In this way, a variety of holographic optical elements operating in transmission or reflection modes (like polarization beam splitter or polarization discriminator) may be realized.

[0036] Moreover, surface relief structures may be generated on the free surface of films made from the material of the present invention by inhomogeneous irradiation with polarized light (holographic, mask or near-field exposure). Surface relief structures may be a result of a photo-induced mass transport upon an E/Z photoisomerization reaction or upon photocycloaddition or photoinduced rearrangement reaction (e.g. caused by shrinkage due to ring formation).

[0037] If a film made of the material of the present invention is irradiated inhomogeneously, formation of surface relief structures (surface relief gratings, SRGs) can be observed along with the generation of inhomogeneous optical anisotropy. However, formation of SRGs can, if required or desired, be suppressed by irradiating a film between two substrates. In respect to reversibility and irreversibility of surface relief structures, the same applies as outlined above for the occurrence of optical anisotropy.

[0038] The lateral size of generated relief structures ranges from tens of nanometers (in the case of irradiation with near-field) to tens of microns provided by holographic irradiation. It is being demonstrated here that the efficiency of the relief formation is comparable to the values reported for the azobenzene functionalized polymers (modulation depth of 2 μm was achieved). Atomic force microscopy (AFM) images of SRG written in the materials of the present invention and, for comparison, in side chain azobenzene polymers of the prior art are shown in Fig. 1.

[0039] There are unique possibilities of the material application, due to the reversibility of the recording process, if a material is selected which allows reversible formation of surface relief structures. Once a relief structure has been recorded, it may be overwritten again. This allows the recording of complicated surface structures by superimposing their simple components. In this way, for example, multidimensional structures may be realized by successive recordings of simple one-dimensional structures; gratings with non-sinusoidal profile may be formed by successive recording of Fourier components or any recorded structure may be in a point way corrected. Another benefit of the reversibility of the process is the possibility of multiple use of the film. A high number of writing cycles without fatigue is possible. On the other hand, if generated in the material with additive as described above, the final relief structure may be "frozen" or fixed, for example, thermally or by flood exposure (exposure of the whole film) in order to obtain crosslinking or the like. and to avoid destruction of the resulting relief.

[0040] In this way a variety of relief holographic elements like diffraction grating, beam coupler, beam multiplexer, splitter or deflector, Fresnel lens and the like may be created. Applications of structured films (in particular gratings) are not restricted to optical elements only. One step all-optical structured surfaces may be used as templates for self-organisation of particles, as command surface for alignment of liquid crystals, as surface with modified wetting/dewetting properties or as antireflective layers.

[0041] If surface relief structures have been prepared according to the invention, such structures may be replicated using a wide variety of different materials. Replication may be performed once or manifold. A replica may again serve as template for replication. Materials which are useful for replication are known in the art. Examples are polysiloxanes, e.g. polydimethylsiloxane. Such materials may be prepared as resins having sufficiently low viscosity to fill the fine structures of the SRG and may be dried or cured after replication to yield a stable material. Other examples are polyacrylate resins, polyurethanes, ene-thiol compositions or a metal, e.g. via electrochemical deposition from a metal solution. The initial surface relief structure can be washed out from the replica, if desired, using an appropriate solvent.

[0042] The materials of the present invention have, inter alia, the following advantages: they can be manufactured from readily available non-expensive commercial materials, namely commercially available polyelectrolytes and photochromic derivatives with ionic groups. There is a great flexibility in their preparation, as well as in the composition of the materials and systems (multi-component systems). It is possible to use environmental friendly water/alcoholic media as solvents. Since the complexes and formulations are prepared in protic solvents like water and/or alcoholic media, films can easily be prepared on polymeric or other (e.g. inorganic) substrates or combined with other polymer layers which are not stable in organic solvents usually used for polymer film manufacturing, but would allow to form another layer from water/alcoholic media. Ink-jet printing will be also readily available with water/alcoholic solvents. In case of a replication of SRGs and other topological surface structures using other polymer or non-polymer material, the initial photosensitive film with the photo-induced structure can be washed out by solvents. Anisotropic films and surface relief structures can be produced using the new material without expensive synthesis and purification of photochromic polymers wherein the photochromic unit must be covalently attached to the polymer backbone. And due to the ionic nature of the using materials, the film and products made from this film, e.g. SRGs, are thermally stable, at least until about 150-200°C.

[0043] Due to their superior chemical and physical (optical, mechanical) properties, the material of the present invention may be used in a wide variety of technical fields, and specifically in the field of technical and other optics, data storage and telecommunication. For example, the material may be used as a photosensitive medium, optical element, functional surface and/or template. Said elements may e.g. be diffractive elements, polarization elements, focusing elements or combinations of such elements. If the light-induced properties thereof are reversible, they can be used as or in elements for optical or optical/thermal switching. In such cases, the material is preferably prepared by a method as claimed in claim 27 or 28. Further, if the light-induced properties are reversible, it may be used as a medium for real-time holography or optical information processing. Alternatively, the photosensitive medium can be a medium for irreversible or reversible optical data storage. If the data storage is reversible, written information can subsequently be eliminated by irradiation or heating, if desired, whereafter another writing cycle is possible. In other applications, the material is used as a template, wherein the template surface is a surface for replication to another material or the command surface for aligning of liquid crystals, self-organization of particles. The surface may determine the chemical, mechanical and/or optical properties of the material, preferably selected from wetting/dewetting, hardness, reflectance and scattering.

[0044] The attached figures illustrate some of the properties of the films of the invention, wherein

Figure 1 is a AFM image of SRG written in material of Example 1a (a) and in poly((4-(4-trifluoromethylphenylazophenyl-4-oxy)butyl)methacrylate)-co- poly((2-(4-cyanobiphenyl-4-oxy)ethyl)methacrylate) (b),

Figure 2 shows the intensity of the 1st order diffracted beam during recording of SRG in the Example 1a,

Figure 3 illustrates the intensities of the 0th and 1st order diffracted beams during recording and erasing of SRG in the Example 2,

Figure 4 illustrates the intensities of the 0th and 1st order diffracted beams by SRG written in Example 1a during erasing at the temperature of 150°,

Figure 5 shows the intensity of the 1st order diffracted beam during the first and the second recordings onto the same spot on the film of Example 1a,

Figure 6 is an AFM image of square SRG written in two steps,

Figure 7 (a) illustrates the induction and relaxation of optical anisotropy of Example 7a: intensity of the orthogonally polarised components of the transmitted probe beam; (b) induction and relaxation of optical anisotropy of Example 7b,

Figure 8 illustrates the intensity of the orthogonally polarised components of the transmitted probe beam: a) switching between two states under alternating irradiation; b) dynamics of single switch.

[0045] Below, the invention shall be exemplified further.

Example 1a. "Recording"

[0046] 54 mg of Alizarin Yellow GG (5-(3-Nitrophenylazo)salicylic acid sodium salt, Aldrich) was dissolved in 20 ml of distilled water, 40 μl of 30% aqueous solution polyethyleneimine was added. The deposit was separated by filtration (30mg after drying) and dissolved in 1 ml of THF, while the mother solution was discarded. A film of about 2 μm thickness was fabricated from the THF solution by casting onto the glass substrate in a close chamber at room temperature. After drying at room temperature in air for 5 h, the film was irradiated with the interference pattern formed by two linearly orthogonally polarized beams with polarisation planes at ±45° to the incidence plane. The irradiation wavelength was 488 nm, and the angle between beams was about of 12° resulting in a period of 2.3 μm. The intensities of interfering beams were equal to 250 mW/cm^2, the irradiation time was 40 min. The 1st order diffraction efficiency measured during the recording is shown in Fig. 2. 1st order diffraction efficiency at the end of recording was measured to be 16.5%. The induced surface relief was investigated by means of AFM and revealed a SRG with amplitude of ca. 350 nm. The measured topography and the related cross-section are shown in Fig. 1.

Example 1b. "Recording"

[0047] 63 mg of Brilliant Yellow (4,4'-bis(4-hydroxyphenylazo)stylbene-2,2'-disulfonic acid disodium salt, Aldrich), were dissolved in 5 ml methanol and then filtered. 130 mg 30% aqueous solution of polyethyleneimine (Aldrich) was added. Since some deposit was formed, the solution was allowed to settle and decanted. The red mother solution was used for the film preparation. A film of about 3 μm thickness was prepared by casting this solution onto the glass substrate in a close chamber at room temperature. After drying at room temperature in air for 5 h, the film was irradiated for 40 min as described in example 1a. The 1st order diffraction efficiency of the SRG recorded was measured to be 14.5 %.

Example 1c. "Recording"

[0048] To 80 mg of Brilliant Yellow (Aldrich) in 2 ml methanol, 130 mg of triethoxy-3-aminopropylsilane (Witco Europa SA) was added. After adding 10μm concentrated HCl, the solution was left to settle. The clear red mother solution was decanted. A film of about 3 μm thickness was prepared by casting this solution onto the glass substrate in a close chamber at room temperature. After drying at room temperature in air for 10 h, the film was irradiated for 30 min as described in example 1a. The 1st order diffraction efficiency of the SRG recorded was measured to be 8%.

Example 1d. "Recording"

[0049] To 28 mg of 4-(dimethylamino)-4'-nitroazobenzene (Aldrich)in 1 ml of MeOH, acidified by HCl was added 0.2 ml of 5% solution of polyacrylic acid Na salt in MeOH. A film of about 1 μm thickness was prepared by spin-coating of this solution onto the glass substrate at 1000 rpm. After drying at room temperature in air for 2 h, the film was irradiated for 30 min as described in example 1a. The 1st order diffraction efficiency of the SRG recorded was measured to be 2%.

Example 1e. "Recording"

[0050] To 34 mg of azobenzene-4-carboxylic acid (Aldrich)in 6 ml of MeOH,. 60 mg of 20% aqueous solution of poly (diallyldimethylammonium chloride) was added. A film of about 1 μm thickness was prepared by spin-coating of this solution onto ink-jet transparency film at 500 rpm. After drying at room temperature in air for 3 h, the film was irradiated for 30 min as described in example 1a. The 1st order diffraction efficiency of the SRG recorded was measured to be 2.5%.

Example 2. "Erasing with light"

[0051] The film from the material of the Example 1a was irradiated with the interference pattern formed by two linearly orthogonally polarized beams with polarisation planes at ±45° to the incidence plane. The irradiation wavelength was 488 nm, and the angle between beams was about of 12° resulting in a period of 2.3 μm. The intensities of interfering beams were equal to 250 mW/cm^2, the irradiation time was 40 min. For the erasing of grating one of the recording beams was used. Thus the polarisation of the erasing light was linear with polarisation plane at 45° to the grating grooves and the intensity of light was 250 mW/cm^2. The 0th and 1st order diffraction efficiencies measured during the recording and erasing of the grating are shown in Fig. 3.

Example 3. "Thermal erasing"

[0052] The film with the inscribed grating as in Example 1a was step-wise heated to a final temperature of 150°. Until 150° the grating was stable. At this temperature thermal erasing evident by decreasing 1st order diffraction efficiency and by increasing 0 order diffraction efficiency started. The erasing was followed for 60 min (Fig. 4).

Example 4. "Rewriting"

[0053] A grating as in Example 1a was rewritten into the film of Example 2. Figure 5 presents the diffraction efficiency measured during recording of the first grating, erasing with linearly polarized light and the recording of second grating onto the same spot of the film. The second recording has been done with a higher intensity thus resulting in a much faster formation of a grating.

Example 5. "Multiple Recording"

[0054] A film of about 2 μm thickness was prepared as in Example 1b. Two gratings were successively inscribed into the same spot on a film. Between the two recording steps the film was rotated at 90° around the normal to the film plane. As a result a 2-dimensional structure was inscribed that is a combination of two linear gratings inscribed in the single steps. The AFM topology image of induced structure is shown in Figure 6.

Example 6. "Comparison of recording configurations"

[0055] The gratings were recorded into the films of the material of the Example 1a. The period of the gratings, recording intensities and irradiation times were kept constant for all gratings. The polarisation of the recording beams was varied: i) linear parallel ss; ii) linear parallel pp; iii) linear orthogonal ±45°; iv) linear orthogonal 0°, 90°; v) circular parallel; vi) circular orthogonal. The obtained diffraction efficiencies and the relief modulation depths are shown in Table 1. It is well seen that the linear orthogonal ±45° polarisation configuration is the most effective one. The circular orthogonal polarisations also result in a formation of SRG although less effective then linear orthogonal ±45°. Among the parallel polarisation configurations the most effective is the linear parallel pp one while the linear parallel ss configuration at the applied recording conditions does not result in any appreciable surface relief.

Table 1. Diffraction efficiency and relief depth for SRG written in different configurations (Example 6).

	linear orthogonal ±45°	linear orthogonal 0°, 90°	linear parallel pp	linear parallel ss	circular parallel	circular orthogonal
1st order DE, %	18.5	0	6	0	0.6	11.2
2nd order DE, %	1.3	0	0.4	0	0	0.9
relief, nm	230	0	80	0	30	180

Example 7a. "Reversible Anisotropy"

[0056] A film of the material of Example 1a was exposed to the linearly polarized light of the wavelength of 488 nm. The induction and the relaxation of the optical anisotropy were detected in real time by means of a probe beam of a He-Ne laser operating at a wavelength of 633 nm. The probe light was linearly polarized at 45° to the polarisation plane of the irradiating beam. The transmitted probe beam was split into two orthogonally polarized beams by means of a Wollaston-prism. The intensities of both orthogonal polarisation components, i.e. the component with the polarisation of the incident probe beam and a new component with orthogonal polarisation rising due to the induced birefringence, were measured. Figure 7a represents the time behaviour of the induced optical anisotropy. Fifteen induction/relaxation cycles are shown, whereas during the first cycle the saturation and the complete relaxation of the signal were reached. It is seen that at the applied intensity and the wavelength of irradiation the induction time is of about 3 min. The time constant of dark relaxation is estimated to be of 8 min. The anisotropy was almost completely erased and then induced again. No fatigue is noticed after 30 induction/erasure cycles.

Example 7b. "Reversible Anisotropy"

[0057] To 36 mg of 4-Phenylazoaniline hydrochloride (Aldrich) in 3 ml of MeOH 17 mg poly(acrylic)acid (Fluka) in 1 ml of water was added. A film of about 2 μm thickness was prepared by casting this solution onto the glass substrate in a close chamber at room temperature. After drying at room temperature in air for 20 h the film was irradiated as described in Example 7a, Optical anisothropy is shown in figure 7b.

Example 8. "Switchable Anisotropy"

[0058] A film of the material of Example 1 was alternatively exposed to linearly polarized light with orthogonal polarisation planes. The wavelength of the irradiation was 488 nm. The induction of the optical anisotropy was detected as in Example 7a. Figure 8a represents the switching of the induced optical anisotropy and Figure 8b shows the switching dynamics. It is seen that the induced optical anisotropy is completely switched between two states by the irradiation with properly polarized light.

Example 9a. "Replication"

[0059] The surface relief structure as in Example 1a was replicated into polydimethylsiloxane (PDMS) by pouring a mixture of Sylgard silicone elastomer 184 and curing agent (10: 1) on the top of the SRG and allowing it to be hardened for 3 h at 60 C. The comparison of grating and replica is shown in the Fig. 9. The original grating had amplitude of ca. 700-800 nm, replica has the same relief shape and amplitude of 400-500 nm.

Example 9b. "Replication"

[0060] Norland optical adhesive NOA65 (Norland corporation) was poured onto the surface of SRG obtained as in Example 1a and immediately irradiated for 30 sec. with UV light to harden. Separation of NOA layer from SRG yields the replica of grating in NOA material.

Example 9c. "Replication"

[0061] Example 9b was repeated, however, instead of NOA65, a two component adhesive (curing time approx. 5 min at 60°C) was used. After pouring the adhesive mixture onto the grating and hardening it for about 10 min at 60°C the replica was easily separated from the grating.

Example 9d. "Replication"

[0062] A surface relief grating as obtained in any of examples 1 was soaked in 1.2 mg/ml solution of $SnCl_2$ (activation solution) for 30 min. and then electroless plated with Ag by pouring onto the surface of the grating the following solution: 120 mg $AgNO_3$ 200 μl 30% NH_3 solution, 80 mg NaOH in 20 ml of water. After washing with water, the Ag covered grating was used as cathode in Ni electrochemical plating in the following Ni plating bath: 50 ml water, 6.4 g $NiSO_4$, 2.4 g $Na_2SO_4x10H_2O$, 1 g $MgSO_4$, 2 g H_3BO_3, 0.25 g Nacl. Plating condition were Ni sacrificial anode, current density 20 mA/cm_2, stirring.

Claims

1. Film forming, photoactive material comprising a complex prepared from

(a) at least one ionic photosensitive compound which may undergo a photoreaction, selected from photoisomerizations, photocycloadditions and photoinduced rearrangements, wherein the photosensitive compound is of formula I or formula II

$$[R\text{-}P\text{-}R']^{n+}\ n/x\ A^{x-} \qquad (I)$$

or

$$n/x\ A^{x+}\ [R\text{-}P\text{-}R']^{n-} \qquad (II)$$

wherein P is a group capable of photoisomerization, and R and R' are independently selected from optionally substituted or functionalised aryl-containing groups at least one of which is positively or negatively charged, A is an oppositely charged cation or anion, n is an integer, and x is 1, 2 or 3, and/or
the photosensitive compound is of formula III or IV:

$$[R^1\text{-}Q\text{-}R^{1'}]^{n+}\ n/x\ A^{x-} \qquad (III)$$

or

$$n/x\ A^{x+}\ [R^1\text{-}Q\text{-}R^{1'}]^{n-} \qquad (IV)$$

wherein Q is a group capable of participating in a photocycloaddition or photoinduced rearrangement reaction, and R^1 and $R^{1'}$ are independently selected from optionally substituted or functionalized groups having electron-accepting properties and optionally substituted or functionalized aryl-containing groups and from such groups which together with Q form an aryl ring or heteroaryl ring, wherein either at least one of R^1 and $R^{1'}$ is positively or negatively charged or the ring structure and/or a substituent thereon will carry at least one positive or negative charge, wherein A, n and x are defined as for formulae I and II
with the proviso that in all compounds of formulae (I) to (IV) contained in one complex, the charge of [R-P-R'] and/or $[R^1\text{-}Q\text{-}R^{1'}]$ has the same sign, and
(b) at least one polyelectrolyte carrying charges which are opposite to those of the active groups [R-P-R'] and/or $[R^1\text{-}Q\text{-}R^{1'}]$ of the photosensitive material.

2. Material according to claim 1, wherein group P and group Q in formulae (I) to (IV) are selected from -N=N-, $-CR^2=CR^{2'}-$ with R^2, $R^{2'}$ being independently selected from H, CN or C_1-C_4 alkyl, and a group containing more than one -N=N- and/or $-CR^2=CR^{2'}-$ moieties in a electron-conjugated system.

3. Material according to claim 1 or 2, wherein in formulae (I) or (II), the aryl moieties of R, R are directly bound to the group P, and/or wherein in formulae.(III) or (IV), R^1 and $R^{1'}$ are selected from aryl moieties directly attached to Q, and —C(O)O- and —(CO)NR^3 groups wherein R^3 is H or a optionally substituted alkyl or aryl group.

4. Material according to any of claims 1 and 2, wherein the at least one photosensitive compound is selected from monoazo compounds, bisazo compounds, trisazocompounds, and preferably from azobenzenes, bisazobenzenes, trisazobenzenes, and further from stilbenes, cinnamates, imines, anthracenes, coumarines, chalcones, p-phenylene diacrylates or diacrylamides, thymin derivatives, cytosine derivatives, merocyanines/spiropyranes and derivatives of maleinic acid anhydride.

5. Material according to any of the preceding claims, wherein the polyelectrolyte is selected from charged polysiloxanes formed *in situ* by hydrolytic condensation of alkoxy- and/or chlorosilanes carrying a positive or negative charge, preferably carboxy group containing silanes, or by hydrolytic condensation of neutral silanes and subsequent introduction of a charged group thereto, preferably an ammonium group into an aminosiloxane.

6. Material according to any of claims 1 to 4, comprising at least one additive which modifies the properties of the material, preferably selected from organic polymers, compounds which have film forming abilities, plasticizers, liquid crystals and photosensitive compounds differing from those as defined in claim 1.

7. Material according to claim 6, comprising a monomeric photosensitive molecule, which is capable to undergo polymerisation or to provide cross-linking, induced either by irradiation with light or by thermal treatment.

8. Material according to any of the preceding claims, in the form of a layer or a film on a substrate or in the form of a free-standing film, the film optionally being patterned.

9. Material according to any of the preceding claims, preferably in the form of a film, the material being capable to change at least one optical property, preferably selected from refraction, absorption, birefringence, dichroism or gyrotropy, upon irradiation with light.

10. Material according to claim 9, wherein the optical properties are either

(a) homogeneous through the material or
(b) varied through the material or through restricted areas thereof.

11. Material according to claim 10, variant (b), wherein optical properties are modulated in one, two or three dimensions including modulation in the direction perpendicular to the film plane, in any direction in the film plane or along the axis tilted to the film plane.

12. Material according to any of the preceding claims in the form of a film on a substrate or of a free-standing film, at least one free surface exhibiting a light-induced relief structure.

13. Material according to claim 12, wherein the relief structure is a regular pattern with height modulated in one or two dimensions.

14. Material according to claims 9 to 13, wherein the induced changes of optical properties or/and the induced relief structure are either

(a) reversible or
(b) irreversible.

15. Material according to claim 14, variant (a), wherein the changes of optical properties or/and of the relief structure are stable when kept at day light below the glass transition temperature or the decomposition temperature.

16. Material according to claims 14, variant (a), and 15, wherein the changes of optical properties or/and of the relief structure are cyclically induced with light and erased optically or thermally.

17. Method for the preparation of a material according to any of claims 1 to 7, comprising separately dissolving the ionic photosensitive compound(s) and the polyelectrolyte(s), combining the respective solutions and optionally redissolving precipitated material in a less polar solvent.

18. Method for the preparation of a material according to claim 8, comprising preparing a material of any of claims 1 to 7 and casting, spin coating, doctor's blading or ink-jet printing it onto a substrate, either in the form of a continuous film or having a predesigned pattern.

19. Method for the preparation of a material according to claim 10, variant (a), comprising preparing a film as defined in claim 18 and irradiating said film or a part of it with a homogeneous light field.

20. Method for the preparation of a material according to claims 10, variant (b), and 11, comprising preparing a film as defined in claim 18 and irradiating said film or part of it with an inhomogeneous light field, provided by a mask or by an interference pattern of at least two intersecting coherent beams.

21. Method according to claims 19 and 20, wherein either the wavelength, the irradiation time, the number of the irradiating beams and/or the polarization, the intensity, the incidence angle of at least one irradiating beam is varied to control the direction, the value and/or the modulation type of the induced optical anisotropy.

22. Method according to claims 20 and 21, further comprising varying the mask spacing or the period of the interference pattern in order to control the spatial modulation of optical anisotropy.

23. Method for the preparation of a material according to claims 12 and 13, comprising preparing a film as defined in claim 18 and inhomogeneously irradiating said film, preferably through a mask, with a focused beam, with near field, or with an interference pattern of at least two intersecting coherent beams.

24. Method for the preparation of a material according to claims 12 and 13, comprising preparing a film as defined in claim 23 and further changing of once inscribed structures (correcting or overwriting) by successive irradiation using method according to claim 23.

25. Method according to claim 23 and 24, wherein structures with complicated (non-rectangular and non-sinusoidal) profile are prepared by multi-step (successive) irradiation, preferably with the interference patterns corresponding to the Fourier components of the desired profile.

26. Method according to claim 23 and 24, wherein complicated multidimensional structures are prepared by multi-step (successive) irradiation, preferably differing by the position of the material, irradiation conditions and/or the interference pattern.

27. Method for the preparation of a material according to claim 16, comprising alternative preparation of a film as defined in claims 19 to 26 and erasure of the induced changes by either homogeneous irradiation of said film or part of it with a light or/and by heating it.

28. Method according to claim 27, wherein either the wavelength, the irradiation time, the polarization, the intensity, the incidence angle of erasing beam and/or the temperature, rate, time of heating is varied to control the velocity and degree of the erasure and the final state of the material.

29. Use of a material as claimed in any of claims 1 to 16 as a photosensitive medium, optical element, functional surface and/or template.

30. Use of a material as claimed in claims 14 to 16 wherein the light-induced property is reversible, as an element for optical or optical/thermal switching, the material preferably being prepared by a method according to claim 27 or 28.

31. Use of a material as claimed in claims 14, variant (a) and 16, wherein the light-induced property is reversible, as a medium for real-time holography or optical information processing.

32. Use according to claim 29, wherein the optical element is selected preferably from diffractive element, polarization element, focusing element or any combination of said elements.

33. Use according to claim 29, wherein the photosensitive medium is a medium for irreversible or reversible optical data storage.

34. Use according to claim 33, wherein written information can be eliminated by irradiation or heating, whereafter another writing cycle is possible.

35. Use according to claim 29, wherein the template surface is a surface for replication to another material or the command surface for aligning of liquid crystals, self-organization of particles.

36. Use according to claim 29, wherein the functional surface is the surface determining the chemical, mechanical, optical properties of the material, preferably selected from wetting/dewetting, hardness, reflectance, scattering.

37. Method for the preparation of a replica of a surface relief structure, comprising the following steps:

(i) preparing a material according to any of claims 12 and 13 ("first material") using a method as claimed in any of claims 23 to 26, to obtain a surface relief structure thereon;
(ii) covering said relief structure or a part thereof with a second material, selected from organic and inorganic-organic polymers and/or metals;
(iii) curing or hardening said second material, if required;
(iv) separating said second material from the surface relief grating of the first material, to obtain a (negative) replica and optionally
(v) repeating steps (ii) to (iv), if more than one replica from the said surface relief structure shall be obtained.

38. Method for the preparation of a reproduction replica of an original surface relief structure, comprising the following steps:

(i) preparating a material according to any of claims 12 and 13 ("first material") using a method as claimed in any of claims 23 to 26, to obtain a surface relief structure thereon;
(ii) covering said relief structure or a part thereof with a second material, selected from organic and inorganic-organic polymers and/or metals;
(iii) curing or hardening said second material, if required;
(iv) separating said second material from the surface relief grating of the firt material or washing out said first material with a suitable solvent to obtain a (negative) replica,
(v) covering the the negative relief structure of the replica with a third material, selected from organic and inorganic-organic polymers and metal,
(vi) curing or hardeing said third metal, if required,
(vii) separating said third material from the surface relief grating of the second material, to obtain a (positive) replication replica of the original surface relief structure, and
(viii) repeating steps (v) to (vii), if more than one reproduction replica from ths said surface relief structre shall be obtained.

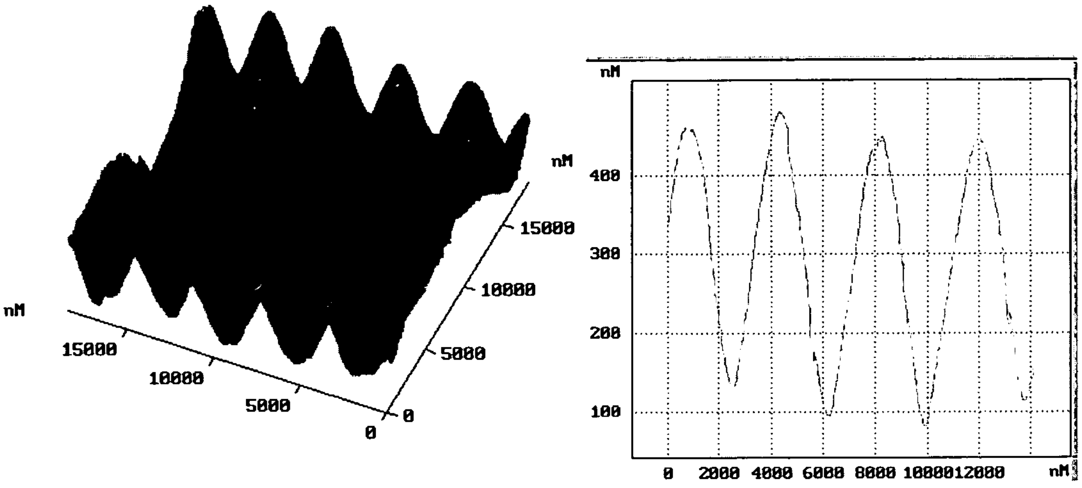


Figure 1a

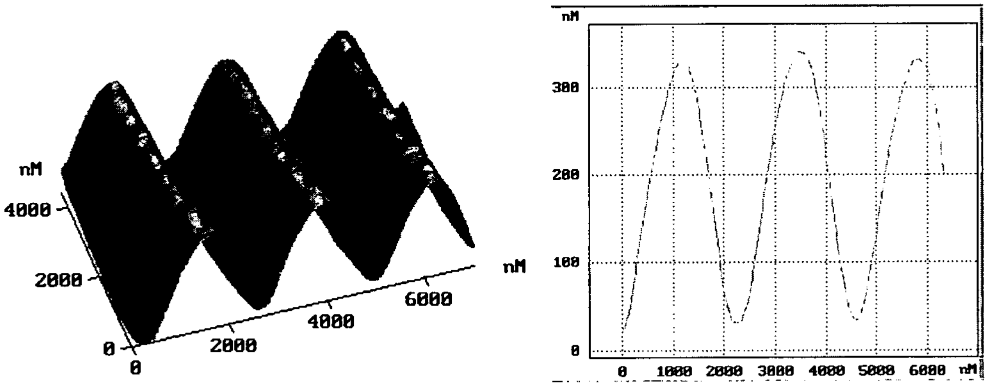


Figure 1b

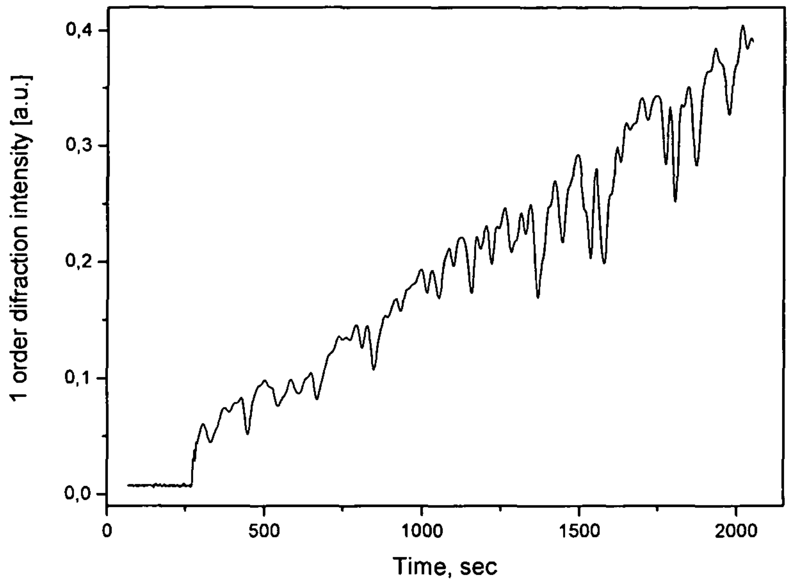


Figure 2

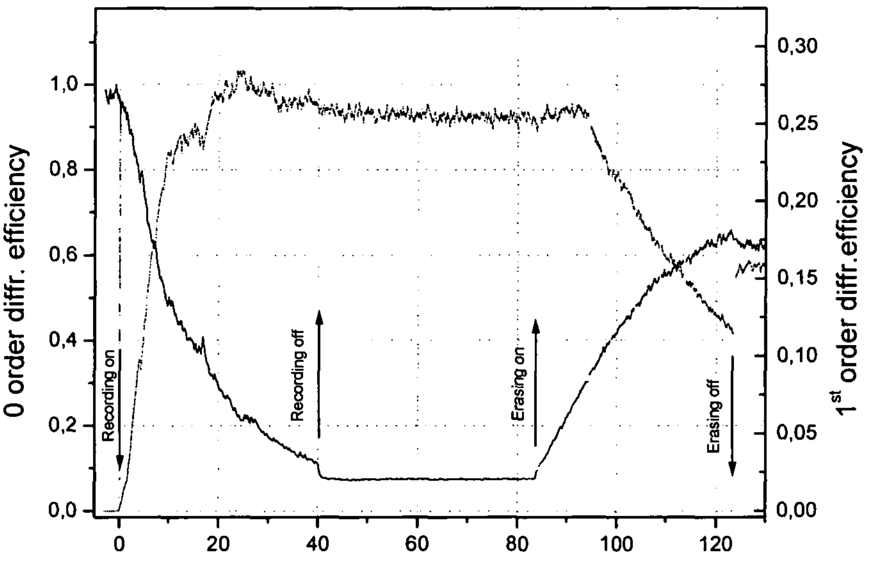


Figure 3

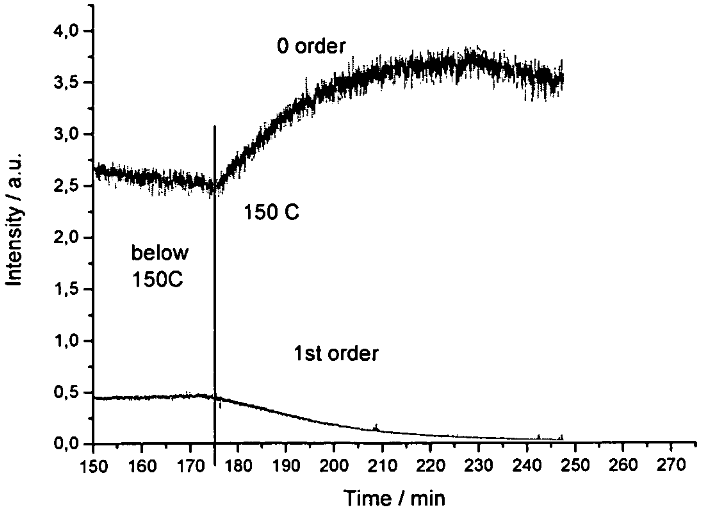


Figure 4

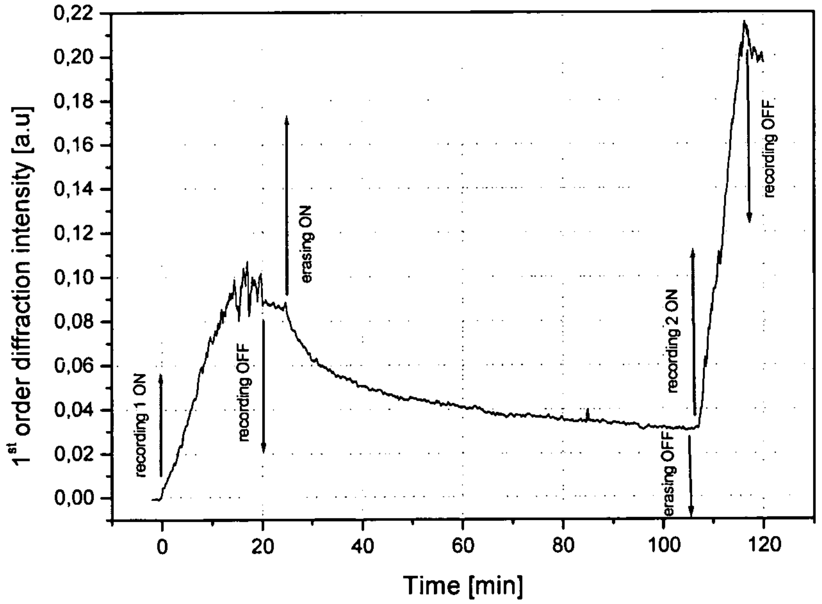


Figure 5

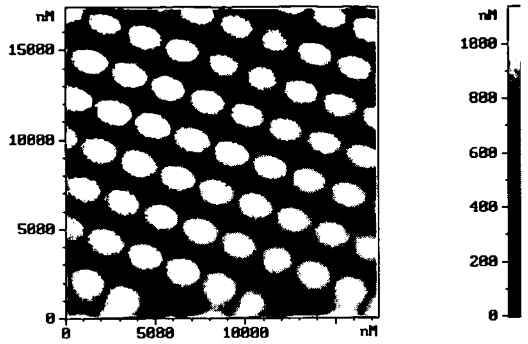


Figure 6

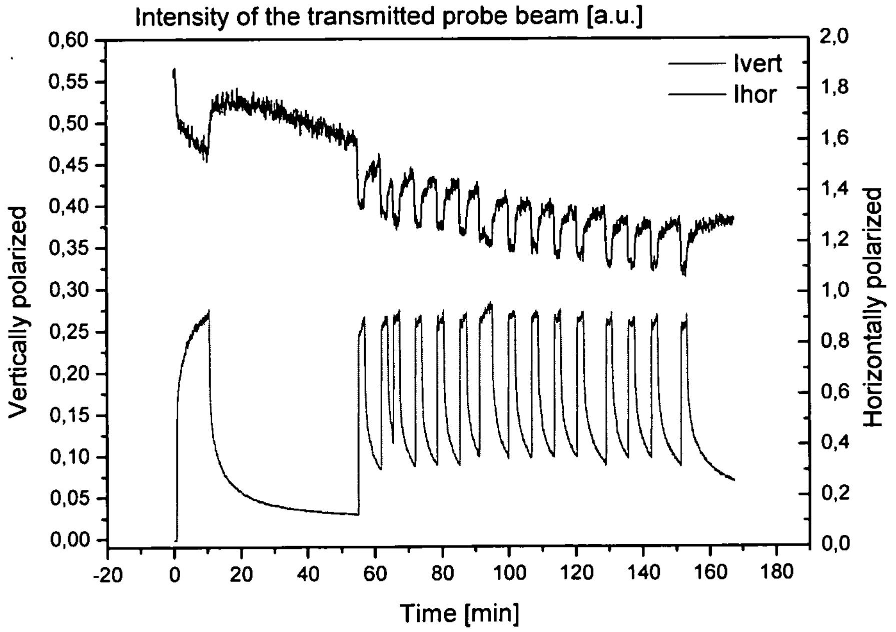


Figure 7a

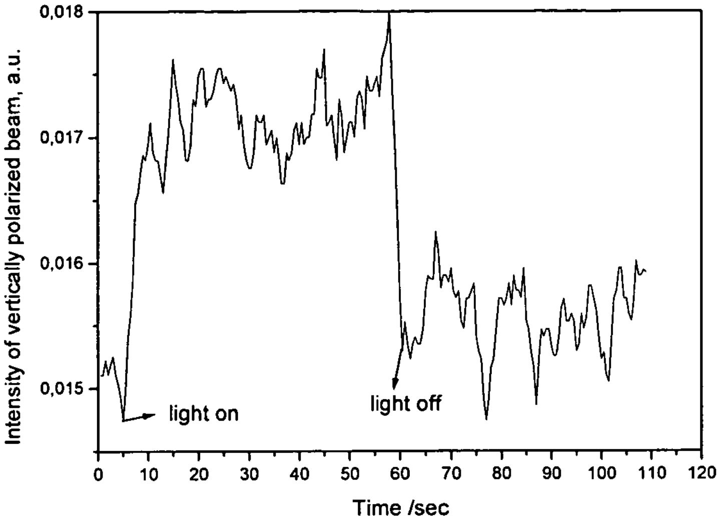


Figure 7b

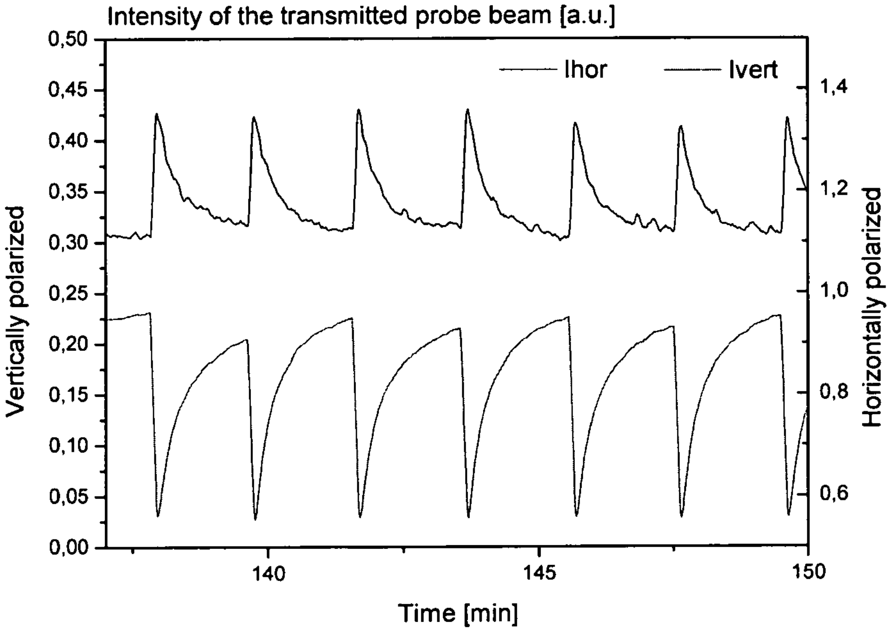


Figure 8a

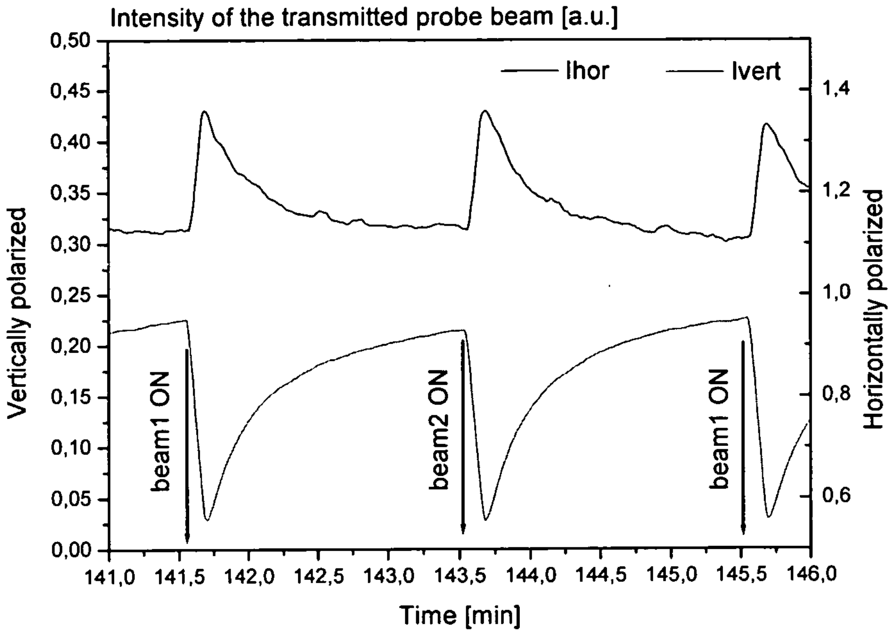
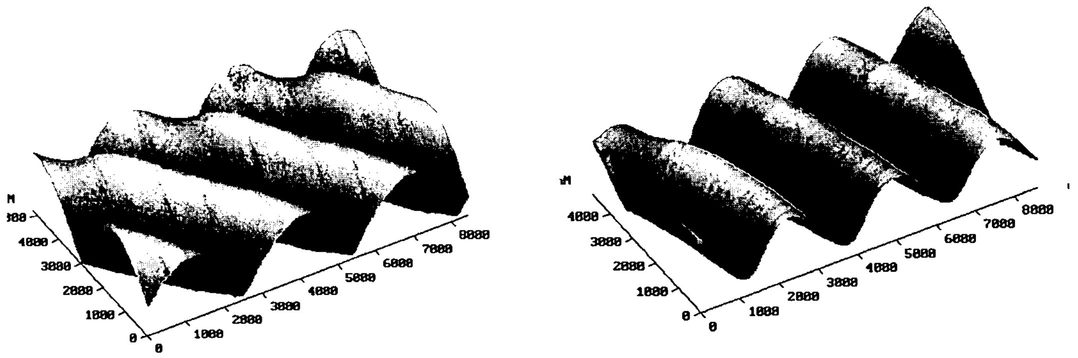


Figure 8b



a

b

Figure 9

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 02 0997

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	ZUCOLOTTO V ET AL: "Mechanisms of surface-relief gratings formation in layer-by-layer films from azodyes" POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 44, no. 20, September 2003 (2003-09), pages 6129-6133, XP004452528 ISSN: 0032-3861 * abstract * -----	1-38	C08G85/00 C08G73/02 C08G77/04 C08F20/06 C08J5/18 G01D5/38 G02B5/18
A	OZAKI M ET AL: "PHOTOINDUCED SURFACE RELIEF GRATING ON COMPOSITE FILM OF CONDUCTINGPOLYMER AND POLYACRYLATE CONTAINIGN AZO-SUBSTITUENT" JAPANESE JOURNAL OF APPLIED PHYSICS, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, JP, vol. 39, no. 6B, PART 2, 15 June 2000 (2000-06-15), pages L614-L616, XP001048939 ISSN: 0021-4922 * the whole document * -----	1-38	**TECHNICAL FIELDS SEARCHED (Int.Cl.7)**
A	HE Y ET AL: "Synthesis, self-assembly and photoinduced surface-relief gratings of a polyacrylate-based Azo polyelectrolyte" OPTICAL MATERIALS, ELSEVIER SCIENCE PUBLISHERS B.V. AMSTERDAM, NL, vol. 26, no. 1, June 2004 (2004-06), pages 89-93, XP004509450 ISSN: 0925-3467 * abstract * ----- -/--	1-38	C08G C08F C08J G01D G02B

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	21 February 2005	Hoffmann, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 02 0997

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	SHARMA L ET AL: "INVESTIGATION INTO THE SURFACE RELIEF GRATING MECHANISM VIA XPS IN NEW AZOBENZENE BASED OPTICAL MATERIAL" POLYMERS FOR ADVANCED TECHNOLOGIES, JOHN WILEY AND SONS, CHICHESTER, GB, vol. 13, no. 6, June 2002 (2002-06), pages 481-486, XP001112859 ISSN: 1042-7147 * abstract * -----	1-38	
A	US 2003/141441 A1 (KAWANO KATSUNORI ET AL) 31 July 2003 (2003-07-31) * the whole document * -----	1-38	
A	DARRACQ B ET AL: "PHOTOINSCRIPTION OF SURFACE RELIEF GRATINGS ON AZO-HYBRID GELS" ADVANCED MATERIALS, VCH VERLAGSGESELLSCHAFT, WEINHEIM, DE, vol. 10, no. 14, 1 October 1998 (1998-10-01), pages 1133-1136, XP000781881 ISSN: 0935-9648 * pages 1133-113, column 6 * -----	1-38	TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	21 February 2005	Hoffmann, K

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